I Basics of the anaerobic degradation

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1 Microbiological basics of the anaerobic degradation

Being an anaerobic biological treatment process, the microbiological basics of the anaerobic degradation shall be discussed first. These basics are fundamental for the evaluation of the anaerobic biological treatment processes and for the understanding of the influencing parameter on the proceedings.

Considering the geological history of our planet it becomes clear that life on earth developed under anaerobic conditions. The primeval atmosphere contained a lot of hydrogen, methane, nitrogen and carbon dioxide, but no oxygen. Through solar radiation and electric discharges simple organic molecules could arise from inorganic compositions which enriched themselves in waterbodies.

The conversion from abiotic organic material to the first living cell did last extremely long (4.5 to 3.1 billions of years ago). The *archebacteria* - which could develop on earth during prehistoric times - at archaic times - belong to the first organisms. The methanogenic (methane forming) bacteria belong to this group. These bacteria play a decisive role in the processes applied today for the anaerobic biological treatment of biomass and are able to produce the methane gas that is used by mankind as a thermal energy source.

The methane formation is, however, only the last step in a multi-step anaerobic degradation process. Besides the methanogenic, various other bacteria groups are involved which make the whole process complicated and easily to be influenced. The most important microbiological interrelationships of the anaerobic degradation, the basics of metabolism, the encymatic kinetics, the catabolism and the growth kinetics shall be explained in the following.

1.1 Basics of metabolism

In order to keep up the state of life and to assure the species' continuity all organisms must provide themselves with food. On the one hand nutrition delivers the necessary energy and on the other hand the components for the synthesis of new cell material. The organism generates energy and components by metabolism, i.e. through a controlled conversion of the nutrients within the cell.

Before the nutrient conversion within the cell takes place the transport of the nutrients from the outside across the cell membrane into the interior of the cell is necessary. The cell walls do not remarkably hinder the small molecules (relative molecule mass <600) and ions. Macromolecules are decomposed in fragments out of the cell by exoenzymes and then are transported into the cell with the help of other enzymes.

The nutrients taken up from the outside are firstly degraded into smaller fragments (decomposition or catabolism). In the intermediate metabolism (amphibolism) new cell material for the basic components of the synthesis is generated from the fragments (e.g. amino acids, organic acids). They build the polymere macromolecules from which the cells are composed of. In microbiology this synthesic metabolism is also called anabolism. As anabolism requires not only the compositions but also energy for its linkage, part of the nutrition is decomposed just for energy generating purposes (SCHLEGEL, 1988).

1.2 Enzymatic control of the metabolic reactions

The participation of the enzymes during the transport processes has already been pointed out. The enzymes play an outstanding role for the total metabolic process within and outside of the cell, for each of the metabolic processes is controlled by enzymes.

Enzymes consist of several complex proteins and have the function of *bio-catalysts*. The catalytic effect is realized by the reduction of the activating energy of a reaction with a strong acceleration of the velocity. A reaction catalyzed by enzymes runs about 10 dimensions faster as a reaction that is not enzymatic. In order to demonstrate the dimension it can be said, that the increase of the velocity by the factor 10^{10} reduces the half-life value of a reaction from 300 years to one second (SCHLEGEL, 1985).

Enzymes are characterised according to the type of reactions catalyzed by them and have the ending *-ase*. For example, permeases catalyze the transport of substrates into the cells (HARTMANN, 1989). In order to absorb and to transport the fragments of the substrates or the hydrogen, lower molecular compositions, the coenzymes and prosthetic groups, are available for the enzymatic proteins. A typical example for a coenzyme is the nicotinamide adeneine dinucleotide (NAD). NAD is the most universal transmitter of hydrogen within a cell.

During the enzyme catalyzed degradation of a nutrient (substrate) the enzyme combines itself with the substrate molecule. Through the effectiveness of the enzyme the substrate molecule is split up. Hereby the unchanged enzyme, the fragments of the substrate and usually a certain amount of energy are released.

The fundament for the description of an enzymatic reaction is the theory of MICHAELIS and MENTEN (HARTMANN, 1989). Accordingly runs the reaction in two steps. In the first instance reacts the substrate (S) with the enzymes (E) and forms the enzyme-substrate complex (ES):

$$E + S \underset{k_2}{\overset{k_1}{\leftrightarrow}} ES$$

A balance between the two reaction partners arises, whereby k_1 and k_2 are the reaction constants of the corresponding reaction. In the second step of the reaction the ES complex degrades into the product (P) and releases the enzyme.

$$ES \xrightarrow{k_3} E + P \qquad \text{where as } k_3 << k_1 \cdot k_2$$

The velocity v of the total reaction is determined by the reaction constant k_3 and the concentration of the ES complex:

$$v = k_3 \cdot ES$$

If the total existing enzyme (E_0) is bound in the ES complex, ES turns to E_0 and a maximal velocity is achieved.

$$v_{max} = k_3 \cdot E_0$$

Resultant from this the MICHAELIS-MENTEN-equation can be deduced by a mathematic transformation, whereby the velocity of the reaction directly depends on the substrate concentration:

$$V = v_{max} \cdot (S) \; / \; (k_m + S)$$

The Michaelis-Menten-constant k_m is hereby the summary of the reaction constants k_1, k_2 and k_3.

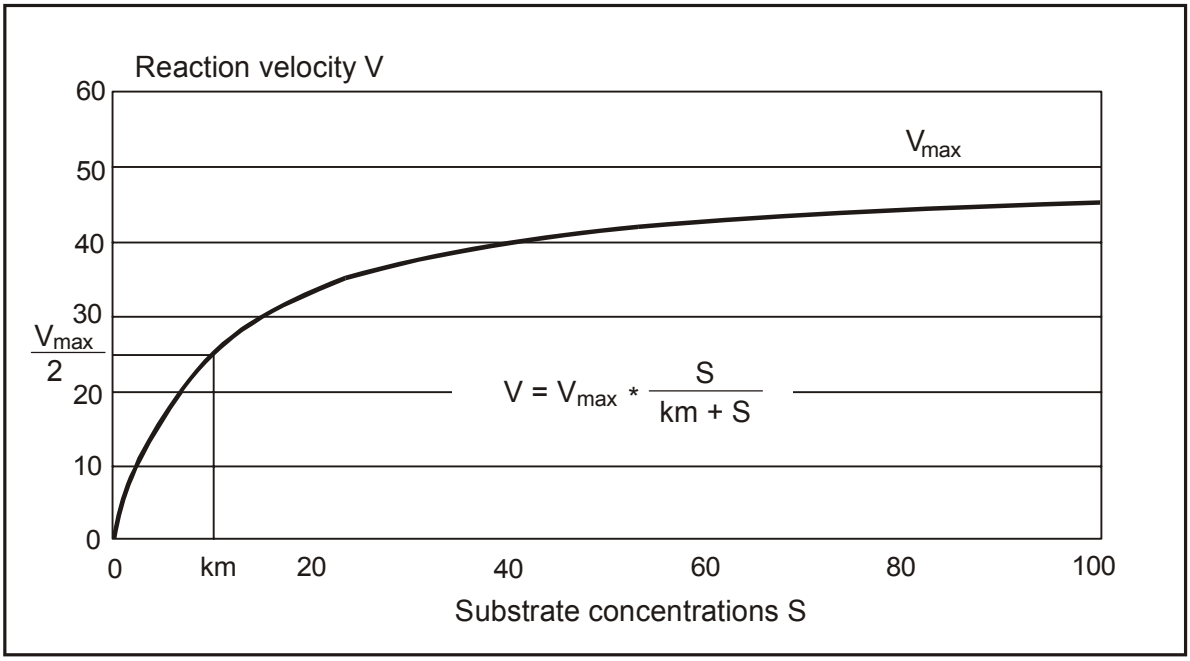


Figure 1: Michaelis-Menten relation

As shown in figure 1 half of the maximum reaction velocity is achieved when the substrate concentration is as high as the reaction constant K_m. Hence the K_m value describes the half-life constant of the reaction. The K_m value is the measure for the enzyme activity. Small K_m values mean that already with low substrate concentrations high reaction velocities can be achieved, i.e. the activity of the enzymes is high. The K_m value is no absolute constant, but dependent on different influences (e.g. pH value, temperature, inhibitors, activators).

1.3 Energy recovery in the cell

During the degradational reactions (catabolism) generally high-molecular compounds, rich in energy, are converted into energy-poor, low molecular products. These reactions always induce a transmission of electrons, i.e. there is always a reaction partner, which is oxidized (electron donor = donation of electrons) and a partner which is reduced (electron acceptor = accepting electrons). The proceeding reaction is therefore called redox reaction. In order that an electron exchange can take place, an electrical potential difference must exist between both partners. The higher this redox potential is the smoother runs the reaction and more energy is released. Table 1 contains the redox potential of selected biologically important reactions:

Table 1: Redox potential of some biologically important reactions (BÖHNKE et al., 1993)

Electron donors	Electron acceptors	Redox potential
H_2	$2H^+ + 2e^-$	-0.414 V
$NADH + H^+$	$NAD^+ + 2H^+ + 2e^-$	-0.317 V
$NADPH + H^+$	$NADP^+ + 2H^+ + 2e^-$	-0.316 V
$FADH_2$	$FAD + 2H^+ + 2e^-$	-0.219 V
Lactate	$Pyruvate + 2H^+ + 2e^-$	-0.180 V
H_2O	$½ O_2 + 2H^+ + 2e^-$	+0.815 V

The redox potential is also a measure for the free energy ΔG' of a reaction. From the difference of the redox potential of two redox systems ΔE', which are reacting with each other, the free energy ΔG' of the conversion can be calculated.

$\Delta G' = n \cdot F \cdot \Delta E'$

with

ΔG' = free energy

n = constant

F = Faraday's constant, corresponds to 96.3 kJ

ΔE' = redox potential

The energy which is released during the decomposition of the substrate molecules, is stored by the cell through the linkage of compounds rich in energy. The universal storage material in the cells of every living organism is the adenosine triphosphate (ATP). The structure of the adenosine phosphates is shown in figure 2. The energy change is achieved by linkage respectively decomposition of the phosphate groups. Approximately 30 kJ are stored respectively released at the connection or disconnection of the third phosphate group.

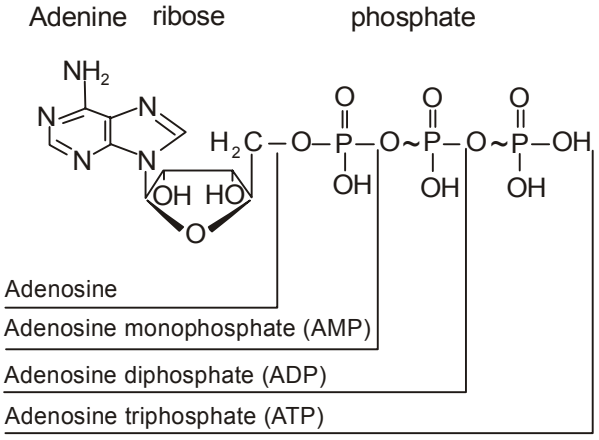


Figure 2: Structure of the adenosine phosphates

1.4 Metabolic processes of the anaerobic degradation

As during the aerobic degradation - e.g. of glucose - a bacterium is able to fully respire the substrate in its cell until the final products carbon dioxide and water, is it not possible under anaerobic conditions. The anaerobic degradation of organic material to biogas (CH_4, CO_2) is a process in four successive steps with the involvement of different bacteria groups (figure 3).

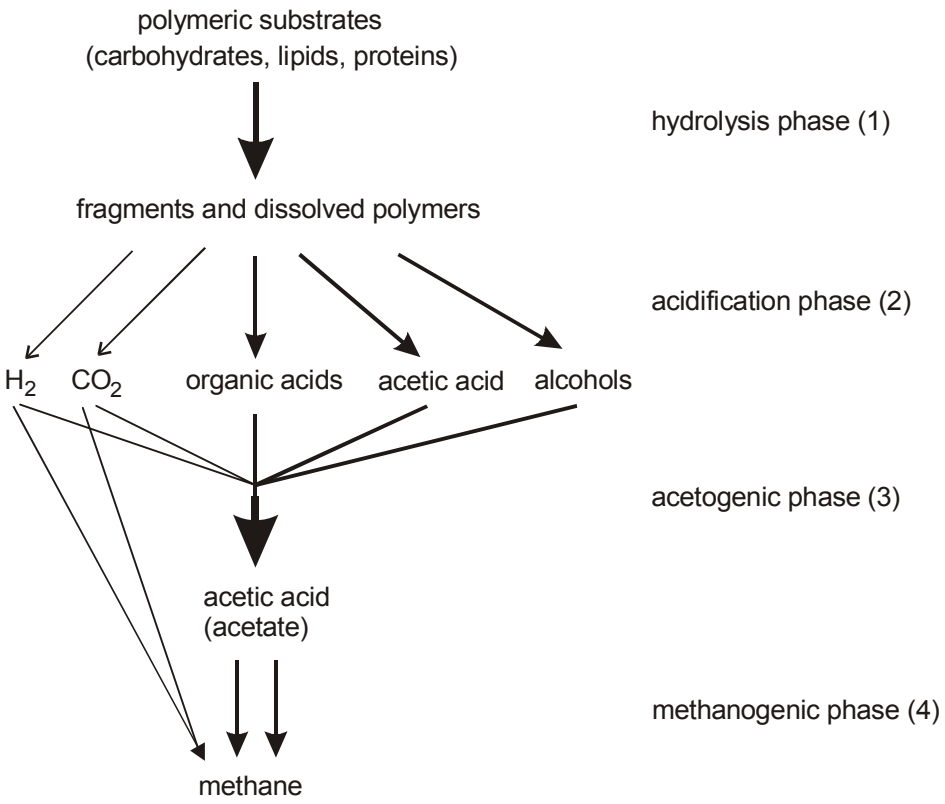


Figure 3: The anaerobic degradation in four steps (according to MUDRACK/KUNST, 1988, modified)

1. During the first step, the **hydrolysis phase**, the highly molecular often undissolved materials (polymers) are decomposed by enzymes in dissolved fragments.

2. In the second step, **the acidification phase**, short-chained organic acids (e.g. butyric acid, propionic acid, acetic acid) alcohols, H_2 and Co_2. are built by the digesting bacteria.

3. The following step is named **the acetogenic phase**, because the acetogenic bacteria are mainly building acetic acid from the previously built organic acids and alcohols.

4. This acetic acid and to a small extent also H_2 and CO_2 are converted in the fourth step, **the methanogenic phase**, of the methane-forming bacteria to CH_4.

Hydrolysis and acidification
Hydrolysis and acidification are carried out by different facultative and obligate anaerobic bacteria. During anaerobic degradation organic material up to energy-poor inorganic end products (CO_2, H_2O) are respired through oxidation. The hydrogen split from the substrate is

finally transmitted over the respiration chain to the oxygen. Hereby the big redox potential between hydrogen and oxygen enables a huge energy yield for the aerobic bacteria.

No oxygen is available for the anaerobic degradation. The involved bacteria must split the organic matter and transform the fission products in such a way that they can absorb the hydrogen. Thus the energy is only released through the redox reactions between organic matters. Hereby the energy yield is essentially lower than during the complete oxidation with oxygen. This anaerobic metabolism is called digestion. The name of the digestion is destined by the major product. If, e.g., lactic acid is mainly formed, digestion is classified as lactic acid digestion.

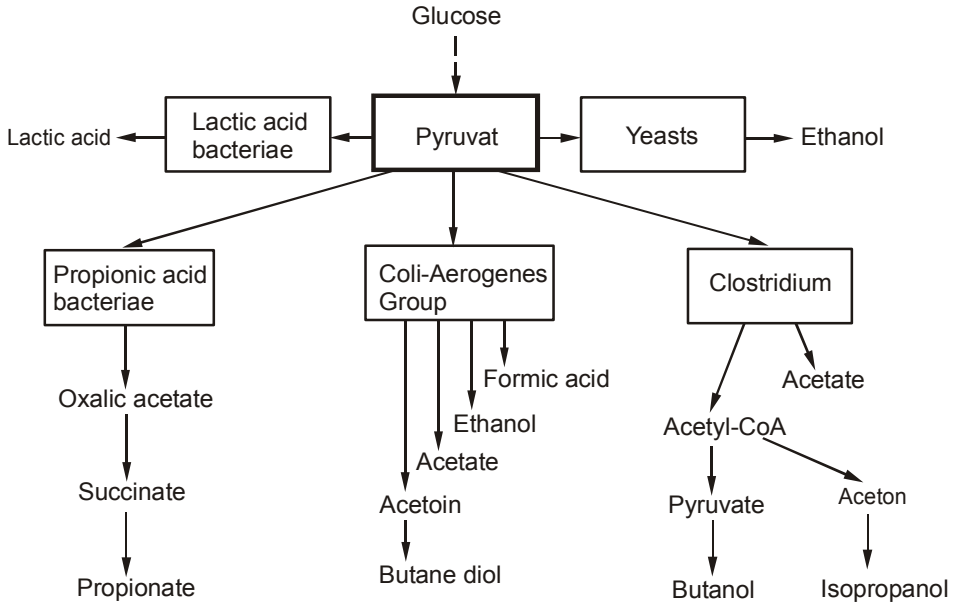


Figure 4: Systematics of digestion reactions (HARTMANN, 1989)

Many of the microorganisms which are able to live in anaerobic conditions cause a mixed digestion, whereby different alcohols and organic acids are eliminated. As in aerobic degradation the pyruvate (the pyruvic acid) takes a central position in the biochemical transactions (HARTMANN, 1989). The flow-chart in figure 4 shows the metabolic products which can be built during anaerobic degradation of the carbohydrates. The end products of digestion are mostly very short-chained organic carbohydrate compounds rich in energy.

Acetogenic and methanogenic phase

During the acetogenic phase digestion products, which were preliminarily built, are used energetically of bacteria which are specialized for this work. A very important aspect, hereby, is, that the transformation under standard conditions (concentration of the reaction partner 1 mol/l, temperature 25 °C, pressure 101.3 kPa) do not deliver energy but consume energy. The acetogenic bacteria can only use the metabolic step energetically if the standard conditions are deviating. In this case the concentration of the reaction product hydrogen plays the decisive role. The reaction process runs only in an exergonic mode at a

low hydrogen concentration. Therefore are the acetogenic bacteria dependent on a constant consumption of the self-built product hydrogen and its low concentration (NÄVEKE, 1997).

Responsible for this are the methane bacteria which transform in the fourth step of the anaerobic degradation the hydrogen to CO_2, whereby methane and water is generated. Figure 5 shows the change of the free energy of the acetic acid from butyrate and methane formation from hydrogen and CO_2 in dependence on the hydrogen concentration in the reaction medium.

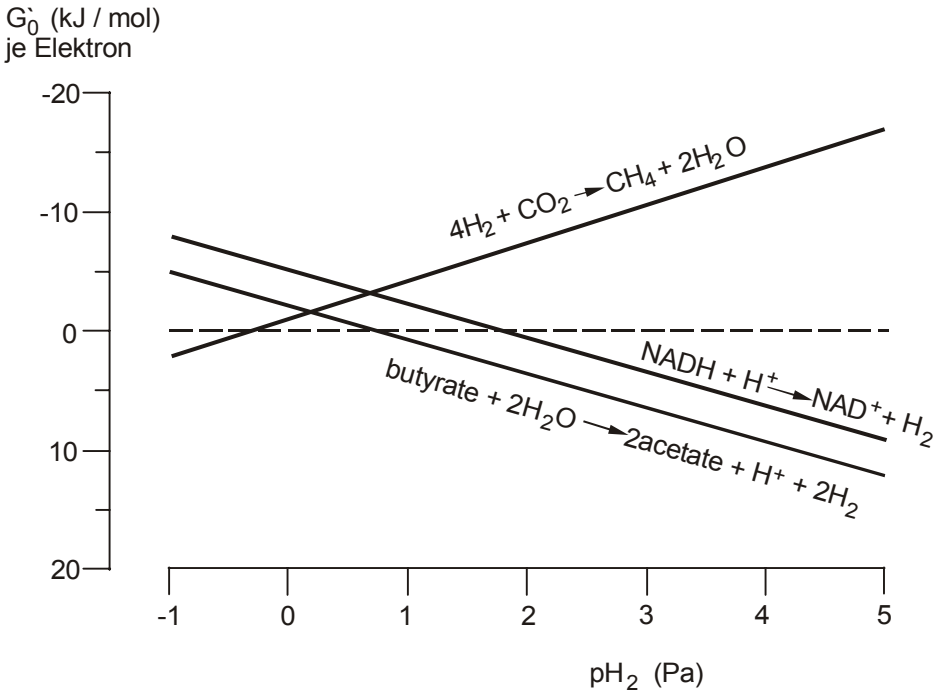


Figure 5: Free energy resulting from acetic acid and methane formation (NÄVEKE, 1997, modified)

Figure 3-5 shows that the acetic acid formation from butyrate runs exergonically only with a very low hydrogen partial pressure under 1 Pa and with an increasing hydrogen concentration becomes more and more endergonic. Contrary to this becomes the methane formation from H_2 and CO_2 more and more exergonic with an increasing hydrogen partial pressure. There is, however, a concentration range where both reactions deliver energy. Therefore acetate and methane formation can only run together, the involved organisms depend on each other. They are building a biocoenosis, a symbiosis for mutual profit. They are living in close neighbourhood, mostly in agglomerates, where they exist mixed up in direct cell contact. The transformation of hydrogen from a hydrogen forming to a hydrogen consuming bacteria group is called "Interspecies Hydrogen Transfer" (NÄVEKE, 1997).

The methane bacteria are substrate specialists, e.g. they can only use a small amount of organic material types for methane formation and energy yield. The most important energy delivering reactions are named in the following (WINTER, 1985).

- Nearly all species

$4\ H_2 + CO_2 \rightarrow CH_4 + 2\ H_2O$ $\quad \Delta G'_0 = -135{,}6\ [kJ / CH_4]$

- Many species

$4\ HCOOH \rightarrow CH_4 + 3\ CO_2 + 2\ H_2O$ $\quad \Delta G'_0 = -130{,}7\ [kJ / CH_4]$

- Few species

$4\ CH_3OH \rightarrow 3\ CH_4 + 3\ CO_2 + 2\ H_2O$ $\quad \Delta G'_0 = -103{,}5\ [kJ / CH_4]$

- Two species

$CH_3COOH \rightarrow CH_4 + CO_2$ $\quad \Delta G'_0 = -31{,}0\ [kJ / CH_4]$

It becomes apparent that methane formation from H_2 and CO_2 is from an energetic point of view essentially more favourable than the conversion of acetic acid which can only be processed by very few specialists. Despite of this fact, approximately 72 % of the produced methane in the biogas is coming from the acetic acid and only 28 % from CO_2 (HARTMANN 1989). This must be so, as the complete anaerobic decomposition can only be realized via the acetate formation. The methane bacteria are not able to use the digestion end products of the acidifying bacteria as substrate. Only formic acid and acetic acid can be used by some of the species, methanol only by very few species. Therefore methane bacteria using acetate deserve special importance in sewage sludge.

1.5 Growth of the anaerobic microorganisms

The growth reactions for the synthesis of new cell material are catalyzed by enzymes, also during the growth of organisms. If one demonstrates the growth rate in dependence on the substrate concentration a similar process is realized as with the MICHAELIS-MENTEN-relation. The growth rate μ rises with the increasing substrate concentration until the maximal growth velocity μ_{max} is reached. Figure 6 shows the growth parameter of two acetate using methane bacteria.

From figure 3-6 can be learnt that the species methanothrix, e.g. grows with a maximal velocity already at relatively low substrate concentrations. All the same, under optimal conditions the bacteria do not split up before 8 days approximately. Other sources do also quote generation periods of several days for the methane bacteria (MUDRACK/KUNST, 1988; BÖHNKE et al., 1993). These values acquired under laboratory tests can only be transferred in practical operation with distinct surcharges. As the environmental conditions in technical application, e.g. in a digestion tank, always deviate in one or the other parameter from the optimal conditions.

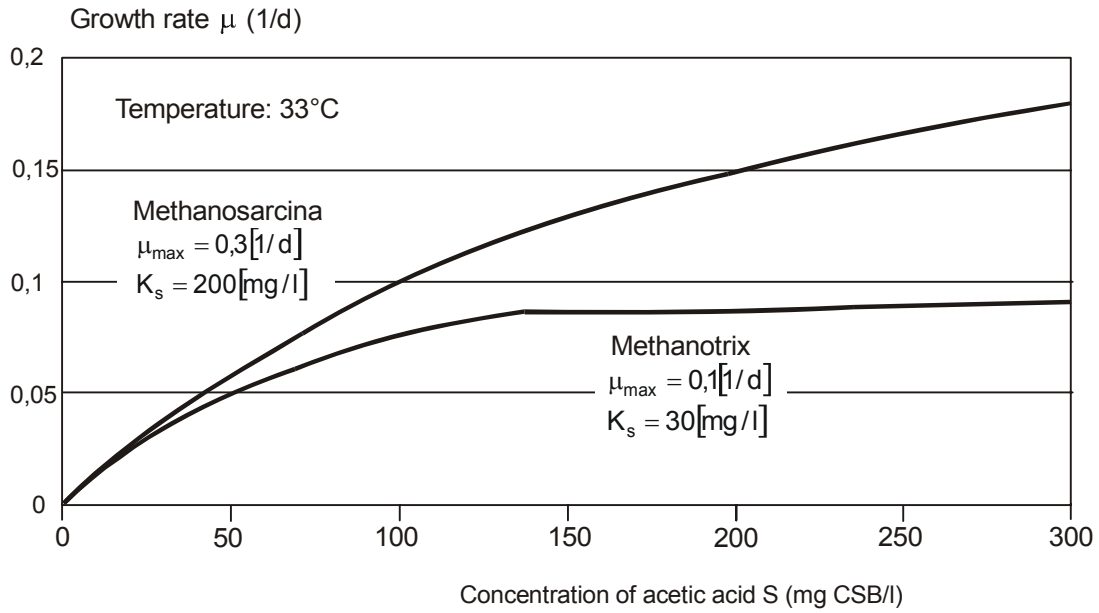


Figure 6: Growth parameter of methanosarcina and methanothrix (GUJER/ZEHNDER, 1983

All, in so far known, acetogenic bacteria are growing very slowly. Their generation periods are in the same dimension as those of the methane bacteria. A butyric acid using acetogenic bacteria for example had in the laboratory a generation period of 84 hours (MUDRACK/KUNST, 1988). GUJER/ZEHNDER (1983) also state maximal growth rates for different acetogenic bacteria. The μ_{max} values are between 0.1 and 0.5 per day, i.e. under optimal conditions are the generation periods lying between two and ten days.

The generation period of the microorganisms is decisive for the dimensioning of the digestion tanks or towers. As the reactors are usually passed continuously, the conditions of the growth of organisms shall be considered here in a continuous culture. The system is relatively simple. A constant liquid flow passes a container (figure 7).

If the flow rate q is divided through the volume V the dilution rate D is achieved:

D = q/V = dilution rate [1/h]

D states how often per hour the volume is exchanged. If the bacteria in the reactor would not grow during the first operation of the fermenter, they would be washed out with the washing out rate:

$D \cdot X = dX/dt$

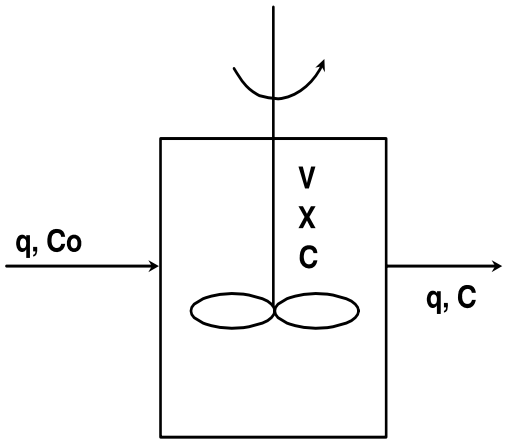
So the bacteria density in the reactor would decrease exponentially:

$X = X_D \cdot e^{-D.t}$

If the bacteria are growing with the growth rate μ [1/h] the increase is also exponential:

$\mu \cdot X = dX/dt$
$X = X_D \cdot e^{\mu \cdot t}$

Hence, the change of the bacteria density in the reactor is determined by the growth rate (μ ▪ X) minus the wash out rate (D ▪ X).



C_0	=	substrate concentration inflow	[g/l]	
C	=	substrate concentration off-flow	[g/l]	
q	=	Inflow rate	[l/h]	
X	=	concentration of organisms in the reactor		[g/l]
V	=	reactor volume	[l]	

Figure 7: Flow chart of a continuously charged fermenter

If the growth rate μ and the dilution rate D are equal the loss of biomass is balanced through the wash out of the biomass growth by reproduction. The system is in a flow balance. If the substrate is enlarged by increasing the supply quantity the system can regulate itself up to certain limits. As the growth rate μ, like shown in figure 3-6, is dependent on the substrate concentration, the growth of the organisms will be increased and a new flow balance is achieved. Not before the growth rate goes toward μ_{max} , i.e. a further increase of the substrate supply does not induce any increase of the growth, the final stage of self-regulation is achieved. The increased wash out cannot be balanced anymore by an increase of reproduction, i.e. the bacteria concentration in the reactor decreases rapidly and simultaneously increases the substrate concentration in the discharge (BÖHNKE et al., 1993, SCHLEGEL. 1989, MUDRACK/KUNST, 1988).

So that a flow balance arises, the growth rate and dilution rate, as mentioned above, must be equal. Hence small growth rates of organisms result in small dilution rates respectively high flow rates. In the waste water technology the flow rate is referred to as hydraulic retention time.

Considering a digestion reactor idealised as a continuously flown-through fermenter, the above mentioned correlations are valid. As the generation periods of the acetogenic and methanogenic bacteria are very long, the growth rates are low and the flow rates correspondingly higher. Regarding exemplarily the growth rate of the methane bacterium methanothrix (figure 3-6), then nearly a maximal growth rate is achieved at a substrate concentration of 300 mg/l (μ = 0.1 per day). Under otherwise normal conditions the bacterium reproduces itself by cell division approximately every 10 days. In order that these bacteria can enrich themselves in the digestion reactor a retention time of distinctly over 10 days is necessary, as the conditions in the digestion reactor usually deviate from the optimal conditions in the laboratory.

2 Factors influencing the anaerobic biological digestion processes

When the microbiological basics were explained it became clear that some reactions can run only under certain boundary conditions. The whole anaerobic digestion process can be influenced by very different factors. It can be differentiated basically according to influences

- which are caused by the effects on the enzymatic system of the participating organisms (temperature, pH value, toxic materials etc.),
- which are determined by the reactor kinetics (mixing, retention time etc.),
- which are caused by the composition of the substrate.

Most of the essential influencing factors are explained in this chapter as they are of decisive importance if anaerobic biological processes shall be applied in technical processes.

2.1 Temperature

The influence of the temperature on biochemical reactions is determined by two effects which are overlaying themselves. According to the principles of thermodynamics an exponential increase of velocity is achieved at rising temperatures. This is also valid for reactions catalyzed by enzymes, however, only up to an enzyme specific optimal temperature value. If this value is surpassed, the second effect becomes active. The linkages within the enzyme are getting looser, for the moment changes the structure reversibly, at a further temperature increase irreversibly. A denaturation of the enzymes takes place. As a result the reaction stops (HARTMANN, 1989). Each organism species has a temperature optimum where the maximal material transformation is achieved.

Two temperature ranges turned out to be optimal in the anaerobic biological treatment of waste water and sewage sludges:

- the mesophile range (33 °C to 37 °C) and
- the thermophile range (50 °C to 65 °C).

The acidifying bacteria are insensible and flexible regarding their ambient temperature (BÖHNKE et al. 1993). Figure 8 shows the optimal temperature at the acidification of glucose.

It becomes apparent that higher conversion rates are achieved in a thermophile optimum than in the mesophile range. In return the mesophile temperature optimum is wider and thus not so sensible against temperature fluctuations. This is not only valid for the acidifying but also for the methanogenic bacteria. As most of the known methane bacteria are allocated to the mesophile temperature range, the mesophile operation of a digestion reactor is more robust and stable than the thermophilic. Temperature fluctuations and substrate compositions resulting from operational conditions can be handled much better by a mixed population with a wide diversity of the species and a wider temperature optimum.

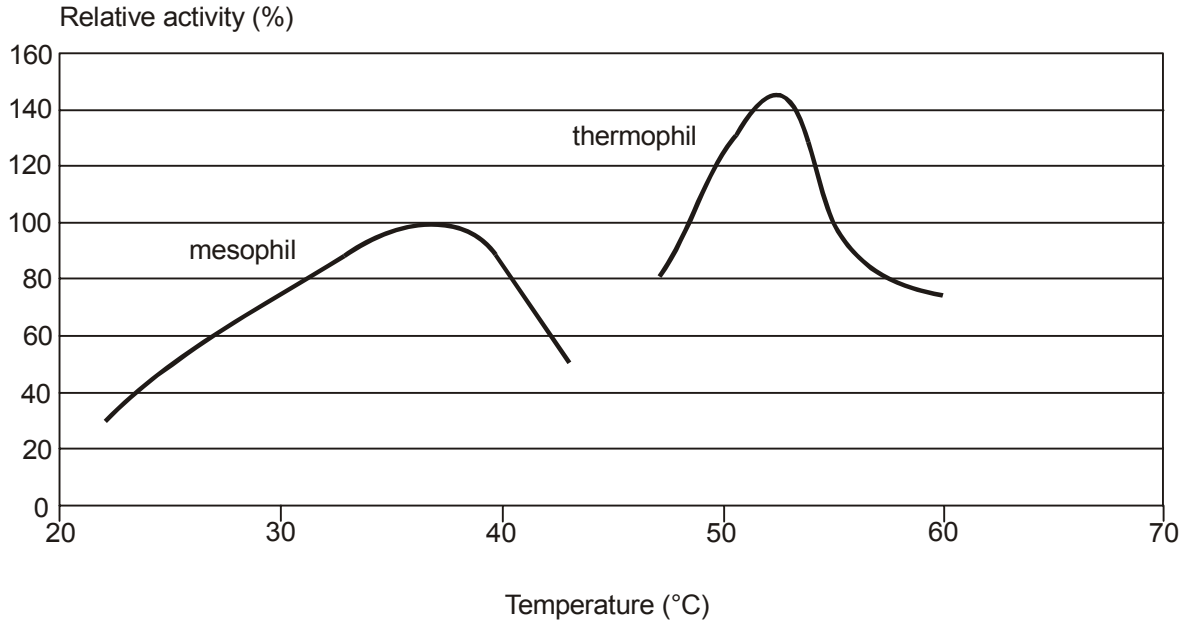


Figure 8: Relative acidification rate of the acid bacteria at acidification of glucose dependent on the temperature (ZOETEMEYER et al. 1982, from BÖHNKE et al. 1993)

2.2 pH value

Each enzymatic reaction has a more or less wide and distinct pH optimum. Changes of the pH values on the one hand can change the dissociation of the functional groups of the enzyme, on the other hand the charges at the substrate or product can be influenced, too (HARTMANN, 1989). Both effects have consequences on the velocity of enzyme-catalyzed biochemical reactions. This is valid for both the catabolism and the anabolism, i.e. the growth of microorganisms.

In the literature the tolerance range of the anaerobe biocoenosis is generally stated from pH = 6.8 to pH = 7.5 (KAPP, 1984). In one-step, mesophile digestion tanks for the treatment of municipal sewage sludges a pH value in a slightly alkaline range usually appears. Only with badly puffered sludges or other substrates the organic acid formation can decrease the pH value more strongly and therefore cause an inhibition of the methane bacteria. As a counter measure the pH value must be increased, e.g, by adding lime.

4.3 Substrate composition

The substrate serves as nutrition source for the microorganisms, from which they gain the energy necessary to maintain their life functions and the components for the reproduction of new cell material, i.e. for their growth. In order to achieve a maximal substrate reproduction for the organisms, not only the ambient boundary conditions must be appropriate (temperature, pH value etc.) but also the composition of the substrate. A lack of vital materials as carbon, nitrogen, phosphorous and trace elements is not acceptable. Therefore certain demands for the composition of the substrates do exist. Sewage sludges from municipal sewage sludge plants or biowastes usually have a very balanced nutrient ratio and rarely cause any problems. This may be contradictory, for instance, if extremely mono-composed organic substrates from industry shall be anaerobically treated. In the course of degradation few materials can be consumed to an extend that they become limiting factors (BÖHNKE et al. 1993).

The composition of the substrate has also a decisive influence on the biocoenosis. A lot of fatty substances contained in a substrate will induce a remarkable rise of bacteria during the anaerobic biocoenosis, which can break down the fats and decompose them. To a certain extent the biocoenosis can respond to changes in the substrate composition. This, however, is only valid if sufficient time is given for adaptation.

2.3.1 Gas structure

A further influence on the substrate composition results from the structure of the biogas. The portion of CH_4 and CO_2 in the biogas can be determined theoretically for any organic material, if the complete anaerobic conversion is assumed. This recognized BUSWELL and MUELLER already in 1952 and drafted the generally valid reaction equation (ROEDIGER et al., 1990):

$$C_cH_hO_o + (c - {}^h/_4 \cdot - {}^o/_2)\ H_2O \quad \rightarrow \quad ({}^c/_2 + {}^h/_8 - {}^o/_4) \cdot CH_4 + ({}^c/_2 - {}^h/_8 + {}^o/_4) \cdot CO_2$$

BOYLE expanded this equation 1976 by the portions of nitrogen and sulphur in the organic matter. ROEDIGER (1990) finally added the phosphorus, so that the complete anaerobic conversion of an organic matter can be described with the following formula:

$$C_cH_hO_oN_nS_sP_p + (c - {}^h/_4 \cdot - {}^o/_2 + {}^{7n}/_4 + {}^s/_2 + {}^{7p}/_4)\ H_2O \quad \rightarrow$$

$$({}^c/_2 + {}^h/_8 - {}^o/_4 - {}^{3n}/_8 - {}^s/_4 + {}^{5p}/_8) \cdot CH_4 + ({}^c/_2 - {}^h/_8 + {}^o/_4 - {}^{5n}/_8 + {}^s/_4 + {}^{3p}/_8) \cdot CO_2$$
$$+ n \cdot NH_4^+ + s \cdot H_2S + (n - p) \cdot HCO_3^- + p \cdot H_2PO_4^-$$

If this formula is used for the degradation of an organic cell substance with an average structure:

$$C_{106}H_{180}O_{45}N_{16}P + 68{,}25\ H_2O \quad \rightarrow \quad 58{,}875\ CH_4 + 32{,}125\ CO_2 + 16\ NH_4^+ + 15\ HCO_3^- + H_2PO_4^-$$

is valid.

This structure has per kilogram decomposed substance (ROEDIGER et al., 1990):

- a water consumption of 0.51 kg
- a gas volume of 0.84 m^3
- a methane portion of 64.7 vol.-%

For the basic substance carbohydrates, fats and proteins, on which all the organic matters can be traced back, follows (BÖHNKE et al., 1993, HARTMANN, 1989, ROEDIGER et al., 1990):

- Carbohydrates (general form):

  $(C_6H_{10}O_5)m + m\ H_2O \rightarrow 3m\ CH_4 + 3m\ CO_2$

- Fats (example tristearin):

  $C_3H_5(C_{17}H_{35}COO)_3 + 26.5\ H_2O \rightarrow 40.75\ CH_4 + 16.25\ CO_2$

- Protein (example):

  $CH_2NH_2COOH + 1.5\ H_2O \rightarrow 0.75\ CH_4 + 0.25\ CO_2 + NH_4^+ + HCO_3^-$

Table 2 contains details about the composition of biogas and the specific gas quantities at the degradation of carbohydrates, fats and proteins (mean values from many stoichiometric calculations and practice trials, ROEDIGER et al., 1990).

Table 2: Composition of biogas and specific gas quantities

	Methane CH_4 in [Vol - %]	Carbon dioxide CO_2 in [Vol - %]	Specific gas quantities in [$Nm^3/kg\ odm_{rounded}$
Carbon hydrates	50	50	0.79
Fats	68	32	1.27
Proteins	71	29	0.70

Basically valid is: the more reduced an organic matter is, i.e. the higher the ratio of carbon and oxygen in the substrate, the higher is the methane content in the biogas (HARTMANN, 1989).

2.3.2 Solid matter content

The solid material content, usually quoted as dry residual DR or dry matter content dm in % or g/l, has two-folded influences on the degradation in an anaerobic reactor. With an increasing solid matter content of the substrate

- the substrate becomes more consistent and the flow behaviour worse,
- the volumetric loading rate of the reactor rises.

If the substrate gets so consistent that no sufficient mixing in the reactor is possible, the bacteria will be insufficiently supplied with the substrate. As a consequence the solid matter degradation and the specific gas production decreases. The same effects also appear when the organic load exceeds a certain value, on account of the substrate amount being too high to be fully utilised by the bacteria.

According to researches by KAPP (1984) and INDEN (1977), solid matter contents of up to 10 % in normal digestion reactors have no significant influence on the specific gas production. Not until higher solid matter contents are achieved, decreases the specific gas production, as shown in figure 9.

2.4 Inhibiting substances and toxic substances

Metabolic activity and the growth of microorganisms can be slowed down or totally suppressed by a series of substances. One differ substances which

- harm the cell boundary layers or the structure of microorganisms (e.g. detergents)
- harm the enzymes of the basic metabolism (e.g. heavy metals)

The harmful effect of these substances is principally dependent on the concentration (SCHLEGEL, 1985). That means, that the existence of a substance must not actually lead to an inhibition or destruction. Not before a certain concentration level is reached starts the destruction.

A short view is given in the following about the toxic substances especially important for the anaerobic processes.

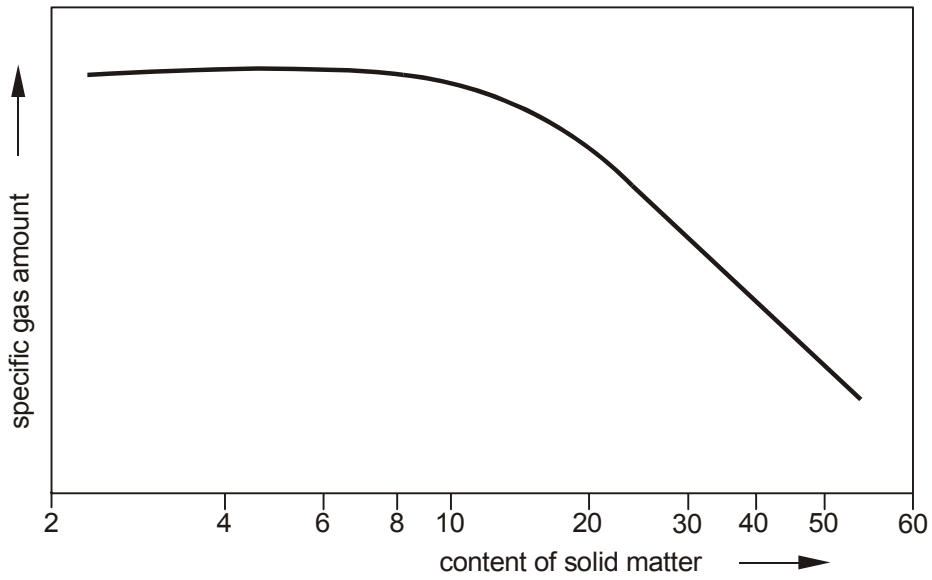


Figure 9: Specific gas generation dependent on the content of solid matter in the digestion reactor (BÖHNKE et al., 1993)

2.4.1 Oxygen

A great part of the acidifying bacteria can be counted among the facultatively anaerobic organisms, which can grow in the absence and presence of oxygen. Therefore plays the presence of small amounts of oxygen no role during the first two steps of the anaerobic degradation, the hydrolysis and acidification. On the contrary, at some two-step processes oxygen is purposefully added in the first step in order to achieve a quicker and more effective hydrolysis and acidification.

The methane bacteria belong to the obligatory anaerobic organisms for which oxygen acts toxic. Therefore, the contact with oxygen must be avoided as far as possible during the one-step processes, where all four steps of anaerobic degradation are proceeding in one reactor. As experience shows, a short oxygen contact, e.g. through opening of the reactor lid, causes no noticeable destruction of the biocoenosis in the reactor.

2.4.2 Sulphuric compositions

When organic matter is degraded the containing sulphurous compositions are also reduced and hydrogen sulphide (H_2S) is formed. All the same the sulphate (SO_4^{2-}), existing in a lot of waste waters, is reduced to hydrogen sulphide under anaerobic conditions. Dependent on the pH value dissociates the produced hydrogen sulphide in the liquid and a balance between the dissociated and not dissociated form appears:

$$H_2S + H_2O \quad \leftrightarrow \quad HS^- + H_3O^+$$

Toxically effective hereby is only the not dissociated hydrogen sulphide. At a pH = 6.5 over 70 % of the total sulphide is available as H_2S, at pH = 7.5 just approximately 25 %, i.e. the lower the pH value in the reactor the higher is the toxic potential through H_2S (BÖHNKE et al., 1993).

It is not only the toxic influence of the H_2S on the methane bacteria that lowers the methane formation in the reactor. At increased sulphurous contents in the substrate the sulphate-reduced bacteria, the so-called desulphurates can increase more strongly and compete with the methane bacteria. Like the methane bacteria the desulphurates can also utilise the substrates hydrogen and acetic acid, and thus undergo a symbiosis with the acetogenic bacteria. The sulphate reduction with hydrogen and acetic acid runs according to the following reaction equation:

$$SO_4^{2-} + 4\ H_2 \quad \rightarrow \quad H_2S + 2H_2O + 2\ OH^-$$
$$SO_4^{2-} + CH_3COOH \quad \rightarrow \quad H_2S + 2HCO_3^-$$

In order to be able to assess whether an increased desulphuration is going on in the reactor and a toxic activity through H_2S, the diagram (figure 4-3), traced back on the research work of KROISS (1986), can be used. Dependent on the ratio of degradable COD (COD_{red}) to reducible sulphur (S_{red}) the inhibition respectively the toxicity through H_2S can be read off.

Moreover figure 10 shows that the inhibition is also dependent on the pH value. Thus the danger of a H_2S inhibition respectively a toxicity of the methane bacteria is so much the minor the less the sulphurous compositions are in the substrate in relation to the degradable carbon compositions and the higher the pH value. KROISS recommends for the planning the following evaluation (KROISS, 1986):

- $COD_{red} / S_{red} \geq 100$ — No problems through H_2S can be expected
- $15 < CXB_{red} / S_{red} < 100$ — Anaerobic treatment is possible, but H_2S problems must be considered
- $COD_{red} / S_{red} < 15$ — Methane production is only possible in special cases

The simplest way to detect a H_2S-toxicity is to monitor the H_2S contents in the biogas. A H_2S content of more than 2 % in the gas can start a beginning inhibition.

A part of the arising hydrogen sulphide is removed from the liquid phase by reacting with heavy metals, especially iron. Metal sulphides of low solubility are formed which fall out and are finally discharged with the solid sludge fraction from the reactor. As an example ferrous hydroxide can react with hydrogen sulphide (ATV, 1996-1):

$$Fe(OH)_2 + H_2S \rightarrow FeS + 2\,H_2O$$

The addition of ferric salts, e.g. ferrous chlorides, in the raw substrate or in the digestion reactor, is therefore also a measure to reduce the H_2S content in the biogas and to avoid the danger of a H_2S toxicity of the methane bacteria.

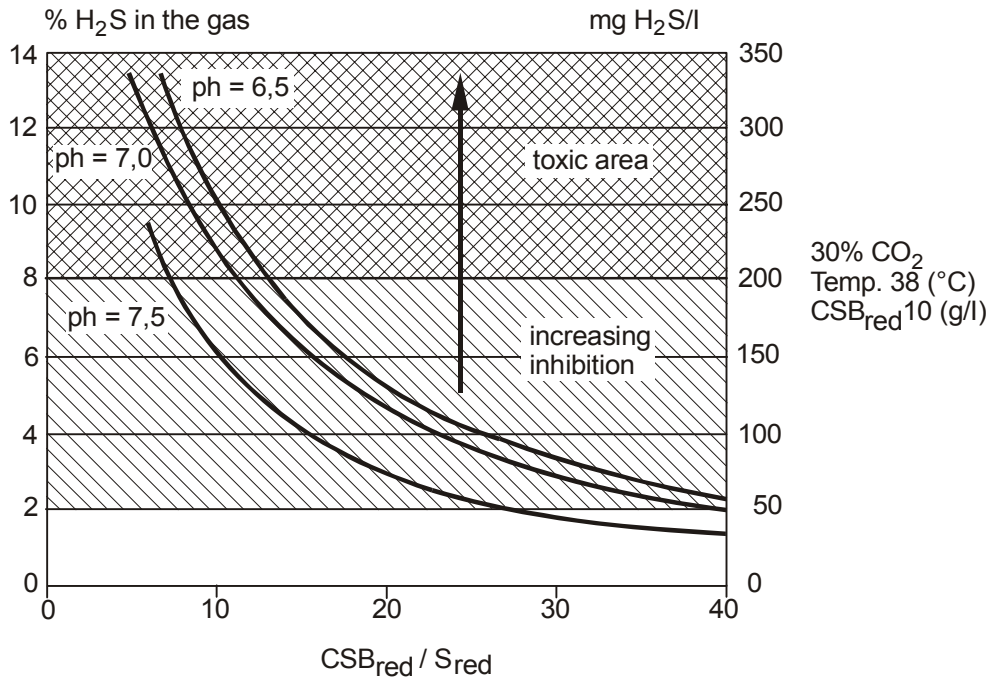


Figure 10: **H_2S concentration in the gaseous and liquid phase dependent on the COD_{red}/S_{red} ratio at different pH values according to KROISS (1986)**

2.4.3 Organic acids

If organic acids are producing themselves in the anaerobic reactor, the following reasons may be relevant:

- A surplus of organic acids is incorporated with the substrate that cannot be fast enough degraded by the acetogenic bacteria.
- The acetogenic and/or methanogenic bacteria in the reactor are inhibited.

High concentrations of organic acids have an inhibitory effect on the methane formers, whereby the not dissociated portions are predominantly toxic. The balance between dissociated and not dissociated portions depends again very strongly on the pH value. As could already be seen with hydrogenic sulphide, the toxically effective, not dissociate portion increases with the decreasing pH value. Figure 11 shows the inhibition of the methane formation dependent on the acetic acid concentration and the pH value.

From figure 11 can be learnt that acetic acid concentrations up to 1000 mg/l do not create inhibitions in a neutral environment. Increases the concentration of organic acids onto more than 2000 mg/l, the pH value can decrease dependent on the buffering capacity. The consequence is an increase of the toxically effective not dissociated organic acids, with a further inhibition of the methane production. As a consequence the organic acids will increase and thus a relatively rapid turnover of the digestion process in an acid fermentation will be the result (ATV, 1996-1).

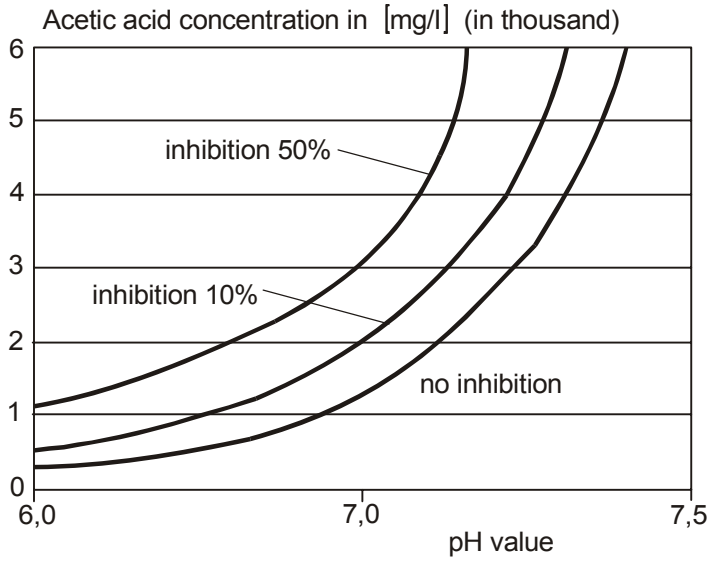


Figure 11: Inhibition of methane formation dependent on the acetic acid concentration and the pH value (KROISS, 1986)

2.4.4 Nitrate, ammonium and ammonia

The methane formation is basically inhibited at the presence of nitrate. Nitrate can occur in certain substrates, which shall be anaerobically treated (e.g. excess sludges from nitrifying sewage plants). Under anaerobic conditions, however, the nitrate will be denitrified very quickly by the facultative bacteria and the inhibition of the methane formation will be stopped.

Ammonium respectively ammoniac is produced by complete degradation of an organic substrate that contains nitrogen. If substrates, containing a lot of proteins, are treated in anaerobic processes or if process waters containing nitrogen are used, e. g. for the slurrying of substrates, high ammonium concentrations can arise in an anaerobic reactor. Depending on the pH value and the temperature a chemical balance is also realised with ammonium between the dissociated ammonium and the not dissociated ammoniac:

$$NH_3 + H_2O \quad \leftrightarrow \quad NH_4^+ + OH^-$$

Like with the hydrogen sulphide and the organic acids the not dissociated portion, i.e. the ammoniac, acts toxic. Figure 12 shows admissible ammoniac concentrations dependent on the pH value at different temperatures. An inhibition starts not before ammonium concentrations of more than 3500 mg/l are reached at a usual mesophile temperature of 38 °C and a pH value of 7.0. With a pH value of 7.5 starts the inhibition already at 1000 mg/l, because the ammoniac portion increases with an increasing pH value.

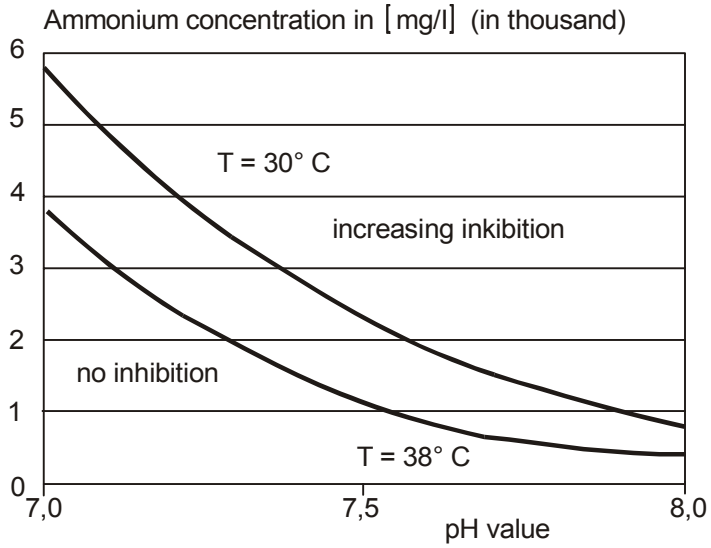


Figure 12: Admissible NH_4-N concentration dependent on the pH value and different temperatures in the reactor (KROISS), 1986

2.4.5 Heavy metals

Depending on their origin sewage sludges and other biowastes can be loaded with strongly varying heavy metals. The toxicity of heavy metals depends on their concentration in the liquid phase. As a rule the heavy metal ions act on certain enzymes and inhibit by this action the metabolism of the bacteria.

As already explained in chapter 2.4.2 heavy metals are forming with hydrogen sulphide very heavily soluble metal sulphides, which precipitate as solid matter and thus are deprived of the liquid phase.

In literature review BÖHNKE et al. (1993) quotes inhibiting or toxic heavy metal concentrations for the anaerobic degradation process. The given values have a relatively high fluctuation range and can only be taken as approximate values, as bacteria are able to adapt themselves to certain heavy metal contents (adaptation) thus becoming less sensible and being able to tolerate higher concentrations. The results of BÖHNKE et al. (1993) are summarised in table 3.

Table 3: Damaging effects of heavy metals (from BOHNKE et al., 1993)

Heavy metals	Inhibitive effects at concentration in [mg/l]	Toxic effects at concentration in [mg/l]
Copper (Cu)	40 - 250	170 - 300
Cadmium	150 - 600	20 - 600
Zinc	150 - 600	250 - 600
Nickel	10 - 300	30 - 1000
Lead	300 - 340	340
Chromium III (Cr)	120 - 300	260 - 500
Chromium VI (Cr)	100 - 110	200 - 420

3 Process for the anaerobic sewage sludge and biowaste treatment

3.1 Sewage sludge digestion

3.1.1 Historic development and targets of the anaerobic treatment of sewage sludge

The anaerobic treatment of waste waters and sewage sludges has a long tradition. The basic principle of the anaerobic purification was already known by the Sumerians (BÖHNKE et al., 1993). The technical application of the anaerobic waste water and sewage sludge treatment was developed in Europe by the end of the 19th century. In 1895 invented the Englishman CAMERON the so-called "septic tank", a closed container through which waste water run. The sediments of the waste water, the solid matter (the sewage sludge) dropped on the floor and converted under anaerobic conditions (in a period of up to one year).

With the beginning of the 20th century the scientists concluded that in order to avoid odour problems the sludge treatment should be separated under exclusion of air from the waste water treatment. This conclusion led to the development of the Emscher tank, the first technical construction for waste water with a separated digestion chamber. In the Emscher tank runs the waste water through a channel with steep funnel-shaped walls with an outlet at the bottom. The settling sludge glides from the steep walls and sinks down in the subjacent digestion chamber, where it can putrefy for 60 days or longer under exclusion of air. The generated digestion gas has been completely collected already in 1921 at the sewage sludge plant in Essen-Rellinghausen and sold to the gas works.

Further developments showed the favourable influence of warm temperatures on the digestion process, which finally led to a purposeful heating of the digestion chambers. A further intensive investment of the digestion process was the turning over of the content of the digestion chamber. Already in 1925 heated and steadily turned containers with a discharge for the digestion gas were built.

ROEDIGER (1967) named the most important measures for a efective construction of a digestion tank and for its operation which are valid until today:

- if possible, a continuous charging of the digestion chamber,
- inoculation of the raw sludge to be charged,
- heating of the digestion chamber,
- mixing and turning of the digestion chamber content,
- surface scum destruction,
- digested sludge discharge and surface scum discharge,
- biogas storage, treatment and utilisation.

Besides the first target of sewage sludge treatment, to change the raw sludge in such a way that it is nearly free of odours and can be supplied to a proper disposal, further targets exist which shall be achieved with the anaerobic sludge stabilisation.:

- reduction of the solid mass of sludge
- improvement of dewatering
- reduction of pathogens
- increase of disposal safety
- generation of biogas

In order to achieve these targets different processes are used today in sewage plants, which are described in the following.

3.1.2 Process of sewage sludge digestion

As already said in chapter 2 approximately 60 % of the raw sludges arising in German sewage sludge plants are treated anaerobically. The standard process is the one-step mesophile sludge digestion. Other processes are basically possible as figure 13 shows:

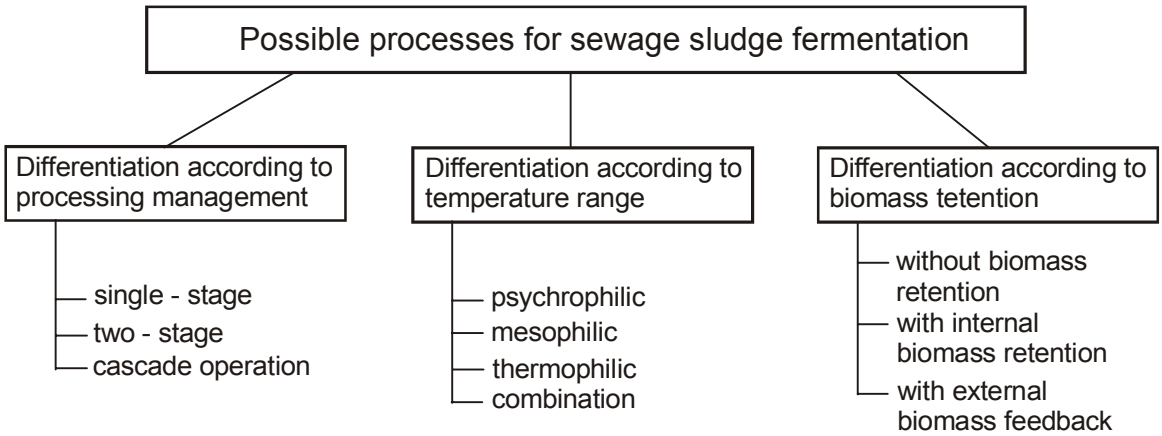


Figure 13: Possible processes for sewage sludge fermentation

3.1.2.1 Process management

The four steps of anaerobic degradation are running simultaneously in all one-step processes. Contrary to this, the hydrolysis and acidification of the two-step processes takes place in the first and the acetogenic and methanogenic phase in the second container. The two-step processes in the range of sewage sludge digestion could not be established, as the sewage sludge, having a complex composition, can be hydrolysed and acidified very difficultly and thus too slowly. Furthermore the raw sludge usually contains some methane bacteria from human faecals or from the sewerage and so methanisation can already start in the first phase. A strict separation of the both steps, as being sensible and advantageous in the anaerobic treatment of highly loaded industrial waste waters, cannot be achieved in sewage sludge digestion.

In some sewage plants, which have two digestion tanks, are the tanks successively flown through, i.e. they are run as cascade. Cascade plants may not be mistaken with two-step plants as in both containers the full anaerobic degradation runs until methane formation. The second container is charged only with somewhat less organic matter because most of the material is degraded in the preceding container. Cascade plants are known for high process stability. Short circuit currents as cannot be totally excluded with continuously charged, fully mixed through systems, can thus be avoided to the greatest possible extent. This can have a positive effect on the germ load and the stabilising degree of the digested sludge.

3.1.2.2 Temperature range

The digestion of sewage sludges can be achieved in a temperature range of 4 °C and 70 °C. Depending on which temperature the participating microorganisms achieve their maximal growth velocity, are they allocated to one of the three temperature ranges:

- psychrophilic (4 °C to approx. 20 °C)
- mesophilic (20 °C to approx. 42 °C)
- thermophilic (42 °C to approx. 70 °C)

The sewage sludge digestion in unheated digestion tanks or digestion chambers (Emscher tank) is classified as *psychrophilic* or *cold digestion*. In Germany this plays presently only a role in simple or small plants (e.g. small sewerages). In a predominant number of sewage plants, digestion is operated in a mesophilic range between 33 °C and 37 °C.
Compared with a fundamentially possible thermophilic operating mode the following advantages result with a mesophilic sludge digestion (BÖHNKE et al., 1993, ATV, 1996-1):

- a more stable and insensitive operation of the digestion tanks, as most of the methane bacteria can be allocated to the mesophile organisms (a higher variety of species) and are insensitive against temperature fluctuations
- compared with the thermophilic solution mesophilically operated digestion tanks need only half of the heat volume

- the mesophilic digested sludge smells less strongly and can be more easily dewatered
- no stricter requirements are necessary for the germ load in agricultural sewage sludge utilisation

Combined solutions are available for individual cases, whereby the sewage sludge is charged into a highly loaded thermophilic short digestion step (2 to 5 days retention time) and is subsequently end stabilised in a conventional mesophilic digestion with a retention time of about 15 days (MITSDÖRFER et al., 1991).

Thermophilically operated sewage sludge digestion plants are scarcely be found, as they have too many disadvantages compared with the mesophilic process. The advantage of a thermophilic operation contrary to the mesophilic system is listed in the following (WEILAND, 1997; BÖHNKE et al., 1993):

- a more rapid degradation of the organic matter
- tendency of a higher degree of degradation
- improved hygienisation
- higher specific gas production

A thermophilic operation for an anaerobic treatment of special industrial waste waters can be reasonable, it is, however, generally not recommended for sewage sludge treatment (BÖHNKE et al., 1993).

3.1.2.3 Biomass retention

The concentration of the active biomass in a system can be increased by the retention of the biomass respectively recirculation. The main advantage is the more rapid degradation that leads to considerably smaller reactor volumes compared with flush out reactors. The biomass retention in anaerobic reactors can be realised e.g. by the installation of carrier material (supporting media), on which the microorganisms can settle (immobilisation). The biomass retention is practiced e.g. in the anaerobic activated process. Hereby the solid matter from the discharge of the anaerobic reactor is separated and returned into the reactor. Both systems didn't become widely accepted in sewage sludge digestion. On the one side a clogging of the packed bed materials (e.g. through coarse or fibrous material in the raw sludge) may arise on the other side fails a biomass retention because of the bad settling properties of the digested sludge (e.g. through post generation of gas in the sedimentation tank). Simple flush out reactors are prevailing in anaerobic sewage sludge treatments, which, on account of the long generation periods of the acetogenic and methanogenic bacteria, must have a correspondingly high hydraulic retention time. Therefore the reactors have a relatively large volume.

3.1.3 Dimensioning and characteristic parameter of the one-step mesophilic sewage sludge digestion

3.1.3.1 Digestion period and volumetric loading rates

Despite of the wide distribution of the one-step mesophilic sewage sludge digestion up to now no generally valid dimensioning principles could be accomplished. Often used reference values for the dimensioning are:

- fermentation period or hydraulic retention time in days [d],
- the volumetric loading rate of the digestion reactor in [kg odm/m^3 ▪ d]
- the specific digestion tank volume per inhabitant equivalent [l/Inh)

Thus the raw sludge amount related to the inhabitant equivalent has a strongly fluctuating quantity, the dimensioning quantity "specific digestion room volume per inhabitant equivalent" is no longer considered in the following. A circumstantial roundup of different dimensioning approaches from the literature for conventional digestion reactors can be found at BÖHNKE et al. (1993). Table 5-1 shows the popular standard values for the dimensioning of one-step mesophilic digestion reactors.

It has to be remarked, that the volumetric loading rates of solid matter quoted in table 4 cannot be achieved with the usual static thickening processes for raw sludge. In order to achieve an volumetric loading rate of 3.5 kg odm/m^3 · d at a digestion time of 15 days a raw sludge with an organic portion of 67 % must be thickened to a 7.8 % solid matter content. This can only be achieved with a specialised machinery for thickening processes (centrifuges).

Further important parameters of the one-step mesophilic sludge digestion are:

- the degradation degree of organic matter,
- the content of organic acids
- the digestion gas yield
- the composition of the digestion gas

Table 4: Guide values for the dimensioning of a digestion tank (BÖHNKE et al., 1993)

Plant size / connection value	Hydraulic retention time in days [d]	Volumetric loading rates of solid matter in [kg odm/m^3 . d]
Small plants < 50.000 inhabitant	20	2.0
Medium size plants 50.000 to 100.000 inhabitants	15 to 20	2.0 to 3.5
Large plants >100.000 inhabitant	15	3.5 to 5.0

3.1.3.2 Degradation degree of the organic matter

KAPP (1984) found in circumstantial tests that the volume of the degradation degree depends on the raw sludge composition (type and degradability of the organic matter in the raw sludge) and on the retention time in the digestion reactor. Figure 144 shows the results determined by KAPP:

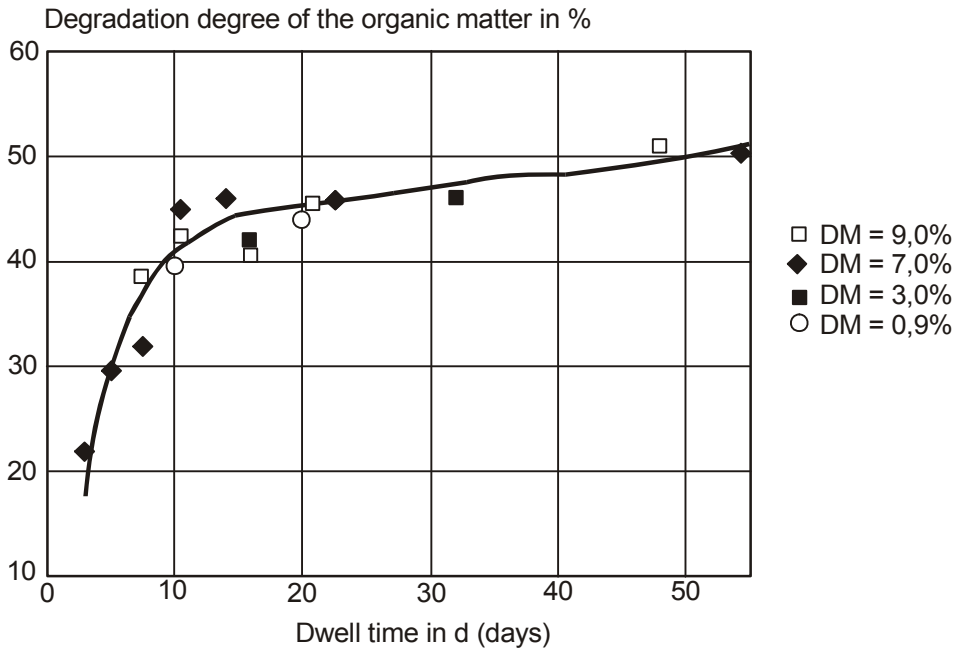


Figure 14: Degradation degree of organic matter dependent on the digestion period according to KNAPP (1984), modified

From the asymptotic course of the balancing line in figure 14 it can be learnt that already after 10 days of digestion period 75 to 80 % of the degradation degree is available, which is reached not before 50 days. Further is to be mentioned that the portion of solid matter in the digested sludge is not of any importance for the achieved degradation degree. At a usual digestion period of 20 and 25 days, regarding mixed sludges from municipalities, a degradation degree of the organic matter of about 45 % will be achieved.

3.1.3.3 Content of organic acids

The content of organic acids in the digestion reactor is the most important criteria for a monitoring of the stability of the digestion process. A low content of organic acids indicates that the anaerobic degradation runs properly. KAPP (1984) points out that the target of the sludge treatment "stabilisation" is completely reached at acid contents below 100 mg/l. ROEDIGER et al. (1990) claims a threshold value of 500 mg/l organic acids, for which the process can be referred to as being stable. A critical value, at which the changeover to acid digestion must be feared, lies at 2000 mg/l (BÖHNKE et al., 1993). A survey can be found in

the ATV-manual "Sewage Sludge" (ATV, 1996-1), from which the stabilisation degree can be concluded on account of the content of organic acids. (table 5):

Table 5: Assessment of the stabilisation degree according to the content of organic acids

Content of organic acids	Stabilization degree
< 100 [mg/l]	very well digested
100 - 1000 [mg/l]	well digested
1000 - 2500 [mg/l]	moderately digested

If there are increasing concentrations of organic acids in the digestion reactor it may have two causes:

- the methanogenic (and / or the acetogenic) bacteria are inhibited
- the anaerobic biocenoesis is overloaded

The most effective counter measure is the reduction of the substrate inflow rate. In order to decrease the inhibition of the methane formation through the concentration of organic acids the pH value in the digestion reactor can be slightly increased (e.g. through addition of lime milk).

3.1.3.4 Gas yield and gas composition

The gas generation in daily operation (gas production per kilogram of feeded organic matter) became accepted as a measure for the intensity of gas production. Other specifications e.g. the specification of a certain gas volume dependent on the inhabitant equivalent (l gas /Inh. ▪ d) fluctuate strongly as being dependent on many other factors (e.g. the waste water purification process). The relation of the produced gas volume to the degraded organic matter is a useful value, too, which, however, is rarely used in daily operation. As it is usually very difficult to determine exact solid matter balances for the digestion reactor. Reasons are the fluctuation of the solid matter content in the raw sludge and the retention time between charge and discharge in the digestion reactor.

At retention times between 20 and 25 days for a mesophilic digestion of usual municipal sewage sludges the gas yield can be determined according to table (KAPP, 1984).

Besides the gas volume the composition of the digestion gas is influenced by the type of the supplied substrates. ROEDIGER et al. (1990) quotes the methane content and the methane generation specific for degradation from the organic matter groups carbohydrates, proteins and fats (table 7).

Table 6: Gas yield at the mesophilic sewage sludge digestion according to KAPP

Gas yield	Preliminary sedimentation tank sludge	Surplus sludge	Mixed sludge
Inflow-specific in [l/kg odm_{inflow}]	540 to 560	270 to 280	430 to 450
Degradation specific in [l/kg odm_{degr}]	900 to 1000	700 to 800	900 to 1000

Table 7: Degradation specific digestion gas- and methane volume (ROEDIGER et al., 1990)

Type of material	Degradation specific gas generation [l/kg odm_{degr}]	Methane content in the digestion gas [Vol.-%]	Degradation specific methane generation [l/kg odm_{degr}]
Carbohydrates	790	50	400
Organic fats	1270	88	860
Protein compositions	700	71	500

The highest volume of methane gas is produced from fats and from carbohydrates the least volume, related to the degraded organic matter. For municipal mixed sludges, which are digested at usual digestion times, a methane portion of 63 and 67 Vol.-% can be calculated (KAPP, 1984; BÖHNKE et al., 1993; ROEDIGER et al., 1990).

The organic portion of municipal sewage sludges is a mixture of the three fractions fats, carbohydrates and proteins, the portions of which can fluctuate according to seasonal conditions. Correspondingly different from plant to plant are the digestion gas volumes and compositions. At the assessment of technical literature a relatively high fluctuation of the gas composition is found, as shown in table 8.

Table 8: Gas composition at the digestion of municipal sewage sludges

Source	Methane portion CH_4 in Vol.-%	Carbon dioxide portion CO_2 in Vol.-%	Hydrogen sulphide H_2S in Vol.-%
ATV (1996-1)	55 - 75	24 - 44	0.1 - 0.7
ROEDIGER et al. (1990)	approx. 67	approx. 33	only traces
KAPP (1984)	62 - 66	32 - 38	only traces
HARTMANN (1989)	61.8 - 77.8	22.2 - 38.2	not available

2.1.3.5 Dewatering ability and specific filter resistance

When leaving the digestion reactor digested sewage sludges usually have water contents between 95 % and 98 %. According to the type of disposal the digested sludges must be more or less strongly dewatered. Relatively high costs arise for the disposal of the sludges. As these costs are subject to the weight of the mass, which leaves the sewage plant, the first obligation is to reduce the volume and the weight by dewatering measures. The digested sludge is normally thickened at the sewage plant, then conditioned and mechanically dewatered. Afterwards the sludge must be thermally dried in order to be disposed of in correspondence to the different systems. Figure 15 shows the most popular disposal paths and the required steps for the separation of the sludge water.

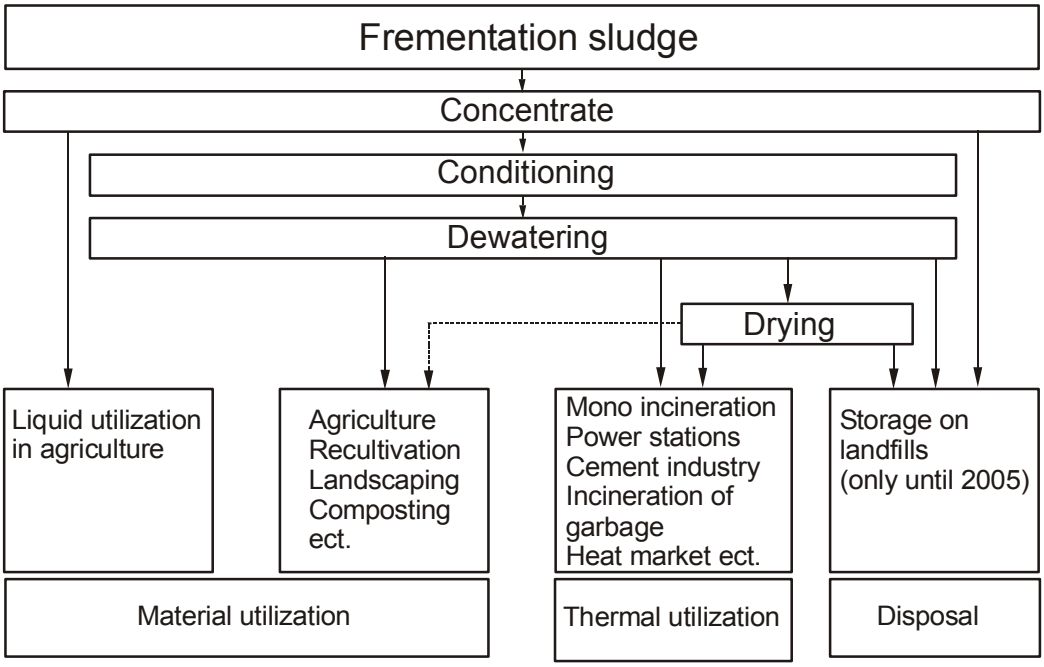


Figure 15: Necessary dewatering dependent on the intended disposal type

The reason for the proportionally high costs for the separation of the sludge water is the high water binding property of the sewage sludges. The linkage between the solid matter of sludges and the sludge water arises from different intermolecular forces which are dependent on:

- particle size distribution
- the organic solid matter portion of the sludge and
- the colloidal and gel-like ingredients.

These influencing factors in turn are decisively dependent on the composition of the waste water and the treatment technology installed on the sewage plant (ATV, 1996-1). This makes it clear that the properties of the sewage sludges, especially in regard to the technical method of dewatering, are differing from sewage plant to sewage plant. There is

no "general municipal sewage sludge" that could be described with few characteristic values. For sludge treatment only a variety of certain characteristics can be given.

The sludge water of digested sludges with, e.g., 5 % solid matter content is variably strongly bound to the solid matter particles. It is composed of:

1. interim- and cavity water (approx. 70 - 80 %)
2. adhesion- and capillary water (approx. 10 - 22 %)
3. adsorption- and internal water (approx. 5 - 8 %)

The linkage forces rise in the given order. The greatest part of the interim- and cavity water can be removed by thickening. When the solid matter content is thickened from 5 to 10 %, more than half of the sludge water is removed. However, the sludge is still liquid and can only be used in agriculture. All other utilisation purposes require a higher solid matter content. Dewatering machines can be used for the removal of adhesion and capillary water, thus achieving solid matter contents of up to about 50 %. A further dewatering of the adsorption and internal water can only be reached by thermal drying processes.

In order to dewater sludges by means of machinery the sludge must be treated by suitable conditioning. Conditioning has the task to loosen the water binding forces, to improve flocculation and to reduce the compressibility of the sludges.

Chemical conditioning processes, partially combined with mechanical conditioning processes, are usually used for sludge dewatering with the help of chamber and membrane filter presses. An approved method is e.g. the conditioning with iron salts and lime. The positively charged ferrous ions respectively hydroxide complexes lead to a charge balance of the negatively charged surfaces of the solid matter particles of the sludge. The particles do not repel each other anymore and it comes to coagulation. Favoured by the polymeric structure of the ferric hydroxide complexes finally micro and macro flocculation are built. The effect is improved through addition of lime suspension and the compressibility of the sludge is reduced, i.e. its water permeability is increased.

The same effects can be achieved by means of conditioning with ion active polymers and mechanical conditioning means like fine coal or ash, but also saw dust, granulated straw or similar. As the solid matter particles in the sludge are usually negatively charged, water-soluble, cationic polymers are used. The charge of the particle surface is destabilised and the particles can make contact through the intensive meddling and can ball together. Through the long polymeric chains flocculation is achieved, the formation of micro and macro flakes. This happens preferably at the gentle thorough mixing so that the macro flakes can ripen and will not be destroyed again. The added mechanical conditioning means has in the subsequent filtration in the press only the task to develop a supporting frame structure in the filter cake, thus improving the water permeability.

The most important characteristic value for the judgement of the dewatering ability of a sewage sludge on filter presses is the specific filtration resistance. It was developed by CARMAN (1938) for the filtration of industrial sludges, however, according to COACKLEY (1955) can also be used for the judgement of waste water sludges. Theoretically considered, the filter resistance can be traced back to the law of DARCY with which filter

velocity in soils can be described. With the following equation the filter resistance can be calculated:

$$r = 2p \cdot F_i^2 \cdot {}^1/\eta \cdot {}^1/c \cdot b \quad [1/cm^2]$$

p: Filtration pressure [N/cm^2)
η: Dynamic viscosity of a filtrate
b: Ascending gradient of a straight line which results from the course of dewatering [s/cm^6]
c: Ratio of dry matter to water content (dm/(100-dm))
F_1: Filter surface [cm^2]

In order to determine the filtration resistance a sludge sample is filtered under heavy pressure and the discharging filter material is measured in certain time intervals. Hereby the necessary size b can be determined and the filter resistance be calculated. On account of the compressibility of the sewage sludges increases the filter resistance with the filtration pressure relatively intensively, i.e., if filter resistances shall be compared among each other, they should have been determined under similar pressures. For a filtration pressure of 8 bar and unconditioned sludges for the following guide values can be given (ATV, 1996-1):

- raw pre-clarification sludge: r = 40 to 80 · 10^{12} [1/cm^2]
- digested pre-clarification sludge: r = 10 to 20 · 10^{12} [1/cm^2]
- surplus sludge: r = > 100 · 10^{12} [1/cm^2]

3.1.3.6 Reloading of the sewage plant

The separated water produced at the dewatering of sewage sludge is called sludge water. This sludge water is usually returned into the sewage plant and leads to a reloading. Sources for sludge waters are:

- static raw sludge pre-thickener (supernatant liquor)
- mechanical raw sludge thickener e.g. decanter (clarified sludge, centrifugal sludge)
- static subsequent digested sludge thickener (supernatant liquor)
- mechanical digested sludge dewatering (centrifugal sludge, filter sludge)

Higher loads can be expected mainly from the pre-clarification thickening at a static raw sludge thickening process. To some extent these thickeners are purposefully operated as pre-acidification thickeners, i.e. the retention times for sludge are chosen as long as the digestion process is going on. The released organic acids are drawn off with the supernatant liquor and discharged again into the anaerobic steps of the sewage plant to support the biological phosphate elimination. The load of the sludge water from the pre-clarification thickening is predominantly affecting the parameters BOD and COD, at badly functioning thickeners, larger solid matter portions can be present in the supernatant liquor which load the sewage plant. As a rule the sludge water from static thickening of surplus sludge is loaded only to a small extent as it corresponds to the process sequence of the sewage sludge plant. However, even higher loads can occur if surplus sludge thickening is carried out mechanically, e.g. with centrifuges. OTTE-WITTE et al. (1991) present a good summary of BOD_{5-} and COD loads of sludge waters from different raw sludge when different dewatering procedures are applied.

The decisive reloads of sewage plants arise at the dewatering of digested sludge. The dissolved organic carbon compositions, which are measured in the sludge as BOD_5 and COD, are largely degraded at anaerobic degradation except for residual contents. Contrary to this at the anaerobic degradation of nitrogen compositions ammonium is released, which concentrates in the sludge water, causing a considerable reloading when it is discharged into the sewage plant.

As stated in ATV (1996 - 1) according to OTTE-WITTE et al. (1991) 10 to 20 %, even up to 30 % of the nitrogen load of a municipal sewage plant can be traced back to this source. KAPP (1984) states nitrogen reloads of 1.38 g N/Inh · d. Other authors state 300 to 1.200 mg NH_4-N/l in the sludge water assume a reload of 25 % ammonium related to the TKN-nitrogen in the inlet (ATV, 1996-1). If certain assumptions are considered the extent of the nitrogen reload can be determined theoretically.

The assessment proves that according to the assumptions made, a nitrogen concentration of 885 mg/l is present in the sludge water after the digestion. As this nitrogen amount is derived from the degradation of organic nitrogen compositions, the nitrogen is exclusively available as ammonium. If this digested sludge amount, related to the inhabitant equivalent, is dewatered to a solid matter content of 40 %, approximately 1.8 l sludge water arise. The nitrogen reload of the sewage plant amounts to 1.59 g N/Inh ··d, nearly 15 %, if a supply load per inhabitant equivalent of 11 g N/ Inh ··d is assumed.

The COD and BOD_5 reloads are very much lower and therefore not so important for the sewage plant. OTTE-WITTE et al. (1991) states BOD_5 values of 300 to 2.000 mg/l and COD concentrations of 300 to 4.000 mg/l for the filtrate from chamber filter presses. Assuming a BOD_5 value of 500 mg/l and for the COD of 2.000 mg/l for a filtrate largely free of solid matter, the following reloads result under the same assumptions as mentioned above:

BOD_5: 0.9 g BOD_5/Inh ··d	corresponds to approx. 1.5 % of the supply load (60 g BOD_5/Inh ··d)
COD: 3.6 COD/Inh ··d	corresponds to approx. 3.0 % of the supply load (120 g COD/Inh ··d)

Table 9: Nitrogen reload through sludge digestion and sludge dewatering

Parameter	Unit	Preliminary sewage sludge	Surplus sludge	Sum
Amount of dry matter	[g dm/Inh · d]	35	50	85
Dry matter in sludge	[%]	5.0	3.85	4.0
Sludge volume	[l/Inh ·d]	0.7	1.3	2.0
Volatile solids	[% v. dm]	65	65	65
Organic portion	[g odm/Inh ·d]	22.75	32.5	55.25
Nitrogen portion in the organic	[% v. odm]	5.0	10.0	7.95
Nitrogen amount	[g N/Inh ·d]	1.14	3.25	4.39
Degradation in digestion	[% v. odm]	55	35	40.3
N-release during degradation	[g N/Inh ·d]	0.63	1.14	1.77
N-concentration in sludge water	[g N/l]	900	880	885
N-reload at dewatering to approx. 40 % dm	[g N/ Inh · d]	-	-	1.59

The phosphate reload can be deduced from a similar approach as was assumed for the nitrogen (ATV, 1996-1). In total the value of 0.17 g P/Inh ··d is achieved, that corresponds to about 7 % of the supply load. If phosphate is precipitated in the sewage plant with ferrous salts the trivalent iron can be reduced to a bivalent iron in the digestion process:

$$6\ FePO_4 + 6e^- \rightarrow 2\ Fe_3(PO_4)_2 + 2\ PO_4^{3-}$$

The re-dissolved phosphate can react with the ferrous hydroxide, which is available in the sludge through the usual surplus dosage of the precipitating agent, and can dissolve again in a not dissolved state. Furthermore the free phosphate in the digested sludge can build hardly soluble compositions with aluminium or magnesium and ammonium and than precipitates. The digested sludge has a considerable cohesive force for phosphorous on account of which nearly no larger re-dissolution of phosphorous arises in sewage plants with biological P-elimination than under conventional conditions (ATV, 1996-1).

3.2 Biowaste digestion

3.2.1 Development and targets of biowaste digestion

The systematic research of biogas generation from agricultural wastes (above all liquid manure) started in Germany during World War II and was carried on until the sixties. The development in Europe came to a standstill because of the high prices for mineral oil. Not

until the energy crisis in the seventies the technology of biogas plants obtained new research impulses. As a consequence some agricultural biogas plants were built in Germany, contrary to the developing countries where up to now a multitude of such plants were built. Predominantly are they operated with a relatively simple technical standard and used for decentralized biogas and energy generation (KULL / PFIRTER, 1994).

The development in the legal waste ordinances in Germany resulted to an countrywide separate collection of biowastes. At the beginning composting plants were built for the treatment of biowastes. Furthermore, composting was increasingly considered critically on account of the environmental awareness, higher demands on emissions and safety technology and thus increasing costs. Discussions about the danger coming from fungus spores, the unfavourable CO_2 and energy balances of composting promoted new impulses for the development of anaerobic biological waste treatment processes (SCHERER, 1995). Meanwhile approximately 30 different processing methods are offered in Western Europe for the digestion of organic residues (KRULL et al., 1995).

The prior targets of anaerobic biological waste treatment are (according to WEILAND, 1997):

- Extensive degradation of the organic components (stabilising, inerting material and reduction of the waste amounts)
- Production of a high-class soil improvers and conservation of the nutrients
- Energy generation
- Reduction of odour and germ emissions
- Reduction of trace gas emissions affecting the climate (CO_2, CH_4, N_2O)
- Short treatment periods
- Compact treatment plants (small site demand)
- Little fault liability

5.2.2 Biowaste digestion procedures

Because of the multitude of procedures offered in the market not all procedures with their advantages and disadvantages will be discussed here. It seems to be more sensible to make a classification of the digestion processes according to the main characteristics. The basic operations are explained in the following which are similar with all procedures. A selection of different biowaste digestion procedures used in Germany will be finally mentioned together with the installed plants and throughput capacities.

The procedures for the anaerobic biological waste treatment can be systematically classified according to different process characteristics (table 10). Table 10 shows a multitude of possible procedures. Despite of this all digestion processes have a similar structure of the process. Figure 16 shows the basic flow-chart of a process, divided up according to the individual basical operations:

Table 10: Classification of the digestion processes (WEILAND), 1997)

Process characteristics	Process modifications		
Water content	Wet digestion dm < 15 %	Semi-dry digestion 15 % < dm < 20 %	Dry digestion dm > 20 %
Temperature	Psychrophilic T < 25 °C	Mesophilic T = 33 - 37 °C	Thermophilic T = 55 - 60 °C
Process management	Single-step	Two-step with solid matter separation after first step	Two-step, without solid matter separation after first step
Type of operation	Batch operation	Repeated Fedbatch (Sequencing batch	continuously
Stirring/mixing	Mechanically	Hydraulically	Pneumatically
Input materials	Mono digestion	Co-digestion	

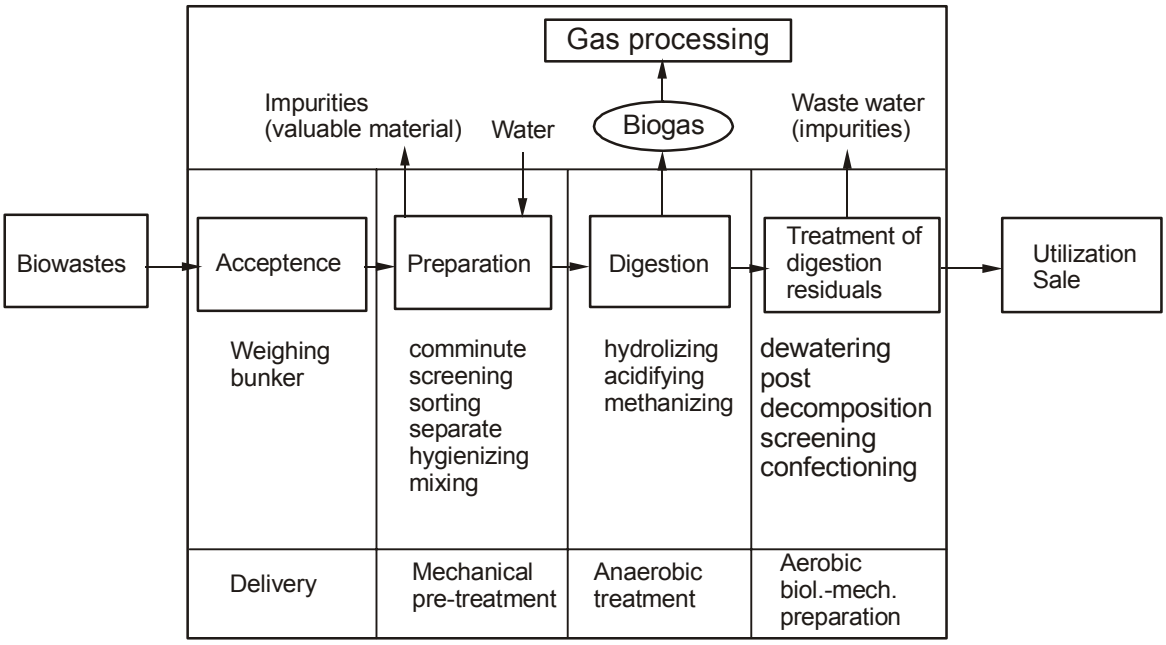


Figure 16: Process flow chart of a digestion plant (accord. to SCHLAG, 1996 and WEILAND, 1997, modified)

The delivered biowastes are weighed and transported into an interim storage (deep bunker or ground-level bunker). In all types of procedures follows a preparation of the biowaste, whereby comminution is obligatory, enabling an extensive and rapid degradation of the biowastes during digestion. Further basic operations like screening, sorting, separating and mixing depend on the procedure. Some procedures have an extensive discharge (sluice out) of impurities (e.g. by a float and sink separation), other procedures separate the impurities at the final treatment of the digestion residues (e.g. by means of screening).

Material that is hygienically critical requires a thermal treatment for hygienisation. However, hygienisation must not obligatorily be carried out during pre-treatment, it can also be achieved by the thermophilic operation of the anaerobic step (at sufficient retention times and prevention of short circuit currents) or through subsequent composting (VDMA, 1995; KÜBLER, 1994).

The individual procedures in the following anaerobical biological step differ from each other considering the substrate humidity, the process management, the temperature and the material flow. The selection of the process depends on the type and composition of the biowastes, the conditions on the location and the intended utilisation of digestion residues (VDMA, 1995; WEILAND, 1997).

A treatment of the digestion residues is normally carried out after digestion. After dewatering the digestion residues correspond to fresh compost with a decomposition degree II to III. In order to be able to sell it as mature compost (decomposition degree IV to V) in the market an aerobic subsequent decomposition and fine preparation is required.

The dewatered waste water can only be returned to some extent into the preparation process. On account of the concentration of ammonium-nitrogen a part of the waste water always must be sluiced out of the process and supplied to a waste water treatment.

Before the biogas is utilised in a district heating station an interim storage of the gas is necessary, in order to balance daily fluctuations and to enable a most effective energy use. Additionally necessary is the installation of an emergency gas flare.

A range of procedures for the digestion of municipal respectively industrial biowastes applied in Germany is shown in table 5-8. A more complete survey can be found in THOMÉ-KOMIENSKY (1995), WIEMER/KERN (1996) or KRULL et al, (1995).

It becomes apparent that already since the beginning of the nineties large scale plants for the digestion of municipal biowastes exist. Experiences with large scale plants for agriculture were carried out essentially earlier, e.g. in liquid manure digestion. It must be realized, too, that, especially with approved procedures, a tendency for plants with higher capacities can be noticed.

A speciality among the processes of biowaste digestion is the co-fermentation with liquid manure in agricultural plants. Plants for the anaerobic treatment of cattle and swine slurry and chicken faeces have been planned and installed already in the eighties in the German Democratic Republic (DDR).

The residues accumulated in such a big volume on account of the intensive husbandry that a preparation for biogas generation was profitable. After the reunion of Germany the intensive husbandry was reduced. The arising free capacities were filled up to some extent by the co-treatment of industrial and municipal biowastes, new plants for co-fermentation of liquid manure and biowastes were also built. Some examples for co-digestion plants on the basis of liquid manure are shown in table 11.

The advantages of the co-digestion plants on liquid manure basis are to be seen in the fact that the digestion residue is usually not dewatered and can directly be applied on arable land as liquid fertiliser. A waste water treatment, which would be very costly on account of the high load of nitrogen from liquid manure, is not necessary.

Table 11: Selection of different digestion procedures and plants for biowastes in Germany (WIEMER/KERN, 1996)

Process (supplier)	Process principle	Reference plants	Capacity [Mg/a]	In operation since [year]
BTA (MAT)	single-step mesophilic wet digestion	Baden-Baden Kehlheim Karlsruhe	5.000 13.000 8.000	1993 1996 1996
DBA/Wabio (Babcock)	single-step mesophilic wet digestion	Bottrop	6.500	1995
ROEDIGER (Roediger)	single-step mesophilic wet digestion	Kaufbeuren Münster	3.000 16.500	1991 1997
LINDE KCA(Linde)	single-step thermophilic wet digestion	Heilbronn	6.100	1997
BTA (MAT)	two-step mesophilic wet digestion	Brunnthal	20.000	1997
KOMPOGAS (Bühler)	single-step thermophilic dry digestion	Burgberg	10.000	1995
AN/Biothane (AN Maschinenbau)	two-step mesophilic perculation process	Ganderkesee	6.000	1994
IMK (BEG-Herten)	two-step therm. / mesophilic dry digestion	Herten	15.000	1998
Plauener (DSD)	Two-step psychro-/mesophilic wet digestion	Zobes/Plauen Sachsen	18.500	1987
HAASE (Schraden-Biogas)	Single-step mesophilic wet digestion	Gröden Brandenburg	110.000	1995
SCHWARTING-UHDE (Uhde)	Two-step meso-/thermophilic wet digestion	Finsterwalde Brandenburg	90.000	1996
LINDE - KCA (Linde)	Single-step thermophilic wet digestion	Behringen Thüringen	23.000	1996

3.2.3 Dimensioning and characteristic parameter of digestion

3.2.3.1 Retention time and volumetric loading rate

As in sewage sludge digestion, the volumetric loading rate or the hydraulic retention time in the reactor is used for the dimensioning of the bio-reactors. Dry matter contents of 8 to 12 % are usually adjusted at the one-step wet digestion processes. At retention times between 15 and 20 days and an organic portion of 75 % in the biowaste, volumetric loading rates arise between 3 and 6 kg odm/m^3 · d.

A distinctly shortened retention time can be achieved in the anaerobic biological system with the separation of hydrolysis/acidifaction and acetic acid/methane formation combined with an intermediately arranged solid matter separation. The retention time in the hydrolysis/acidification is from one to four days. The solid matter separation enables the instalment of fixed beds in the methane reactor thus immobilizing the biomass. Retention times of one to two days are sufficient to convert the dissolved organic matter into biogas.

The retention times in the reactors for the dry digestion process lies between 15 and 25 days, according to the high solid matter content distinctly higher loading rates of organic solid matter arise in the reactors, up to 20 kg odm/m^3.

3.2.3.1 Gas yield and composition

The gas yield is generally given with 80 to 150 m^3/Mg input, whereby the lower volumes arise in the one-step processes, respectively with preponderantly municipal biowastes, higher values are achieved with the two-step processes respectively a treatment together with wastes rich in solid matter with relevant fatty portions. To relate the gas yield to the weight of the biowastes is only sensible, if the biowastes can be compared among each other (solid matter content, organic portion, origin, composition).

Biogas yields of about 100 m^3/Mg input are named for municipal biowastes from separate collection (bio bin). When different substrates are processed it is advisable to relate the gas production on to the organic matter supplied to the reactor (kg odm_{to}) respectively the degraded organic matter (kg odm_{degr}). At wet processes the relation of the supplied respectively degraded COD fraction to the gas production may be reasonable and, to some extent, can render comparable values. Literature mostly provides supply specific gas volumes from application. Table 5-10 shows some values.

An average of 65 Vol.-% CH_4, 33 Vol.-% CO_2, 0.4 vol.-% H_2S is given for the biogas composition together with traces of H_2, N_2 and olefins (KRULL et al., 1995).

3.2.3.3 Waste water volume quality

The specific waste water volume at the wet digestion processes lies between 400 and approx. 800 l per Mg input. Less waste water arises at dry digestion processes on account of the lower substrate humidity (100 to 450 l/Mg input, KRULL et al., 1995). Only some

publications exist for the composition of these waste waters. THOME-KOZMIENSKY (1995) published a summary of the waste water qualities of the two-step wet fermentation after the BTA-process. Tests for the mesophilic and thermophilic digestion of biowastes and kitchen wastes have been carried out in the INFA Institute for waste and waste water management in Ahlen (Germany) (INFA, 1997). The tests were carried out to enlarge the momentary state of the art of process water composition data. The following table 12 contains bandwidths for some waste water parameters from the above mentioned publications for the mesophilic digestion.

Table 12: Gas volume at the digestion of different biowastes

Substrate	Gas volume [l / kg odm_{to}]	Treatment process / source
Municipal biowaste	475 - 500	DBA-WABIO (THOME-KOZMIENSKY, 1995)
Municipal biowaste	380 - 550	MAT (THOME-KOZMIENSKY, 1995)
Organic fraction from mixed waste	450	GOSCH (1997)
Kitchen wastes, liquid manure and contents of fat separator (Mixture)	420	DSD (THOME-KOZMIENSKY, 1995)
Liquid manure	160 - 640, average 340	Agricultural biogas plant (ATV 1996-1)
Grass	550	20 d, 30° C, (MUDRACK/KUNST, 1988)

As the load of waste waters are very high it is absolutely necessary to carry out a waste water purification before a direct discharge in a water body, sometimes even before an indirect discharge in the sewerage system. Offers for the BTA process include therefore integrated biological waste water purification with nitrification/denitrification. A separate waste water purification can be avoided only if a leachate treatment plant, e.g. on a landfill, can be used or the waste water can be directly discharged into a nearby sewage plant.

Table 13: Load of waste water from digestion plants (THOME-KOZMIENSKY; 1995 and INFA, 1997

Parameter	BTA process (test plant Munich)	INFA biowaste	INFA kitchen waste
COD_{fil} [mg/l]	3.000 - 23.800	3.060 - 6.430	2.760 - 12.450
BOD_5 [mg/l]	700 - 10.000	1.940 - 4.980	2.330 - 8.650
N_{total} [mg/l]	305 - 1.558	1.050 - 1.510	1.520 - 1.830
NH_4-N [mg/l]	229 - 963	870 - 1.280	1.230 - 1.710
$P_{total, fil}$	35.4 - 198*	32 - 51	28 - 38

* = only PO_4-P

5.2.3.4 Digestion residues

The digestion residue must usually be subsequently composted after dewatering if the product shall be sold as mature compost. Hereby the material is mixed with structure material and subsequently composted in an open windrow. The time for subsequent decomposition lies between 8 and 84 days depending on the different processes (KRULL et al. 1995). On an average two to three weeks are enough in order to produce mature compost with decomposition degree IV to V.

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