Chapter 5

The Anaerobic Digestion Process

Anaerobic digestion (AD) is the process in which microorganisms break down organic matter in an anaerobic (that means oxygen-free) environment. It is the process which is used to produce biogas in the anaerobic digesters of a biogas plant. As organic matter all kind of biodegradable material can be used such as wastewater, manure, agricultural and food waste, organic fraction of municipal solid waste, microalgae, grass, energy crops and many others (Nallathambi Gunaseelan, 1997).
Biogas is a mixture of different gases containing, in decreasing concentration, methane, carbon dioxide, water vapor, nitrogen, oxygen, hydrogen, ammonia and hydrogen sulphide. As methane is an energy carrier the general idea is to maximize methane production. Its concentration in biogas is usually around $50\ \% - 75\ \%$ (cf. Besgen (2005)).
In this chapter the anaerobic digestion process is described very briefly (see Section 5.1 and 5.2) focusing on those aspects that are important out of the view of process control.
Sections 5.3 and 5.4 are written in the style of glossaries and are dedicated to those which want to familiarize themselves with the most important terms, definitions and reactor configurations used in the field of anaerobic digestion.
For a more complete treatment of the anaerobic digestion process please refer to e.g. Gerardi (2003), Gujer and Zehnder (1983) or Bischofsberger et al. (2005).

5.1 Process Description

The anaerobic degradation (or digestion) process can be separated into four consecutive following steps, which are described in the following four paragraphs.

Hydrolysis The anaerobic degradable part of any substrate is seen to be a composite out of carbohydrates, proteins and fats. During the first step, the hydrolysis, the three biomolecules carbohydrate, protein and fat are decomposed into their constituent

parts. All of the three biomolecules are bonds of smaller molecules. Carbohydrates are bonds of monosaccharides, proteins are bonds of proteinogenic amino acids and fats are bonds (so-called esters) of the alcohol glycerol with fatty acids. During hydrolysis these bonds are separated using water, which is available in the digester, and enzymes. The products of the hydrolysis step therefore are monosaccharides, proteinogenic amino acids, glycerol and fatty acids.

Acidogenesis During the acidogenesis the microorganisms process the products of the hydrolysis mainly to different acids such as propionic, acetic and butyric acid. During these fermentation processes carbon dioxide and hydrogen are produced as well. The acidogenesis of some proteinogenic amino acids also releases the toxic substances ammonia and hydrogen sulphide.

Acetogenesis The acids produced in the acidogenesis step are degraded further to become acetic acid, therefore this step is called acetogenesis. Those fermentation processes are performed by bacteria as well.

Methanogenesis In the last step, the methanogenesis, the methane is produced. There are two path ways of how bacteria produce methane. The first one is the acetoclastic methanogenesis (eq. (5.1)), where acetic acid (CH_3COOH) is converted to methane (CH_4) and carbon dioxide (CO_2)

$$CH_3COOH \longrightarrow CH_4 + CO_2 \tag{5.1}$$

and the second one is hydrogenotrophic methanogenesis (eq. (5.2)), where carbon dioxide and hydrogen (H_2) is converted to methane as well (Gerardi, 2003).

$$CO_2 + 4\ H_2 \longrightarrow CH_4 + 2\ H_2O \tag{5.2}$$

5.2 Important Process Values

As the anaerobic process is performed by living organisms it must be assured that the environmental conditions in the digester are such that the organisms can survive and reproduce. The participating bacteria have different preferences with respect to pH value, temperature and other environmental factors (Appels et al., 2008). Therefore a compromise has to be found. Most often the environmental conditions are set to the preferences of the methanogenic bacteria, which produce the methane (eqs. (5.1) and (5.2)), Besgen (2005). The reason is, that those are inhibited by the starting material of their performed reactions, thus acetic acid and hydrogen. This has as consequence, that once the methanogens are inhibited the educts in eqs. (5.1) and (5.2) increase, inhibiting the methanogens even more. In the long run, due to the increasing acid

concentration, the pH value drops, that inhibits the methanogens as well (Weiland, 2010), killing them in the end. So, to guarantee a stable process of methanogenesis, it must be assured by all means that this chain reaction never commences.
There are a few more process variables next to pH value, acetic acid and dissolved hydrogen concentrations that affect the well-being of the bacteria. An automatism that stabilizes the pH value around an equilibrium is called a buffer. The buffer in anaerobic digesters mainly depends on the equilibria of ammonia/ammonium, carbon dioxide/bicarbonate and the equilibria of the volatile fatty acids and their salts. A large buffer can compensate an increase of acids, before the pH value and thereby the methanogens are affected. But, as the pH value does not change as long as there is still buffer capacity, based on the pH value no process imbalances can be recognized. Therefore, it is important to monitor the buffer capacity. The most important component of the buffer is the total alkalinity (TA), defined in eq. (7.61), which is a sum of bicarbonate and the salts of the volatile fatty acids. The ratio of volatile fatty acids over total alkalinity (VFA/TA) then is an often used indicator to measure the size of the buffer with respect to the acid concentration in the digester, see Section 7.3.3.8. Ammonia and hydrogen sulphide are important as well, because they are toxic for the microorganisms (Appels et al., 2008, Chen et al., 2008).

5.3 Important Definitions and Terms

This section should be seen as a glossary and only needs to be read if some terms in the field of anaerobic digestion used in this thesis are not familiar to the reader.

5.3.1 Amount of Substance & Molar Mass

The amount of substance is a standards-defined quantity with the unit mol, called mole, that measures the size of a collection of any substance. An amount of 1 mol particles is a number of around $6.02214199(47) \cdot 10^{23}$ of that particles (Avogadro constant) (Tipler and Mosca, 2007). Mole is defined that way, such that 1 mol of the carbon atom ^{12}C weighs 1 g.
Using amount of substance the term molar mass M with the unit $[\mathrm{M}] = \frac{\mathrm{g}}{\mathrm{mol}}$ can be introduced. Molar mass defines how much gram (g) an ensemble of 1 mol particles weighs. Given the relative atomic mass (which is defined relative to the mass of the carbon atom ^{12}C) of an element, e.g. oxygen, taken from a periodic table, being $16.00\ \frac{\mathrm{mol_C}}{\mathrm{mol_O}}$, the molar mass M of oxygen is

$$\mathrm{M_O} = 16.00\ \frac{\mathrm{mol_C}}{\mathrm{mol_O}} \cdot 1\ \frac{\mathrm{g}}{\mathrm{mol_C}} = 16\ \frac{\mathrm{g}}{\mathrm{mol_O}}.$$

Molar mass M is used in Section 5.3.3 to calculate the chemical oxygen demand of a molecule.

5.3.2 Biomass

As the term biomass has two meanings that are both related to the topic of this thesis, it is specified here which of the two meanings is referred to when we speak about biomass.
On the one hand biomass is a renewable energy source such as organic garbage, wood or plants (McKendry, 2002). On the other hand biomass is used in ecology to specify the mass of living biological organisms. In this thesis, if not stated otherwise, the term biomass is used in the second sense. Therefore, biomass is the mass of bacteria and enzymes living in a digester and being part of the conversion process of substrate to biogas.

5.3.3 Chemical Oxygen Demand

The chemical oxygen demand (COD) of a material defines the amount of oxygen needed to completely oxidize the material. The amount of oxygen O_2, measured in g, needed to oxidize 1 mol of a biomolecule is defined as $g_{COD} := g\ O_2$. To calculate the amount of oxygen to oxidize a biomolecule $C_cH_hO_oN_n$ the general combustion equation for biomolecules (eq. (5.3)) can be used (Koch et al., 2010).

$$C_cH_hO_oN_n + \left(c + \frac{h}{4} - \frac{o}{2} - \frac{3\cdot n}{4}\right) O_2 \longrightarrow c\ CO_2 + \left(\frac{h}{2} - \frac{3\cdot n}{2}\right) H_2O + n\ NH_3 \quad (5.3)$$

Therefore, with the molar mass of oxygen $M_{O_2} = 32.00\ \frac{g\ O_2}{mol_{O_2}}$ (see Section 5.3.1), the COD of one mole of the biomolecule $C_cH_hO_oN_n$ is

$$\begin{aligned}&\left(c + \frac{h-3\cdot n}{4} - \frac{o}{2}\right)\frac{mol_{O_2}}{mol_{C_cH_hO_oN_n}} \cdot 32.00\ \frac{g\ O_2}{mol_{O_2}} = \\ &(32\cdot c + 8\cdot(h-3\cdot n) - 16\cdot o)\ \frac{g_{COD}}{mol_{C_cH_hO_oN_n}}.\end{aligned} \quad (5.4)$$

As an example, the COD of 1 mol methane (CH_4) is $(32 + 8\cdot 4)\,g_{COD} = 64\ g_{COD}$.
In simulation models of the anaerobic digestion process the chemical oxygen demand is a property of conservation and therefore very important, see Section 7.1.

5.3.4 Dilution Rate & Volumetric Flow Rate

Given the volume ΔV of a material passing through a given surface in the time Δt, the volumetric flow rate Q of the material is defined as:

$$Q := \lim_{\Delta t\to 0}\frac{\Delta V}{\Delta t} = \frac{dV}{dt} \qquad [Q] = \frac{m^3}{d}. \quad (5.5)$$

On biogas plants the material could e.g. be a substrate (or substrate mix) or the produced biogas. The volumetric flow rate of substrates is denoted by Q_{IN} and the volumetric flow rate of the produced biogas is symbolized by Q_{gas}, see equation (7.3).

The dilution rate D is defined as the ratio between the volumetric flow rate Q_{IN} of the substrate feed of a digester and the liquid volume of the digester V_{liq}, as given in eq. (5.6).

$$D := \frac{Q_{\mathrm{IN}}}{V_{\mathrm{liq}}} \qquad [D] = \frac{1}{\mathrm{d}} \tag{5.6}$$

The dilution rate D is the most often used manipulated variable for substrate feed control (see Chapter 6). On the one hand increasing the dilution rate, increases the amount of substrate fed to the digester and therefore increases biogas production, but on the other hand the biomass is washed out in the rate given by the dilution rate. Therefore, the dilution rate should be smaller than the specific growth rate of the slowest growing biomass, such that the organism can reproduce and survive. Exceptions are high-rate digesters (Section 5.4), where washout of biomass is not directly proportional to the value of the dilution rate.

5.3.5 Fresh Mass

The substrate, as it is fed, is referred to as fresh mass (FM), often but not always referring to the mass of the substrate. To avoid confusion, the initials FM are always (if needed) appended to an unit, when a parameter of the fresh mass substrate is measured. Examples are the mass, measured in $\mathrm{kg_{FM}}$, or the volume, measured in $\mathrm{m^3{}_{FM}}$, of the fresh mass.

5.3.6 Hydraulic & Sludge Retention Time

In this thesis, the hydraulic retention time HRT of a digester is defined as the ratio of the liquid volume of the digester V_{liq} and the volumetric flow rate of the sludge leaving the digester Q:

$$\mathrm{HRT} := \frac{V_{\mathrm{liq}}}{Q} \qquad [\mathrm{HRT}] = \mathrm{d}. \tag{5.7}$$

With the approximation $Q \approx Q_{\mathrm{IN}} \cdot \left(1 - \frac{\mathrm{m_{gas}}}{\mathrm{m_{influent}}}\right)$ the hydraulic retention time can be related to the volumetric flow rate of the substrate feed Q_{IN}. Here, the mass of the biogas leaving the digester is given as $\mathrm{m_{gas}}$ and the mass of the influent as $\mathrm{m_{influent}}$. For details see Lübken (2009).
If $Q_{\mathrm{IN}} \approx Q$, then the HRT is equal to the inverse of the dilution rate D, see Section 5.3.4, as it is often given in textbooks, see equation (5.8).

$$\mathrm{HRT} \approx \frac{V_{\mathrm{liq}}}{Q_{\mathrm{IN}} \cdot \left(1 - \frac{\mathrm{m_{gas}}}{\mathrm{m_{influent}}}\right)} \overset{\mathrm{m_{gas}} \ll \mathrm{m_{influent}}}{\approx} \frac{V_{\mathrm{liq}}}{Q_{\mathrm{IN}}} \overset{(5.6)}{=} \frac{1}{D} \tag{5.8}$$

As said above in Section 5.3.4, for high-rate digesters the washout of the biomass is not related to the dilution rate D. For such digesters the retention time of the biomass

is not equal to the hydraulic retention time, but to the so-called sludge retention time SRT with SRT $\gg$ HRT.

5.3.7 Organic Loading Rate

The organic loading rate OLR is defined as:

$$\mathrm{OLR} := \frac{Q_{\mathrm{IN}} \cdot \rho_{\mathrm{IN}} \cdot \mathrm{VS}_{\mathrm{IN}}}{V_{\mathrm{liq}}} \overset{(5.8)}{\approx} \frac{\rho_{\mathrm{IN}} \cdot \mathrm{VS}_{\mathrm{IN}}}{\mathrm{HRT}} \qquad [\mathrm{OLR}] = \frac{\mathrm{kg_{VS}}}{\mathrm{m^3 \cdot d}}. \tag{5.9}$$

In equation (5.9) the raw density ρ_{IN} of the substrate is given in $\frac{\mathrm{kg_{FM}}}{\mathrm{m^3}}$ and the volatile solids content of the substrate $\mathrm{VS}_{\mathrm{IN}}$ is given in $\frac{\mathrm{kg_{VS}}}{\mathrm{kg_{FM}}}$, see Section 5.3.11.
The organic loading rate OLR is the relation between organic mass in the substrate feed, that is $(Q_{\mathrm{IN}} \cdot \rho_{\mathrm{IN}} \cdot \mathrm{VS}_{\mathrm{IN}})$, and the liquid volume of the digester V_{liq}. With a rising OLR also biogas production increases, but only until a critical point, where the organically available material inside the digester increases to such an amount that it inhibits the work of the bacteria in the digester. Therefore, the organic loading rate is an indicator for potential process stress, but not a very good one, because it only refers to the substrate feed and not to a process value inside the digester.

5.3.8 Temperature Specifications

Anaerobic digesters are operated in three different temperature regions, with the temperature in the digester T, given as follows (Bischofsberger et al., 2005):

- psychrophilic: $T < 20\ ^o\mathrm{C}$
- mesophilic: $20\ ^o\mathrm{C} \leq T \leq 40\ ^o\mathrm{C}$
- thermophilic: $T > 40\ ^o\mathrm{C}$

Each temperature region has its advantages and disadvantages and each bacteria species has their individual preferred ambient temperature (cf. Besgen (2005)). In general the higher the temperature the faster biochemical reactions occur, on the other hand equilibria are changed, such as the ammonia/ammonium equilibrium which is shifted towards the toxic ammonia, see Section 5.2 (Appels et al., 2008).

5.3.9 Theoretical Oxygen Demand

Bringing the chemical oxygen demand of a substance (COD, Section 5.3.3) in relation to its molar mass (M, Section 5.3.1) results in the theoretical oxygen demand (ThOD), Koch et al. (2010). The ThOD of the biomolecule $\mathrm{C}_c\mathrm{H}_h\mathrm{O}_o\mathrm{N}_n$ is thus defined as

$$\mathrm{ThOD} := \frac{\mathrm{COD}_{\mathrm{C}_c\mathrm{H}_h\mathrm{O}_o\mathrm{N}_n}}{\mathrm{M}_{\mathrm{C}_c\mathrm{H}_h\mathrm{O}_o\mathrm{N}_n}} \overset{(5.4)}{=} \frac{32 \cdot c + 8 \cdot (h - 3 \cdot n) - 16 \cdot o}{12 \cdot c + h + 16 \cdot o + 14 \cdot n} \cdot \frac{\mathrm{g_{COD}}}{\mathrm{g}}, \tag{5.10}$$

where the molar masses of the C, H, O and N atoms were used. The theoretical oxygen demand is used in Section 7.2 to calculate the COD out of the cell content of a substrate.

5.3.10 Total Solids

The total solids (TS) content of a substrate (or a digester probe) is the part of the substrate (or digester probe) which is left over after thermal removal of water. Usually the water is removed by drying for 24 hours at 105 ^{o}C or by drying until a constant weight is achieved, VDI (2006). Given the definition of the fresh mass in Section 5.3.5, the water content of a substrate (or a digester probe) is given as the difference of FM and TS. The unit of the TS content is

$$[\mathrm{TS}] = \frac{\mathrm{g_{TS}}}{\mathrm{kg_{FM}}} = 0.1\ \%_{\mathrm{FM}}.$$

The volatile organic substances which escape together with the water vapour are not measured by this method and have to be determined separately. As an alternative, the TS content can also be corrected by the estimated loss of organics, see Weiß bach and Strubelt (2008a,b,c).

To distinguish between the total solids content of a substrate $\mathrm{TS_{IN}}$ and the total solids content inside a digester TS the two different symbols are used.

5.3.11 Volatile Solids

The organic dry-weight content, or volatile solids (VS), is the loss of weight of the total solids TS (Section 5.3.10) of a probe, while reducing it to ashes at a temperature of 550 ^{o}C, DIN (2001b). This loss of weight is predominantly due to organics, therefore it is called the organic dry-weight content, VDI (2006). The volatile solids is measured in

$$[\mathrm{VS}] = \frac{\mathrm{g_{VS}}}{\mathrm{kg_{TS}}} = 0.1\ \%_{\mathrm{TS}} \qquad \text{or} \qquad [\mathrm{VS}] = \frac{\mathrm{g_{VS}}}{\mathrm{kg_{FM}}} = 0.1\ \%_{\mathrm{FM}}.$$

The organic substances which already escaped during TS determination are not measured by this method and have to be determined separately, see above in Section 5.3.10.

To be able to distinguish between the volatile solids content of a substrate $\mathrm{VS_{IN}}$ and the volatile solids content inside a digester VS the two different symbols are used.

5.4 Typical Reactors

In this section a few typical types of anaerobic reactors are described very briefly. The number of different reactor types and their description is by no means complete. Here only those reactors are listed, which are referred to in the control review in Chapter 6. For a more elaborate review please refer to the literature, e.g. Henze and Harremoës (1983), Hickey et al. (1991), Iza et al. (1991) or Skiadas et al. (2003).

5.4.1 Continuous Stirred-Tank Reactor

A continuous stirred-tank reactor (CSTR) is an idealized standard chemical reactor. Its key characteristic is that the concentration values of all substances have the same value all over the reactor. Therefore, a CSTR is often modeled as a perfectly mixed reactor using ordinary differential equations (ODEs). In anaerobic digestion a CSTR has a liquid phase in the bottom and a gas phase in the top with a liquid/gas transfer (Figure 5.1a). The CSTR is the most common reactor employed for wet fermentation (Weiland, 2006).

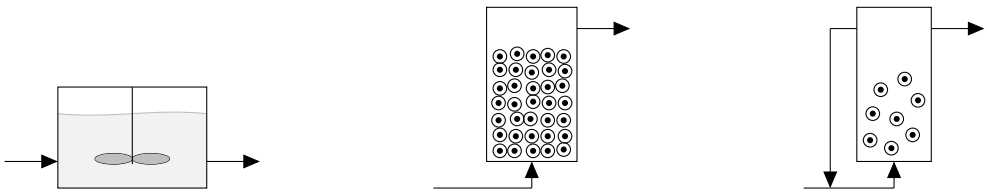
5.4.2 High-Rate Reactors

High-rate reactors can only be used for the anaerobic treatment of liquids such as wastewater, which flows vertically through the digesters. They are termed high-rate because of their low hydraulic retention time (eq. (5.7)). To avoid washout of biomass the biomass in these reactors is either attached to support material or is fixed in conglomerates of microorganisms (so-called granules) which have a very good settling behavior and therefore are not washed out. Thus, by fixating the biomass the sludge retention time (Section 5.3.6) is decoupled from the hydraulic retention time.

Expanded Granular Sludge Bed / Fluidized Bed Reactor Expanded granular sludge bed (EGSB) and fluidized bed reactors (FBR) are tall and thin reactors, where a high degree of recycle leads to the expansion (fluidization) of the sludge bed, Chou et al. (2011). Therefore, the wastewater to sludge contact is improved by enlarging the active surface of the sludge (Seghezzo et al., 1998). In FBR the biomass is attached to inert support media, such as sand or gravel (Figure 5.1c) (Henze and Harremoës, 1983) and in EGSB the biomass is granular, see UASB below. Furthermore, both digesters are distinguished from each other based on the degree of bed expansion (Iza et al., 1991).

Fixed Bed Reactor Key characteristic of anaerobic fixed bed reactors (AFB) (also called anaerobic filters (Zaher, 2005)) is the fixed support media inside the digester where the microorganisms are attached to (see Figure 5.1b). In general, AFBs are operated without recycle (Henze and Harremoës, 1983).

Upflow Anaerobic Sludge Blanket Reactor In upflow anaerobic sludge blanket (UASB) reactors (Lettinga et al., 1980) aggregations of microorganisms are formed, which are termed granules. Granules have very good settling behavior, such that UASB reactors can be operated with low hydraulic retention times without being concerned with washout of biomass. Different models exist about anaerobic granulation, a review is given in Liu et al. (2003).



(a) CSTR **(b)** AFB reactor **(c)** FBR

Figure 5.1: Schematics of CSTR, AFB reactor and FBR, cf. Henze and Harremoës (1983).

Upflow Anaerobic Sludge Blanket-Anaerobic Filter Reactor The upflow anaerobic sludge blanket-anaerobic filter (UASB-AF) reactor is a combination of an upflow anaerobic sludge blanket (UASB) reactor, located in the lower part, and an anaerobic filter (AF), located in the upper part. The UASB-AF combines the advantages of both single reactors and diminishes their disadvantages, Rajesh Banu and Kaliappan (2007). The filter in the upper part protects for sudden washout of biomass in extreme cases as it can happen in UASB reactors, Ramakrishnan and Surampalli (2012).