# Biofuels

## Lec 3-Biogas: part 2

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## Content

- Anaerobic digestion Systems
- Parameters for the biogas process
- Landfills
- The world markets for biogas

# AD systems

➢ AD processes can be classified according to

- The total solids (TS) content of the slurry in the digester reactor.
  - o Low solids systems (LS) contain less than 10 % TS,
  - o Medium solids (MS) contain about 15%-20%,
  - o High solids (HS) processes range from 22% to 40%

- o Number of reactors used,
- o Single-stage the three stages of anaerobic process occur in one reactor and are Separated in time (i.e., one stage after the other)
- o Multi-stage. two or more reactors that separate the acetogenesis and methanogenesis stages in space are used.



# AD systems

- Operation mode
  - o Batch reactors: used where the reactor is loaded with feedstock at the beginning of the reaction and products are discharged at the end of a cycle
  - o Continuous flow reactor for low solids slurries, is where the feedstock is continuously charged and discharged
- Total Solid content
  - o Wet (<10 % total solids)
  - o Dry (>20 % total solids),
- Digester temperature
  - o Mesophilic (35-40oC)
  - o Thermophilic (> 55oC)

# AD systems

- Dry anaerobic digestion offers several advantages over wet digestion process like,
  - Lesser water addition and lesser pretreatment needed ,
  - Due to low water content and small reactor volume, energy requirement for heating is less for dry digester.
  - technical simplicity in design due to plug flow movement of substrate
  - no mechanical devices required inside the reactor for mixing
  - easy handling of digested residues (Guendouz et al. 2010; Yabu et al. 2011).
- higher volumetric biogas production rate as compared to wet digestion.
- Moreover, high solid content of the digestate makes it simpler and easier to handle as compared to liquid digestate of wet digestion that adds dewatering cost as well.



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# AD systems

- Similarly, better process conversion efficiency and maximum net energy gains are reported especially with the thermophilic operations of dry anaerobic digestions systems (Fdez-Guelfo et al. 2010; Forster-Carneiro et al. 2008).
- the Dranco and Kompogas processes are single stage, dry, thermophilic systems, which have been commercialized in Europe and other parts of the world.



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# Aerobic or anaerobic

- Anaerobic processes have many advantages over the corresponding aerobic processes, such as
  - low consumption of energy
  - low sludge production,
  - smaller space requirements
  - lower overall costs .
  - aerobic digestion requires energy input to provide aeration.
  - The anaerobic route has an obvious advantage in that it produces methane, a combustible gas with a high calorific value (24 $MJ/m^3$).
- In nature this process occurs in environments such as hot springs, swamps, paddy fields, lakes and oceans and the intestinal tract of animals (Garcia et al., 2000).



# Aerobic or anaerobic

- Aerobic treatment or composting involves the use of oxygen as an electron acceptor by microorganisms during the degradation of organic matter into $CO_2$, water, nitrates and sulphates.
- Of all biological waste treatment methods, aerobic treatment is the most widespread process used throughout the world (more than 95% of biological treatment).
- The compost contains nutrients and is used as a soil conditioner

# Aerobic or anaerobic

**Table 1.** Comparison of aerobic and anaerobic biological waste(water) treatment.

| | Aerobic digestion | Anaerobic digestion |
|---|---|---|
| Start-up | • Short start-up period. | • Long start-up period. |
| Process | • Integrated nitrogen and phosphorus removal possible.<br>• Production of high excess sludge quantities.<br>• Large reactor volume necessary.<br>• High nutrient requirements. | • No significant nitrogen or phosphorus removal, nutrients removal done via post treatment.<br>• Production of very little excess sludge (5-20%).<br>• Small reactor volume can be used.<br>• Low nutrient requirements. |
| Carbon balance | • 50-60% incorporated into $CO_2$; 40-50% incorporated into biomass. | • 95% converted to biogas; 5% incorporated into microbial biomass. |
| Energy balance | • 60% of available energy is used in new biomass; 40% lost as process heat. | • 90% retained as $CH_4$, 3-5% is lost as heat, and 5-7% is used in new biomass formation. |
| Residuals | • Excess sludge production.<br>• No need for post-treatment. | • Biogas, nitrogen mineralised to ammonia.<br>• Post-treatment required for removal of remaining organic matter and malodorous compounds. |
| Costs | • Low investment costs.<br>• High operating costs for aeration, additional nutrient and sludge removal, and maintenance. | • Often moderate investment costs.<br>• Low operating costs due to low power consumption and additional nutrients hardly required. |
| State of development | • Established technology. | • Still under development for specific applications. |

(Adapted from Lepisto and Rintala, 1997; Banerjee *et al.*, 1999; Zoutberg and Eker, 1999; Gijzen, 2001; Lettinga *et al.*, 1984; Lettinga, 2001).





# Parameters for the biogas process

**Loading rate** Amount of substrate added to the digester. Expressed e.g. as kg VS per $m^3$ digester and day.

**Biogas production** Amount of produced biogas expressed e.g. $Nm^3$ per ton TS.

**C/N-quota** Relation between carbon and nitrogen content in the substrate.

**Pretreatment** Prior to digestion, many substrates needs to be pretreated. This pretreatment can be pasteurisation, thickening or disintegration.

**Volatile Solids – VS** Weight of organic matter in the substrate. Normally expressed as percentage of TS.

## Parameters for the biogas process

| | |
|---|---|
| **Mesophilic Digestion** | Digestion at 25-40°C. Usually around 35-37°C. |
| **Methane concentration** | Amount of methane in the biogas. Normally expressed as percentage by volume. |
| **Methane yield** | Amount of produced methane expressed e.g. $Nm^3$ per ton TS. |
| **Thermophilic Digestion** | Digestion at 50-60°C. Usually around 50-55°C . |
| **Total Solids – TS** | The weight of the substrate after drying. Normally expressed as percentage of wet weight. Also called dry matter (DM) |



## Parameters for the biogas process

| | |
|---|---|
| **Dry Digestion** | Digestion of substrate with TS around 15-35 %. |
| **Hydraulic retention time** | The average time that the substrate is inside the digester. |
| **Degradation of VS** | Describes how much of the substrate that is degraded in the digester. Usually expressed as percentage of VS. |
| **Wet digestion** | Digestion of substrate with TS around 2-15 %. |
| **Wet weight** | The weight of the substrate including water. |

# What parameters affect anaerobic digestion?

- The rate at which the microorganisms grow is of paramount importance in the AD process.

**The most important determinants of good living conditions for anaerobic bacteria and therefore efficient gas production, are :**

- Temperature
- Retention Time
- pH-level
- Carbon/Nitrogen ratio (C/N ratio)
- Proportion of dry matter in substrate = suitable viscosity
- Agitation (mixing) of the substrate

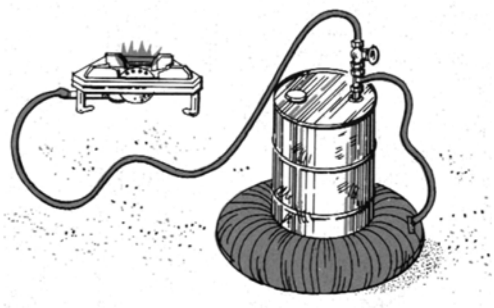
**If any one of these determinants is outside acceptable range, the digestion may be inhibited**

*Pedro Kraemer, BORDA, India*



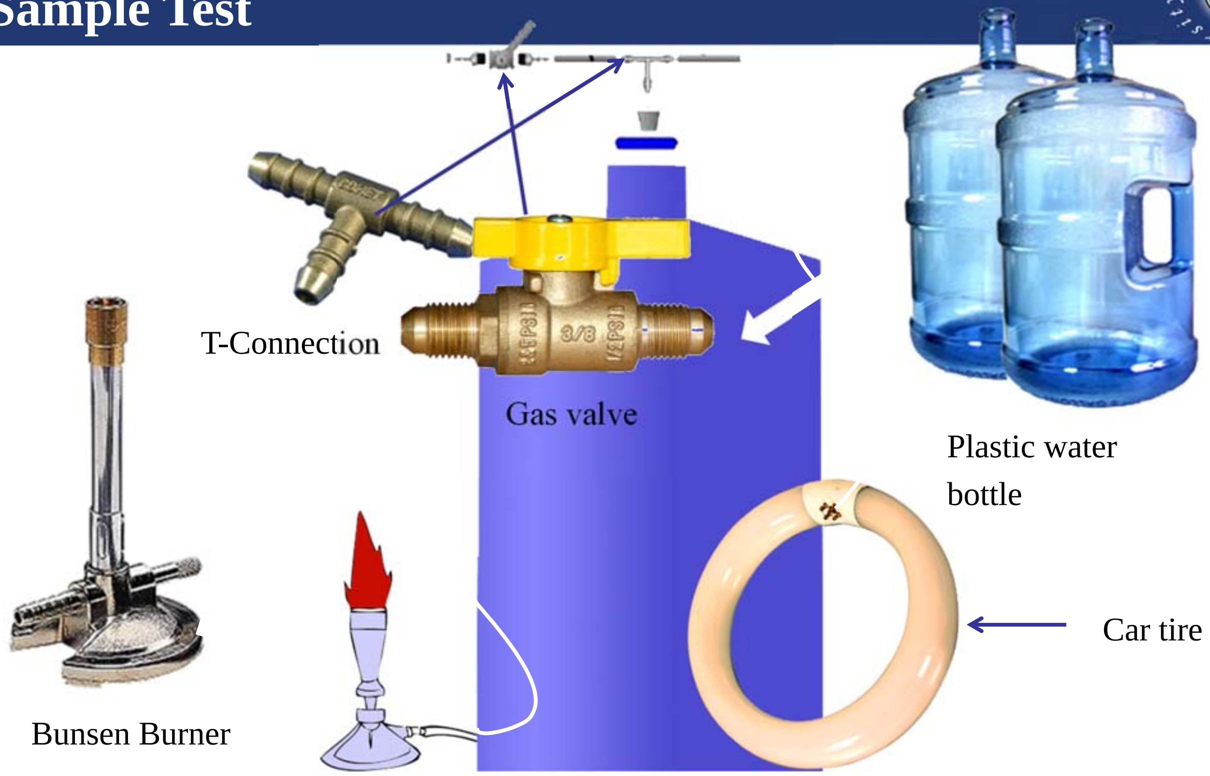
# Sample Test

- ✓Reduction in scum accumulation
- ✓Temperature Control
- ✓Ease of operation
- ✓Durable
- ✓Low cost



Prototype

# Sample Test






# Sample Test

# Substrate temperature in the digester

- Methane production is very sensitive to changes in temperature

Anaerobic fermentation can work in an ambient temperature between 3°C and 70°C and, if colder, the reactor has to be insulated and/or heated.

**Common temperature ranges for bacteria**:

| | |
|---|---|
| Psychrophillic bacteria | below 20°C |
| Mesophillic bacteria | 20 – 40°C |
| Thermophillic bacteria | above 40°C-75°C |

- Mesophilic processes require long hydraulic retention time and are not efficient in killing pathogenic microorganisms.
- Thermophilic anaerobic digestion characterized by
  - A higher growth rates of the bacteria involved and



# Substrate temperature in the digester

  - Therefore, high activities per unit biomass,
  - Higher loading rate of organic materials that can be employed
  - Ability for treating high-temperature industrial effluents and specific types of slurries

- The higher temperatures facilitates greater sterilization of the end digestate

- The disadvantage of thermophilic digestion is the often-found high effluent VFA concentrations

# Substrate temperature in the digester

| Performance characteristics | Mesophilic digestion | Thermophilic digestion |
|---|---|---|
| Gas production rate | Contradictory reports | Contradictory reports |
| Pathogen reduction | Lower | Higher |
| Effluent VFAs | Lower | Higher (contradictory) |
| Dewaterability | Contradictory reports | Contradictory reports |
| Process stability | Higher | Lower (contradictory) |
| Methane content | Higher | Lower |
| Energy requirement | Lower | Higher |
| Odour | Lower | Higher |
| Product/substrate inhibition | Lower | Higher |



# pH –value is crucial for a good result

- pH is a central parameter for controlling the anaerobic process because each of the microbial groups involved in the reactions has a specific pH range for optimal growth.

**Optimal production when pH 6.8 – 7.2**

- Inhibition (due to acids) if pH < 6.2 (The growth rate of methanogenic microbes decreases)
- Inhibition (due to ammonia) if pH > 7.6

Deviation from the optimum range results in:

Lower gas yield

Inferior gas quality

# pH –value & VFA

- The decrease in pH accompanying accumulation of VFAs is the main cause of toxicity and reactor failure in the anaerobic digestion process
- This is because the toxicity of VFAs is pH dependent since only the nonionized forms are toxic to microorganisms.
- VFAs are toxic at pH values where they exist in protonated forms, as they then can penetrate the cell membrane.
- When they are inside the cell, where the pH is around 7, they are ionized and the hydrogen ion released will cause a decrease in the intracellular pH.
- The pH gradient across the membrane is essential for ATP formation and therefore bacterial growth.

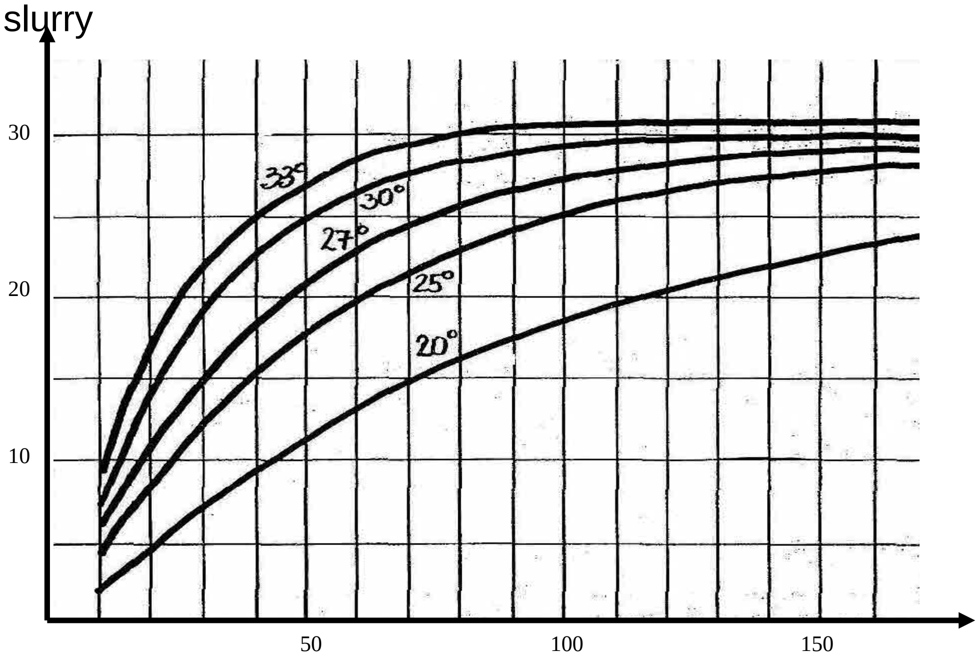


# Retention (or residence) Time

- The retention time of digestate affects the pH value and in a batch reactor acetogenesis occurs at a rapid pace.
- Acetogenesis can lead to accumulation of large amounts of organic acids resulting in pH below 5.
- Excessive generation of acid can inhibit methanogens, due to their sensitivity to acid conditions.
- Reduction in pH can be controlled by the addition of lime or recycled filtrate obtained during residue treatment. In fact, the use of recycled filtrate can even eliminate the lime requirement.

# Biogas production with continuous feeding

Litres of biogas per
litre of slurry




Hydraulic retention time in days



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# C/N ratio is important

- Microorganisms need N (nitrogen) and C (carbon) for their metabolism

**Methanogenic organisms prefer a**

**C/N ratio of between 10:1 and 20:1**

N must not be too low, or else → shortage of nutrient

- A high C/N ratio is an indication of rapid consumption of nitrogen by methanogens and results in lower gas production.
- On the other hand, a lower C/N ratio causes ammonia accumulation and pH values exceeding 8.5, which is toxic to methanogenic bacteria.
- Optimum C/N ratios of the digester materials can be achieved by mixing materials of high and low C/N ratios, such as organic solid waste mixed with sewage or animal manure.



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# Nitrogen inhibition

- If N concentration is too high (>1,700 mg/l of NH4-N) and pH is high, then the degradation of nitrogenous compounds will release ammonium.

→ growth of bacteria is inhibited due to toxicity caused by high levels of (uncharged) ammonia

- Methanogens, however, are able of adapt to 5,000 - 7,000 mg/l of $NH_4$-N given the pre-requisite that the uncharged ammonia ($NH_3$ controlled by pH) level does not exceed 200-300 mg/l



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# Nutrients

- The most important nutrients are nitrogen and phosphorus, and the optimum C:N:P ratio for high methane yield is reported to be 100:3:1
- If the C/N ratio is high there is a risk of nutrient deficiency and a low buffering capacity will result in a more sensitive process
- Inhibitory effects of copper and zinc in batch digesters in the range of 1-10 mg/l for copper and 5-40 mg/l for zinc,
- Copper was more toxic than zinc to acidogens.
- Heavy metals inhibit the degradation of VFAs to methane in anaerobic digestion



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# Organic loading rate (OLR)

- Organic loading rate (OLR) is a measure of the biological conversion capacity of the AD system.
- Feeding the system above its sustainable OLR results in low biogas yield due to accumulation of inhibiting substances such as fatty acids in the digester slurry.
- In such a case, the feeding rate to the system must be reduced. OLR is a particularly important control parameter in continuous systems.
- Many plants have reported system failures due to overloading



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# Waste composition/Volatile Solids (VS)

- The wastes treated by AD may comprise a biodegradable organic fraction, a combustible and an inert fraction.
- The biodegradable organic fraction includes kitchen scraps, food residue, and grass and tree cuttings.
- The combustible fraction includes slowly degrading lignocellulosic organic matter containing coarser wood, paper, and cardboard.
- As these lignocellulosic organic materials do not readily degrade under anaerobic conditions, they are better suited for waste-to-energy plants.
- Finally, the inert fraction contains stones, glass, sand, metal, etc.
- This fraction ideally should be removed, recycled or used as land fill.



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# Waste composition/Volatile Solids (VS)

- The removal of inert fraction prior to digestion is important as otherwise it increases digester volume and wear of equipment.
- In waste streams high in sewage and manure, the microbes thrive and hydrolyses the substrate rapidly whereas for the more resistant waste materials, such as wood, digestion is limited.
- The volatile solids (VS) in organic wastes are measured as total solids minus the ash content, as obtained by complete combustion of the feed wastes.
- The volatile solids comprise the biodegradable volatile solids (BVS) fraction and the refractory volatile solids
- Lignin is a complex organic material that is not easily degraded by anaerobic bacteria and constitutes the refractory volatile solids (RVS)



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# Ammonia-N inhibition

- Ammonia is produced by the biological degradation of the nitrogenous matter, mostly in the form of proteins and urea.
- About 60-80% of total nitrogen (especially the proteins and other organic nitrogen compounds) is converted to ammonia during anaerobic digestion of organic waste
- Microorganisms responsible for anaerobic digestion need low concentration of ammonia for their growth and multiplication.
- However, the excess ammonia accumulates in the digester and hinders the process.
- In dry anaerobic digestion, apart from low C/N ratio of the feedstock, recycling of a fraction of leachate or digestate intended to optimize solid contents and inoculate fresh waste) has also been found to increase the ammonia concentration



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# Ammonia-N inhibition

- Inhibition happens at total ammonia nitrogen (TAN) concentration range of 1200-6000 mg/L or more depending on TS content, pH, temperature and degree of acclimation of reactor medium.
- Ammonia-N accumulation is, however, identified as a major issue with dry thermophilic anaerobic digestion systems, which can affect the overall methane yield.
- Generally, the OFMSW is characterized with the average of 4% of protein content, a major source of nitrogen, which is removed via ammonification process and accumulated as ammonia-N (Jokela and Rintala, 2003).
- Also, the chances of ammonia-N accumulation are higher, if the feedstock is mixed up with the large portions of food processing waste and animal waste.



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# Ammonia-N inhibition

- Even though, the protein degradation process is found to be very slow, the released ammonia-N tend to accumulate in anaerobic digesters because of leachate recycling and there is no mechanism to remove it except by leachate removal or leaching.
- Thus, the leaching is the only mechanism proposed to overcome this issue, through which the ammonia-N concentration is reduced with the external water addition.
- But water addition is not desirable in the case of dry anaerobic digestion systems.
- Also, ammonia-N stripping is not considered as good option for organic wastes with the high solid contents due to their poor fluidity and difficulty in handling.



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# Ammonia-N inhibition

- On the other hand, it can be governed possibly through adjusting the carbon to nitrogen (C/N) ratio of the feedstock, which determines the overall ammonia-N concentration within the digester (Straka et al. 2007).
- The optimum C/N ratio for anaerobic digestion is agreed to be in the range of 20 to 30 (Li et al. 2011), with a higher C/N ratio, the release of lower concentrations of ammonia-N can be expected within the anaerobic systems.



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# Stirring the substrate

- **Stirring improves the efficiency of digestion by:**
  - Removing metabolites (gas removal)
  - Bringing fresh material in contact with bacteria
  - Reducing scum formation and sedimentation
  - Preventing temperature gradients in the digester
  - Avoiding the formation of blind spots (short cuts)
- **However, excessive stirring disturbs the symbiotic relationship between the different bacteria species**
- Simple biogas units normally do not have mechanical stirring devises



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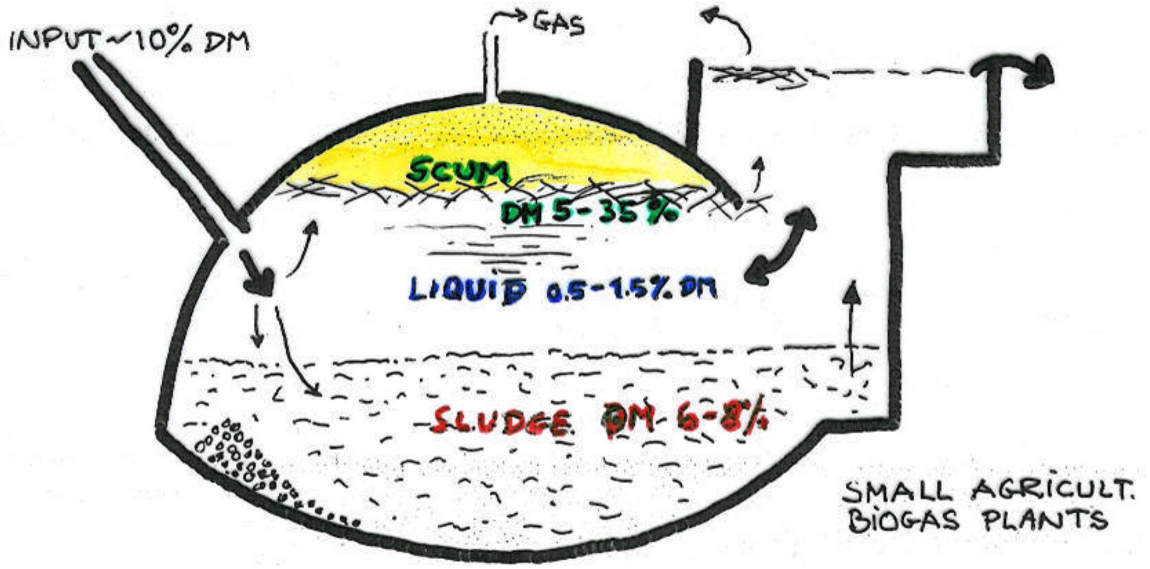
# Changes in dry matter (DM) concentration inside the digester



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# Changes in dry matter (DM) concentration inside the digester

- During digestion, properties of waste change considerably:
  - Total solids, organic carbon, volatile organic compounds (odor), GHG emissions potential, pathogens and weed seeds in the waste decrease because of digestion.
  - pH of the digester medium increases.
  - Organic N is transformed to $NH_4$-N, so N availability to plants increases, if the digestate is applied to agricultural land.
  - Moreover, fluidity, homogeneity and infiltration properties of waste are also improved by digestion, which further increases the nutrient availability of digestate (Lantz et al., 2007).
  - However, the increased concentrations of $NH_4$-N and high pH also increase the loss potential of N in $NH_3$ form through volatilization.



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# Changes in dry matter (DM) concentration inside the digester

- There is no much effect of fermentation on P and K availability.
- Digestion also improves handling and solids separating characteristics if manure is used as
- feedstock, and reduces attractiveness of the manure to rodents and flies.



# Changes in dry matter (DM) concentration inside the digester

**Effect of Digestion on Properties of Waste**

| Parameter | Feedstock | Before Digestion | After Digestion | % Change | Reference |
|---|---|---|---|---|---|
| pH | Primary sludge + OFMSW | 3.5 | 7.5 | +114 | Gomez et al., 2007 |
| | Cattle slurry | 7.2 | 8.4 | +16.7 | Mokry et al., 2008 |
| | Pig slurry | 7.0 | 8.1 | +15.7 | Mokry et al., 2008 |
| | Cattle manure | 6.9 | 7.6 | +10.1 | Gomez et al., 2007 |
| Total Solids | OFMSW | 90 g | 43.4 g | -52 | Rao and Singh, 2004 |
| | Primary sludge + OFMSW | 60 g/L | 23.6 g/L | -60.66 | Gomez et al., 2007 |
| | Cattle manure | 263 g/L | 122.6 g/L | -53.38 | Gomez et al., 2007 |
| | Cattle slurry | 9.9 % | 7.1 % | -28.28 | Mokry et al., 2008 |
| | Pig slurry | 7.6 % | 4.9 % | -35.52 | Mokry et al., 2008 |

# Changes in dry matter (DM) concentration inside the digester

| | | | | | |
|---|---|---|---|---|---|
| Volatile Solids | OFMSW | 79.65 | 33.10 | -58.44 | Rao and Singh, 2004 |
| | OFMSW | 82.32 % | 40.95 % | -50.25 | Eliyan, 2007 |
| | Primary sludge + OFMSW | 55.2 g/L | 16.5 g/L | -70.10 | Gomez et al., 2007 |
| | Cattle manure | 226.2 g/L | 105.4 g/L | -53.40 | Gomez et al., 2007 |
| | Cattle slurry | 86.9[a] %TS | 75.35 %TS | -13.25 | Mokry et al., 2008 |
| | Pig slurry | 78.5[a] %TS | 73.26 %TS | -6.66 | Mokry et al., 2008 |
| Total N | OFMSW | 1.4 g | 1.06 g | -24.28 | Rao and Singh, 2004 |
| | Cattle slurry | 4.1 kg/t | 4.5 kg/t | +9.75 | Mokry et al., 2008 |
| | Pig slurry | 4.1 kg/t | 4.5 kg/t | +9.75 | Mokry et al., 2008 |
| $NH_4$-N | Cattle slurry | 1.7 kg/t | 2.5 kg/t | +47 | Mokry et al., 2008 |
| | Pig slurry | 2.0 kg/t | 3.5 kg/t | +75 | Mokry et al., 2008 |
| | Manure | 70 % of TN | 85 % of TN | +21.42 | Berglund, 2006 |



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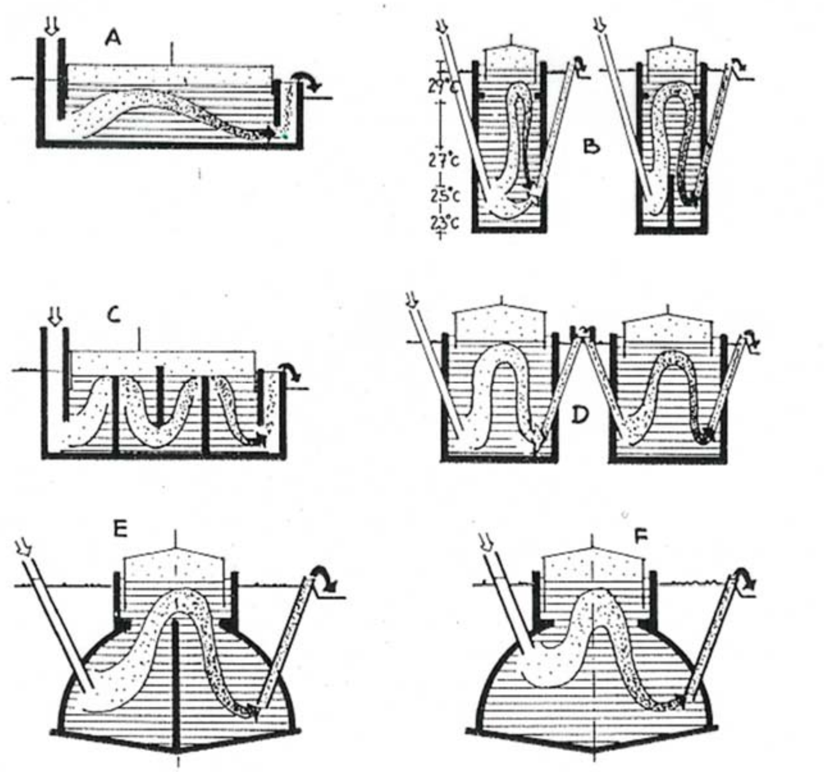
# Behaviour of the substrate inside the digester



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# Summary: Biomethanization Inhibitors

**Table 2.1 Biomethanization Inhibitors and their Inhibitory Concentration**

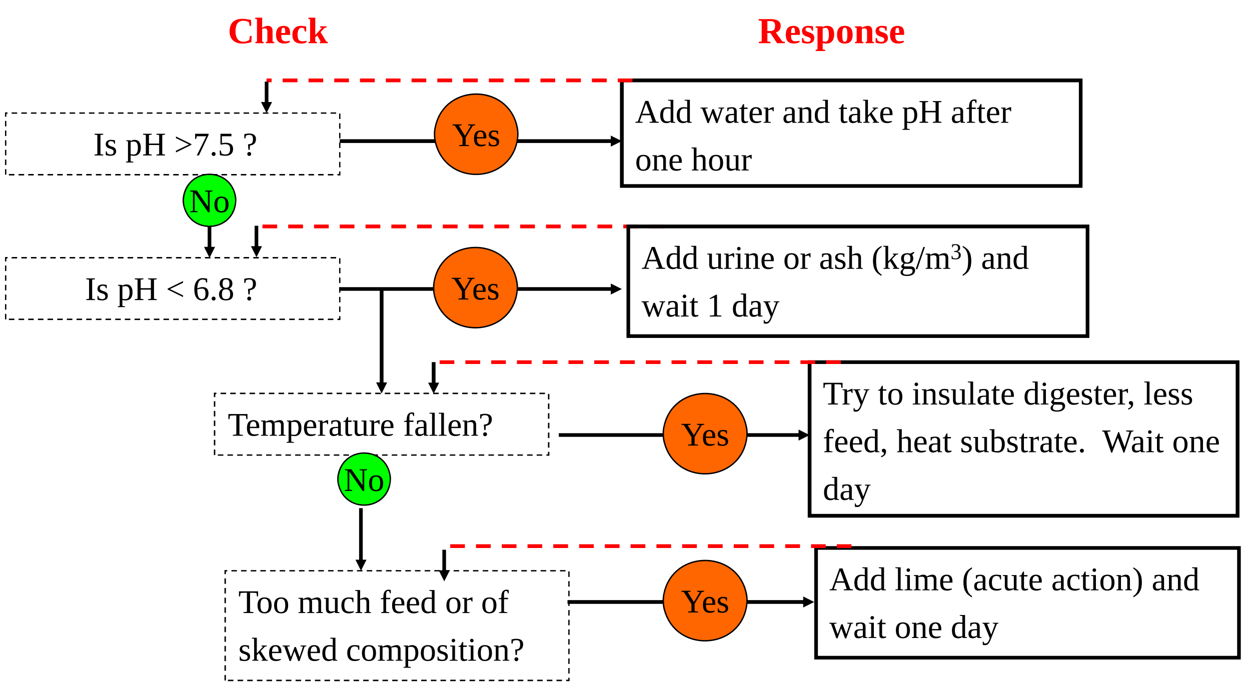
| Parameter | Concentration of inhibition (g/L) |
|---|---|
| Volatile fatty acids | >2 (as acetic acid) |
| | > 6-8 (as overall volatile acids) |
| Total ammonia nitrogen | 1.5-3 (at pH>7.6) |
| Free ammonia | 0.6 |
| Sulfide | 0.25 (as $H_2S$ at pH 6.4-7.2) |
| | 0.09 (as $H_2S$ at pH 7.8-8.0) |
| Sulfide | >0.1 (as soluble sulfide) |
| Calcium | 2.5-4.5 |
| | 8 (strongly inhibitory) |
| Magnesium | 1-1.5 |
| | 3 (strongly inhibitory) |
| Potassium | 2.5-4.5 |
| | 12 (strongly inhibitory) |
| Sodium | 3.5-5.5 |
| | 8 (strongly inhibitory) |
| Heavy metals | |
| Copper (Cu) | 0.0005 (soluble metal) |
| | 0.15 [a] |
| Cadmium (Cd) | 0.15 |
| Iron (Fe) | 1.71[a] |
| Chromium ($Cr^{3+}$) | 0.003 |
| Chromium ($Cr^{6+}$) | 0.5 |
| Nickel | 0.002 |

Source: Chen et al., 2008; Polprasert, 2007; Dong et al., 2010

[a] mole/kg dry solids



# Check-list if gas production is lower than expected

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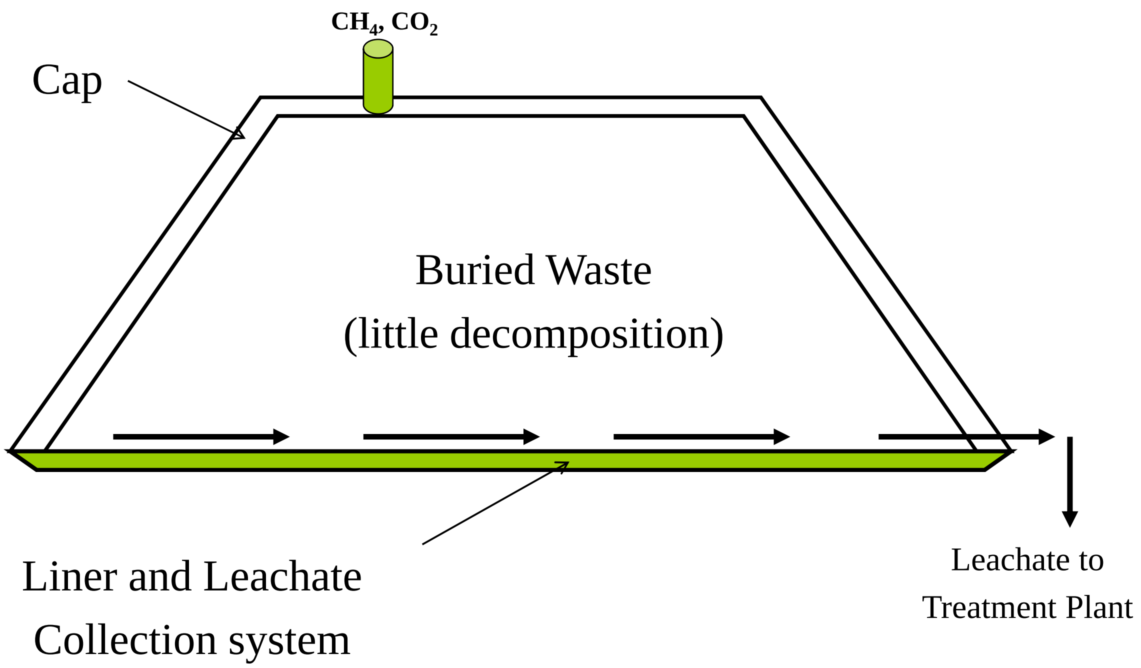
➢Drangert & Ejlertsson, Linkoping university, Sweden

## Traditional Landfill



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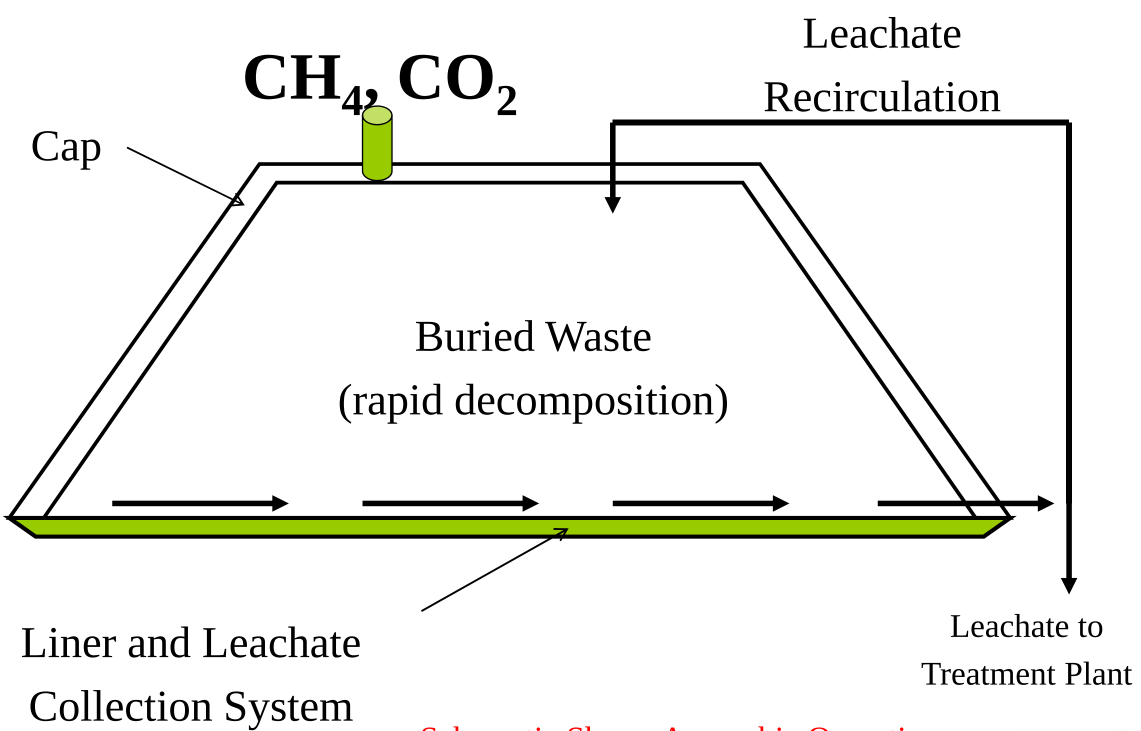
## Bioreactor Landfill




Schematic Shows Anaerobic Operation



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## Bioreactor Landfill

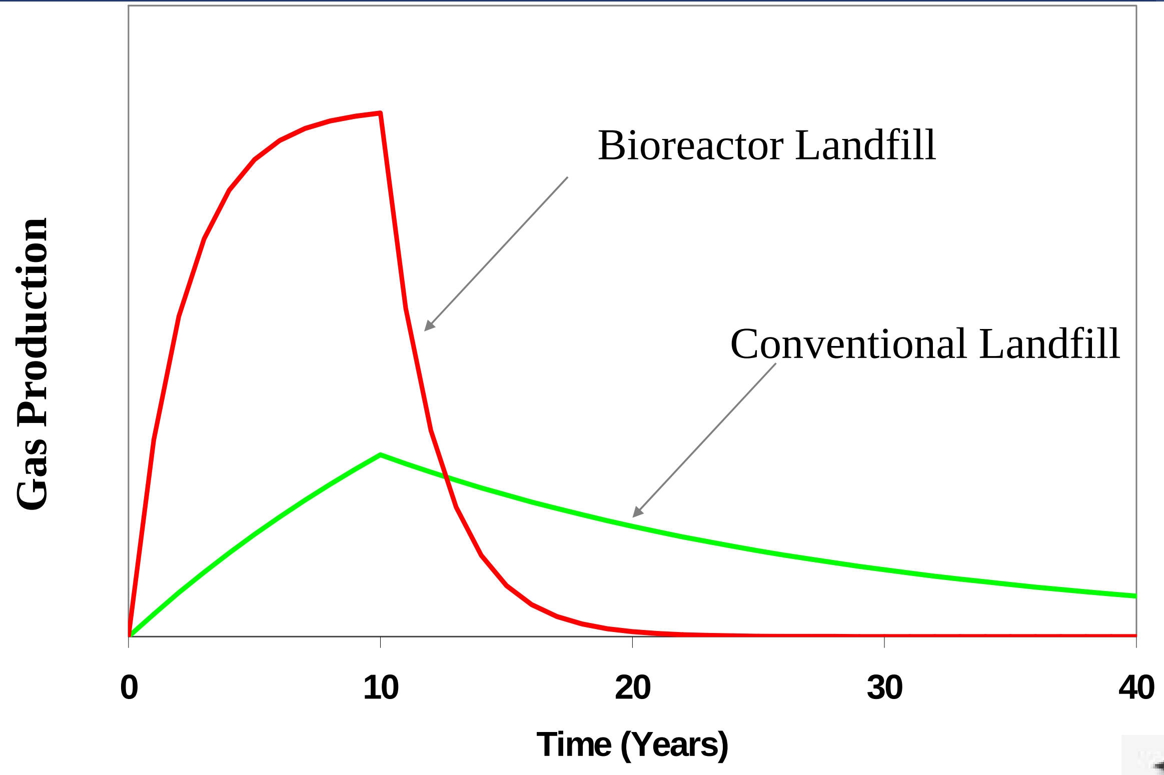
- Create conditions for waste degrading organisms to thrive
- Most typically performed by increasing moisture content
  - Leachate recirculation (A moisture content above 40 % can be achieved)
  - Water addition
- Methods of leachate recirculation
  - Spray irrigation
  - Surface ponding
  - Vertical wells
  - Horizontal trenches
- liquid or air is injected in a controlled fashion into the waste mass in order to or enhance biostabilization and accelerate degradation of waste due to enhanced hydrolysis



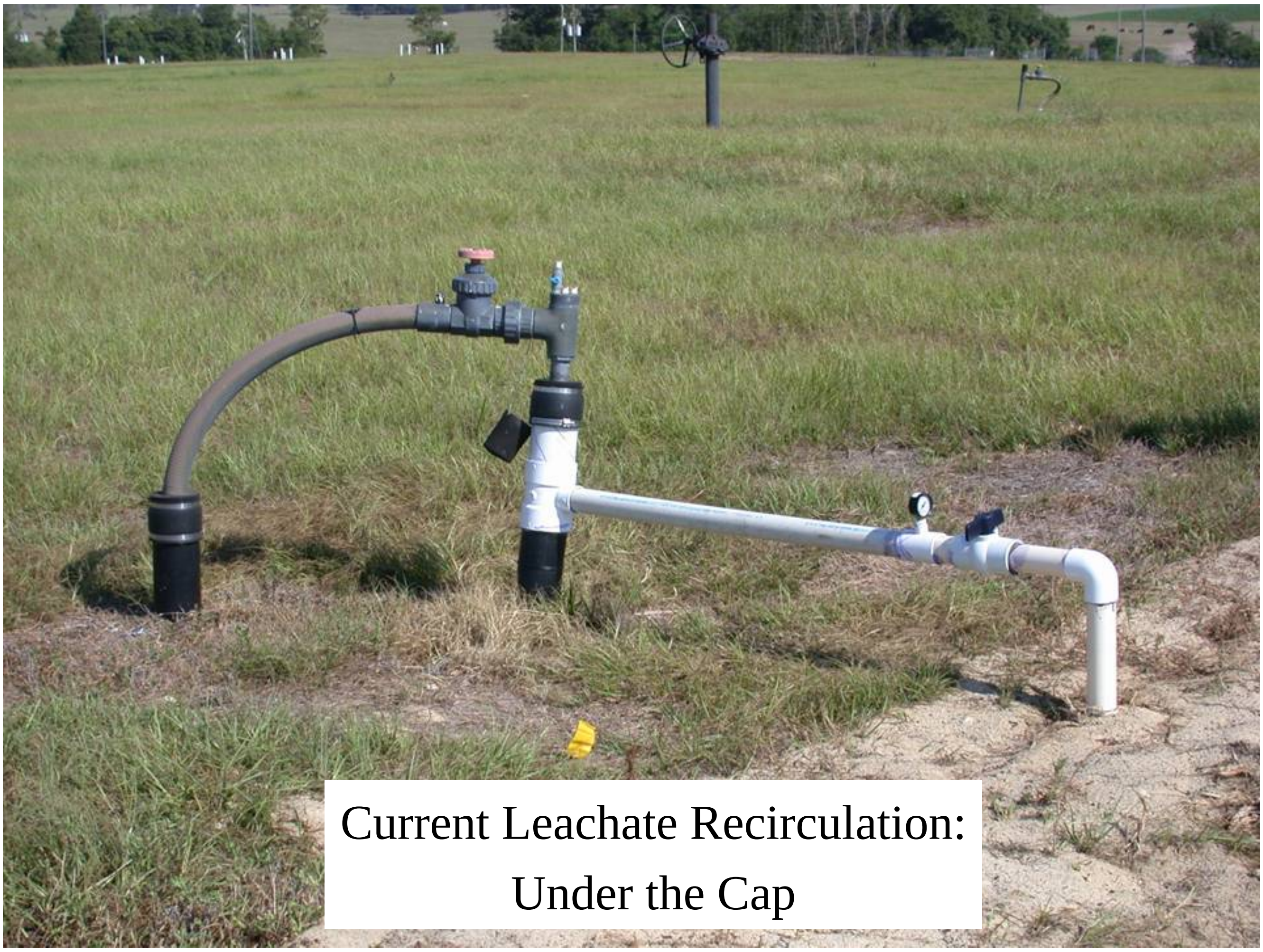
## Bioreactor Landfill

- The advantages of the bioreactor landfill also include earlier gas generation, quicker stabilization of leachate, enhanced landfill gas generation and quicker settlement
- Challenges
  - Getting the moisture to the right place
  - Waste heterogeneity
  - Monitoring progress and determining completion
  - Collecting gas
  - Avoiding problems caused by too much moistures
  - Slope stability

# Bioreactor Landfill and Traditional Landfill








## Aerobic Bioreactors Landfill

- Relatively new technique
- Aerobic conditions are maintained in the landfill by air injection and lecheate recirculation.
- The odors produced by the aerobic reactors are not foul.
- The main advantage of these landfills is rapid stabilization of waste based on the fact that aerobic bacteria grow faster
- Concerns
  - Air injection to a landfill results in a decrease in the concentrations of methane and carbon dioxide leading to increased hydrogen sulfide concentration
  - Fire potential
  - Explosive gas mixtures
  - Air emissions
  - Cost

## The world markets for biogas

- European biogas sector
  - thousands of biogas installations,
  - Germany, Austria, Denmark and Sweden :
    the technical forerunners with the largest number of modern biogas plants)
- Asia
  - -Small-scale biogas plants
  - -Simple technologies, and therefore cheap to construct
- Vietnam: 200 thousand rural household biogas digester
- China: 30 million rural household biogas digesters
- India: 5 million



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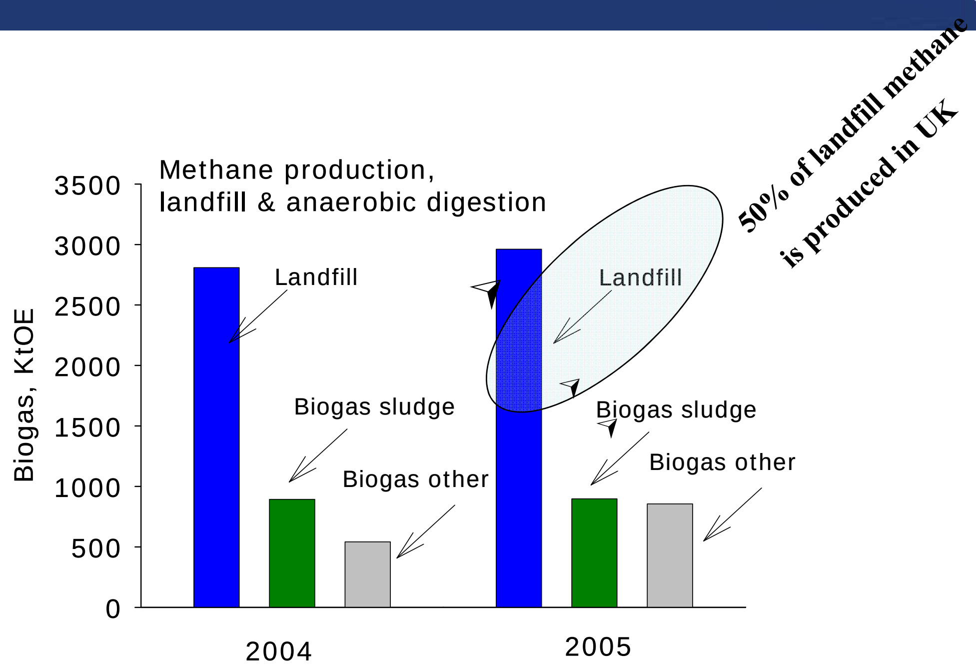
## Biogas production in Europe



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# Global potential of biogas production

- ❑ Very small part of this potential is utilized today
- ❑ European Biomass Association (AEBIOM)
  - – The largest potential lies in biomass originating from agriculture.
  - – Up to 20 to 40 million hectares (Mha) of land can be used for energy production in the European Union alone, without affecting the European food supply.