A REVIEW OF THE ANAEROBIC DIGESTION PROCESS

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ABSTRACT
As one of the oldest biological waste treatment processes, anaerobic digestion offers the advantages of low energy requirement, high treatment efficiency, low excess sludge production, low nutrient requirement, no oxygen requirement and energy recovery. This paper reviews the process covering its fundamental requirements, factors affecting it, effect of mixing as well as mixing regimes. The fundamental stage-wise processes of hydrolysis, acidogenesis, acetogenesis and methanogenesis were described. The factors affecting the performance of anaerobic digesters include feeding rate, feeding mode (retention time), temperature, pH and alkalinity, nutrient content, toxicity, mixing frequency and intensity as well as the method of mixing. The factors affecting mixing in digesters are in turn reviewed in considerable detail. The relevance of anaerobic digestion in the light of the enforcement of the Kyoto Protocol was also discussed, together with the rationale for waste treatment options for minimisation of greenhouse gases. It is concluded that treatment options for waste management should include anaerobic digestion in which methane is captured for power generation, a planned process flow to minimise pumping of wastewater, planned biosolid flow to minimise internal transport and systems that avoid incineration using fossil fuel. Finally, more recent developments in the areas of microbial fuel cell as well as biological production of hydrogen were discussed. With the emergence of "white biotechnology" leading to the pursuit of bio-refinery projects, it is suggested that anaerobic digestion should now be integrated with bio-refinery activities to find its exclusive niches.

INTRODUCTION

Anaerobic digestion is one of the oldest biological waste treatment processes. It was a century ago that anaerobic digestion was first applied in wastewater treatment. With the use of digester heating and mixing, it has become the most common method of sewage sludge stabilisation. It has also been applied to processing wastes originating from industries such as dairy, abattoir, piggery, palm oil, brewery and other food processing forms. These agricultural wastes are relatively concentrated, having a high content of biodegradable organic matter. Anaerobic digestion offers the advantages of low energy requirement, high treatment efficiency, low excess sludge production, low nutrient requirement, no oxygen requirement and energy recovery. It has been shown that both the capital and operational costs of anaerobic treatment increase relatively slowly with increasing waste strength, compared with aerobic treatment (Eckenfelder *et al.*, 1988).

Recognition of the potential of anaerobic processes has led to the development of highly advanced reactor configurations for improved biomethanation. Anaerobic microorganisms being used in waste management are present ubiquitously in many natural ecosystems. Whether studied under natural conditions or within controlled systems, anaerobic processes have become a focus of multidisciplinary research resulting in a broadening of their application throughout the world. Anaerobic processes are being studied in fields as diverse as soil and sediment systems, gastrointestinal tracts of animals, geothermal vents, municipal landfills, and of course, liquid waste management.

There have been significant efforts to promote small-scale biomethanation plants for

methane production and fertiliser conservation in both China and India. In 1930, the Chinese government granted a patent for a biogas production system to an entrepreneur who then built up a gas production company with branches in 13 provinces (Xu, 1983). In 1939, biomethanation research was initiated in India at the then Imperial Agricultural Research Institute, largely due to concern over increased use of manure as cooking fuel, with its consequent loss as fertiliser. The aim then was to make use of manure as a fuel source without destroying its usefulness as a fertiliser (Idnani and Acharaya, 1963). The research resulted in the development of the well-known floating-dome biogas plant, which was promoted by the Khadi and Village Industries Commission as well as the Gobar Gas Research Station for rural areas of India. Similarly, interest shown by the Chinese government in the 1970's resulted in the building of over 6.5 million units of family-size fixed-dome type biogas plants in 30 million villages (Xu, 1983).

Meanwhile in the west, advanced anaerobic configurations such as the anaerobic filter were developed in the 1970's, while the Upflow Anaerobic Sludge Blanket (UASB) process was developed in 1979. As a result of its effectiveness and low cost, anaerobic treatment has received considerable attention throughout the world.

FUNDAMENTALS OF ANAEROBIC DIGESTION

Conceptually, anaerobic digestion of complex organics can be described as a stage-wise process involving:

1. Hydrolysis
2. Acidogenesis
3. Acetogenesis and homoacetogenesis
4. Methanogenesis

At least five groups of bacteria are known to be involved, namely, fermentative bacteria, hydrogen-producing acetogenic bacteria, hydrogen-consuming acetogenic bacteria, carbon dioxide reducing methanogens and acetoclastic methanogens. However, the division is only arbitrary and schematic since in actual fact the bacteria cannot be separated due to the fact that each group is metabolically dependent on one another, i.e. they are ecologically syntrophical (McInerney *et al.*, 1979).

Hydrolysis

Hydrolysis and liquefaction are achieved due to the presence of hydrolytic enzymes produced and excreted by bacteria. Once complex organics are hydrolysed, they are converted to short chain organic acids, sugars, amino acids and eventually to acetic, propionic, butyric and valeric acids. This stage is commonly called the "acid-forming" or acidogenic phase and is described in the following section. During hydrolysis, no stabilisation of the organic waste occurs. The overall rate of stabilisation and methanogenesis of complex polymeric compounds is often limited by the rate of hydrolysis, particularly for agricultural wastes containing insoluble solids. There must be sufficient hydrolytic enzymes having intimate contact with the organic fraction. This fact emphasizes the importance of having a large, active microbial population, sufficient organic substrate and uniform mixing. Acid-forming bacteria may be facultative, obligate anaerobes or a combination of both. They are inhibited by hydrogen which, however, is an energy source for some methanogenic bacteria which reduce carbon dioxide to methane.

The rate of hydrolysis is dependent on the type of biopolymer as well as on environmental factors. The anaerobic rate of hydrolysis for each type of complex substrate varies, with that of carbohydrates being generally more rapid than that of proteins. Gujer and Zehnder (1983) found that the hydrolysis rate constants for lipids, protein, cellulose and hemicellulose were 0.08 to 1.7, 0.02 to 0.03, 0.04 to 0.13, and 0.54 day^{-1}, respectively. The hydrolysis and fermentation of cellulose by a continuous culture of *Ruminococcus albus* follows first-order kinetics while its rate constant was found to be 1.18 day^{-1} (Pavlostathis *et al.*, 1988). The rate of hydrolysis appears to be affected by pH, with the highest rate for cellulosic materials being at pH 6.7 (Eastman and Ferguson, 1981). It is also influenced by temperature, with optimum hydrolysis being found to be at 40° C (Tong and McCarty, 1991). A detailed review of

microbial hydrolysis in anaerobic digestion of cellulosic materials has been published (Tong and McCarty, 1991).

Fermentation

A second group of anaerobic bacteria ferments the hydrolysed products to short chain organic acids, the most common of which is acetic acid. This group of bacteria is called the acidogenic bacteria. Hydrogen is produced by the acidogenic bacteria; the hydrogen plays a key role in regulating the next stage termed acetogenesis. The non-methanogenic bacteria, collectively known as acidogens include *Clostridium spp, Peptococcus spp, Bifidobacterium spp, Desulphovibrio spp, Corynebacterium spp, Lactobacillus, Actinomyces, Stayphylococcus* and *Escherichia*.

After sugar and other monomers have been formed by hydrolysis, they can then be metabolised to provide energy and synthesis materials. Since metabolic products formed from the energy source are used as energy acceptors, no external electron acceptors are required. Production of ATP is accomplished by substrate level phosphorylation. There is no utilisation of pathways that lead to complete oxidation of the energy source. During this stage of fermentation, the Embden-Meyerhof-Parnas (EMP) pathway plays the most important role. Other pathways such as the tricarboxylic acid (TCA) and hexose monophosphate (HMP) pathways only occur in reactions required for conversion of substrates to intermediates of the EMP pathway (Gaudy and Gaudy, 1981). The EMP pathway converts sugars into pyruvic acid. In the process, $NADH_2$ is oxidised and additional ATP may be generated by substrate level phosphrylation.

Another common product is lactic acid, formed as a result of acceptor replacement for the hydrogen removed during formation of pyruvate. However, only low levels of lactic acid are usually found in stable digesters, possibly due to its rapid consumption. Lactic acid bacteria are represented by the genera *Lactobacillus, Leuconostoc* and *Pediococus* (Linden, 1988). Due to the low level of lactic acid found in most anaerobic digesters, it was excluded in early modeling work as an intermediate product. However, Costello (1989) proposed its inclusion in anaerobic modeling, demonstrating its importance during shock loading, particularly of carbohydrates, and its significance in two-stage anaerobic digestion, where a separate acidification reactor is provided.

Anaerobic fermentation produces three major types of volatile fatty acids, namely acetic, propionic and butyric acids, as represented by the following three reactions:

$$C_6H_{12}O_6 + 2H_2O \Rightarrow 2CH_3COOH + 2CO_2 + 4H_2 + 4\ ATP$$
$$C_6H_{12}O_6 \Rightarrow CH_3CH_2CH_2COOH + 2CO_2 + 2H_2 + 3\ ATP$$
$$C_6H_{12}O_6 + 2H_2 \Rightarrow 2CH_3CH_2COOH + 2H_2 + 2\ ATP$$

The conversion of glucose to acetic acid, as represented by the first reaction, is the preferred reaction (Mosey, 1983). It produces four ATP with another two ATP being produced during the EMP pathway resulting in pyruvic acid, while two additional ATP are produced from each mole of acetic acid formed. Propionic acid is formed by some anaerobic bacteria, notably by the genus *Propionibacterium*, which consumes lactic acid produced by lactic acid bacteria. It may also be formed as the metabolic end product of long-chain fatty acids which contain odd numbers of carbon atoms (Gaudy and Gaudy, 1981). Butyric acid is produced by anaerobic metabolism of butyric clostridia such as *Clostridium butyricum* and *Clostridium tyrobutyricum*. In this reaction, it was assumed by Mosey (1983) that only two moles of ATP were produced. Other workers such as Gaudy and Gaudy (1981) and Sheehan (1981) had earlier suggested the production of one additional mole of ATP for each mole of butyric acid formed. The more recent research work on anaerobic modeling by Costello (1989) adopted the latter view.

Other intermediate metabolic products of anaerobic fermentation are ethanol, succinic acid and formic acid. Ethanol can be produced from glucose through the heterolactic pathway of *Leuconostoc* and some species of *Lactobacillus*. It can also be produced via the Entner-Douderoff pathway by *Zymomonas mobilis* (Gaudy and Gaudy, 1981; Linden, 1988). Succinic acid is produced as an intermediate product in the cyclic

pathway which produces propionic acid. Other species such as *Escherichia coli* and *Enterobacter aerogenes* produce lactic acid, ethanol, acetic acid, carbon dioxide and hydrogen. Accumulation of formic acid may be found in the fermentation of some enteric bacteria which lack enzyme-synthesis ability (Gaudy and Gaudy, 1981). More complex metabolic pathways resulting in the formation of acetone and butanol also occur. These have been reviewed by Datta (1988).

Acetogenesis and Homoacetogenesis

Methanogenic bacteria can utilise only a very limited number of substrates as energy sources. These are acetate, methanol, methylamine, carbon dioxide and formate, Fermentation products such as propionic acid, butyric acid and ethanol have two carbon atoms and therefore must be converted to acetic acid before they can be utilised by methanogenic bacteria. This conversion is accomplished by acetogenic bacteria which suffer from thermodynamic product inhibition by hydrogen gas. At the same time, their growth rate is dependent on the simultaneous removal of reduced products and acetate (Lannotti *et al.*, 1973 ; Wolin, 1974). The hydrogen-utilising bacteria play a pivotal role in the degradation process by removing hydrogen generated by the hydrolytic and acetogenic bacteria. Such bacteria produce methane from hydrogen and carbon dioxide. In such a situation, acetogenic bacteria are provided with favorable growth conditions while their metabolic partners are simultaneously provided with carbon as an energy source. Under standard conditions of acetogenesis, the chemical free energy change is positive for most reactions (Thiele and Zeikus, 1988).

This is demonstrated in Table 1 which shows that the free energy change for propionate oxidation is more positive than those for ethanol and butyrate, indicating that propionate suffers from a greater sensitivity to product inhibition than ethanol or butyrate. In other words, the oxidation of propionate is thermodynamically less favorable than those of ethanol and butyrate, considering that one mole of propionate produces three moles of hydrogen compared with only two moles of hydrogen produced from one mole of ethanol or butyrate. A small amount of acetate is formed by homoacetogenic bacteria which convert carbon dioxide to acetic acid. Two bacterial species have been reported to be involved in this conversion, namely *Acetobacterium woodee* and *Clostridium aceticum* (Braun *et al.*, 1981).

Table 1. Important reactions and free energy change in anaerobic ecosystems (after Thiele and Zeikus, 1988)

No	Reaction	DG
	Acidogenic fermentative bacteria	
1	Glucose + 2 H_2O Æ 2 ethanol + 2 HCO_3 + 2H^+	-225.4
2	Glucose Æ 2 lactate$^-$ + 2H^+	-198.1
3	Glucose + 2 H_2O Æ butyrate$^-$ + 2 HCO_3 + 3 H^+ + 2 H^+	-254.4
4	Glucose Æ 3 acetate$^-$ + 3 H^+	-310.6
5	3 lactate$^-$ Æ 2 propionate$^-$ + acetate$^-$ + HCO_3^- + H^+	-164.8
	Acetogenic bacteria	
6	Ethanol + H_2O Æ acetate$^-$ + 2H_2 + H^+	+9.6
7	Lactate$^-$ + 2 H_2O Æ acetate$^-$ + 2H_2 + HCO_3^- + H^+	-3.96
8	Butyrate$^-$ + 2 H_2O Æ 2 acetate$^-$ + 2H_2 + H^+	+48.1
9	Propionate$^-$ + 3 H_2O Æ acetate$^-$ + HCO_3^- + 3 H_2 + H^+	+76.1
	Methanogenic bacteria	
10	Acetate$^-$ + H_2O Æ methane + HCO_3^-	-31.0
11	4 H_2 + HCO_3^- + H^+ Æ methane + 3 H_2O	-135.6
12	4 HCO_3^- + H^+ + H_2O Æ methane + 3 HCO_3^-	-130.4

Methanogenesis

During methane formation, a further group of microorganisms, the methanogens, which are strict anaerobes, convert the hydrogen and acetic acid formed by acid formers to methane and carbon dioxide. These include *Methanobacterium, Methanobacillus, Methanococcus, Methanosarcina* and *Methanothrix*. They are known to use carbon dioxide, hydrogen, formate, acetate, methanol, methylamines and carbon monoxide as substrates. All methanogenic bacteria belong to the archae kingdom and differ from bacteria in ribosome composition, membrane lipids and cell wall components. The structure and physiology of these bacteria are excellently reviewed by Zeikus *et al.* (1985) and Jones *et al.* (1987).

The main pathways involved in methane formation are conversion of hydrogen and carbon dioxide to methane and water, and conversion of acetate to methane and carbon dioxide. Approximately 72% of methane formed in anaerobic digestion of wastewater sludges originate from acetate cleavage (Jeris and McCarthy, 1965; Kaspar and Wuhrmann, 1978). The acetoclastic methanogens perform the function of carbon removal. Approximately 30-40% of biological methane is produced by reduction of carbon dioxide (Thiele and Zeikus, 1988). As shown in Table 2, most of the reactions producing acetic acid from fermentative products are thermodynamically unfavourable.

However, these reactions are made possible by the removal of hydrogen from the system by the hydrogen-utilising methanogens. Although only a third of methane is produced from this reaction, the hydrogen transfer is important in regulating the partial pressure of hydrogen (Mosey, 1983). A detailed review of the kinetics of methanogenic bacteria has been published by Pavlostathis and Giraldo-Gomez (1991).

FACTORS AFFECTING PERFORMANCE OF ANAEROBIC DIGESTERS

Feeding Rate (Retention Time)

The feeding rate determines the residence times of the substrates in a digester. In a continuous and completely mixed digester, the mean cell residence time equals the mean hydraulic retention time (HRT). To prevent bacterial wash-out, the mean cell residence time must be at least the reciprocal of the net growth rate of the anaerobic bacteria. Under optimum, steady state conditions, this would be minimally 3 or 4 days (Lawrence, 1971). Generally, the organic loading rate is a yardstick for measuring the efficiency of the available reactor volume utilisation. It is generally calculated as

$$B_v = \frac{C_i \cdot Q}{V}$$

where B_v is the volumetric organic loading rate (kg COD/m^3.d), C_i the raw wastewater biodegradable COD concentration (mg COD/L); Q the wastewater flow rate (m^3/day) and V the bioreactor volume (m^3).

The primary purpose of anaerobic digestion is the partial biological destruction of the volatile solids in the sludge to enhance dewaterability and reduce putrescibility of the sludge. Since volatile solids degradation is time dependent, the design criteria for most anaerobic digesters is based on the hydraulic detention time required to achieve a specific reduction in the volatile solids content of the digested sludge. That the hydraulic detention time affects the rate and extent of methane production has been elucidated as early as 1960 (Hindin and Dunstan, 1960). For an anaerobic digester with no recycle, the hydraulic retention time is the same as the mean cell residence time. Methane-forming bacteria have a relatively long generation time compared with those of aerobic and facultative bacteria. This refers to the time required to double the number of bacteria.

The generation times of methane-forming bacteria range from less than two days to more than 20 days at around 35° C. Thus, typical detention times for anaerobic digesters are about 15-20 days. The design detention time is a function of the final disposal of the sludge (perhaps land application or incineration). This is because the conversion of volatile solids to gaseous products

is dependent on the hydraulic detention time. It follows therefore, that for a given detention time, the digester volume is controlled by the solids loading. Typically the design solids loading to most anaerobic digesters ranges from 3.2 to 7.2 kg VS/m^3.day (Anon. 1987). The bulk of the data gained from practical digestion of sewage sludge indicates that the design HRT should be at least ten days (Malina, 1992).

Feeding Mode

Feeding can be continuous or intermittent. Continuous feeding is recommended because it provides a more uniform environment for the microorganisms involved. Intermittent feeding tends to promote a "feast or famine" type of situation for the bacteria. In cases where continuous feeding is impossible, frequent intermittent feeding is the next best cause of action.

Temperature

Anaerobic digestion may be carried out under psychrophilic (below 20° C) mesophilic (30-38° C) or thermophilic (50-60° C) conditions. However, optimal efficiency is found only at the mesophilic and thermophilic ranges. Low rates of digestion between these two optima may be due to a lack of adaptation (Macki and Bryant, 1981). With temperatures at or above 70° C, methanogenic rates have been reported to decrease (Zinder *et al.*, 1984). For conventional single-stage digesters, it is generally recognised that the economic optimum temperature is around 35° C.

Nutrient Content

Like other biological processes, nutrients including nitrogen, trace elements and vitamins are required in anaerobic digestion. However, since there is a very low net cell yield, the nutrient requirement is correspondingly much lower compared with aerobic processes. For feedstocks such as sewage, agricultural and food processing wastes, available nutrients are usually in excess of requirements. The elemental composition of bacterial cells is roughly $C_5NH_7O_2$ (Parkin and Owen, 1986) and about 15% of carbon substrate is assimilated by the bacteria. Thus, a carbon to nitrogen ratio of 100:3 (wt/wt) may be necessary to maintain bacterial growth. If there is too much nitrogen in the substrate, ammonia may accumulate in the mixed liquor and at high concentrations, it is toxic to methanogenic bacteria. Occasionally, the C:N ratio may be affected by substrate specificity. If measured as chemical oxygen demand, COD:N ratios of about 400:7 and 1000:7 have been estimated as high (Henze and Harremoes, 1983) and low (Van den Berg and Lentz, 1978) substrate loadings, respectively. Similarly, a N:P ratio of 7:1 has been reported to be required (Stronach *et al.*, 1986). Other nutrients considered as necessary for various conditions of active methanogenesis include trace elements such as iron, nickel, magnesium, calcium, sodium, barium, tungsten, molybdate, selenium and cobalt. Under normal circumstances mixed-substrate systems, particularly those originating from wastes, have an abundance of essential nutrients.

pH and Alkalinity

pH is a measure of the hydrogen ion concentration and is important to digester stability because it is thermodynamically unfavorable for methanogens to oxidize molecular hydrogen to methane at a low pH against a proton gradient (Parkin and Owen, 1986). Generally, a pH between 6.8 and 7.2 is preferred. As the pH drops below 6.8, significant inhibition of methanogenesis occurs. The acid formers continue to produce excess volatile fatty acids (VFA), further reducing the pH. With the addition of a strong base such as sodium hydroxide or a carbonate salt, ionic equilibrium occurs rapidly and carbon dioxide is removed from the gas phase to form the required bicarbonate alkalinity, which is a measure of the buffering capacity of the reactor content. If the buffering capacity is low, relatively small increases in VFA concentration will have a severe effect on pH, resulting in reduced methanogenic activity.

On the other hand, if there is adequate alkalinity, the system can tolerate significant changes in VFA concentrations without large changes in pH. A bicarbonate alkalinity of 2.5-6.0 g calcium carbonate/L usually provides sufficient buffering capacity. However, methane production is not limited to near neutral pH, since

methanogenesis is known to occur in both acidic and alkaline environments. Two acetate-degrading methanogens, *Methanosarcina barkeri* and *Methanosarcina vacuolata* are known to grow well at low pH when cultured on hydrogen and methanol (Maestrojuan and Boone, 1991). Similarly, hydrogen-utilizing methanogens have been found at very alkaline pH (Boone *et al.*, 1986).

Toxicity

The toxicity of a substance to a mixed substrate depends on its concentration, degree of acclimation by microorganisms, effects of pH, valency, synergism, antagonism, temperature and biomass characteristics. An ammonia-nitrogen concentration above 1,500 mg/L is inhibitory at pH values greater than 7.4 while at 3,000 mg/L regardless of pH, ammonia is toxic (McCarty, 1964). Due to the degradation of protein present in most wastewater sludges, nitrogen is released either as ammonium ion or as dissolved free ammonia, depending on the pH. Free ammonia in excess of 150 mg/L is severely toxic to anaerobic digestion. Soluble heavy metals in the range of 0.1-10 mg/L are inhibitory (Kugelman and Chin, 1971).

Chlorinated hydrocarbons such as those that may be used to wash piggery and dairy parlors are inhibitory at about 115 mg/L (Meynell, 1976). Soluble sulphides at concentrations above 200 mg/L decrease methane gas yield (Lawrence *et al.*, 1964). However, if sufficient solid retention time (SRT) is provided to allow bacterial acclimation, toxic substances at 20-50 times the inhibitory levels may be tolerated (Parkin and Speece, 1983). In terms of volatile fatty acids, the effects manifested are related to other factors particularly pH and buffering capacity. Recent work on anaerobic modeling has incorporated regulation and inhibition of hydrolytic bacteria as well as propionic and butyric acetogenic bacteria (Mosey, 1983; Costello *et al*, 1991a; Costello *et al.*, 1991b).

Mixing

Initial attempts at mixing digesters were directed at breaking the scum or keeping the scum moist so that the gas could escape (Malina, 1992). Most of the current knowledge on mixing is gained from experience with sewage sludge digestion. Mixing is variously achieved by pumping supernatant to moisten the scum, transferring from one digester to another, using a vertical screw pump, re-circulating gas or mechanical stirrers. However, the effects of mixing on the process of anaerobic digestion are not well understood (Verhoff *et al.*, 1974; Stuckey, 1983). The benefits of mixing are generally attributed to the following (U.S. EPA, 1979; Monteith and Stephenson, 1981; Rundle and Whyley, 1981; Cooper and Tekippe, 1982):

a. minimisation of solid deposition and dead space;
b. uniform substrate distribution, thus reducing short circuiting;
c. elimination of scum formation;
d. intimate contact between microorganism and feed;
e. uniformity of environmental factors; and
f. even distribution of buffering alkalinity.

Lack of mixing has been identified as one of the causes of poor digester performance (Swanwick *et al.*, 1969). Finney and Evan (1975) hypothesised that the transport of biogas to the gas phase was the rate-limiting step in the anaerobic digestion process. Thus, at high substrate levels, bubbles of methane and carbon dioxide would surround the bacteria, hindering the transport of substrate to the cells. This hypothesis implied that gas transport and hence the rate of biodegradation would be improved by efficient mixing, which reduces the film thickness of gas bubbles (Chapman, 1989). Jones and Greenfield (1982) found that mixing promotes carbon dioxide removal by increasing the rate of nucleation for bubble formation. The work of Yaziz (1989) demonstrated that *Salmonella* organisms survive longer in the stagnant zones of a digester, indicating the importance of mixing in *Salmonella* destruction. Two disadvantages are found in mixed digesters. Firstly, the cost of mixing can be substantial. Secondly, there is a need for providing a separate vessel for separation of the digested sludge from the liquid phase.

FACTORS AFFECTING MIXING IN DIGESTERS

Fluid Properties and Sludge Characteristics

Fluid properties and sludge characteristics depend on the nature and concentration of the raw waste. Table 2 shows the ranges and typical values of solid concentrations for sludge produced from different unit operations (Metcalf and Eddy, 1991). Sludges are two-phase fluids consisting of water and flocculent particles. Typically, their flow is non-Newtonian. The apparent viscosity of a digesting sludge is a function of both total solids concentration and its volatile content (Buzzell and Sawyer, 1963). Early work by Hartfield (1938) showed that sewage sludge exhibits pseudoplastic characteristics with slight thixotropic behaviour. Later work confirmed that sewage sludge is pseudoplastic with a relatively small but definite yield stress (Buzzell and Sawyer, 1963; Mackay, 1991).

Rheological measurements are now used to characterise both sludge and slurries (Campbell and Crescuolo, 1982; Zhang and Day, 1990). Rheological properties are dependent on the concentration of total suspended solids for sewage sludge, being Newtonian, Bingham plastic and pseudoplastic for TSS concentrations of less than 1.0%, 1.0 to 2.0% and more than 2.0% respectively (Chapman, 1989). In the case of fresh swine slurry, the flow properties are Non-Newtonian, dilatant and pseudoplastic for total solids contents of 1 to 2%, 2 to 4% and 6 to 8%, respectively (Zhang and Day, 1990). Further, for fresh swine manure slurry with a total solids content of 2 to 8%, the relationship between shear stress and shear rate follows a power law.

As the applied shear rate decreases, the apparent viscosity of sludge increases. The fluid properties are therefore a function of the complex three-dimensional flow within the digester. The apparent viscosity of sludge is high in the regions of the digester away from a mixing device. Stagnant zones are found in these regions. Near the mixing device, the apparent viscosity of sludge is low and velocity gradients are large. The apparent viscosity of sludge increases with an increase in solids concentration, resulting in increased power requirements for mixing. Sawyer and Grumbling (1960) suggested that it was impractical to thicken sludges to more than 8% unless the volatile fraction of the sludge exceeded 65%.

Chapman (1989) made the following assertions regarding the effects of sludge characteristics:

a) anaerobic digesters require large power inputs to induce motion in all parts of the digester;
b) analysis of mixing requirements is made more complex by the fact that rheological properties vary from plant to plant and that

Table 2. Percent sludge solids from various unit operations (Metcalf and Eddy, 1991)

Process	Range	Typical
Primary settling tank:		
primary sludge	4.0-10.0	3.0-8.0
primary and waste activated	5.0	4.0
Secondary settling tank:		
waste activated sludge with primary settling	0.5-1.5	0.8-2.5
waste activated sludge without primary settling	0.8	1.3
Gravity thickener:		
primary sludge only	5.0-10.0	2.0-8.0
primary and waste activated	8.0	4.0
Anaerobic digestion:		
primary sludge only	5.0-10.0	2.5-7.0
primary and waste activated	7.0	3.5

the apparent viscosity of sludge is dependent on its previous shear history and relative zone within digester;

c) a knowledge of the sludge rheological characteristics is required for proper selection of mixing equipment.

Mixing Systems

Current mixing systems in anaerobic digesters can be divided into four types, viz.,

a) Unconfined gas injection
b) Confined gas injection
c) Mechanical stirring
d) Mechanical pumping

In unconfined gas injection systems, gas is collected at the top of the digester, compressed and then discharged through bottom diffusers or mounted lances. Mixing is accomplished by gas bubbles which rise to the surface, carrying and moving the sludge. In a confined gas injection system, gas is released within a tube known as a draft tube. In one type, known as a gas lifter, several lances are located in the draft tube. Increasing the depth of submergence of the lances within the draft tube increases the pumping rate (Baumann and Huibregtse, 1982). Multiple gas lifters are generally provided for digesters with diameter larger than 18 m (Metcalf and Eddy, 1991).

However, in the case of agricultural waste slurries, especially for fibrous cattle slurry, draft tubes pose a greater risk of fouling and blockages (Cumby, 1990). In another type of confined gas injection device, known as a gas piston, gas bubbles are intermittently released at the bottom of a cylindrical tube. Acting like a piston, the bubbles rise, pushing the sludge to the surface. Generally, multiple gas pistons are provided when digester diameters are wider than 9 m. Mechanical stirring systems consist of either low speed turbines or low speed mixers. Mixing is accomplished by rotating impellers. Digesters using low speed turbines are usually equipped with wall-mounted baffles to prevent vortexing.

Mechanical stirring systems usually have cover-mounted motors and are not suitable for digesters with a gas holder cover since submergence is reduced as the cover rises. Mechanical pumping systems consist of propeller-type pumps mounted in draft tubes which can be inside or outside the digester. Mixing is accomplished by creating a fluid pumping action. Multiple draft tubes are generally provided for digesters with diameters wider than 9 m. Another type of mechanical pumping is pumped re-circulation which consists of pumps and associated pipe work to withdraw sludge near the top of the digester and discharge it through nozzles at the base.

Advantages and disadvantages of mixing systems

The advantages and disadvantages of each system are listed by Metcalf and Eddy (1991). There is no single design parameter which can be applied to all mixing systems to establish a basis of comparison (US EPA, 1987). Common design parameters are:

a) Unit power, defined as motor power of mixing equipment in watts divided by digester volume in m^3 (W/m^3);
b) Unit gas flow, defined as quantity of gas delivered by the gas injection system in m^3/min divided by digester volume in 1000 m^3 ($m^3/min/km^3$);
c) Turnover time, defined as digester volume divided by sludge flowrate (min);
d) Velocity gradient defined as the square root of the ratio of the power used per unit volume divided by the absolute viscosity of the sludge (sec^{-1}).

Typical values of design parameters for mixing in anaerobic digesters are shown in Table 3 (US EPA, 1987). The most common design parameter is the velocity gradient, which identifies the power delivered to the digester contents. This power is an indicator of the degree of mixing regardless of the mixing systems (US EPA, 1979). However, the use of velocity gradient is limited for the following reasons:

a) Limited information on flow properties of unstabilised sludge; calculation of velocity gradient is based on absolute viscosity,

whereas, being a pseudoplastic fluid, sludge is described by an apparent rather than absolute viscosity. Apparent viscosity is dependent on shear rate applied, so that within a digester, a range of viscosities can be found, depending on the position of a quantity of sludge relative to the mixing device.

b) Sludge viscosity is affected by many factors including temperature, solid concentration and volatile content.
c) Limited data is available which can be used to define acceptable values for the optimum velocity gradient.
d) There is a lack of data demonstrating a correlation between mixing efficiency and velocity gradient values for different mixing systems.

Choice of mixing equipment

In the absence of definitive knowledge on design parameters for a mixing system in anaerobic digestion, its design and choice are based on practical considerations. Chapman (1989) identifies the following practical considerations in the choice of mixing equipment for anaerobic digesters:

a) Safety;
b) Effect of mixing action on foaming within digester;
c) Maintenance requirement;
d) Potential for plugging by rags and other inert materials;
e) Suitability of mixer for use with selected heat exchanger and digester cover;
f) Ease of cleaning; and
g) Suitability of mixer for use in upgrading an existing digester.

Tank Geometry

Anaerobic digesters are conventionally cylindrical in shape with a large diameter relative to the side water depth. In the U.S.A., sizes range from 6-38 m in diameter and 6-12 m in depth (US EPA, 1979). In the U.K., depth to diameter ratios (aspect ratios) commonly range from 0.4:1 to 2:1 (Brade and Noon, 1981). The use of centrally located gas mixers is restricted to tanks with an aspect ratio of between 0.25:1 and 0.7:1 (US EPA, 1979). Hertle and Lever (1987) recommended that an aspect ratio exceeding 1.0 be used for digesters operated at relatively high loadings with continuous mixing. Increased aspect ratio results in higher mixing efficiencies. This translates into the same degree of mixing for less power input in taller digesters. Heat loss is minimized at an aspect ratio of 1:1 (Brade and Noone, 1981).

Alternatives to conventional cylindrical digesters are the rectangular and egg-shaped digesters. Uniform mixing in rectangular digesters is difficult to maintain since dead zones usually develop at the corners.

Egg-shaped digesters are common in Europe. Designs of such digesters are described in detail by Hamman and Sastry (1965). They are usually constructed with scum doors at the top of the tanks and gas spargers along the inside wall near the bottom of the tank. Energy requirements for mixing in egg-shaped digesters are low because of enhanced self-mixing due to the high aspect ratio, although construction costs are high (Garvin and Hills, 1987).

Level of Mixing

Both the capital and maintenance costs of mixed digester are higher that those of conventional digesters. The level of mixing is often empirically

Table 3. Common design parameters for mixing systems

Parameter	Typical value
Unit power	Mechanical system: 5-8 W/m^3
Unit gas flow	Unconfined gas: 4.5-5 m^3/min/1000m^3 Confined gas: 5-7 m^3/min/1000m^3
Turnover time	Confined gas and mechanical mixing systems: 20-30 min.
Velocity gradient	All mixing systems: 50-80 sec^{-1}

determined by a compromise between increased digester stability and achievable digestion rate.

In the case of livestock wastes, intermittent mixing in anaerobic digesters under mesophilic conditions is recommended by Mills (1979) and Smith *et al.* (1979). The data of Hashimoto (1982) also showed that an increased rate of gas production was not large enough to justify for continuous mixing. However, intermittent mixing results in considerable inertial power inputs to start mixing (Brade and Noone, 1981). This is exacerbated by the fact that most slurries and sludges are non-Newtonian in bahaviour. If a sludge exhibits a generalized Bingham plastic behavior, continuous rather than intermittent mixing is recommended (Hertle and Lever, 1987). For sewage sludge digestion, continuous mixing ensures temperature homogeneity (Hwang, 1989). More recently, Ong et al (2000) devised an operational strategy for improved biomethanation of cattle slurry in an unmixed digester. This strategy took advantage of the different rates of biomethanation and biochemical methane potentials of the different layers of the slurry. It was achieved by allowing the slurry to digest without mixing and discharging the effluent from the middle liquid layer rather than from the bottom or top layers.

Power requirements

Owen (1982) suggested that a power level of 13 W/m^3 is adequate for effective mixing. A survey of digesters in the United Kingdom showed that mixing power inputs in digesters of high effective volumes were in the order of only 4 W/m^3 (Brade and Noone, 1981). For mechanical mixing, the recommended power level is 5 to 8 W/m^3 (U.S. EPA, 1987). Power level per se does not ensure a high mixing efficiency. In one digester with a power input of 2.7 W/m^3, the active digester volume was 72%, while in another with a power input of 17 W/m^3, the active volume was still 74% with a short circuit component of 21% (Hertle and Lever, 1987).

Power requirements for mixing are affected by the degree of self-mixing which, in turn is induced by gas-production. Self-mixing is enhanced in digesters with higher aspect ratio (ratio of height to diameter) due to the minimal area at liquid surface available for scum formation and maximal gas generating rate per unit surface area. This point is an important consideration in the development of egg-shaped digesters.

To achieve "off-bottom suspension" of sludge, a minimum mixing intensity in terms of impeller speed was determined as 20 rpm in the case of potato-processing wastewater (Lin and Pearce, 1991). However, the power requirement of high-solid wastes cannot be obtained by extrapolating from that of low-solid wastes. This was proven by the work of Rivard *et al.*, (1995) who showed that increasing the sludge solids up to 30% required similar horsepower per digester volume as that for low-solids sludge (2 to 8%). This could be explained by the fact that in low-solid sludge, sufficient power is still needed to prevent solids settling and scum formation. In the case of high-solid sludge, mixing is required only to provide gentle contact of microorganisms, substrates and nutrients, while releasing in-trained pockets of biogas (Rivard *et al.*, 1995).

RELEVANCE OF ANAEROBIC DIGESTION UNDER THE KYOTO PROTOCOL

The Kyoto Protocol

The Kyoto Protocol (agreed in 1997 and implemented on 16th Feb 2005) is the first of a series of international initiatives to set legally binding, national targets for greenhouse gas (GHG) emissions. Therefore reference should be made to this protocol with regards to GHG emission assessments as well as selection of options for waste management. The protocol has three main objectives, namely: a) to reduce GHG emissions; b) to produce a framework for commoditization of fixed carbon; c) to be a driver for the development of renewable energy and carbon sequestration technology. The outcomes of Kyoto Protocol and any other subsequent protocols would affect the mode of waste treatment. National environmental standards are typically based on water quality criteria.

Waste management methods are mostly based on the utilisation of relatively inexpensive stationery energy, with little consideration for energy production. In most cases, waste treatment facilities are net importers of energy

rather than net generators of energy. Furthermore, most waste treatment plants are actual generators of GHG released from the biological metabolic processes typically used to achieve the desired degree of treatment. In addition to that, most waste treatment plants or animal farms are net exporters of embodied carbon in the form of biosolids or sludge that have the potential to generate GHG in another location where it is exported to. While the Kyoto Protocol is silent on the import/export of energy or embodied carbon, the choice of treatment option should take into consideration the impact of the whole environment in a holistic way.

Rationale for Waste Treatment Option

In the light of the issues mentioned above, it is pertinent to consider the energy and material flows in a waste treatment facility so that an appropriate treatment option could be selected that is in line with the Kyoto Protocol objectives. Figure 1 summaries such a flow. From the energy and mass flows indicated, it is envisaged that any regulations aimed a GHG reduction would influence three important areas in waste treatment, namely, a) the use of non-renewable energy to power pumping, aeration, solid separation, transport, etc within the treatment facility concerned; b) the generation of GHG from waste treatment processes; c) the transport of biosolids from the waste treatment site to another location.

The major GHG that can be produced during waste treatment are carbon dioxide, methane and nitrous oxide. Their greenhouse effect is typically weighted by their Global Warming Potential (GWP), which are dependent on considered timeframe, usually for 100 years. The GWP factors for a 100-year period are CO_2 = 1, CH_4 = 21 and N_2O = 310. This means that over 100 years, one tonne of methane will have a warming effect equivalent to 21 tonnes of carbon dioxide. It is specified in IPCC Guildelines (IPCC, 2000) that emissions of carbon dioxide generated from biomass sources are not counted in GHG inventory. Thus, emissions of CO_2 generated from treatment processes, and those generated from flaring of methane produced from biomass are excluded in the inventory. However, releases of CO_2 from incineration of wastes, unutilized methane from anaerobic waste treatment as well as nitrous oxide from nutrient removal processes are counted in this methodology. In other words, only the anthropogenic but not the biogenic CO_2 are considered.

It is apparent that in the treatment of waste, the following points should be avoided in order to minimize GHG emissions:

a) use of open anaerobic lagoons where methane is released continuously;
b) heavy use of fossil fuel;
c) incineration using fossil fuel;
d) land-filling of waste or biosolids;

On the other hand, the following should be considered:

a) anaerobic digestion in which methane is captured for use;
b) use of methane for power generation;
c) planned biosolid flow to minimize internal transport;
d) planned waste treatment flow to minimized pumping of wastewater;

RECENT DEVELOPMENT

Biological electricity

Electricity could be produced using bacteria in a microbial fuel cell (Kim et al, 1999). It is fundamentally an anaerobic process, in which the bacteria oxidise a substrate and pass the electrons to an electrode (anode). The potential difference between the cathode and the anode forms the basis of the microbial fuel cell (MFC). Thus simultaneous generation of electricity in wastewater treatment becomes potentially feasible. Liu *et al.* (2004) have demonstrated that up to 26 mW/m^2 of reactor surface area could be continuously generated using domestic wastewater in which up to 80% of the BOD was removed at the same time.

Biological production of hydrogen

Another related area in the field of clean energy is the biological production of hydrogen, sometimes called bio-hydrogen production. This has been recently pursued actively, since organic

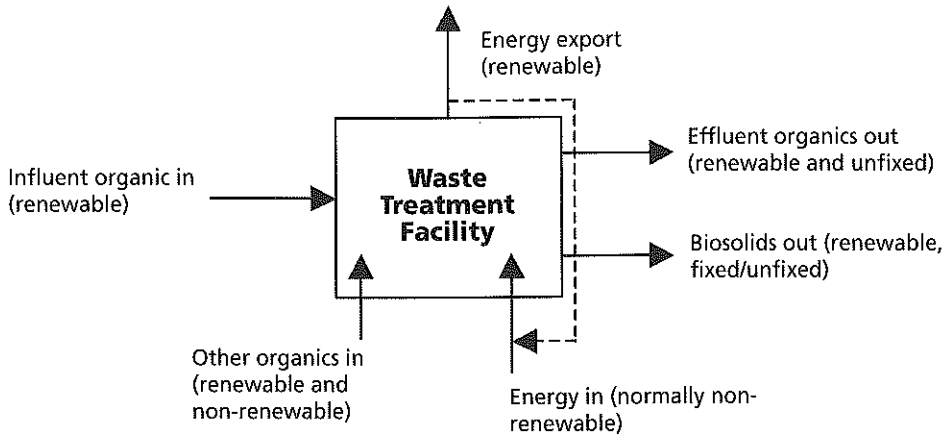

Figure 1. Key energy and waste streams that have a potential impact on GHG release (after Greenfield and Bastone, 2004)

wastes could be a potential feed for hydrogen-producing bacteria via anaerobic process (Levin et al, 2004). An important key to successful bio-hydrogen production is the isolation and identification of efficient anaerobic bacteria responsible for such a hydrogen conversion (Tanishio and Ishiwata, 1994; Yokio *et al.*, 1995; Taguchi *et al.*, 1994; Oh *et al.*, 2003). Among the fermentative bacteria, the clostridial type has been found to be promising for bio-hydrogen production and its metabolic pathway has been well-investigated by Lay (2000). The low yields of hydrogen fermentation, typically only 10-25% of methane yields from anaerobic digestion have limited their applications (Hallenbeck and Benemann, 2002). In the long term, yields may be increased through genetic engineering efforts. In the nearer term, it may be better to combine hydrogen and methane fermentations to produce hydrogen-methane mixed fuel that can reduce NOx emissions during power generation using more conventional internal combustion engine (Benemann *et al.*, 2004).

Solid oxide fuel cell

There is yet another method of clean electricity production, i.e. the electro-chemical oxidation of biogas in a solid oxide fuel cell (Spiegel et al., 1999; Spiegel and Preston, 2000; Staniforth and Ormerod, 2002; Van Herle *et al.*, 2004). With the biogas generated by an anaerobic digester, the solid oxide fuel cell system generally consists of a coalescing filter, an activated carbon bed, a dry reformer, a steam reformer and a hydrogen storage tank (Caner *et al.*, 2004).

Anaerobic digestion re-examined

Anaerobic digestion has traditionally been regarded as end-of-pipe treatment technology for organic waste and wastewater. It has played a key role in the treatment of sewage sludge and animal manure as well as co-digestion of food waste or household waste with animal manure. However, in the whole realm of global waste management, as well as in the overall utilization of renewable energy, anaerobic digestion does not feature prominently. Its only valuable product is biogas, but with it comes its major drawback, i.e. its residual organic and mineral nutrients are problematic for the eco-systems (Verstraete et al., 2004). There is a limit to receiving compost and sewage sludge on normal agricultural lands.

Anaerobic digestion is also sidelined by the emergence of "white biotechnology", which is the production of energy, fuel and other value-added products from bio-materials, leading to the new field of bio-refinery (Kamm and Kamm, 2004). It uses physical, chemical and biotechnological processes to create products such as ethylene, acetic acid, ethanol, polymers, aromatic compounds, etc. Anaerobic digestion would continue to exist in exclusive niches if it ties in

with new processes that could take care of the residual organics produced by anaerobic digestion. Furthermore, ways to integrate anaerobic digestion with bio-refinery efforts should be explored. A case in point is the integration of anaerobic digestion in bio-ethanol production (Ahring and Westermann, 2004). Another opportunity is in biological dechlorination (Verstraete *et al.*, 2004).

CONCLUSION

It can be seen that a multitude of factors affect the process of anaerobic digestion. A host of areas offer opportunities for further research and development covering microbiology, process design, mixing regimes for different substrates, as well as gas utilisation. However, in the light of the Kyoto Protocol, there are incentives to avoid methane emission to the environment and utilise this source of renewable energy more fully. At the same time, new areas such as microbial fuel cell development and bio-hydrogen production are being vigorously pursued for eventual clean energy production and utilisation. In the process, new disciplines such as genetic engineering are being used as tools. With the emergence of "white biotechnology" and the coming into effect of the Kyoto Protocol, the role of anaerobic digestion should be re-examined to integrate itself with bio-refinery activities. The final objective should be the achievement of sustainable development on this planet.

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