8.3.1 Theory of anaerobic digestion

When activated sludge is kept in an anaerobic environment, specialised bacteria will develop that use the excess sludge as a source of organic matter for fermentative metabolic processes. The end products of the fermentation are mainly methane and carbon dioxide. The overall conversion process of complex organic matter into methane and carbon dioxide can be divided into four steps (Gujer and Zehnder, 1983), as shown in Fig. 8.12: hydrolysis, acidification, acetogenesis and methanogenesis.

In an anaerobic digester, the four processes occur simultaneously. When the anaerobic digester performs properly, the conversion of the intermediate products (i.e. the products of the first three steps) is virtually complete, so that the concentrations of these are low at any time. In the hydrolysis process, macro molecules like proteins, poly saccharides and fats that compose the cellular mass of the excess sludge are converted into molecules with a smaller atomic mass that are soluble in water: peptides, saccharides and fatty acids. The hydrolysis- or solubilisation process is carried out by exo-enzymes excreted by fermentative bacteria. Hydrolysis is a relatively slow process and generally it limits the rate of the overall anaerobic digestion process.

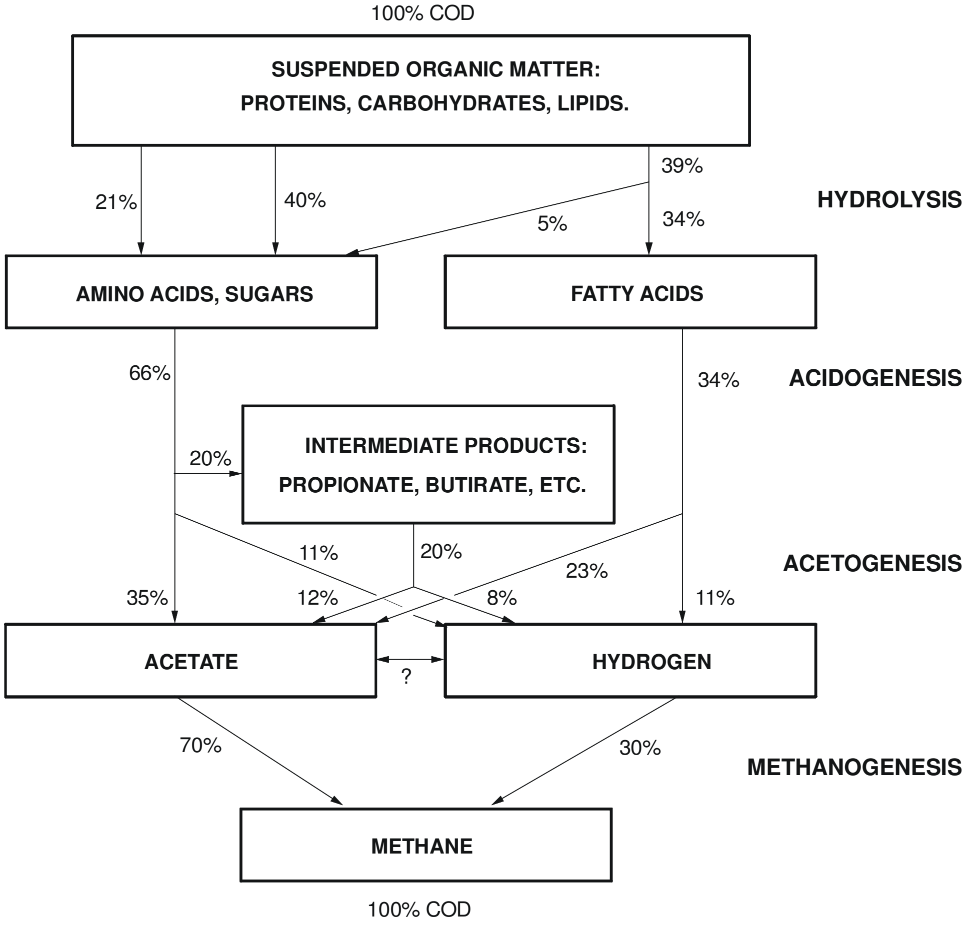

Figure 8.12 Schematic representation of the decomposition of excess activated sludge (and other organic material) by anaerobic digestion

The second step of the anaerobic digestion process is acidogenesis or acidification, a process that results in the conversion of the hydrolysed products into simple molecules with a low molecular weight, like volatile fatty acids (e.g. acetic-, propionic- and butyric acid), alcohols, aldehydes and gases like CO_2, H_2 and NH_3.

Acidification is effected by a very diverse group of bacteria, the majority of which are strictly anaerobic, i.e. the presence of oxidants like oxygen or nitrate is toxic. Luckily for these strict anaerobes, there are always bacteria present that will use oxygen whenever it is available. The presence of these bacteria is important to remove all oxygen that might be introduced into the system, for instance together with the excess sludge. The acidogenic bacteria are able to metabolise organic material down to a very low pH of around 4.

In the third step, acetogenesis, the products of the acidification are converted into acetic acids, hydrogen, and carbon dioxide by acetogenic bacteria. The first three steps of anaerobic digestion are often grouped together as acid fermentation. It is important to note that in the acid fermentation, no organic material is removed from the liquid phase: it is transformed into a form suitable as substrate for the subsequent process of methanogenesis.

In the final step of the anaerobic digestion process, the products of the acid fermentation (mainly acetic acid) are converted into CO_2 and CH_4. Only then will organic material be removed, as the produced methane gas will largely desorb from the liquid phase. In each of the four sequential steps, the catabolic reactions described above develop together with anabolic activity. The free energy released in the reactions is partially used for synthesis of the anaerobic bacterial populations.

As the energy release from fermentative catabolism is relatively small (refer to Chapter 2), the yield coefficient is much lower than in aerobic processes. Therefore, a large fraction of the digested organic matter is converted into biogas (85 to 95 percent).

In order to maintain an anaerobic sludge with a high metabolic activity, it is necessary to apply favourable environmental conditions. Among these factors the most important ones are temperature, pH, the absence of toxic materials and the availability of nutrients. The methanogens are very sensitive to adverse environmental conditions and for this reason it is always attempted to maintain optimal conditions for these bacteria. These conditions are discussed in Section 8.3.3.

The fundamental problem in the anaerobic digestion process is that equilibrium has to be maintained between acid- and methanogenic fermentation. While this equilibrium exists, the concentration of intermediate products from the conversion of organic material into biogas (many of which are acids) will be low and at any time the conversion of hydrolysed products to the final products is substantially complete.

However, if for some reason the equilibrium is disrupted, there will be an accumulation of (acid) intermediates and consequently the pH of the digester will decrease. As methanogenesis requires a pH near the neutral value ($6.5 < pH < 7.5$), the decrease in pH might lead to a reduction of the methane production rate and a further accumulation of acids. As a consequence, the process of anaerobic digestion as a whole may fail due to “souring” of the reactor contents. The digester will only return to activity when the pH of the reactor is restored to a value near neutral pH, which can be effected through the addition of alkalinity.

When anaerobic digestion is compared with other methods of sludge stabilisation (particularly aerobic digestion), the following advantages and disadvantages can be distinguished:

Advantages:

- Production of a useful energy source in the form of biogas, which can be used for power generation (for instance to be used for aeration of the mixed liquor), or can be converted into liquid gas for car fuel, as is currently done by the waste water companies in São Paulo (Sabesp) and Paraná (Sanepar);

- Reduction of the mass of excess sludge and production of a stabilised sludge with excellent rheological properties for water removal;
- Substantial improvement in the hygienic quality of the digested sludge because of the efficient removal of pathogens.

Disadvantages:

- The construction costs of an anaerobic digester are considerable. It will be necessary to construct a relatively large unit which is closed to the atmosphere and equipped with complicated devices for feeding, mixing, and (in case of low temperatures) heating of the digester contents;
- The supernatant of the digester contains a high concentration of biodegradable material, principally ammonium. The reintroduction of the supernatant into the activated sludge process results in a significant increase of the nitrogen load;
- Toxic material or operational errors may cause a disruption of the equilibrium between acid and methanogenic fermentation. The correction of the operational problems is difficult and may require considerable time.

There are two important aspects related to the stoichiometry of anaerobic digestion: (1) the effect of digestion on alkalinity and consequently on pH and (2) the potential biogas production and more specifically that of methane. If a structural formula of $C_5H_7O_2N$ is assumed to be representative for secondary sludge, acid- and methanogenic fermentation can be expressed as:

(a) Acid fermentation:

$$C_5H_7O_2N + 3H_2O \rightarrow 2.5\ CH_3COOH + NH_3 \quad (8.56a)$$

$$\rightarrow 2.5\ CH_3COO^- + 1.5\ H^+ + NH_4^+$$

(b) Methanogenic fermentation:

$$2.5\ CH_3COO^- + 2.5\ H^+ \rightarrow 2.5\ CO_2 + 2.5\ CH_4 \quad (8.56b)$$

The overall anaerobic digestion can be summarised as:

$$C_5H_7O_2N + 3\ H_2O + H^+ \rightarrow 2.5\ CO_2 + 2.5\ CH_4 + NH_4^+ \text{ or} \quad (8.56c)$$

$$C_5H_7O_2N + 4\ H_2O \rightarrow HCO_3^- + 1.5\ CO_2 + 2.5\ CH_4 + NH_4^+$$

Equation (8.56a) shows there is a production of 2.5 mole of acetic acid and 1 mole ofammonia per "mole" (113 grams) of digested biological sludge. After the dissociation of acetic acid (which is virtually complete at neutral pH) and the reaction of the hydrogen ion with ammonia, there is a net production of 1.5 mole H^+ per mole of sludge or, equivalently, there is a consumption of $1.5 \cdot 50 = 75$ g $CaCO_3$ per 113 g of acidified sludge. Hence, during acid fermentation there is an alkalinity consumption of $75/113 = 0.66$ g $CaCO_3$ per gram of acidified sludge.

During methanogenic fermentation, there is consumption of H^+ i.e. there is alkalinity production. With the aid of Eq. (8.56b), the alkalinity production is calculated as $2.5 \cdot 50 = 125$ g $CaCO_3$ per mole of digested sludge. Hence in the overall process (acid- plus methanogenic fermentation) there is an alkalinity production of 50 g $CaCO_3$ per 113 g of digested sludge or $50/113 = 0.44$ g $CaCO_3$ per gram of digested sludge. This increase can be attributed mainly to the mineralisation of organic nitrogen into NH_4^+ and is more than sufficient to maintain the pH in the suitable range for methanogenesis (Van Haandel, 1994).

It is known that the nitrogen content of primary sludge is lower than that of biological sludge. Probably a better approximation of the composition of primary sludge is to consider it as a mixture of proteins, carbohydrates and fats with the average structural formula $(CH_2O)_n$. The following reaction equations can be written:

(a) Acid fermentation:

$$(CH_2O)_n \rightarrow n/2\ CH_3COOH \rightarrow n/2\ CH_3COO^- + n/2\ H^+ \qquad (8.57a)$$

(b) Methanogenic fermentation:

$$n/2\ CH_3COO^- + n/2\ H^+ \rightarrow n/2\ CH_4 + n/2\ CO_2 \qquad (8.57b)$$

For the overall anaerobic digestion process:

$$(CH_2O)_n \rightarrow n/2\ CH_4 + n/2\ CO_2 \qquad (8.57)$$

Equations (8.57 a and b) indicate that during anaerobic digestion of primary sludge there will be a consumption of 1 mol (50 g $CaCO_3$) of alkalinity per “mol” of primary sludge (60 grams) or 50/60 = 0.83 g $CaCO_3.g^{-1}$ VSS. During the methanogenic fermentation, the consumed alkalinity will be recovered and the overall effect of complete anaerobic digestion of primary sludge is that alkalinity remains unchanged. In most situations when primary sludge is digested together with the biological excess sludge, there is always alkalinity production during anaerobic stabilisation of sludge. The numerical value of the alkalinity increase will depend upon the TKN/VSS ratio in the mixed sludge, but it can be shown that for sewage the generation of alkalinity is always more than sufficient to maintain an optimal pH value in the digester (van Haandel 1994). However, at lower TKN/VSS ratios, both the alkalinity production and the buffer capacity in the digester will be small, so that souring may occur more easily. Even in the case of purely proteinic matter, souring is possible if for some reason methanogenic fermentation is reduced.

The potential of methane generation in the digester can be calculated from stoichiometry by remembering that l gram of CH_4 (with a COD content of 4 grams) will be generated from the digestion of 4 grams organic matter expressed as COD. Thus the mass of produced methane is calculated from the total digested excess sludge production and the composition in terms of the mass fractions of primary and secondary sludge.

Under the conditions prevailing in the digester (atmospheric pressure, temperature of 30°C), the volume of l mole of methane (16 gram) is about 25 litre or 25/16 = 1.6 $litre.g^{-1}$ CH_4. Eqs. (8.56 and 8.57) show that for both primary and secondary sludge, an equal number of moles of CO_2 and CH_4 are produced. However, as CO_2 is more soluble in water where it will form bicarbonate, the released biogas is always richer in methane. In practice, the methane percentage in digester biogas is in the range of 55 to 70 percent.