CO-DIGESTION OF AGRICULTURAL AND INDUSTRIAL WASTES

by

FERGAL JAMES CALLAGHAN

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Faculty of Engineering
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Abstract

Anaerobic digestion technology has not gained widespread acceptance on UK farms due mainly to the long return on investment periods involved. It has been suggested that co-digestion of agricultural and industrial wastes may enhance the economic viability of such installations. Batch and continuous digestion of cattle slurry and organic industrial wastes was carried out in specially constructed pilot plant digesters, to determine optimum mixtures of waste and digester loading rates. A total of 10 different wastes were tested, on a batch digestion basis, for their potential to co-digest with cattle slurry. Of these, 3 were chosen for continuous pilot plant trials, due to either a need to provide a disposal route for the waste, or positive effects of the waste on methane productivity. Chicken manure was found to slightly enhance methane productivity, but ammonia inhibition of methanogenic bacteria was noted over time. The organic fraction of municipal household waste (OFMSW) significantly enhanced digester methane productivity, while fish offal (FO) slightly enhanced methane productivity when added to the digester in small quantities, but quickly caused digester failure when added in larger amounts. An economic model of a digestion facility was developed and used to show the financial benefits of co-digestion.

Dedication

To Ger, Mam, Dad, Diarmuid and Ruairi

Thank you

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2. Co-digestion of cattle slurry and chicken manure, The World Congress of Chemical Engineering, San Diego, California, 1996.

3. Co-digestion of agricultural and industrial wastes, *Avert* (The magazine of the Environmental Protection Subject Group, Institute of Chemical Engineers),Issue No. 7, page 4, 1996.

4. Co-digestion of cattle slurry and waste milk under shock loading conditions, *Journal of Chemical Technology and Biotechnology*, volume 68, pages 405 - 410, 1997.

5 Further studies on the co-digestion of cattle slurry and waste milk under shock loading conditions, *Environmental Technology*, volume 18, pages 647 - 654, 1997.

6. An examination of the continuous anaerobic digestion of cattle slurry and fish offal. *Trans. IChemE, in press*, 1998.

7. Co-digestion of waste organic solids. *Bioresource Technology, in press*, 1998.

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Chapter 1

Introduction

1.1 General background

Pollution of land, water and air is generally regarded as an un-avoidable product of economic and social progress. Much pollution is caused by organic material, which is not toxic to life forms, but actually encourages the growth of bacteria, plants and animals. Problems with this form of pollution arise from the un-controlled release of organic material into the environment (The Environment Agency, 1996). The majority of major water pollution incidents recorded in the UK between 1990 and 1995 were caused by organic material (Central Statistical Office, 1997).

Some of the processes which naturally degrade organic material have been adapted in order to control the environmental impact of these wastes. One such process is anaerobic digestion, carried out by bacteria in the absence of air, which converts organic material to methane, carbon dioxide and other gasses (McInerney and Bryant, 1981).

Most organic wastes, if dumped in a landfill site or spread un-treated on land, carry the potential to pollute ground and surface waters, by increasing their nutrient loading, and air by odour and methane emissions. It has recently been recognised that methane

emissions from agricultural wastes and landfill sites constitute a significant contribution to global warming (The ENDS Report, 1996). By converting some of the polluting material to methane and other gasses in a controlled environment, the anaerobic digestion process can reduce the environmental impact of organic wastes.

1.2 The microbiology of anaerobic digestion

The bacteria involved in anaerobic digestion derive energy from the metabolism of organic carbon compounds in the absence of oxygen or other electron acceptors such as nitrate or sulphate (Schoberth, 1981). Anaerobic metabolism also occurs in the muscles of mammals, to provide energy during periods of extreme exertion. Lactic acid is formed as a by-product and removed by respiratory enzymes within the mammalian cell, by conversion to water and carbon dioxide, which leave the cell in the gaseous phase (Conn *et al.*, 1987). In an anaerobic digestion system, methanogenic bacteria take over the function of respiratory enzymes. Together with other groups of non-methanogenic anaerobes they form an anaerobic food chain, completely converting complex organic material to gaseous carbon dioxide and methane which can then escape the anaerobic bacterial system. These anaerobes may be separated into 5 main groups of bacteria (Parkin and Owen, 1986), see Figure 1.1.

Figure 1.1 (see over) The microbiology of anaerobic digestion

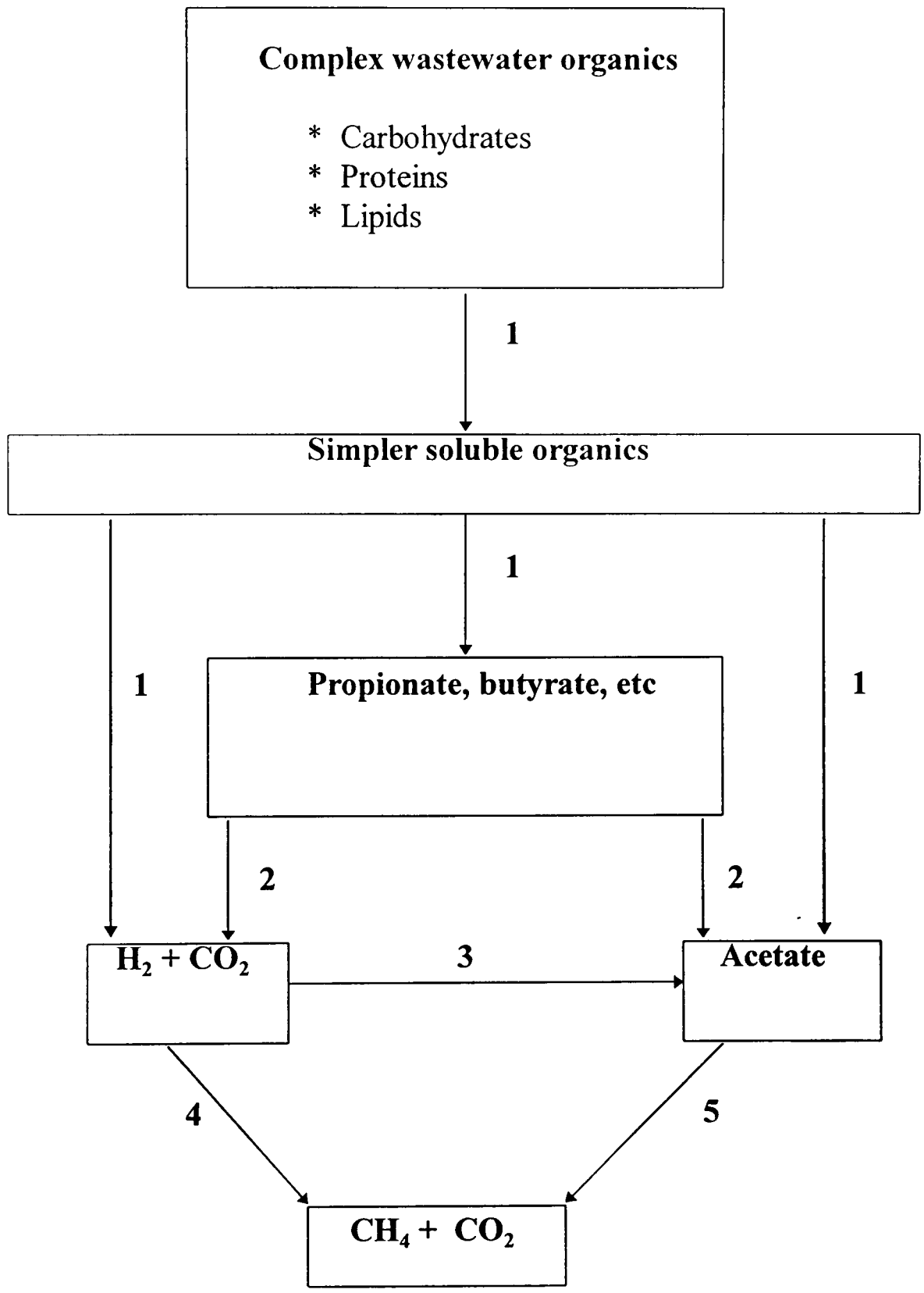
1 Fermentative bacteria

2 Hydrogen-producing acetogenic bacteria

3 Hydrogen-consuming acetogenic bacteria

4 CO_2-reducing methanogens

5 Acetoclastic methanogens


Complex wastewater organics
* Carbohydrates
* Proteins
* Lipids
1
Simpler soluble organics
1
1
Propionate, butyrate, etc
1
2
2
$H_2 + CO_2$
3
Acetate
4
5
$CH_4 + CO_2$

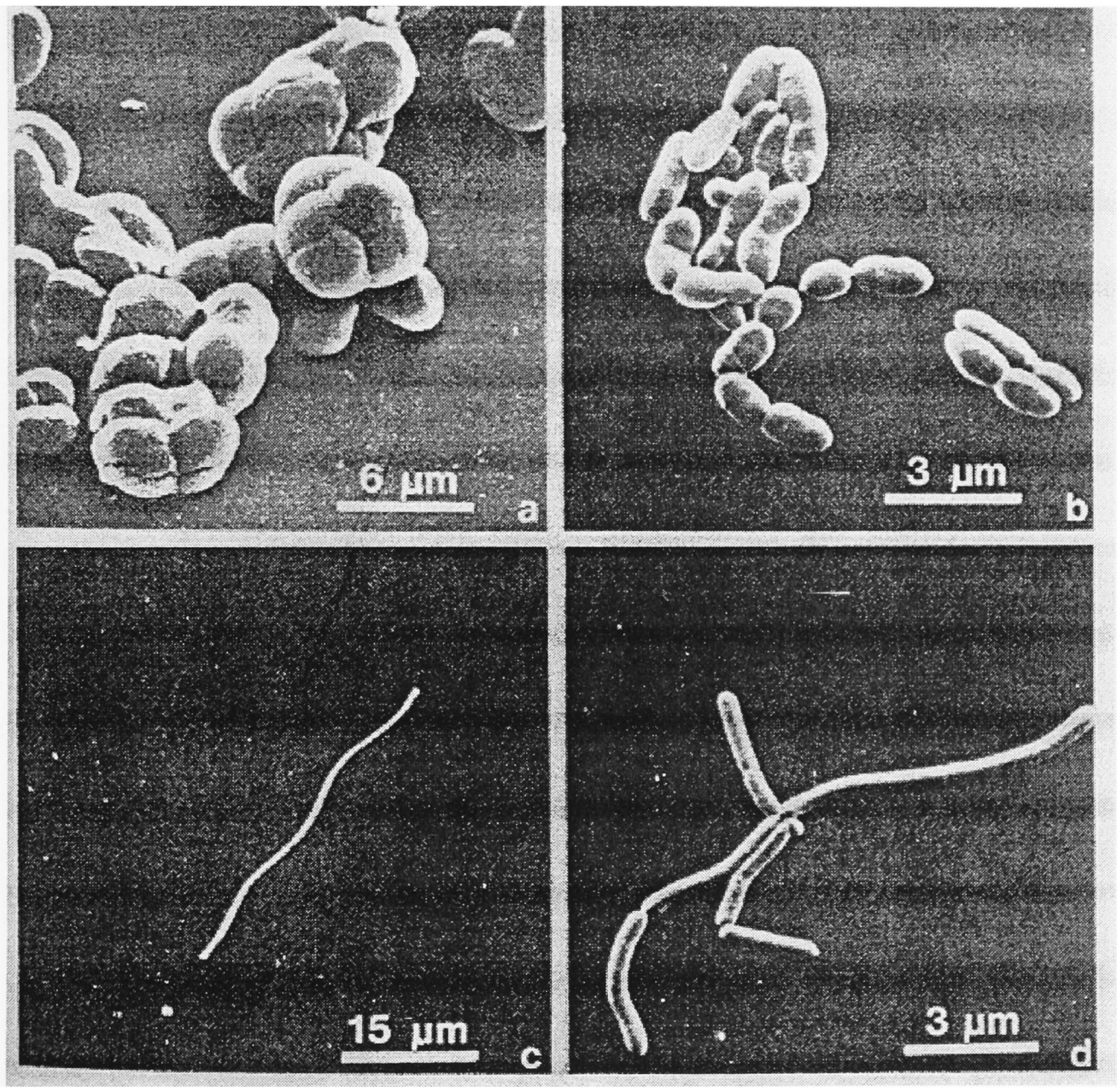
1.2.1 Fermentative bacteria

The first step in the anaerobic process is the liquefaction of in-soluble organic matter. This material, which may consist of complex carbohydrate, lipids, and proteinaceous materials, is then further broken down to simpler compounds such as poly and mono-saccharides and amino acids, which can be easily transported across the bacterial cell wall for use as a source of energy and metabolites. The fermentative process is accomplished by extra-cellular hydrolytic enzymes excreted by the fermentative bacteria (Kotze *et al.*, 1969). Propionic, butyric and other long and short chain fatty acids, as well as CO_2, NH_3, and H_2 are also produced in this stage. It is important to note that this step is often the rate-limiting stage of the anaerobic digestion process. Noike *et al.* (1985) operated anaerobic reactors on a number of substrates and showed that if refractory compounds such as cellulosic materials are the main substrate for an anaerobic reactor the hydrolysis of these materials limits the overall digestion rate. They also demonstrated that if soluble hydrolysed materials were fed to a digester the methanogenic phase becomes rate limiting.

1.2.2 Acetogenic bacteria

Acetogenic bacteria convert the volatile fatty acids produced in the fermentative step to acetic acid, hydrogen and carbon dioxide. The predominant species in an anaerobic reactor tends to be the hydrogen producing acetogens, a small proportion of the hydrogen generated by these bacteria is converted to acetic acid by hydrogen consuming methanogens (Kaspar and Wuhrman, 1978).

Figure 1.2 4 types of methanogenic bacteria. (a) *Methanosarcina barkeri* strain MS (b) *Methanobrevibacter smithi* strain PS (c) *Methanospirillum hungatei* strain JF 1 (d) *Methanobrevibacter arboriphilus* strain AZ. (Schoberth, 1981)



1.2.3 Methanogenic bacteria (carbon dioxide reducing and acetoclastic)

Most of the characterisation work on the bacterial population of an anaerobic digestion system has attempted to identify the methanogenic bacteria present. The methanogens in Figure 1.2 are commonly found in animal slurry digesters (Schoberth, 1981). Most methanogens contain an enzyme co-factor called F_{420} which has been found to fluoresce under ultra-violet (UV) light, and hence these methanogens can be easily identified using a UV microscope (Mink and Duggan, 1977)

Methanogenic bacteria are capable of metabolising only acetic (and possibly formic) acid, hydrogen and carbon dioxide, and hence are dependent on the other species in the anaerobic food chain (Kaspar and Wuhrman, 1978). The methane formation step of the anaerobic digestion process may be labelled the waste stabilisation step, as acetic acid is converted into methane, which being insoluble in water, leaves the system. Carbon dioxide is also produced and either leaves the system or is converted to bicarbonate. Approximately 70% of the methane produced by an anaerobic system is formed by the cleavage of acetic acid, the remaining 30% is formed from the reduction of carbon dioxide (Jeris and McCarty, 1965).

1.2.4 Syntrophy and interspecies hydrogen transfer

The relationship between the hydrogen producing acetogens and the carbon dioxide reducing (hydrogen consuming) methanogens has been shown to be syntrophic in nature. The word syntrophic comes from the words *syn*, meaning together and *trophic*, meaning to eat. The concept is based on the observation that syntrophic acetogens cannot grow in the absence of hydrogen oxidising bacteria such as

methanogens (Kaspar and Wuhrman, 1978). The syntrophy is mutual as the methanogens require hydrogen and acetic acid for growth and metabolism. It has been suggested that the bacteria communicate by a process known as interspecies hydrogen transfer (Sadettin *et al.*, 1989). Hydrogen partial pressures above 10^{-4} atmospheres cause inhibition of hydrogen producing acetogens (Mosey, 1983), hence by removing hydrogen from the system (transferring hydrogen from acetogens to methanogens) optimum growth conditions are maintained for both groups of bacteria. For this reason the anaerobic food chain shown in Figure 1.1 can perhaps be likened to a symphony of biochemical reactions played by an orchestra of bacteria, conducted by the methanogens!

1.3 The biochemistry of anaerobic digestion

The biochemistry of anaerobic digestion can be described as the complete reduction of carbon atoms within the digester feedstock to methane or their complete oxidation to carbon dioxide (Buvet, 1981).

Some aspects of the biochemistry of an anaerobic system have been mentioned in the preceding sections. This section will further explore some of the topics mentioned earlier and also discuss the degradation of various materials under anaerobic conditions. The various parameters used to monitor the state of the anaerobic digestion process will also be discussed.

The exact composition of a farm digester feedstock will vary depending on the source of the waste but generally most farm digester feedstocks consist of a large fraction of

carbohydrate along with some protein and other nitrogen based compounds (Hawkes, 1981).

1.3.1 Feedstock composition - carbohydrate

Carbohydrates are the principal carbon source for methane production in an anaerobic digester and are generally present as insoluble polysaccharides (such as cellulose) from vegetable residues, some soluble polysaccharides (such as starch) and a variety of sugars (Cowley and Wase, 1981). Farm animals have digestive tracts which allow degradation of starch and plant structural polysaccharides such as cellulose and hemicellulose. However degradation of the latter materials is not complete, hence some residues will remain (Hobson and Wheatley, 1993). These materials, having passed un-degraded through the digestive tract of an animal, degrade slowly in the digester under enzymatic attack from fermentative bacteria mentioned earlier.

Farm wastes may also contain bedding materials such as straw or wood shavings which can be an additional carbon source for methane formation. The structural polymer lignin is present in these materials and makes them difficult to degrade anaerobically. Lignin is a complex 3-dimensional highly cross-linked polymer which is resistant to both chemical and biological degradation (Conn *et al.*, 1987). Pfeffer showed that wheat straw was only 38% degraded in an anaerobic reactor at a retention time of 13.7 days and calculated that maximum degradation, at an infinite retention time, would be approximately 50% (Pfeffer, 1978). Robbins *et al.* (1979) reported 32% degradation of straw in a commercial cattle slurry digester.

Hence most of the carbon present in a farm digester feedstock is in the form of insoluble carbon compounds which must first be hydrolysed to make them available to fatty acid forming bacteria, ensuring that the rate of methane formation in a digester operating on animal waste can be quite slow.

1.3.2 Feedstock composition - nitrogenous compounds

Carbohydrates are the principal source of energy for cell growth. Cells also require nitrogen to form amino acids and structural proteins. Proteins in cattle slurry are one of the principal sources of nitrogen for bacterial growth in an anaerobic system, and in farm wastes are likely to have come from plant leaves, animal feed stuffs and intestinal secretions (Hawkes, 1981).

Proteins are polymers of amino-acids and are hydrolysed in anaerobic systems to release amino acids (Conn *et al.*, 1987). These amino acids may in turn be broken down to release ammonia (NH_3), which is the form in which nitrogen is directly available to digester bacteria (Rivand *et al.*, 1988). Other major sources of nitrogen within the digester include urea excreted by animals and uric acid excreted by poultry. These are converted to ammonia by anaerobic bacteria within the system.

1.3.3 Parameters for controlling and monitoring the anaerobic digestion process

The main parameters involved in the control and monitoring of the anaerobic digestion process, and the relevant biochemistry, will be discussed in the following sections.

1.3.3.1 Operating temperature

Temperature plays a significant part in the performance of anaerobic digestion system. There are 3 temperature ranges in which bacteria grow and generally speaking different bacterial strains or species grow in each temperature range (Hobson and Wheatley, 1993). The psychrophilic range is from 0 ^{o}C to about 15 ^{o}C and is generally of no great significance in the field of anaerobic digestion. The mesophilic stage, from around 15 ^{o}C to 45 ^{o}C, is the range within which most commercial anaerobic digestion systems operate. Thermophilic digesters operate between 50 ^{o}C and 70 ^{o}C, and although much research is being conducted in this area, there are few commercial systems in operation (Aitken and Mullennix, 1992).

The optimum temperature for mesophilic operation is generally accepted as being 35 ^{o}C. Sudden decreases in temperature, as can happen with the failure of a digester heating system, can lead to sharp drops in methane production rate. However, it has also been shown that rapid restoration of operating temperature tends to lead to rapid system recovery (Peck *et al.*, 1986).

1.3.3.2 pH

The generally accepted pH range for optimum operation of an anaerobic digestion system is between 6.8 and 7.6. Methanogenic bacteria are significantly inhibited below pH 6.2 (Metcalf and Eddy, 1991). pH also affects parameters such as ammonia (NH_3) concentration. In turn pH is affected by levels of alkalinity and volatile fatty acids present in the system. All these parameters will be discussed in the following paragraphs, beginning with alkalinity.

1.3.3.3 Alkalinity

Alkalinity is one of the most commonly used parameters for monitoring digester performance. It is a measure of the acid neutralising potential of the digester liquor. Most of the alkalinity available in a stable digester will be in the form of HCO_3^- which is known as bicarbonate alkalinity (or BAlk) and is produced during digestion by the conversion of nitrogenous organics (mostly proteins) to NH_3 and then by the reaction of NH_3 with CO_2 to form NH_4^+ and HCO_3^-. This can be represented by the following equation developed by McCarty for the digestion of primary sewage sludge (McCarty, 1974).

$$C_{10}H_{19}O_3N + 4.69\,H_2O \longrightarrow 5.74\,CH_4 + 2.45\,CO_2 + 0.2\,C_5H_7O_2N\ \text{(bacteria)} + 0.8\,NH_4^+ + 0.8\,HCO_3^-.$$

However alkalinity, as measured by the standard laboratory method for wastewaters which involves titration of digester liquor with dilute H_2SO_4, is a measure of all titratable bases present, and is measured as mg l^{-1} $CaCO_3$ (Standard Methods, 1992). Hence, it should be noted that any constituent of the digester liquor which reacts with H^+ ions, such as NH_3, amines or sulphides will be measured as part of total alkalinity (TAlk).

In a stable sewage sludge digester most of the alkalinity can be expected to be in the form of HCO_3^- (McCarty, 1974). However in animal waste digesters the presence of other constituents mentioned above, specifically NH_3 and other organic bases may account for a significant percentage of TAlk. The high TAlk values reported for a

cattle slurry digester of around 11,000 mg l^{-1} $CaCO_3$ (Chayovan *et al.*, 1988) and a poultry manure digester, up to 21,000 mg l^{-1} $CaCO_3$ (Webb and Hawkes, 1985), are most likely to be in part due to the high NH_3 levels associated with these wastes.

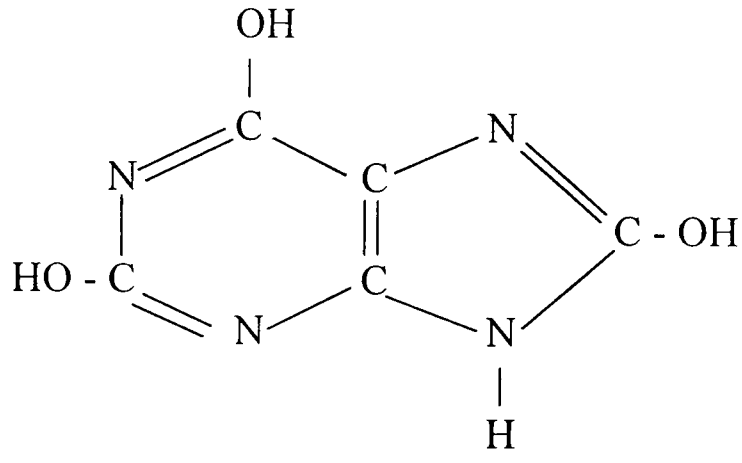
An important point to note is that TAlk levels found in animal slurry digesters are significantly higher than those in sewage digesters, which are typically around 2000 - 4000 mg l^{-1} (Standard Methods, 1992). Therefore animal slurry digesters should be able to withstand much higher shock organic loadings, and consequent volatile fatty acid production, due to the higher acid neutralising capacity of these systems.

1.3.3.4 Ammonium (NH_4^+) and ammonia (NH_3)

Bacterial degradation of nitrogenous compounds produces NH_3 in both aerobic and anaerobic systems. As has been mentioned earlier, proteins are a major source of NH_3 in animal slurry digestion systems. Urea, which is the form in which nitrogen is excreted by mammals, is also a major source of NH_3. Bacterial action converts urea to NH_3 in the following manner:

$$CO(NH_2)_2 + H_2O \longrightarrow CO_2 + 2\,NH_3$$

Birds excrete nitrogen as uric acid which is relatively insoluble in water and has the following structure (Fessenden and Fessenden, 1986):



Uric acid is also converted to NH_3 by microbial action.

NH_3 becomes hydrated to form NH_4^+. The pH of the system is one of the main factors which determine the relative concentrations of NH_3 and NH_4^+ in an anaerobic digestion system (the other being temperature) according to the following equilibrium.

$$[NH_4^+] \rightleftharpoons [NH_3] + [H^+]$$

Hence the NH_3 concentration increases with increasing pH. This is an important point as both NH_3 and NH_4^+ have an inhibitory effect on methanogens.

Inhibition of methanogenesis by NH_4^+ concentration and NH_3 has been the subject of much debate. Van Velsen found that, in un-adapted methanogenic bacterial sludge, methanogenesis ceased when the NH_4^+ concentration was raised to approximately 1700 - 2000 mg N l^{-1} (Van Velsen, 1979). However, other authors have shown that

methanogenesis is possible at much higher NH_4^+ concentrations. Melbinger and Donnellon showed a high rate anaerobic sludge digester could function successfully at up to 2,700 mg l^{-1} NH_4^+(1971). Webb and Hawkes (1985) found that 2 digesters operating on 10% TS chicken manure, with similar NH_4^+ concentrations, had quite different methane productivity values, 0.376 compared with 0.399 m^3 CH_4 kg VS^{-1} added. This was shown to be due to the quite different pH values of the systems, 7.97 and 7.78 respectively, which meant that the NH_3 concentration of the system with the lower productivity was 435 mg l^{-1}, whereas that of the other system was 29 mg l^{-1}. This is a clear demonstration that NH_3 concentration plays a large part in contributing to the inhibition traditionally associated with high NH_4^+ concentrations. Work done by Koster and Lettinga (1988) also showed that for a number of batch digestion systems, a slight decrease in system pH and consequent decrease in NH_3 concentrations led to an increase in methanogenic activity compared to other systems with similar NH_4^+ concentrations but higher pH values.

Webb and Hawkes 1985) also suggested that NH_3 concentrations of between 138 and 225 mg l^{-1} would cause significant inhibition of methanogenesis, but that after adaptation to increasing levels of NH_3, it was possible to operate digesters at 330 - 370 mg l^{-1} NH_3 with little apparent inhibition. McCarty and McKinney also concluded that the ammonia toxicity threshold was around 150 mg l^{-1}(McCarty and McKinney, 1961)

1.3.3.5 COD and BOD

COD (Chemical Oxygen Demand) is a measure of the amount of oxygen theoretically required to oxidise a given volume of effluent completely. It is therefore a measure of the polluting potential (or oxygen removing potential) of the material if it were to enter a water course. COD is determined by reacting an effluent sample with a powerful oxidising agent. It is commonly used to measure the organic loading on a digestion system, most often defined in terms of kg COD m^{-3} d^{-1} (Parkin *et al.*, 1994). While a useful tool for analysing and quantifying the polluting strength of effluents containing mostly dissolved material, COD is of little practical use in analysing animal slurries, due to the very high COD values (up to 150,000 mg l^{-1} for cattle slurry) and high total solids (up to 15 % TS) values of these wastes. COD analysis methods generally have a range of 0 - 1500 mg l^{-1} (Standard Methods, 1992), hence large dilutions are required to analyse animal slurries. Also these slurries are not homogenous materials, even after maceration in a laboratory blender. Therefore, it can be concluded that COD analysis of animal slurries can give un-reliable results, unless the slurry has been extensively macerated and sieved to remove all large particles. Even then, because much of the particulate matter present is organic material, and would be expected to contribute to the overall COD of the slurry, the COD values obtained for sieved slurry would be lower than the actual slurry COD.

BOD (Biological Oxygen Demand) is a measure of the amount of biodegradable organic matter present in a given volume of effluent. It is determined by measuring how much oxygen is consumed by a sample of the waste over a period of time. If this time period is set at 5 days, the result is known as the BOD_5 of the effluent. Again, as for COD, due to the high strength and non-homogenous nature of animal

slurries this parameter is of little practical use in measuring the polluting strength of animal slurries.

1.3.3.6 Total, fixed and volatile solids and VS/TS ratio

The parameter most commonly used to define the polluting potential of animal slurries is the percentage of volatile solids present (% VS) (Parkin *et al.*, 1994). The % VS of an effluent is determined by firstly drying a known weight of sample at 105 ^{o}C for 24 hours and then, after determining the dry weight (which gives the percentage of total solids present (% TS)), ignition at 550 ^{o}C to determine the percentage inorganic or fixed solids present (% FS). Subtracting % FS from % TS gives the percentage by weight of VS present in the sample (Standard Methods, 1992). The loading rate to an animal slurry digester is commonly expressed in kg VS m^{-3} d^{-1} (Singh *et al.*, 1985). As the method does not rely on dilutions or colourimetric analysis it is quite accurate and gives reproducible results, although attempt is made in the analysis procedure to account for VFA and NH_4^+ losses during the drying stage. Nevertheless this method has become the standard for slurry analysis.

The VS/TS ratio of an effluent is a useful concept which allows ready assessment of the biodegradability, and suitability, of an effluent for anaerobic digestion. The parameter is commonly used by the water industry to measure the potential degradability of mixtures of sewage sludge from a number of different sites (Finch, 1997).

Sewage sludge and cattle slurry have similar VS/TS ratios (in the range of 0.72 - 0.78) (source: laboratory measurements), but values for poultry manure are generally lower (range 0.5 - 0.65) (source: laboratory measurements). Fish offal and the organic fraction of household waste were found to have VS/TS ratios of 0.99 and 0.93 respectively. Hence the VS/TS ratio can be used to predict the likely effect of adding a particular waste to a digestion system. The addition of large quantities of fish offal to a stable digester operating on sewage sludge would most likely lead to digester failure, as the material is almost entirely organic matter. Similarly, adding materials with much lower VS/TS ratios than the material on which the digester is operating would most likely lead to a decrease in methane productivity.

1.3.3.7 Volatile Fatty Acids (VFA)

The production of VFAs by acidogenic and fermentative bacteria in an anaerobic system was discussed in sections 1.2.1 and 1.2.2.. The VFAs of interest in monitoring the anaerobic digester performance are acetic, propionic, butyric, and to a lesser extent isobutyric, valeric, isovaleric and caproic. VFAs are so named because they can be distilled at atmospheric pressure and hence can be analysed using a distillation apparatus or gas chromatography (GC) (Parkin *et al.*, 1994). If analysed by distillation apparatus the result is expressed in terms of mg l^{-1} of acetic acid. GC analysis allows the separation and measurement of each individual acid. A stable sewage sludge digester will typically have a VFA concentration of around 300 mg l^{-1} acetic acid (Simpson, 1960). The values reported for cattle slurry digesters are similar, generally within the range 100 to 400 mg l^{-1} of acetic acid (Chayovan *et al.*, 1988).

In a stable anaerobic digester, methanogenic and acidogenic bacteria are in a state of dynamic equilibrium, hence VFAs are converted to methane at roughly the rate they are produced. An increase of VFAs in the digester effluent indicates a kinetic uncoupling between acidogens and methanogens (McCarty and McKinney *b*, 1961), suggesting that a shock loading has been applied to the system or inhibition of methanogenesis has occurred. Normal procedure to counteract this imbalance is to cease feeding the digester until VFA levels return to normal.

The VFA to total alkalinity ratio(VFA:TAlk) has been proposed as a parameter for monitoring the status of an anaerobic digester and as a useful "early warning sign" of digester instability (Hickey and Switzenbaum, 1991). Switzenbaum (1990) and others have concluded that the recommended ratio is in the range 0.1 to 0.35 for a stable anaerobic digester.

1.3.3.8 Biogas composition

Biogas produced by sewage sludge digesters typically consists of 60 to 75% CH_4 and 25 - 40% CO_2, and contains traces of H_2, H_2S and CO (Dague, 1968). CH_4 and CO_2 concentrations are usually measured by gas chromatography.

Reported values for cattle slurry digesters are lower, ranging from 43 to 60% CH_4 for a farm based anaerobic digester (Sarapatka, 1994) to 58 to 63% for a laboratory digester (Chayovan *et al.*, 1988). Values available for poultry litter digesters include

32 to 58% CH_4 for a farm based digester (ETSU, 1994) to 56 to 61% for a laboratory digester (Webb and Hawkes, 1985).

Biogas CH_4 concentration is an indicator of system stability in an anaerobic digester. However, it is of limited use due to the time taken for a shock load applied to an anaerobic system to have a significant effect on biogas CH_4. Hickey and Switzenbaum (1991) demonstrated that one of the first parameters to show a significant response to an organic shock load to a digester was the VFA:TAlk ratio, which showed a significant change 6 days after the initiation of shock loading, whereas biogas CH_4 concentration did not decrease significantly until day 8. Callaghan *et al.*(1997) have shown that the addition of a shock-load of readily degradable organic material (milk) to a batch anaerobic digestion system produced a rapid decrease in biogas methane concentration (from 70% to 30% in 48 hours). This was due to the rapid production of CO_2 immediately after the shock-loading, anaerobic digesters operating on a continuous basis are obviously more resilient to a shock-load event.

Hydrogen sulphide (H_2S), formed by the reduction of sulphate, is also present in trace quantities in the biogas from sewage digesters (Metcalf and Eddy, 1991), and at higher concentrations in the biogas from cattle slurry and poultry manure digesters (ETSU, 1994). Concentrations in biogas from poultry manure digestion are typically around 3000 ppm (ETSU, 1995). H_2S is not corrosive itself, but dissolves in water and is converted to H_2SO_4 by bacterial action, hence H_2S in the biogas must be

removed before the biogas comes in contact with steel or iron surfaces, this can add significantly to the overall process cost.

1.3.3.9 Redox potential

Redox potential is a measure of the oxidising or reducing power of a substance or mixture. It is generally measured in millivolts and most commonly is determined using a silver/silver chloride electrode couple (MacKay and MacKay, 1981). A negative redox potential indicates reducing potential and a positive redox potential indicates oxidising potential. The redox potential of a system can also be defined as the electron activity of the system (Parkin et *al.*, 1994).

It has been suggested that redox potential may provide an accurate measurement of intermediate product composition in an anaerobic digestion system (Grune, 1965). This author monitored redox potential during a shock-loading event and found it could be correlated with VFA accumulation. However, Switzenbaum (1990) concluded that in multi-redox component systems such as anaerobic digesters one cannot be sure which redox couples are being measured by the redox probe, and hence redox is more than likely of little practical benefit in monitoring an anaerobic digestion system.

1.4 Methane production rates of cattle slurry digesters

Much work has been done to determine the range of methane production values which can be expected from the addition of known amounts of cattle slurry to an anaerobic digester. The most common method of expressing the methane producing potential of

a slurry or a digester is refer to m^3 CH_4 produced per kg volatile solids added to the digester (m^3 CH_4 kg VS^{-1} added) The principal factors governing this factor are the type of foodstuffs given to the cattle, the total solids level of the slurry, the % volatile solids removal rate in the digester, the digester loading rate (kg VS m^{-3} day $^{-1}$), the retention time (RT) in the digester and the digester operating temperature (Cowley and Wase, 1981).

As these factors can vary considerably from farm to farm, it is not surprising that a wide variety of figures for m^3 CH_4 kg VS^{-1} have been reported. Erdman (1985) found that laboratory digester, operated on a cattle slurry feedstock of 6.5% TS, and a loading rate of just over 1 kg VS m^{-3} day $^{-1}$, produced 0.49 m^3 CH_4 kg VS^{-1} added, at a retention time of 10 days and a temperature of 30°C. However, Peck *et al.* (1985) found that a laboratory digester fed on 8 % TS cattle slurry, with a retention time of 25 days, produced 0.162 m^3 CH_4 kg VS^{-1} added, and Hobson (1984) reported a similar figure of 0.165 m^3 CH_4 kg VS^{-1} added for a digester fed on 6% cattle slurry at a 20 day retention time. Both slurries used in these experiments came from similar sources, namely cattle housed in indoor units and fed on a relatively rich diet of concentrates and silage. It is not clear why Erdman obtained such a high methane production rate. Hobson (1984) reported that the values similar to the value measured by him (0.165 m^3 CH_4 kg VS^{-1}) have also been measured by other authors. Liao *et al.* (1984) found that a laboratory digester, operated on a feedstock of 6% solids, a retention time of 10 days and with a reduction of 25% volatile solids, produced only 0.08 m^3 CH_4 kg VS^{-1} added. It is not clear why the slurry these workers used produced a lower value than that used by Hobson and Peck *et al.*, it is possible that the

cattle which produced the slurry were not fed such a rich diet, and perhaps were fed mainly on grass. Linke (1997) recorded methane productivity values of 0.2 m^3 CH_4 kg VS^{-1} added for a laboratory cattle slurry digester, which was closer to the values recorded by Hobson than those recorded by Liao *et al.*

Hawkes and Horton have shown that the methane productivity of a digester, measured as m^3 CH_4 kg VS^{-1} added, increases with increasing volatile solids loading rate. This may be another reason for the difference in methane productivity values noted by various authors. It can be concluded that the expected methane production rate, from a laboratory digester operating on cattle slurry, would be some where between 0.08 and 0.20 m^3 CH_4 kg VS.

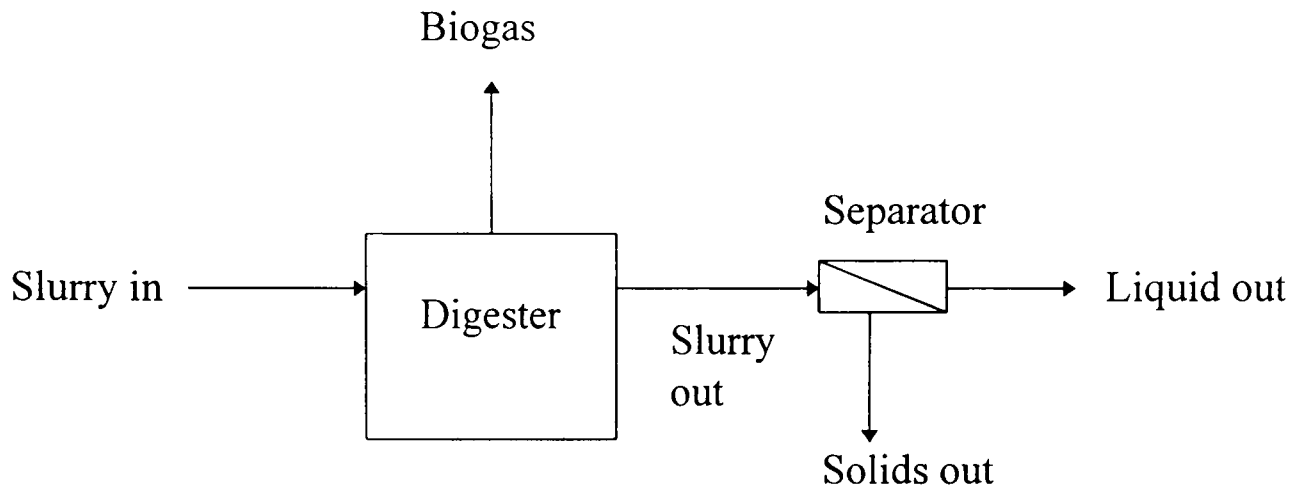
1.5 Design and engineering of farm scale anaerobic digester

A modern farm anaerobic digestion system is shown schematically in Figure 1.3. Figures 1.4 and 1.5 show a digester installation on a farm near Birmingham. The unit processes which comprise a farm digester are described in the following paragraphs.

1.5.1 Slurry collection and storage

On this particular site slurry from 100 head of dairy cattle is collected and brought to the digester loading bay using a tractor driven scraper. The digester is fed every day with the entire slurry arisings from that day. The slurry is loaded into the digester using a screw auger, driven by an electric motor.

Figure 1.3 Schematic diagram of modern farm anaerobic digestion system



1.5.2 The digester vessel

The digester is constructed from steel sections coated in (glass reinforced polystyrene) GRP. The vessel shown in Figures 1.4 and 1.5 has a working volume of $100m^3$ and is fed at a rate of about 4 m^3 of slurry per day, giving a 25 day retention time, and a loading rate of about 3 kg VS m^{-3} d^{-1}. The system achieves about a 40% reduction in TS levels. Biogas is collected over water using a floating lid collector (see Figure 1.5, left foreground). Biogas production rates are not known, but sufficient biogas is produced to heat the digester itself, produce hot water for the dairy and farm-house, and supply the gas cooker in the farm house.

The vessel contents are mixed with biogas blown through a network of PVC (poly vinyl chloride) pipes of 50 mm diameter which are at the bottom of the vessel.

1.5.3 Slurry removal and treatment after digestion

Slurry is removed from the digester using a screw auger and flows to a swept brush belt separator, housed in the building on the right of the digester vessel in Figure 1.4. The separator produces 2 streams, a liquid stream of about 5% total solids (TS), which flows to an irrigation pond is then spread on pasture, and a filter cake of about 20% TS which drops from the separator into a trailer below the building housing the separator and is used as a soil conditioner on arable land around the farm.

Figure 1.4 Farm digester, showing digester vessel set into earth bank for insulation purposes, and building on the right which houses the slurry extraction auger and the slurry separator.

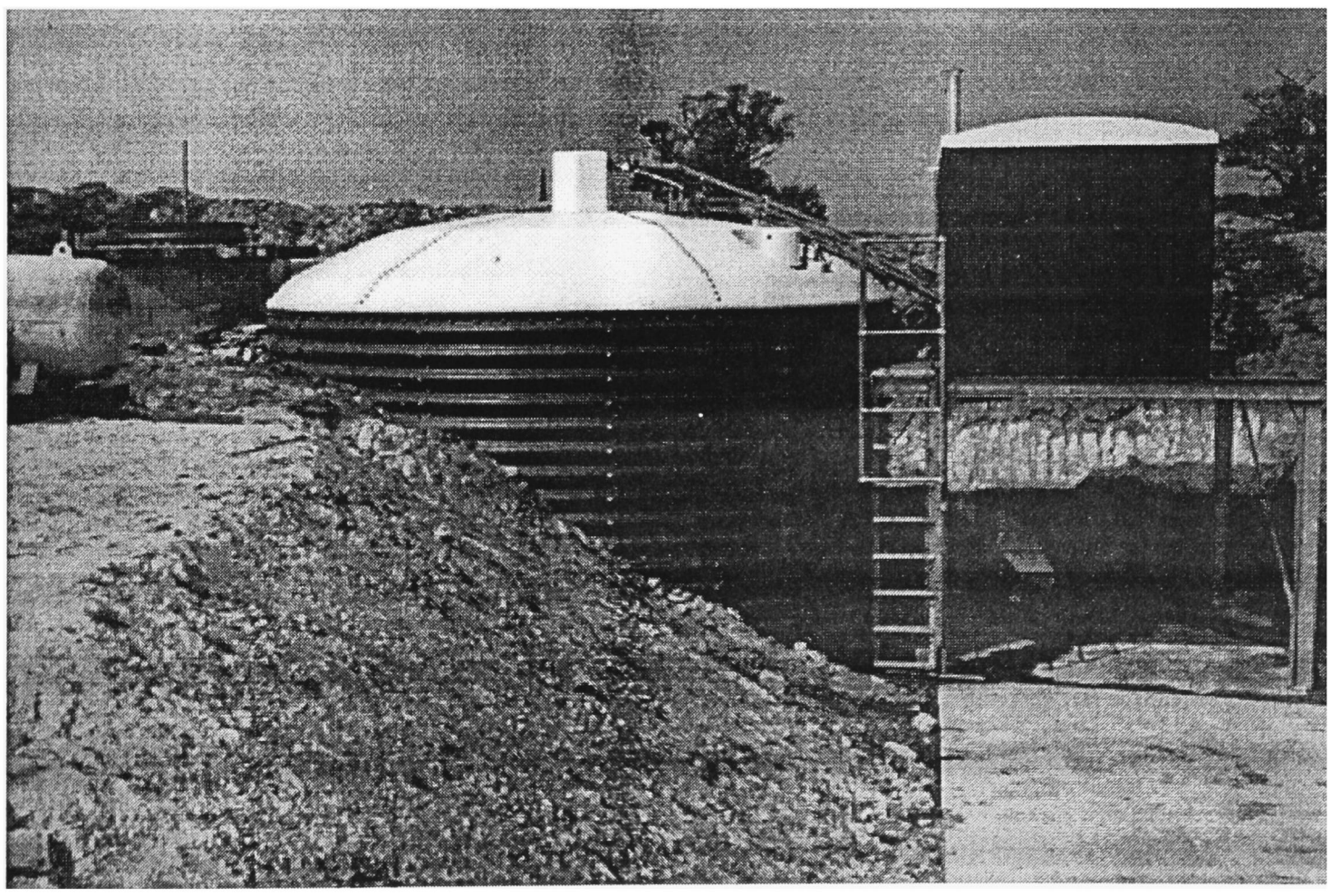
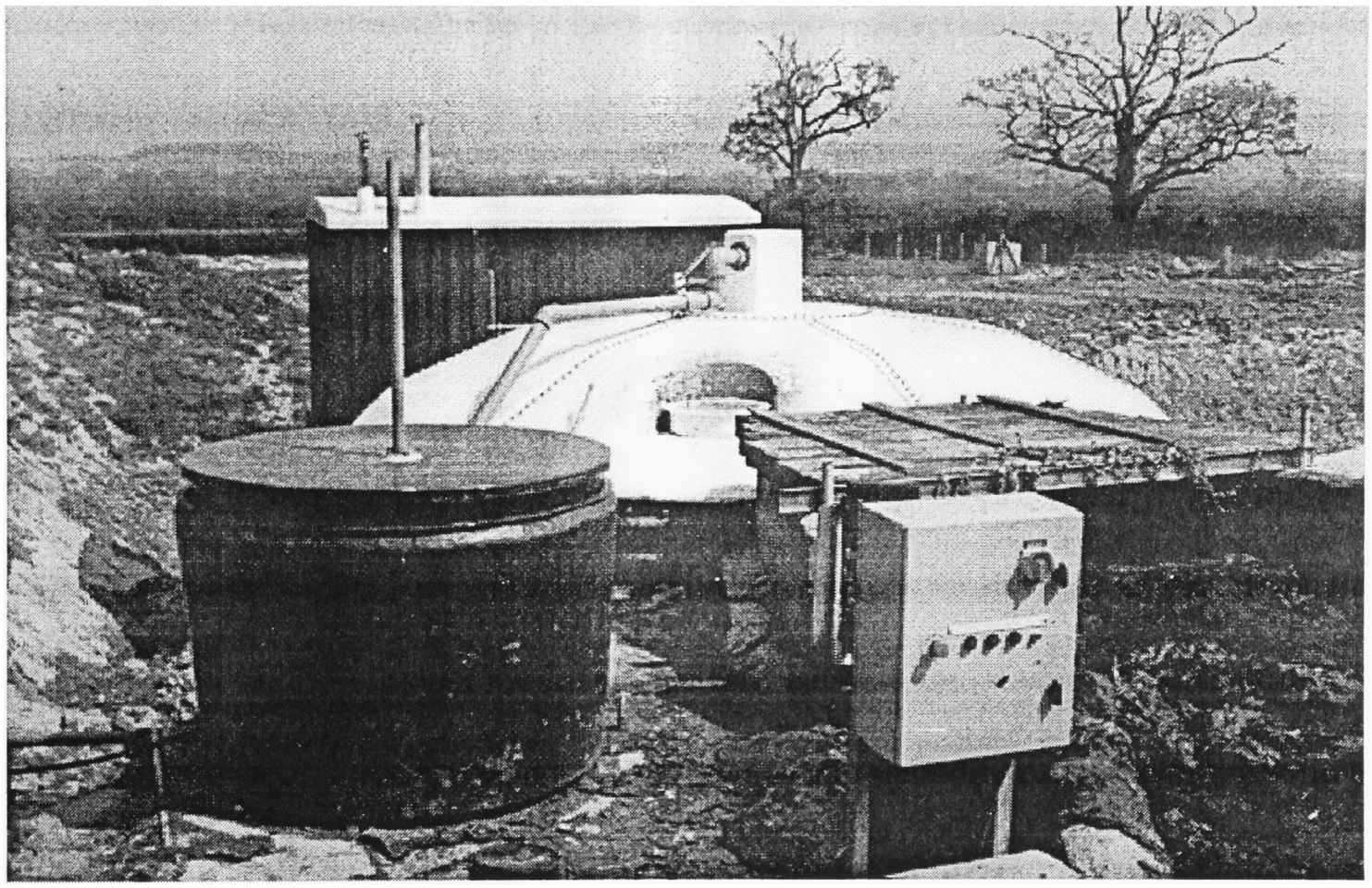


Figure 1.5 Farm digester, showing biogas collecter in the left foreground, and the biogas collection pipework leading from the top of the digester. The slurry feed auger controls are in the right foreground. The auger itself is underneath the slurry on the extreme right of the picture



1.6 The farm digester industry in the UK

The early farm anaerobic digester systems were poorly engineered and suffered numerous mechanical breakdowns, making them un-economical to operate in many cases (Cowley and Wase *b*, 1981). Although recent improvements in solids handling and mixing technology have led to the development of systems, (such as the one

described above) which are reliable and quite robust, the technology has yet to gain widespread acceptance, in the UK, as a slurry treatment technique.(Wase and Thayanithy, 1993). There are only 14 anaerobic digestion systems currently operating in the UK, mostly on cattle slurry, with two using pig slurry as a feedstock. (ETSU, 1995)

The main reason for the slow up-take of farm based anaerobic digestion systems is economic. The payback on investment time involved can be up to ten years for many systems (Wase and Thayanithy, 1993).

1.7 The concept of co-digestion

The principal revenue streams from a farm digester are the energy value of the biogas produced, the fertiliser value of the liquid portion of the digester effluent and the soil conditioning or commercial compost value of the solid portion. Adding other organic wastes to the digestion system could increase the value of some, or all, of these streams. For instance, the addition of another organic waste containing significant quantities of nitrogenous materials, and degradable matter, could increase biogas production and enhance the fertiliser value of the solid and liquid streams produced by the digester. Dagnall (1995), in a review of the prospects for centralised co-digestion facilities in the UK, suggested that the most suitable wastes for co-digestion would be those produced by the food industry, as they would be the most likely of all industrial wastes to be free from heavy metal or organic chemical contamination, and hence be acceptable for spreading on farmland after digestion.

In many cases, the digester operator may be able to charge for disposal of the waste, creating an additional revenue stream. It may be that it would be more financially viable for a farmer, or group of farmers, or a developer, to set up a centralised anaerobic digestion unit, which would take slurries from a number of farms, and wastes from a number of industries. This facility would then be operated as a waste treatment plant as opposed to a farm based unit. There are a number of these units in Denmark, operating in such a fashion, although they tend to be operated largely as treatment facilities for farm slurries, with only a small fraction of other wastes being included in the digester feedstock (Danish Energy Agency, 1995).

Little work has been done in the laboratory on co-digestion. Wong and Cheung (1989) observed the co-digestion of pig slurry and cardboard, newspaper, sawdust and sugar-cane waste. They found that sawdust at a ratio of 4:1 pig slurry:sawdust, and cardboard at 4:1 and 3:1 pig slurry:cardboard, gave significantly higher methane yields than the pig slurry control.

Marques *et al.* (1997) also used pig slurry for co-digestion work, combining it with olive oil mill effluents, to provide a feedstock for an upflow anaerobic filter. They operated the filter at COD loading rates of between 3 and 10 kg COD $m^{-3}d^{-1}$, and at ratios of olive oil mill effluent to pig slurry of between (6 : 1 and 30 : 1 olive oil mill effluent to pig slurry), with no adverse effects on methane production. However, for reasons given in Section 3.1.1, pig slurry is not considered an appropriate material for a full-scale co-digestion plant.

1.8 Project Aims

Overall it can be concluded that little is known about what types and quantities of wastes digest best together, and which mixtures of animal slurries and other wastes would maximise some, or all, of the revenue streams mentioned above. This project has been set up to identify wastes which may digest well together, and demonstrate the digestion of these wastes in pilot scale anaerobic digesters.

The aims of the project were:

1. Design and construction of laboratory apparatus for batch co-digestion of wastes.

2. Design and construction of 20 litre pilot plant anaerobic digesters.

3. Obtain a range of wastes from different industries, and assess which digest best together on a batch digestion basis.

4. Digestion of the wastes which performed best under batch conditions, on a continuous basis in the anaerobic digestion pilot plant, to determine the optimum ratio of cattle slurry and waste .

5. Assessment of the impact of co-digestion of agricultural and industrial wastes on the economic viability of an anaerobic digestion facility.

Chapter 2

Methods and materials

2.0 General

Many of the methods listed in the following paragraphs are taken from Standard Methods for Water and Wastewater Analysis (APHA, 1992) and are marked by an asterisk (*). Mean and standard deviation values are quoted for each method. As a rule a method is accepted as being accurate if the within batch standard deviation is less than 5% of the mean value measured. All tables referred to in this chapter can be found in Appendix 1.

2.1 Chemical Oxygen Demand (COD)

The Hach sealed tube/colourimetric method, approved by the US Environmental Protection Agency, (Federal Register, 1980) was used for COD analysis.

The method is based on the oxidation of organic matter by dichromate in acid solution, followed by measurement of the residual dichromate. Initially the dichromate is present in excess as $Cr_2O_7^{2-}$, and the solution is orange in colour with a low absorbance at 610 nm in a spectrophotometer. Oxidation of matter present in the sample reduces the Cr(VI) ions to Cr (III) ions causing a colour change to blue/green, which can be measured using a spectrophotometer, and hence can be used to

determine the amount of organic matter present. The procedure for sample analysis was as follows.

The sample was diluted by an appropriate amount with distilled water as the Hach method has an upper limit of 1500 mg l^{-1} COD, and slurry samples were found to have COD values of up to 80, 000 mg l^{-1}. 2 ml of sample was then added to a pre-prepared tube, supplied by Hach, containing all the necessary reagents. The samples were placed in a heating block for 2 hours at 150 ^{o}C. At the end of this period samples were removed from the block and allowed to cool to approximately room temperature, and were then read in a Hach spectrophotometer, model DR/700. The spectrophotometer compared the absorbance of each sample with a standard curve determined by the manufacturer, and displayed the result in mg/l COD. The accuracy of the spectrophotometer was checked regularly using a potassium hydrogen phthalate (KHP) standard. This was prepared by dissolving 1275.5 mg of KHP, which had been previously dried at 120 ^{o}C to a constant weight, in 1000 ml of distilled water. KHP has a theoretical COD of 1.176 mg O_2 mg^{-1} (Pitwell, 1983), hence the above solution has a COD of 1500 mg l^{-1}. Table 2.1 (see Appendix 1) shows values produced by the assay for this standard and a diluted standard, 750 mg l^{-1} COD.

Cattle slurry can have COD values over 100,000 mg l^{-1}, so a dilution of at least a hundred -fold is required to bring the sample within the range of the COD assay. As cattle slurry is non-uniform in composition, often containing pieces of partially digested feed or straw, this dilution can be a major source of error. To check the accuracy of the dilution step portion of fresh cattle slurry, which had been

homogenised in a Magimix food blender (see Section 2.10.3 1), was divided into 5 parts and each part was diluted a hundred-fold and the diluted sample analysed for COD. The results obtained are displayed in Table 2.2 (Appendix 1). It will be noted that a relatively wide range of values were measured, with a difference of over 14,000 mg l^{-1} COD between the highest and lowest values recorded. This difference, most likely due to particles mentioned above, shows that COD values for cattle slurry must be interpreted with caution, unless the slurry has been extensively treated using a sieve or other type of filtration system to remove all large particles.

2.2 Total, fixed and volatile solids*

Total solids

Total solids were determined by placing 25 g of sample in a clean ceramic evaporating dish (which must have a volume appreciably larger than the slurry sample, or alternatively, be lidded) which had previously been ignited in a muffle furnace at 550 ^{o} C, allowed to cool in a desicator and weighed (weight A). The dish and sample were then weighed (weight B). The dish was then placed in an oven overnight at 105 ^{o} C, after which time the dish was removed from the oven, placed in a desicator and allowed to cool to room temperature. The dish was then weighed again (weight C).

The percentage of solids in the sample was determined using the formula:

$$\% \text{ total solids} = \frac{(\text{weight C} - \text{weight A}) \times 100}{\text{weight B} - \text{weight A}}$$

Fixed and volatile solids

The dish containing the dried residue was transferred to a muffle furnace operating at 550 ^{o} C, and left there for 1 hour, or until no further combustion was observed, whichever was longer. The dish was then removed, and due to the high operating temperature of the muffle furnace, was placed in an oven at 105 ^{o} C for 20 minutes, to allow the dish to cool to around 105 ^{o} C, as placing a dish at 550 ^{o} C in the glass desicator could have caused the glass to crack. Once the dish was cool it was re-weighed (weight D).

The percentage of fixed (inorganic) solids in the sample was determined using the following formula:

$$\% \text{ fixed solids} = \frac{(\text{weight D - weight A}) \times 100}{\text{weight B - weight A}}$$

The percentage of volatile solids in the sample was determined using the following formula:

$$\% \text{ volatile solids} = \frac{(\text{weight C - weight D}) \times 100}{\text{weight B - weight A}}$$

The main source of error in the measurement of volatile solids comes from the loss of volatile material such as volatile fatty acids on drying, see Section 1.3.3.6.

2.3 Measurement of pH*

An Ingersol Combination Electrode pH probe (model 465-35-K9) connected to a pH meter (Model 80, Fisons Scientific) was used to measure the pH of samples. The

probe was regularly calibrated using aqueous buffers of pH 4, 7 and 10. The pH of samples taken from reactors was measured immediately after removal from the reactor.

2.4 Total alkalinity*

The alkalinity of a wastewater was defined to be the measure of its ability to neutralise acids, and was measured by titration to pH 4.5 with standard acid (Parkin *et al.*, 1994). The resulting value was expressed as mg l^{-1} calcium carbonate ($CaCO_3$).

Standard sulphuric acid (0.357 N) was made up by adding 10 ml of 98% conc. H_2SO_4 to 989 ml of distilled water. Standard Methods suggests using 0.1N acid, however due to the high alkalinity values associated with animal slurries (up to 30,000 mg l^{-1}), it was decided to use a stronger solution to avoid the errors associated with refilling the burette during the analysis of each individual sample.

The acid used was standardised in the following manner:

40.00 ml of 0.05N Na_2CO_3 solution was added to 60 ml of distilled water in a beaker and titrated using the acid to pH 5. The pH electrode was removed and rinsed into the same beaker using distilled water, and the solution was boiled gently under a watch glass for 5 minutes. The solution was then cooled to room temperature, the watch glass rinsed into the beaker, and the titration continued to the inflection point, around pH 4.5. The normality of the acid was calculated using the following equation:

$$\text{Normality, } N = \frac{A \times B}{(53.00 \times C)}$$

A = g Na_2CO_3 weighed into 1 litre flask to make up 0.05N Na_2CO_3 solution

B = ml 0.05N Na_2CO_3 solution used for titration

C = ml acid used

Total alkalinity was measured as follows:

10 ml of sample were placed in a beaker and diluted with 10 ml of distilled water, although this may have altered the initial pH slightly, it was considered necessary due to the high solids levels of some samples (up to 10% solids). Acid was slowly added from a burette until the pH stabilised at 4.5. Total alkalinity was calculated using the formula:

$$\text{Alkalinity, mg } l^{-1}\ CaCO_3 = \frac{A \times N \times 50{,}000}{\text{ml sample}}$$

Where:

A = ml of standard acid used

N = normality of standard acid

No suitable standard could be found to check the accuracy of the method, so a slurry sample was assayed 5 times to check the reproducibility, the results are listed in Table 2.4.

2.5 Ammonium and ammonia*

Ammonium (NH_4^+)

Ammonium (NH_4^+) was measured using an ammonia selective electrode (Hach electrode no. HH/44470-01) and an ion selective electrode meter (Hach model no. HH/45400-00) both supplied by Camlab Ltd, Cambridge, UK. The method involved raising the sample pH to above 11 to convert all NH_4^+ ions present to $NH_{3\ (aq)}$ ions. The electrode membrane allowed only $NH_{3\ (aq)}$ ions to cross into the internal electrode solution where a pH probe measured the change in pH caused by the presence of $NH_{3\ (aq)}$ ions.

A stock solution of 1000 mg l^{-1} NH_4^+ was prepared by dissolving 2972.2 mg of NH_4Cl in 1000ml of distilled water. Solutions of 100 and 1000 mg l^{-1} NH_4^+ were used to produce a standard plot from which sample NH_4^+ concentrations could be determined, see Figure 2.1. A 2-point calibration was considered sufficient as all values measured fell within this range when diluted. Also, it has been shown that if the electrode is functioning properly and in a linear manner, a tenfold change in NH_4^+ concentration should result in a change in electrode potential of 59 mV ($\pm$ 1mV) (Hach, 1997). In Figure 2.1 the tenfold change in concentration resulted in an electrode potential change of 58.2 mV.

Samples were measured by adding 5 ml of sample and 15 ml of distilled water to a 50 ml beaker. The pH was then adjusted to above 11 with powdered lithium hydroxide (which was supplied by the probe's manufacturers and reccomended as being more suitable than sodium hydroxide), and the sample placed on a magnetic stirrer to ensure complete mixing and a constant flow across the electrode surface. The electrode was then immersed in the liquid and a covering of laboratory Parafilm placed around the

top of the beaker and the electrode to ensure no NH_3 escaped to atmosphere. The meter was then switched on and the milli-volt reading was allowed to stabilise, this took up to 5 minutes in some cases. Milli-volt readings could then be converted to mg l^{-1} NH_4^+ using the standard plot.

The concentration of NH_4^+ was calculated by determining the slope of the line in Figure 2.1 (see Appendix 1) and using this value to obtain a value for the constant c in the equation for a line, y = mx + c, where:

y = the milli-Volt value

m = the slope of the line

x = the NH_4^+ concentration

c = a constant

The values of m and c were found to be -0.064667 and -10.4667 respectively.

Hence the equation of the line becomes:

$$mV = -0.064667\ [NH_4^+] - 10.4667$$

The electrode was calibrated daily and periodically checked throughout the assaying of samples using a standard of 1000 mg l^{-1} NH_4^+. The results obtained are listed in Table 2.5.

Although the standard deviation is low (0.6 % of the mean value) the measured values were on average 3.4 % less than the expected value of 1000 mg l^{-1} NH_4. This may have been due to fouling of the membrane by materials contained in the animal slurries being analysed. Some brown discolouration of the membrane was noted over the course of the assay. Measured samples were adjusted to compensate for this change in membrane performance.

Ammonia (NH_3)

Ammonia (NH_3) is the un-ionised form of ammonium (NH_4), and was calculated using a formula developed by Abeling (1994). The formula used was as follows:

$$NH_3 \text{ (mg } l^{-1}) = \frac{17}{14} \times \frac{N \text{ (as mg } l^{-1} N) \times 10^{pH}}{\exp\{6334/T\} + 10^{pH}}$$

2.6 Redox potential

Redox potential within the anaerobic reactor was measured using a silver/silver chloride combination redox electrode(model no. P14 805-SC-DPAS-K85/225, Mettler Toledo Ltd.), and a volt meter with a range of +1000 to -1000 milli-Volts (Model 80 voltmeter, Fisons Scientific). The accuracy of the probe was monitored using standard solutions of +276 and +468 milli-Volts (supplied by Mettler Toledo Ltd.).

2.7 Volatile Fatty Acids (VFA)*

It was initially intended to measure volatile fatty acid (VFA) concentrations using gas chromatography (GC), but this method had to be abandoned in favour of the standard

distillation method due to insurmountable problems caused by the high concentration of dissolved material in the samples, which rapidly caused blocking of the capillary column used for analysis. The samples analysed on the GC had first been centrifuged at 12,000 rpm for 20 minutes and filtered through a 0.2 μm disposable filter, so it could be concluded that all suspended material had been removed , and the problem was caused by dissolved material present in the sample. The possibility of using specialised separation cartridges to selectively recover the fatty acids was investigated but found to be too expensive, due to the large number of samples requiring analysis.

The eventual solution was to use distillation to separate the fatty acids from the waste samples, and measure total VFA by titration with NaOH.

2.7.1 VFA analysis using the distillation method*

25 ml slurry samples were diluted to 125 ml with distilled water and centrifuged at 12,000 rpm for 20 minutes. 100 ml of supernatant from the centrifuge tube was placed in a 500 ml round bottomed distillation flask, together with 100 ml of distilled water, 5 ml of 5 M H_2SO_4 and 4 to 5 fused alumina anti-bumping chips. The flask was connected to a standard condenser, approximately 76 cm long, and distillation was commenced at the rate of 5 ml min^{-1}. As H_2S and CO_2 were liberated early on in the distillation process the first 15 ml of distillate was discarded. 150 ml of distillate was then collected in a 250 ml graduated cylinder. This was titrated with 0.1 N NaOH, using a phenolpthalein indicator, and the first pink colour which persisted on standing for a short time, as an end point.

As heating rate and other factors unique to each distillation apparatus affect recovery of VFA, a recovery factor was determined for the apparatus, using a stock solution of 2000 mg l^{-1} acetic acid.

The concentration of VFA present, expressed as mg l^{-1} acetic acid, was calculated using the equation:

$$\text{mg VFA } l^{-1} = \frac{\text{ml NaOH x N x 60,000}}{\text{ml sample x f}}$$

where f is the recovery factor. The recovery factor, f, was calculated by analysing the standard solution of 2000 mg l^{-1} acetic acid using the distillation apparatus and determining the amount recovered using the above equation with the recovery factor equal to 1. As the concentration of acetic acid in the standard was known, the recovery factor could be calculated by dividing the mean concentration of acetic acid in the distillate by the concentration of acetic acid in the standard. Table 2.6 shows the concentration of acetic acid actually recovered in the distillate from 5 samples and the mean concentration of the acetic acid in the distillate. f was calculated using the equation:

$$f = \frac{\text{concentration of acetic acid in the distillate}}{\text{concentration of acetic acid in standard}}$$

Table 2.7 shows the results of analysis of 5 samples of acetic acid standard solution using the assay and the factor f determined above

Therefore:

$$f = \frac{1736}{2000} = 0.87$$

2.8 Methane and Carbon Dioxide

Methane and carbon dioxide concentrations in the biogas were measured using a Pye Unicam series 104 gas chromatograph fitted with a Porapak Q packed column (3mm ID and mesh size 80-100) and a thermal conductivity detector (TCD). Helium was used as a carrier gas, at a flow rate of 40 ml min^{-1} and the oven temperature was 50 ^{o}C.

The GC was calibrated using a function in the software control package which allowed a single point calibration, using a standard comprising 48% methane (CH_4)and 52% carbon dioxide (CO_2).

Running this standard on the GC five times yielded the results listed in Table 2.8.

2.9 Hydrogen Sulphide (H_2S)

H_2S levels in the biogas were measured using a Draeger Tube System (supplied by Draegerwerk AG). The system involves drawing a sample of the gas to be analysed through a graduated tube which has been pre-filled with a lead salt, using a bellows supplied by the manufacturers of the kit. The lead salt is initially white in colour, but changes to brown as the lead reacts with the H_2S to form PbS. The graduated scale on the side of the tube gives a reading of H_2S in ppm. No calibration of the assay was performed due to the extremely toxic nature of H_2S, and associated handling and

disposal problems. The manufacturer indicates the assay is accurate to ± 5 - 10 %. Zero to 2000 ppm and 2000 to 70,000 ppm tubes were used, depending on the levels of H_2S present in the biogas.

An important point to note is that H_2S is soluble in water. An air sample containing 2000ppm H_2S, in contact with a water sample for a period of time at 20 °C, would produce a saturation H_2S concentration in the water of 195ppm (Metcalf and Eddy, 1997). However, as the acidified water in the gas collection equipment was in permanent contact with biogas and was not replaced over the course of the experiment, it could be assumed that water was saturated with H_2S from an early stage in the experiment, and therefore would not contribute to changes in measured H_2S levels.

2.10 Experimental Equipment

Batch digesters were used for waste selection trials and the most suitable waste combinations were then tested using 2 x 18 l working volume pilot plants which were constructed as part of the project. The following paragraphs and illustrations describe both sets of apparatus. The detailed design calculations for the 18 l working volume units can be found in Appendix 3.

2.10.1 Batch digesters

Waste selection trials were conducted using 1 litre shake flasks, kept at 35 °C in an incubator. Figure 2.2 (Appendix 2) is an outline sketch of the apparatus. Figures 2.3

and 2.4. are black and white plates and are included in the body of the text for illustration.

2.10.1.1 Selection of construction materials and design of batch digestion apparatus

Neoprene stoppers and PVC tubing were used due to these materials being relatively impervious to methane. PVC - Simona glass was chosen as a suitable material for the biogas collection vessels due to its acid-resistant properties. Nipro stopcock 3-way luer slip valves (NIPRO Medical Industries Ltd., Japan) were used as gas sampling ports, as they are cheap, reliable and allow direct connection to a gas-tight syringe. Nickel plated steel ball valves (AIGNEP compressed air valves, Major Fluid Power Control Ltd., Birmingham) were used as gas valves on the PVC - Simona glass cylinders. All joints were sealed with silicone sealant.

2.10.1.2 Start - up and operation of batch digesters

Cattle slurry and waste material were combined in the desired proportions using a Magimix food blender (Magimix SA, France) and 750 ml of this mixture was placed in a 1 litre flask. The flask was stoppered with a neoprene bung and placed in the incubator which was maintained at 35 ^{o}C. The flasks were mixed by hand once a day. Daily biogas production was measured by calculating the volume of water displaced form the biogas collection cylinder. Atmospheric pressure and the pressure head supplied by the reservoir of acidified water were also measured and used to adjust the biogas volume to a standard pressure of 760 mm Hg and a temperature of 25 ^{o}C.

Biogas composition was monitored daily by flushing the vent line with biogas from the collection cylinder, and then taking a biogas sample from the sample port. The syringe was flushed 3 times with biogas from the vent line, the 4th sample taken was retained for immediate analysis by GC as previously described.

Figure 2.3 Batch digestion flasks inside incubator, connected by PVC tubing to gas collecters outside the incubator housing

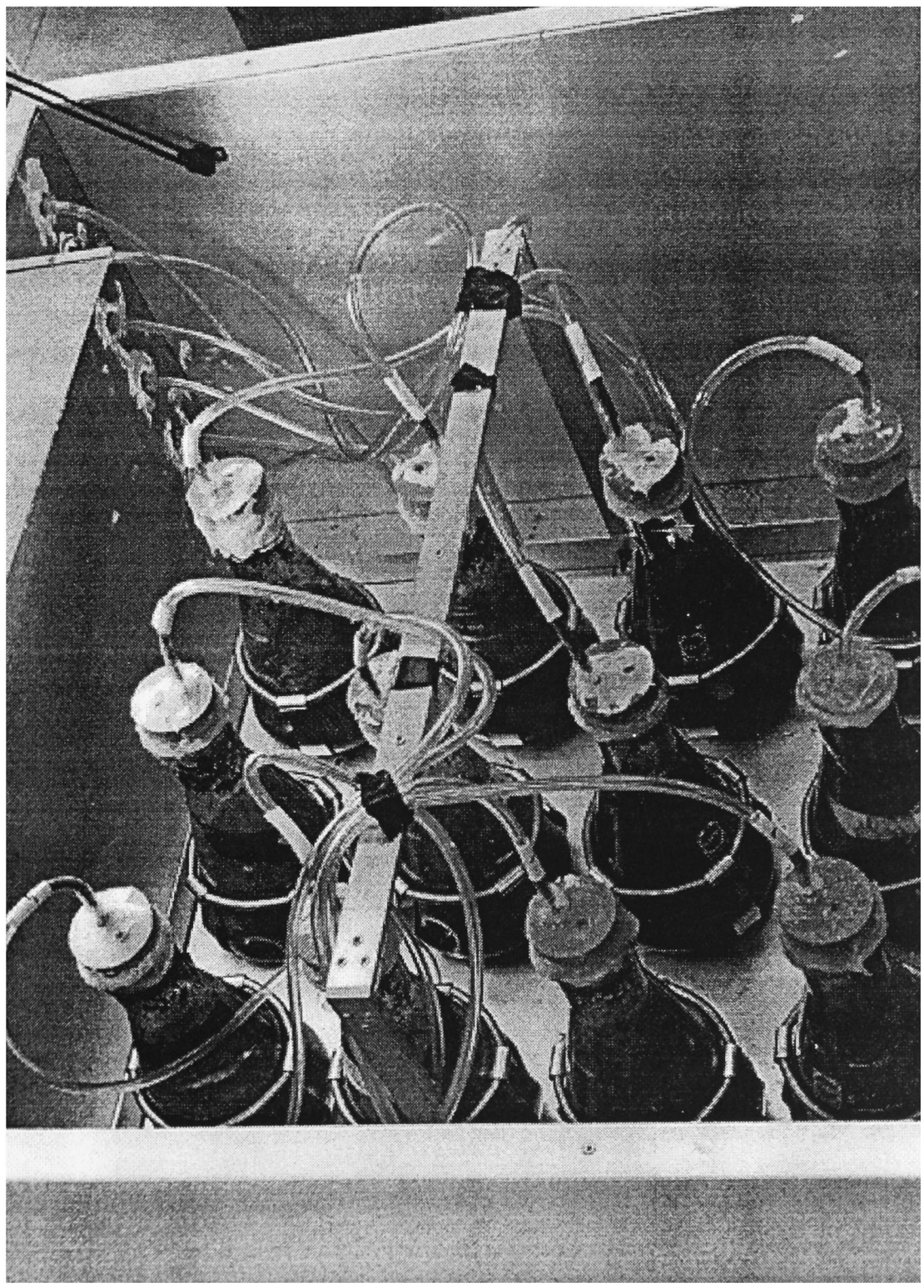
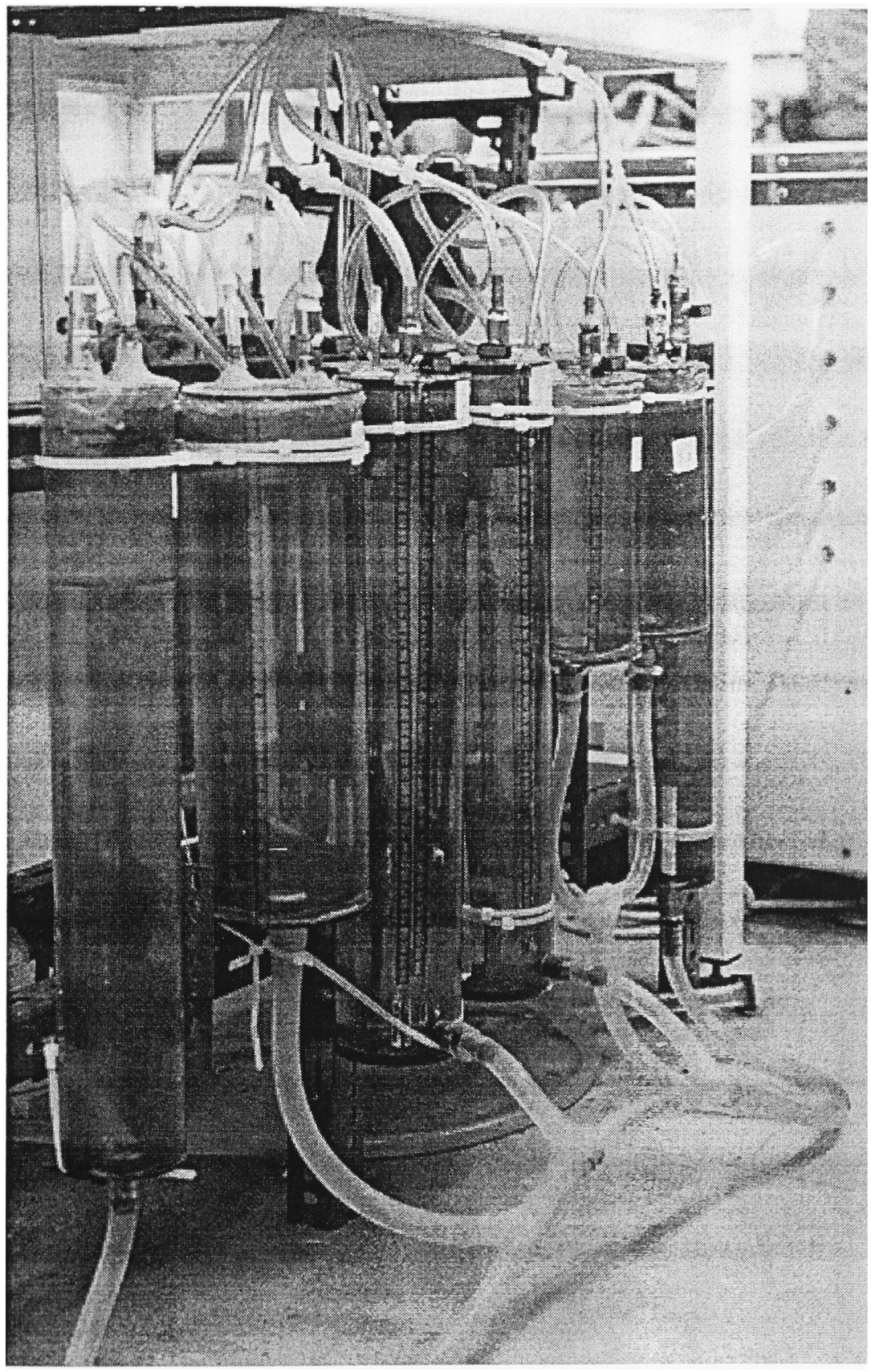


Figure 2.4 Gas collecters for batch digestion flasks



2.10.2 Selection of construction materials and design of pilot plant anaerobic digesters

Figures 2.5 (Appendix 2), 2.6, 2.7, 2.8 (Appendix 2) and 2.9 (Appendix 2) show the pilot plant units which were designed and built as part of this project. It was decided to construct 2 units to allow waste mixtures to be trialed in duplicate, or to offer the possibility of running 2 different waste mixtures concurrently.The component parts of the pilot plant unit are described in the following paragraphs.

2.10.2.1 Safety enclosure around pilot plant

A wooden frame 2400 mm high x 2000 mm wide by 1300 mm deep was constructed in the laboratory. The frame was then covered with heavy duty polythene, and a centrifugal extraction fan (0.37 kW motor, Westmid Fans, Birmingham) was fitted on top of the frame with ducting to atmosphere. The fan was specified to provide approximately 2 air changes of the space inside the frame per minute.

2.10.2.2 Pilot plant frame

The framework for the pilot plant, see Figure 2.6, was constructed from laboratory Dexion steel sections (Dexion Ltd, UK), and painted with commercial metal emulsion paint (Andrews Coatings, Birmingham).

2.10.2.3 Reactor

The reactor sections were QVF glass sections (QVF Ltd Staffordshire) of internal diameter of 300 mm, height 300 mm and wall thickness 10 mm (see Figure 2.7) The sections were sealed at either end with 12 mm mild steel end plates, coated in 2 pack

epoxy paint (Andrews Coatings Ltd., Birmingham). PTFE O-rings (supplied by QVF) and silicone sealant were used to effect a water and gas tight seal. The reactors were designed to have a working volume of 18 litres, giving a headspace volume of 3.2 l and a headspace height of 45mm. 4 baffles with a horizontal length of 10% of the reactor diameter, were installed at 90° intervals around the reactor wall. The reactor endplates, see engineering drawings Appendix 2 , were machined from 12 mm mild steel plate at the School of Chemical Engineering workshops. Once assembled the reactor was leak tested to 5 psi with nitrogen.

Figure 2.6 Both anaerobic digester pilot plant in operation. The plant on the right has had its motor removed for clarity.

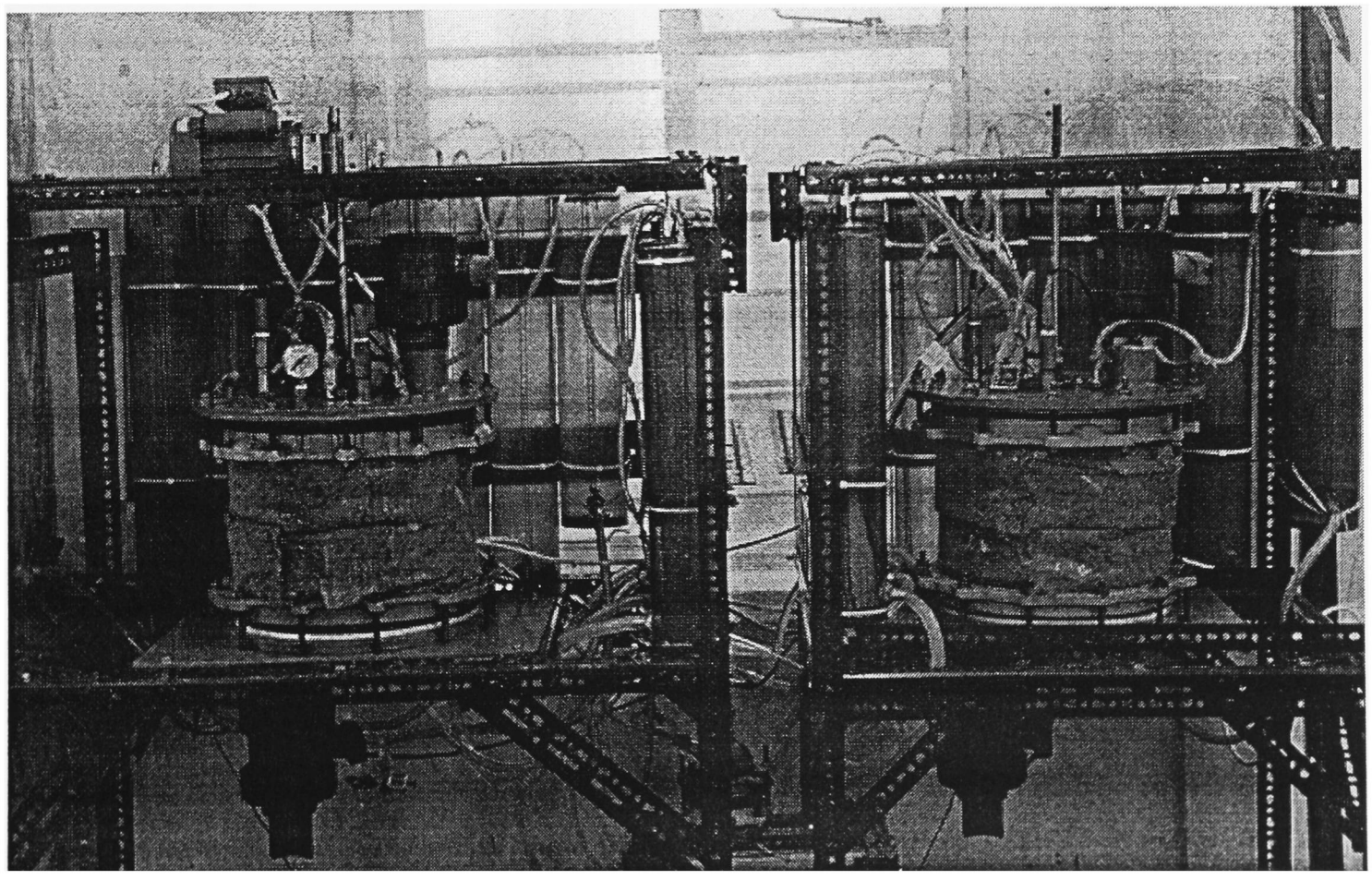
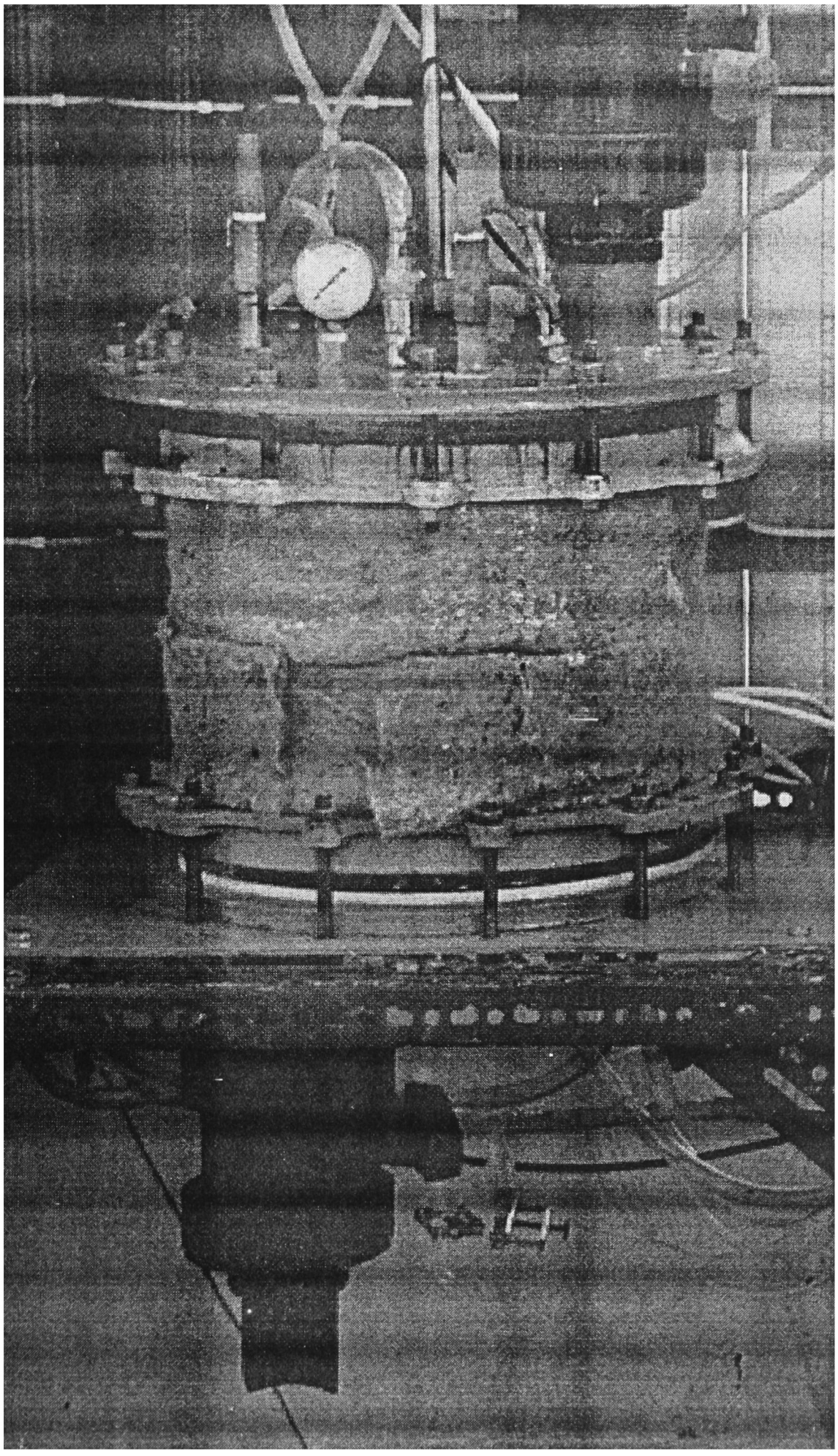


Figure 2.7 Close-up of digester vessel. Note pressure gauge to indicate pressure build-up caused by gas outlet blockages.



2.10.2.4 Biogas collection and monitoring system

The system used was a larger version of the apparatus used in the batch experiments, see Section 2.10.1.1 for a full description of this system. Each pilot plant unit had 11 biogas collection cylinders, each with 4 litres capacity. See Appendix 3 for the calculations used to determine biogas production rate and storage capacity required.

2.10.2.5 Waste addition and withdrawal system

Waste was added and withdrawn through 2 inch ABS ball valves (Capper PC, Birmingham). Waste was withdrawn from the bottom of the reactor and added at the top. A gas reservoir system was devised to prevent ingress of air during withdrawal of waste, see Figure 2.10 (Appendix 2). The materials of construction and components used were of the same type as those used to construct the batch digestion biogas collection system, see Section 2.10.1.1.

2.10.2.6 Mixing system

The pilot plant digesters were mixed using a 6 blade, pitch-blade impeller, manufactured in the Engineering Workshops, School of Chemical Engineering, University of Birmingham. The impeller had a diameter, 15 cm (the reactor diameter (D) divided by a factor of 2) and was mounted 7.5 cm above the base of the tank (D/4) both dimensions were calculated using the method suggested by Chapman *et al*

(1983). The impeller was mounted on a stainless steel shaft with a diameter of 10 mm, and driven by a 0.12 kW single phase motor (Powerpak Ltd, Birmingham) see Appendix 3, for detailed mixing design calculations.

Sealing of the shaft presented a number of problems, namely the requirement for the sealing system to be able to operate in a corrosive (H_2S) and abrasive (grit) environment. Initially the system shown in Figure 2.11 (Appendix 2) was designed and installed. The headspace in the reactor was kept isolated from the atmosphere by the flange and pipe system (A) which ensured the shaft entered the reactor below the level of the slurry. After 4 months satisfactory operation the bearings failed due to damage to the bearing assembly caused by grit. The supplier of the bearings had guaranteed the bearing housings would exclude liquid and grit, but the housings could not cope with the exceptionally aggressive conditions present in an anaerobic slurry digester. The system was re-designed using spring-loaded lip seals to ensure greater protection for the bearings, see Figure 2.12 (Appendix 2). This system performed satisfactorily for over 7 months, at the end of which period the reactors were shut down and the bearings examined and found to be in good working order.

2.10.2.7 Digester temperature control system

Digester temperature was controlled using a set-point controller (manufactured by the Electronic Engineering Workshop, School of Chemical Engineering, University of Birmingham), linked to a thermistor inside the reactor, see Figure 2.8. The set-point unit controlled a centrifugal pump (Eheim AG, Germany) by an on/off switch, see Figure 2.9. The pump was capable of pumping 10 l water min^{-1} from a water bath

containing water at 60 °C, through an external water jacket which was wrapped around the outer wall of the reactor. The water jacket was manufactured from 6 mm copper tubing (Capper PC, Birmingham, UK). The unit kept the reactor temperature at 35 °C (± 0.5 °C). Initially an internal coil was used heat the reactors, but on dismantling the system after the first set of experiments this was found to be coated with straw and slurry, which would increase the resistance to heat transfer into the digester liquor, and hence make the system inefficient, therefore an external heating jacket was used for the remainder of the project.

2.10.3 Waste collection, pre-treatment and storage

2.10.3.1 Cattle slurry

Fresh cattle slurry was collected from a dairy farm near the University about once a month during the operation of the digesters. The cattle were housed in-doors, during the winter and early spring, and fed on ensiled grass supplemented by a ration of sugar beet and seed-cake. From late spring on-wards the cattle were put out to pasture, and received a supplement of seed-cake at milking time. Pre-treatment, before addition to the digesters, consisted of manual removal of all long straw, usually defined as straw longer than 50 mm, followed by maceration in a commercial Magimix food blender (Magimix SA, Montceau en Bourgougne, France). The manure was then stored at 4 ^{0}C. The required portion of manure was diluted to 8% total solids with tap water, immediately prior to digestion.

2.10.3.2 Chicken manure

Chicken manure was collected once a month, on average, from Attwells Farms Ltd., whose site was near the University. The farm operated a system where the laying hens were housed in the upper storey of a number of 2 storey sheds, each containing 20,000 birds. Manure collected in heaps on the concrete floor below and was removed twice a year. The manure was diluted with tapwater to 15% total solids immediately before digestion. However, due to the un-even solids distribution of the raw manure, caused by the drying effect of the ventilation system within chicken sheds, it was impossible to achieve a constant total and volatile solids concentration.

Prior to co-digestion, the required amounts of chicken manure, cattle slurry and tap water were combined in a 1 litre graduated cylinder and mixed vigorously for 30 seconds using a plunger with a diameter about half that of the cylinder. This method of combining the materials was chosen over using a blender as it was noted that the blender tended to mix a lot of air into the material, producing a mousse like effect. Air is toxic to methanogens, and regular addition of air could have had a negative effect on the performance of the system.

2.10.3.3 Sugar beet processing effluent

This waste was the wash water and carrier water from the sugar extraction process at British Sugar's Kidderminster site. The waste sample was obtained from the pipe carrying effluent to the site's activated sludge effluent treatment plant. No pre-treatment of the waste was necessary before co-digestion. The effluent was stored at -10 °C until it was required for experimental work, as were all the effluents described in the following paragraphs.

2.10.3.4 Chocolate manufacturing effluent

Cadburys chocolate manufacturing site in Birmingham supplied this wastewater, which was produced by the tank washing process in the first stages of chocolate manufacture. Again no pre-treatment of this waste was necessary before co-digestion.

2.10.3.5 Potato processing effluent

The potato processing effluent was produced by Everest Foods Ltd, Wombourne, near Wolverhampton, who manufacture frozen potato chips. The effluent was a combination of tank and floor washings, and was obtained from the effluent line which fed the site's UASB (Upflow Anaerobic Sludge Blanket) digester. No pre-treatment of this waste was undertaken prior to co-digestion.

2.10.3.6 Brewery sludge

This material was taken from the sludge settling tanks at the Whitbread brewery in Maygor, South Wales. The site employs high rate trickling filters to treat the effluent produced by the brewing process. These filters produce quite a lot of sludge, which is very high in nitrogen, and has a very strong odour, (Walsh, 1997). No pre-treatment was considered necessary prior to co-digestion.

2.10.3.7 Dissolved Air Floatation (DAF) sludge

This sludge was obtained from a DAF unit on Yeo Valley Farm's yoghurt manufacturing site near Bristol. The unit removed particulate matter from the

wastewater produced by the yoghurt manufacturing plant, using ferric sulphate as coagulating agent. The wastewater included tank washings and yoghurt batches which had been dumped to waste. No pre-treatment was required before co-digestion.

2.10.3.8 Silage effluent

Silage effluent is the name commonly given to the liquid produced by the anaerobic fermentation process, known as ensiling, which is used on many farms in the UK to produce a feed for cattle during the months when pasture land is not available for grazing. The effluent used was obtained from the channels draining the silage pit of a farm near Birmingham.

2.10.3.9 The organic fraction of household municipal solid waste (MSW)

This material was obtained from the kitchen of a student residence, using a rubbish bin which was for organic material only. The bin was emptied once a week, and the material was macerated using the Magimix food blender described in Section 2.10.3.1. The macerated waste was then stored at -10°C until required. During the pilot plant trials using this waste sufficient material for one weeks operation was thawed out at the beginning of each week and stored at 4°C for the week.

2.10.3.10 Fish offal

Fish offal was obtained from the Donnington Fish Farms site near Stow-on-the Wold, Gloucestershire. The company reared and harvested rainbow trout for the restaurant trade. The offal consisted of fish viscera, heads and tails. The first batch of waste collected, which was used in the batch digestion trials, described in Chapter 5, had

been stored at room temperature for over a week prior to collection. The waste samples used during the work described in Chapter 7 were collected on the day the fish were processed, macerated using Magimix food blender and then stored at -10°C until required. For the pilot plant trials involving this material a quantity sufficient for one weeks operation was thawed out at the beginning of each week and stored at 4°C for the week.

Chapter 3

Batch co-digestion of agricultural and industrial wastes - trial 1

3.1 Selection of slurry for digester feedstock

The first issue to be tackled was the type of agricultural slurry to be used as feed for a digester to which other wastes could then be added. Cattle slurry, pig slurry and chicken manure (manure from laying hens housed in battery cages) were all considered as possible digester feedstocks.

3.1.1 Pig slurry

Pig slurry contains high levels of copper which is fed to pigs as a growth promoter (McGrath *et al.*, 1982). High copper concentrations in the slurry from a digester could limit the land available for spreading the slurry, as repeated applications of pig slurry on land have been shown to raise soil and herbage copper levels to a point where they can be dangerous to livestock (McGrath *et al.*, 1982). Limited land availability could in turn limit the size of a digester operated as a co-digestion facility,

as described in Section 1.6 of Chapter 1, and hence reduce the economic viability of the digester. Hence pig slurry was not considered suitable for use as a digester feedstock.

3.1.2 Chicken manure

Aubart and Fauchille, (1983) in a review of the anaerobic digestion of chicken manure concluded that an extremely long retention time (up to 60 days) in a digester was required for stabilisation of the waste (defined by the authors as odour reduction and removal of a significant amount of volatile solids). While numerous laboratory studies have shown that chicken manure can be successfully digested on a laboratory scale (Webb and Hawkes, 1985, Pechan *et al.*, 1987), studies of farm based digesters operating on chicken manure in the UK have shown that the systems have poor methane production rates and produce a malodorous semi-digested slurry. Also, due to the high solids levels of chicken manure (typically 25 - 30% total solids), dilution with large volumes of water is necessary to reduce solids levels to about 10%, as it is difficult to mix systems with solids levels greater than this value. This adds greatly to the operating cost of a farm based digester.

For example for a farm producing 14,000 wet tonnes of chicken manure per year, with a total solids level of around 30%, 28,000 tonnes of water would be required to reduce the total solids level to 10%. The typical cost of water supplied to UK industry is about £0.60 per m^3 (Tyler, 1995). Hence the dilution water alone represents an annual operating cost of £16,800. Additional costs would also be incurred in building tanks for storage of diluted slurry and ancillary pumping equipment.

For all these reasons, chicken manure is unlikely to be an acceptable material for co-digestion. It is interesting to note that two of the three chicken manure digestion systems built in the UK have recently been de-commissioned as they were found to be un-economical to operate due to a combination of the factors mentioned above (ETSU, 1994).

3.1.3 Cattle slurry

The principles of the anaerobic digestion of cattle slurry have been well established for a number of years, and there are currently 14 digesters successfully processing cattle slurry on farms around the UK (ETSU, 1995). Cattle slurry does not contain heavy metals as pig slurry does and generally can be stabilised in an anaerobic digester in 15 - 20 days, a third of the time taken to stabilise chicken manure, hence it was deemed to be the most suitable material for the co-digestion trials. The high alkalinity values associated with cattle manure, typically around 11,000 mg l^{-1} $CaCO_3$ (Chayovan *et al.*, 1988) should also ensure that a cattle slurry digestion system could accept significant quantities of volatile fatty acids, which may be generated by adding a readily degradable organic waste to the digestion system, and still maintain the pH of the system within the range at which anaerobic bacteria can survive.

3.2 Selection of wastes for co-digestion

The wastes chosen as co-digestates for the first waste selection trials were **potato processing effluent**, **sugar beet processing effluent**, **wash-water from the manufacture of chocolate** and **chicken manure** (also known as layers muck, that is manure from laying hens housed in battery cages).

Each was chosen for a particular reason. Potato effluent is high in starch and refractory COD (COD which is difficult to breakdown using bacteria) (Barlow, 1995). Sugar beet effluent is high in particulates and has a very strong odour making it unsuitable for aerobic treatment at many sites (Sexton, 1995). Chocolate manufacturing wash waters are very high in COD, which can cause overloading problems in effluent treatment plant, or incur significant charges from water companies if discharged to sewer (Hebbleswaite, 1995).

Intensive poultry farming is practised in many areas of the UK. The industry currently produces about one million dry tonnes of excrement per year (ETSU, 1995). There are two main types of intensive poultry farming; rearing of poultry for meat (known as broiler farming) and keeping hens for laying eggs; each of which produces a waste which has quite different characteristics. Broilers are housed in large sheds. They nest on the floor of the shed, which is spread with a layer of sawdust bedding, usually about one inch thick, and are fed for six weeks on a diet designed to achieve optimum weight gain. At the end of six weeks the poultry are removed for slaughter and the waste which has built up is also removed. This mixture, known as poultry litter, tends to have a solids content of about 50% and is friable and relatively odour

free. A typical example of a broiler farm was studied and was found to produce 80,000 chickens for slaughter every 6 weeks. The farmer used 10 tonnes of sawdust to line his sheds and total litter production was 160 tonnes per 80,000 chickens produced (Bright, 1997). As poultry litter is quite dry and friable, it is suitable for composting (Hayward, 1997) or as fuel for specially adapted power stations, 3 of which are currently operating in the UK. Hence this material although produced in large quantities, does not cause any major disposal problems in the UK.

The other major waste arising from intensive poultry farming, one which causes disposal problems at many sites, is chicken manure, also known as layers muck, which is produced by laying hens. The poultry in this case are housed in cages with wire mesh floors, on the upper floor of two-storey sheds. The excrement produced falls from the cages and builds up in heaps on the floor of the shed from where it is periodically removed. This material usually has a solids content of 25 - 30% and has quite a strong odour. Due to economies of scale, egg producing units tend to be quite large, and hence produce large volumes of waste. One poultry producer near Birmingham produces about 14,000 wet tonnes of chicken manure each year, which is currently disposed of to land around the UK, some of this waste has to be transported to farmland in south Wales for disposal, such is the demand for land for spreading organic waste in the West Midlands (Attwell, 1995).

The land disposal route has been closed or severely restricted in many areas of the UK due to new rules governing nitrate pollution of ground and surface water by agricultural slurries (ENDS Report, 1994). Chicken manure contains high levels of ammoniacal nitrogen which, when spread on land, can be converted to nitrite and nitrate by nitrifying bacteria in the soil, and hence can make a large contribution to this type of pollution, even if the slurry itself is not discharged directly to the watercourse (ETSU, 1995)

As has been noted in Section 3.1.2, anaerobic digestion of chicken manure has not been successful on farms in the UK. Composting of the material has also been unsuccessful, due to the difficulties involved in mixing this paste like material with bulking agents (Hayward, 1997) and the high moisture content of the material means it is not very suited to incineration. No other treatment method is currently available, hence the disposal of this material represents a major problem in the UK today.

3.3 Analysis of wastes

Samples of waste were obtained from Everest Frozen Foods Ltd., Wombourne (potato), British Sugar Ltd., Kidderminster (sugar beet), Cadburys Ltd. Bournville (chocolate) and Attwell Farms, Redditch (chicken manure) and analysed for pH, COD, NH_4^+ and for total, fixed and volatile solids, see Table 3.1

3.3.1 Chocolate manufacturing effluent

An analysis of the wastes highlighted some interesting points. The chocolate manufacturing effluent proved to be very high in COD (244,000 mg/l) mostly due to the glucose present (Cadburys estimated the amount of glucose in the sample to be about 18%). This should make it an ideal co-digestate, as glucose is readily converted to acetate and hence to methane under anaerobic conditions (Nicholson, 1996).

3.3.2 Cattle slurry

The cattle slurry used was obtained from a local farm, where cattle were housed in a barn and slurry was collected twice a day using a tractor driven floor scraper. Some evaporation of water had occurred during the time the slurry lay on the ground and it was found to be quite high in total solids (13.6%). Reported values for cattle slurry range from 8.5% total solids (Singh et al., 1985) to 12.7% (Hobson and Robertson, 1977). Storage conditions before digestion, animal feedstuff, water consumption and rainwater or drainage water ingress, dictate the solids level of cattle slurry being fed to a farm digester. Generally it is difficult to mix a digester by conventional means if the contents have a solids level greater than 10% (Bujawlski, 1986). Dilution of the slurry to 10% total solids was therefore considered necessary.

3.3.3 Chicken manure

The solids levels in the chicken manure sample were found to be quite similar to published data (ETSU, 1994). The ETSU study found 34.8% total solids, 9.5% fixed solids and 25.3% volatile solids in a typical chicken manure sample. The sample from Attwell Farms had 30% total solids, 8.1% fixed solids and 21.9% volatile

solids. Dilution to 7.5% total solids with water, on a commercial farm digester, would probably not be feasible due to cost of the water, see Section 3.1.2. It was decided to test the 7.5% total solids mixture in case the 15% total solids mixture caused digester failure. To bring the solids levels in raw chicken manure down to a level suitable for digestion in a CSTR, some dilution would be necessary. From observations of various dilutions of chicken manure, 15% total solids was considered to be the minimum dilution necessary. At solids levels higher than this the slurry was thick and did not easily flow and hence would be difficult to handle on a full scale plant.

3.3.4 Sugar beet processing effluent

The sugar beet waste water was not a very good example of an effluent of this type as it was collected from the water recirculation system of a lagoon where the effluent had been stored for one month. Hence some bacterial action and some settling of solids had occurred. The effluent retained its very strong odour which causes a lot of complaints from the general public when the effluent is treated aerobically.

3.3.5 Potato processing effluent

The pH of the potato processing effluent was found to be quite low for reasons which were not quite clear. However the buffering capacity of the cattle slurry ensured the pH was 7.3 in the digestion flask. This type of effluent tends to produce a lot of NH_3 during digestion as it is quite high in protein (Koster and Lettinga, 1988).

3.4 Waste selection trials

Ten one litre flasks fitted with baffles were used as digesters for these trials. See Section 2.10.1 for a full description of the apparatus. 750 g of waste mixture was placed in

each flask, this comprised, 75g of inoculum from a working digester and 675g of a mixture of 80% (by weight) raw slurry and 20% (by weight) of the waste being studied.

The flasks were maintained at 35^0 C an incubator, and mixed by hand once a day. The

contents of each flask are described in Table 3.2. Each flask was analysed for pH, COD, NH_4^+, total, fixed and volatile solids before being placed in the incubator, see Table 3.3. The experiment lasted for 22 weeks. Biogas production was recorded weekly and biogas analysis for methane and carbon dioxide was also carried out weekly. After 22 weeks biogas production had become negligible and the experiment was terminated. Samples from each flask were again analysed for pH, COD, NH_4^+, total, fixed and volatile solids, see Table 3.4. Samples from each flask were also analysed for methanogens under a UV (ultra-violet light) microscope. This method involved taking a sample of slurry, smearing it on a slide, covering with a coverslip and observing under a microscope fitted with a UV lamp. Methanogenic bacteria fluoresce under UV and can be easily counted and identified. A full description of above-mentioned analysis methods can be found in Chapter 2, Sections 2.1 - 2.5.

The COD loading figures mentioned in the following sections were used to compare the different waste loadings on the flasks and were calculated in the following

manner, using the flasks receiving additions of sugar beet effluent as an example. The total weight of material present in each flask was 750 g, this was approximately equal to 0.75 l of material and was taken to be the working volume of the flask. 150 g (20% by weight) of this material was sugar beet effluent, which had a COD of 5,600 mg l^{-1}. 150g of sugar beet effluent, which had a volume of 150 ml, contained 0.84 g of COD, or 0.00084 kg of COD. The working volume of the flask was 0.00075 m^3 so the COD loading, as sugar beet effluent, was 0.00084 kg COD added to 0.00075 m^3, which was 1.1 kg COD m^{-3}. The COD loadings for the other flasks were calculated in a similar manner.

Table 3.1 Composition of wastes selected for co-digestion trials

Waste type	pH	NH_4^+ mg/l	Total solids %	Fixed solids %	Volatile solids %	COD mg/l
Chocolate manufact. washwater	7.0	0	22.6	0.3	22.3	244,000
Potato processing effluent	4.6	1,525	1.2	0.2	1.0	15,000
Sugar beet processing effluent	6.8	300	0.50	0.2	0.3	5,600
Cattle slurry	7.8	1,925	13.7	3.0	10.7	108,750
Chicken manure	7.3	12,800	30.0	8.1	21.9	271,000

Table 3.2 Contents of each flask

Flask	70% of flask contents (by weight)	20% of flask contents (by weight)	10% of flask contents (by weight)
1	Cattle slurry	Cattle slurry	Digester inoculum
2	Cattle slurry	Sugar beet processing effluent	Digester inoculum
3	Cattle slurry	Sugar beet processing effluent	Digester inoculum
4	Cattle slurry	Chocolate manufacturing eff.	Digester inoculum
5	Cattle slurry	Chocolate manufacturing eff.	Digester inoculum
6	Cattle slurry	Potato processing effluent	Digester inoculum
7	Cattle slurry	Potato processing effluent	Digester inoculum
8	Cattle slurry	Chicken manure (7.5% total solids)	Digester inoculum
9	Cattle slurry	Chicken manure (7.5% total solids)	Digester inoculum
10	Cattle slurry	Chicken manure (15% total solids)	Digester inoculum

Table 3.3 Analysis of flask contents before digestion

Flask	pH	NH_4^+ (mg l^{-1})	NH_3 (mg l^{-1})	Total solids %	Fixed solids %	Volatile solids %	COD (mg l^{-1})
Flask 1	7.6	1275	34	10.6	2.3	8.3	104,500
Flask 2	7.5	1925	41	10.6	2.3	8.4	116,500
Flask 3	7.8	1925	65	10.2	2.1	8.1	110,500
Flask 4	7.1	250	<10	13.4	2.0	11.4	134,750
Flask 5	7.1	150	<10	13.2	1.3	11.9	133,000
Flask 6	7.3	1600	22	10.5	2.2	8.3	126,250
Flask 7	7.3	1600	22	11.0	2.3	8.7	128,000
Flask 8	7.3	2500	34	12.1	2.9	9.2	94,250
Flask 9	7.3	2250	31	11.8	2.8	9.0	99,500
Flask 10	7.2	3350	60	13.8	3.8	10.0	98,000

Table 3.4 Analysis of flask contents after 22 weeks digestion

Flask	pH	NH_4^+ (mg l^{-1})	NH_3 (mg l^{-1})	Total solids %	Fixed solids %	Volatile solids %	COD (mg l^{-1})
Flask 1	8.0	1600	104	5.3	1.3	4.0	67,500
Flask 2	8.0	1925	126	5.9	1.6	4.2	63,300
Flask 3	8.0	1400	87.5	5.1	1.4	3.8	57,500
Flask 4	4.5	970	< 10	8.7	1.5	7.2	105,000
Flask 5	4.5	1770	< 10	9.5	1.5	7.9	105,000
Flask 6	8.0	2400	150	5.8	1.7	4.1	67,700
Flask 7	8.0	3200	200	5.9	1.8	4.2	53,100
Flask 8	8.1	3200	260	6.5	1.7	4.8	56,000
Flask 9	8.1	3300	267	6.3	1.7	4.5	54,500
Flask 10	8.3	8800	1087	7.4	5.5	1.9	71,300

Figure 3.1 Weekly methane production: digesters 2 and 3 (sugar beet processing effluent/cattle slurry)

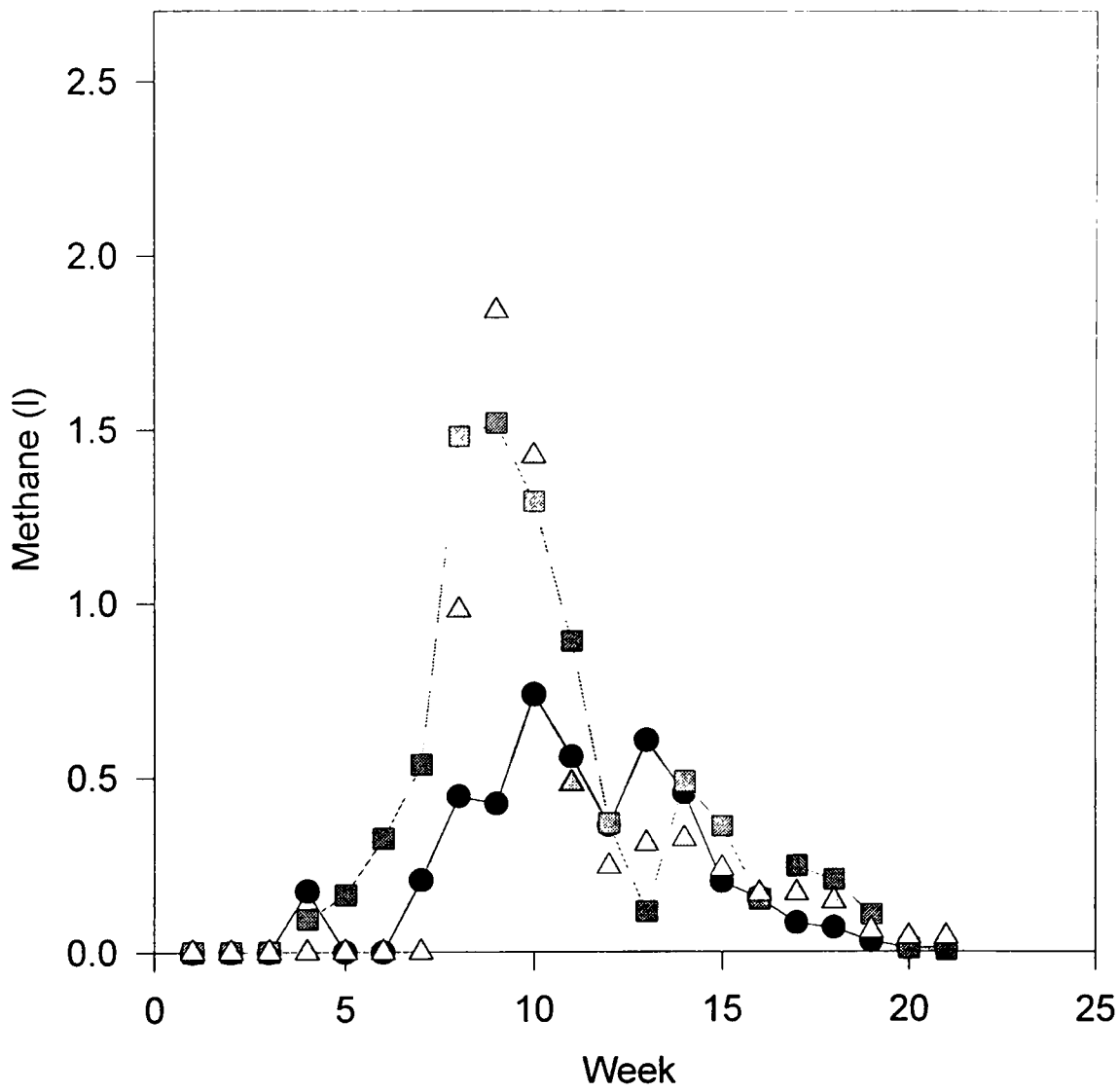


Figure 3.2 Weekly methane production: digesters 6 and 7 (potato processing effluent/cattle slurry)

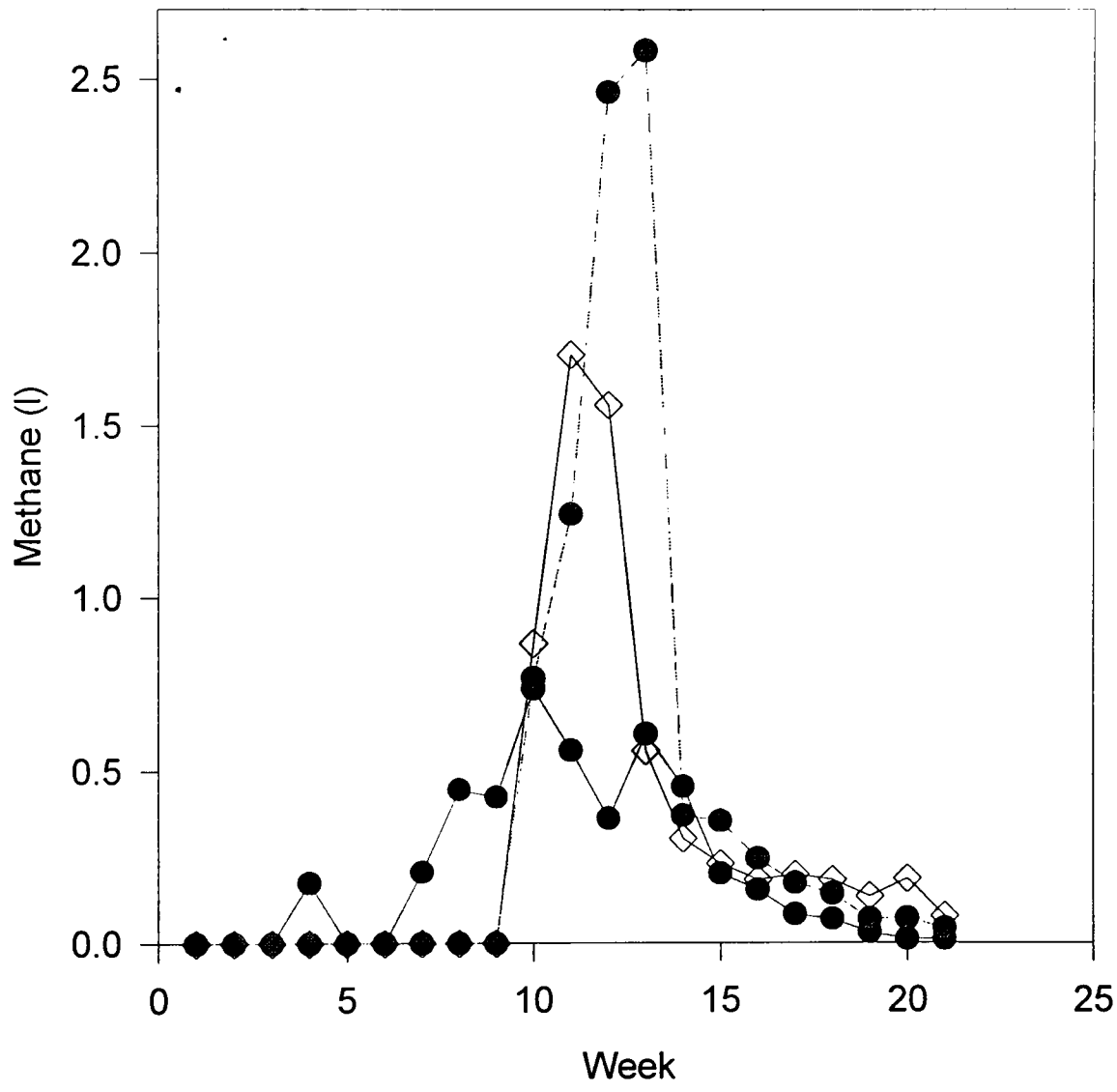


Figure 3.3 Weekly methane production: digesters 8 and 9 (chicken manure, 7.5% solids/cattle slurry)

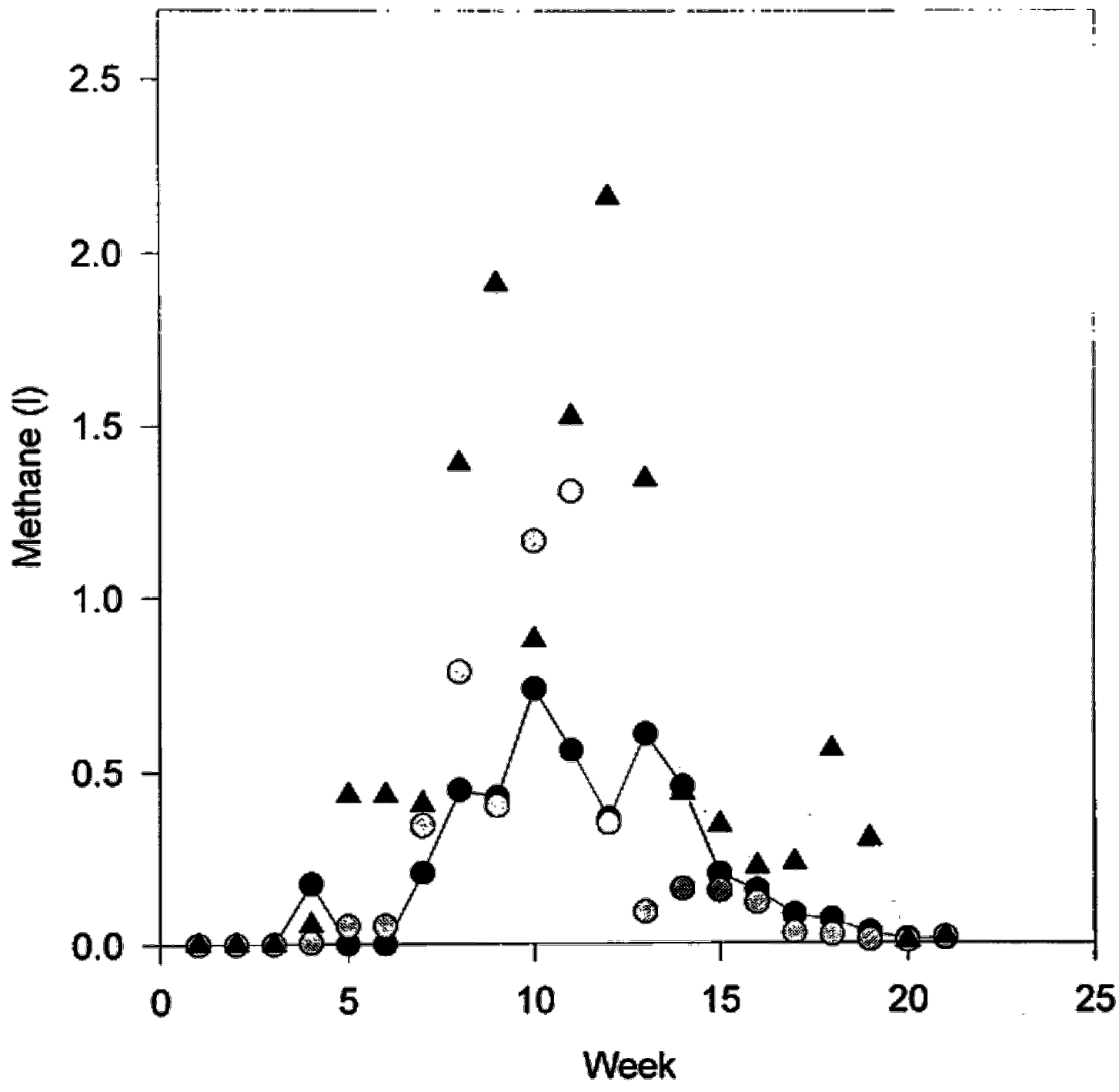


Figure 3.4 Weekly methane production: digester 10 (chicken manure, 15% solids/cattle slurry)

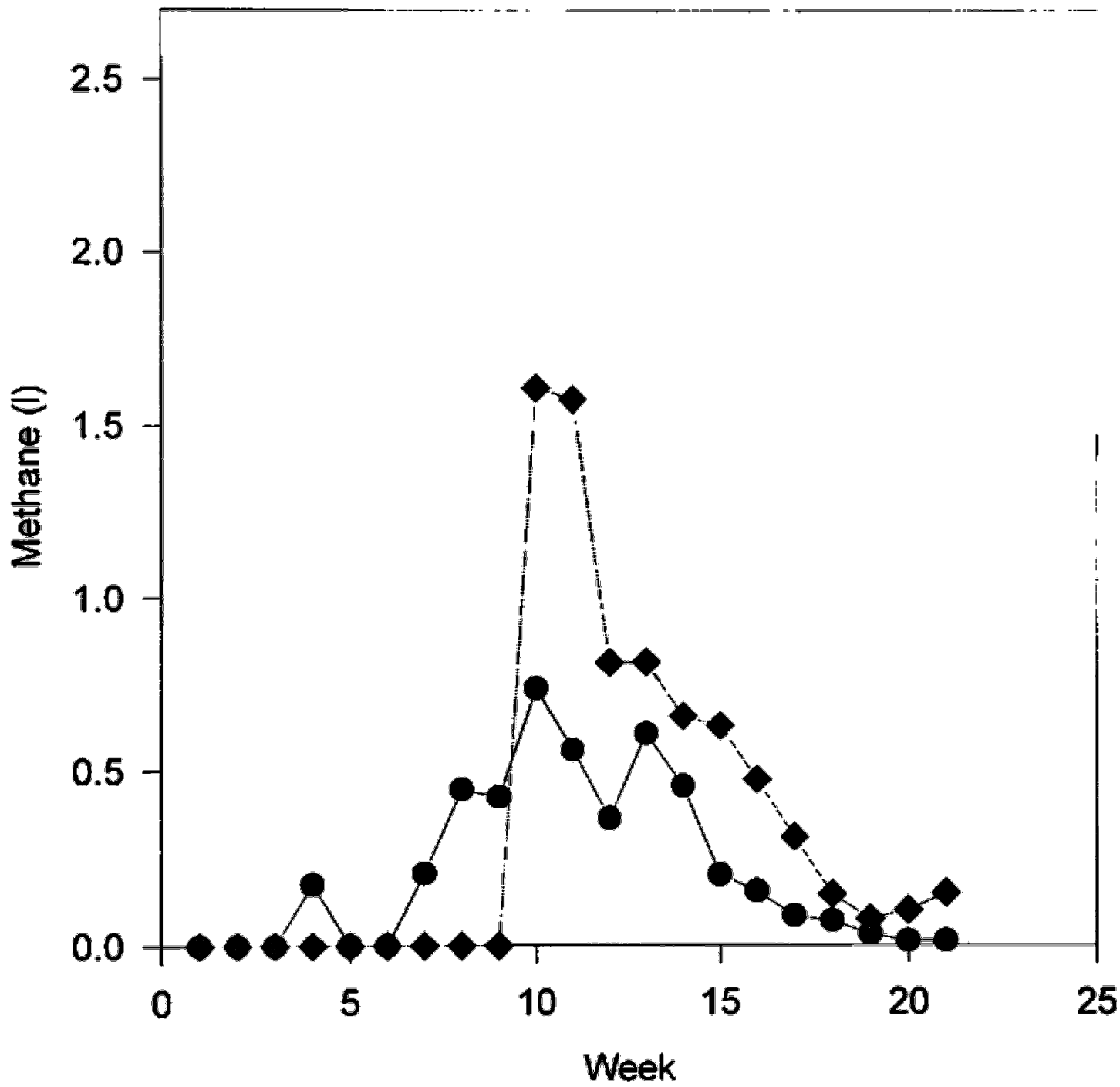


Figure 3.5 % solids reduction for each flask over 22 week digestion period

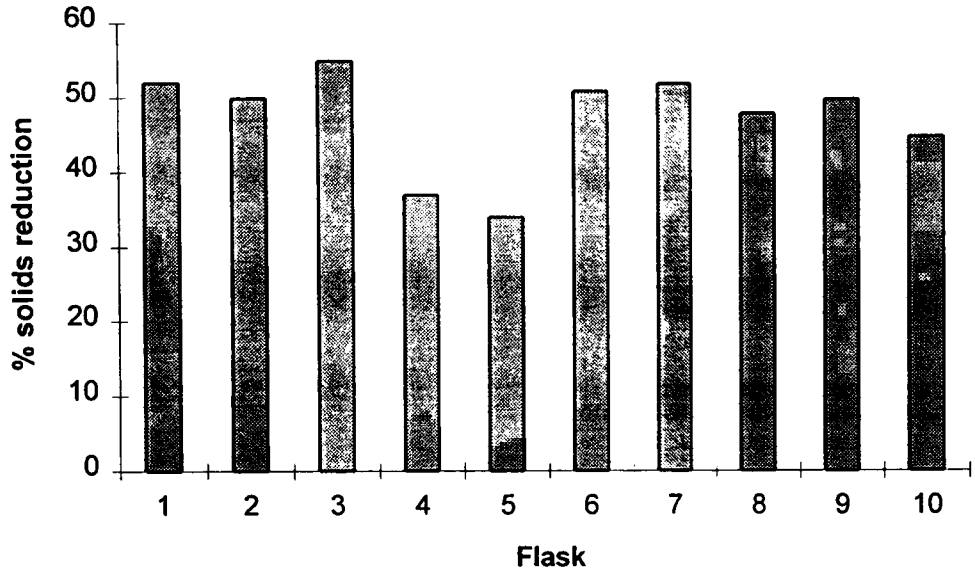


Figure 3.6 Maximum methane production rate for each flask

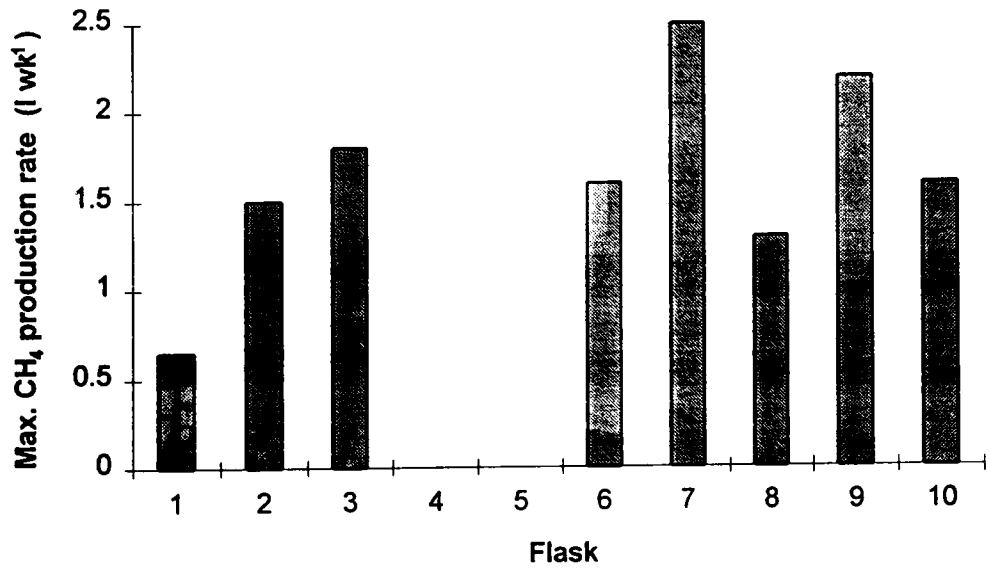
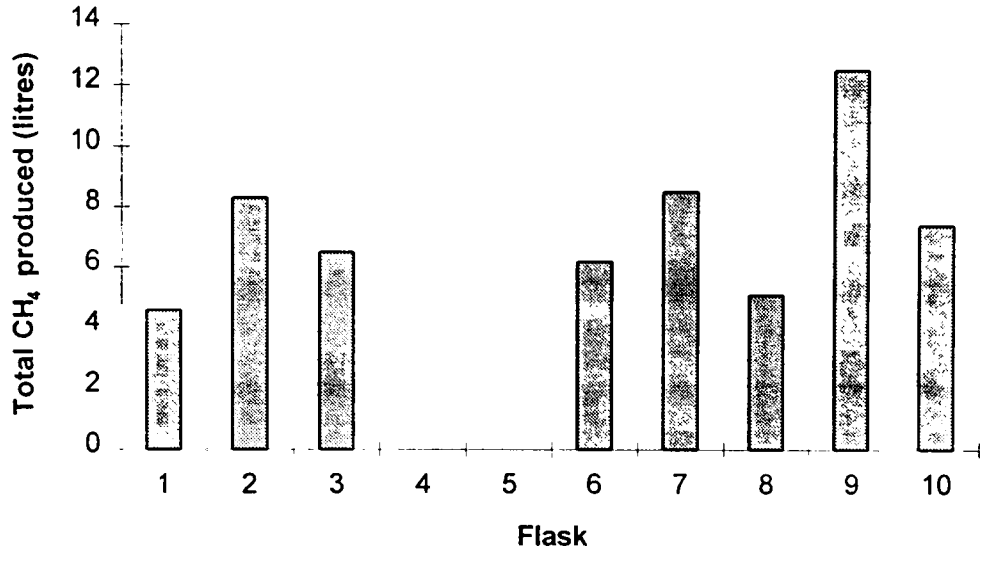


Figure 3.7 Total methane production from each flask over 22 week digestion period



3.5 Criteria used for assessing performance of the co-digestion mixtures

Figures 3.1 to 3.4 show weekly methane production from each flask over the 22 week period of the experiment. The maximum methane production rate, the total methane volume produced over the course of the experiment and the reduction in volatile solids levels were determined for each flask and are displayed in Figures 3.5 to 3.7.

As all the cattle slurry used in the experiment was from the same homogenised sample. It could be assumed that the methane production potential of the cattle slurry in each flask was roughly the same, and therefore any difference in methane production rates or total methane volumes between any flask and the control flask, was assumed to be due to the addition of the other waste. Using these criteria it was then possible to determine which wastes made the greatest contribution to enhancing methane production.

3.6.1 Sugar beet processing effluent

Both sugar beet effluent/cattle slurry mixtures produced significantly more methane than the control digester over the course of the experiment, see Figure 3.1. The % reduction in volatile solids was similar to the control, indicating that no inhibition of the digestion process had been caused by the addition of the waste, see Figure 3.5. The COD load (as sugar beet effluent) applied to the flasks 2 and 3 was only 1.1 kg COD m^{-3}, compared to 21.3 kg COD m^{-3} added to the control digester as cattle slurry.

The difference in maximum methane production rates (0.65 l wk^{-1} for the control versus 1.5 and 1.8 l wk^{-1} for flasks 2 and 3), was most likely due to much of the volatile solids in the sugar beet effluent being present as sucrose (Sexton, 1995, Fessenden and Fessenden, 1986). The volatile solids present in cattle slurry are mainly insoluble polysaccharides, proteins and lipids (Hawkes, 1981). These materials are much more chemically complex than sucrose, which is simply one unit of glucose joined to one unit of fructose (Conn *et al.*, 1987), and hence are only slowly converted to methane in an anaerobic system. Also, whereas it would be expected that all the sucrose available would be consumed by the anaerobic bacteria present, only a percentage of the complex polysaccharide present would be digested. Pfeffer (1978) found that wheat straw was only 38% digested after 14 days in a digester and would only be 50% digested at an infinite retention time.

This highlights how important it is to determine not only the COD or volatile solids concentration of a waste before adding it to a digester, but also the form in which the COD or volatile material is present.It can be concluded that the sugar beet processing

effluent enhanced the digestion process and could be considered as a co-digestate for the pilot plant trials.

3.6.2 Chocolate manufacturing effluent

It was expected that this effluent would be an ideal co-digestate due to the large concentrations of glucose it contained, about 18%, in this particular sample. The COD loading on the flask was quite high,at 48 kg COD m^{-3} more than double the loading on the control digester. As can be seen from Figure 3.7 no methane production was observed from digester 4 or 5 over the course of the experiment. The pH of the mixture in these digesters at the end of the experiment was found to be 4.5 as compared to a pH of about 8 for the control digester. It appears that the large concentration of glucose was readily converted to volatile fatty acids (VFA) by the acidogenic bacteria present, at a faster rate than the methanogens could convert the VFA produced to methane, hence the VFA concentration built up within the flask and the pH fell. Although the flasks were not analysed for VFA it was noted that the mixture had the sour odour indicative of a failed digester. The optimum pH range for methanogenic bacteria is between pH 6.8 and 7.6, and they cannot survive below pH 6 (Parkin and Owen, 1986) hence any methanogens in the mixture would have been quickly destroyed and prevented from re-growing. Microbiological analysis, using a UV microscope, confirmed that methanogens were absent from both flasks. It may be possible to introduce lower concentrations of this kind of effluent into a working digester without adversely affecting its performance, if careful monitoring of the total volatile fatty acid concentration in the system was carried out to ensure the digester pH did not drop a level which inhibited methanogenic growth. It is interesting to

note, from Figure 3.5, that although methanogenesis did not take place, measurements indicated that a significant proportion of volatile solids had been removed from flasks 5 and 6. This was partly due to carbon dioxide production, which was observed during the experiment, and partly due to an inherent flaw in the analysis method for measuring volatile solids levels of samples which have high VFA levels. Drying at 105 ^{o}C (see Section 2.2 for a full description of the method) to remove moisture from the sample, also has the effect of removing any volatile material present and hence the weight of this material is not included when the amount of non-volatile organic matter is determined. This has also been noted by Hayward and Pavlicik (1990), who have proposed an alteration to the standard method which takes this error into account.

3.6.3 Potato processing effluent

Both flasks containing this mixture (flasks 6 and 7) produced significantly more methane than the control, see Figure 3.2. The COD of the flasks containing potato waste was significantly higher than the control , between 126,000 and 128,000 mg l^{-1} , compared to 104,500 mg l^{-1} for the control, see Table 3.3. The methane production pattern in each system was very different from the control flask, see Figure 3.3. Neither flask produced any methane until week 9 of the experiment, 6 weeks after the control flask began producing methane. Methane production peaked sharply over weeks 10 to 12 in both systems and then dropped off quite sharply.

The COD loading, as potato processing effluent, was higher (2.93 kg COD m^{-3}) than that applied to the flasks containing sugar beet effluent (1.1 kg COD m^{-3}). However, total methane production, in the 6 - 8 litre range, was similar to the flasks containing

sugar beet effluent, see Figure 3.7, indicating that a lower proportion of the organic material present in potato effluent was available for conversion to methane.

As the control sample began producing methane 6 weeks earlier and as the same slurry sample was used in both control and the potato effluent samples, the delay in the onset of methane production was due to inhibition of the methanogenic bacteria present. This hypothesis is supported by the maximum methane production rates for flasks 6 and 7, at 1.6 and 2.5 l wk^{-1} respectively. The large difference between the methane production rates observed in flasks 6 and 7 was probably due to the slightly higher COD noted in flask 7. The potato effluent samples used contained a significant quantity of suspended material and large potato particles, it is likely that flask 7 received a more particulate sample than flask 6, accounting for the higher methane production rate and total volume of methane produced by this flask. Potato effluents contain significant quantities of protein (Koster, 1986). The most likely cause of inhibition was the ammonia (NH_3) produced during anaerobic digestion of the protein present, see Chapter 1, Section 1.3.3.4 for a full discussion of the effects of NH_3 on the anaerobic digestion process.

The anaerobic breakdown of proteins may be described by the following equation (Scharer and Moo-Young, 1979):

$$2\,C_5H_7NO_2 + 6\,H_2O \longrightarrow 5\,CH_4 + 5\,CO_2 + 2\,NH_3$$

Koster and Lettinga (1988) have demonstrated how methanogenic sludges can be adapted to high NH_3 concentrations. While the initial NH_3 concentrations in the flasks containing potato effluent were similar to that in the control system, NH_3 levels would have quickly built up as described by the above equation. The lag period observed before methane production began was due to the methanogens adapting to the high levels of NH_3

present. This adaptation may have been due to either a mutant form of methanogen or the selection of one strain of methanogen which could tolerate higher levels of NH_3.

An analysis of the methanogenic population of flask 6 and 7 using a UV microscope found that a coccus type methanogen, often occurring in clumps and identified as *Methanosarcina barkeri* (using photographs in Schoberth, 1981) was present. Some chains of between 5 and 7 bacterial units in length, of a smaller bacterium, identified as *Methanibrevibacter smithii* were also present. The cattle slurry control system was found to have large numbers of *Methanosarcina barkeri* and clumps of 2 units of *Methanibrevibacter smithii* (no chains of more than 2 units were observed) and similar numbers of rod shaped bacteria, which were identified as a strain of *Methanobacterium* and which are known to be acetoclastic. No *Methanobacterium* were noted in flasks 6 and 7. Poggi-Varaldo *et al.* (1991) have shown that the growth rate of acetoclastic methanogens was halved by NH_3 levels above 100 mg l^{-1} but that levels below this value had little effect on the growth rate and McInerney and Bryant (1981) have noted that acetoclastic methanogens are exclusively rod shaped. The NH_3 levels present at the end of the experiment were in the range 150 to 200 mg l^{-1} in flasks 6 and 7 and just over 100 mg l^{-1} in the cattle slurry control.

It can be concluded that the rising NH_3 levels in flasks 6 and 7 inhibited the growth of the *Methanobacterium*, and that M*ethanosarcina barkeri* and M*ethanibrevibacter smithii*, after a lag period, became the dominant methanogenic species. The *Methanibrevibacter smithii* bacteria were also seen to form chains of bacterial units in the potato effluent flasks, whereas none of these chains were seen in the cattle slurry control. It is possible that the bacteria formed chains to establish a micro-environment in which they could continue to flourish in a material with high NH_3 levels.

Wiegant and Zeeman (1986) put forward the theory that M*ethanosarcina* strains should be more resistant to high NH_3 levels than smaller rod shaped cells. They suggested that the inhibiting effect of NH_3 is exerted after it diffuses across the bacterial cell wall. Therefore the larger the cell and the greater its surface to volume ratio, the smaller the diffusion of NH_3 into the cell, measured as kg NH_3 per kg cell mass per hour.

The total methane production and methane production rates observed suggest that potato processing effluent could also be a suitable substrate for co-digestion trials on the 18 litre pilot plants, but that some acclimatisation of the methanogenic bacteria to the NH_3 levels present would be necessary

3.6.4 Chicken manure (7.5% solids)

The flasks containing theses mixtures produced an interesting gas production profile, see Figure 3.3. Although flask 9 produced over twice as much methane as flask 8 (see

Figure 3.7) both had the same unique methane production profile. Essentially flask 8 produced a peak in gas production in week 7 of the experiment, and flask 9 produced a peak one week later, both peaks then dropped substantially during the week after the gas peak and then rose again in the following week to an even higher level before dropping away sharply with another slight peak recorded for flask 8 in week 14 and for flask 9 in week 18.

One possible explanation for the growth pattern suggests 2 groups of methanogenic bacteria with the second group growing rapidly about a week after the growth rate of the first group had peaked. Microbiological analysis of the mixtures at the end of the experiment revealed rod shaped *Methanobacterium*, *Methanosarcina barkeri* and *Methanibrevibacter smithii*. Again, as in the potato effluent samples, the *Methanibrevibacter smithii* bacteria were present in chains of around 5 bacterial units. However, unlike the potato effluent samples, the rod shaped *Methanobacterium* was present in these samples, even though the final NH_3 concentration was around 260 mg l^{-1} in both flasks. It is not known why *Methanobacterium* was present at NH_3 levels which, according to literature, should have severely inhibited its growth. The chief source of NH_3 in the chicken manure/cattle slurry systems would be uric acid, the form in which nitrogen is excreted by birds (Hawkes, 1981). Uric acid is converted by bacterial action to NH_3 in anaerobic systems. As has been mentioned earlier, the chief source of NH_3 in the potato effluent/cattle slurry systems would have been protein breakdown. If the rate of uric acid breakdown was slower than the rate of protein degradation, the rate at which NH_3 concentrations built up in the chicken manure systems would be slower, and it is possible that the *Methanobacterium* could

have acclimatised to a gradual increase in NH_3 levels, although there is nothing in the literature to support this. As uric acid is insoluble, and would have first of all to be solubilised by bacterial action before conversion to NH_3 and the protein in the potato effluent was already dissolved in the effluent, this may be a valid explanation.

Maximum methane production rates for flasks 8 and 9 (1.3 and 2.2 l wk^{-1} respectively) were both significantly greater than the control value (0.65 l wk^{-1}), and total methane production in flasks 8 and 9 (5.1 l and 12.5 l) was above the control value also. The low value in flask 8 may have been due to an un-detected leak in the biogas collection system.

The methane production data suggest that digestion of the mixture of 7.5% chicken manure and cattle slurry would be worth investigating on the 18 litre pilot plant. However, as has been discussed in Section 3.1.2, the cost and volumes of water necessary to reduce the quantities of raw chicken manure produced by a modern egg production unit, from 30% total solids to 7.5% total solids, and the volumes of waste generated by this procedure, would make it unlikely that a full scale commercial digester could be operated on a feedstock containing chicken manure at 7.5% total solids. Hence operating the laboratory pilot plant on this mixture would be of little practical value in providing a disposal route for chicken manure.

3.6.5 Chicken manure (15% solids)

The methane production profile for flask 10 was quite similar to that of flasks 6 and 7, no methane production was observed until week 9 of the experiment, then a sudden

peak in methane production occurred, followed by a sharp drop. Again this pattern suggests inhibition of the methanogenic bacteria or selection of a strain more tolerant of high NH_3 levels. Microbiological analysis of the flask at the end of the experiment revealed that only *Methanosarcina barkeri* were present. The reasons for the observed tolerance of this bacterial strain to high NH_3 levels are discussed in Section 3.6.3. The final NH_3 concentration in the mixture was over 1000 mg l^{-1}. In experiments on the digestion of chicken manure, Webb and Hawkes (1985) demonstrated that inhibition of methanogenesis occurred in the range of 138 - 225 mg l^{-1} NH_3, but that after a period of adaptation it was possible to operate a digester at NH_3 concentrations of 370 mg l^{-1} with little sign of inhibition. Pechan *et al.*(1987) operated a laboratory digester, which had been acclimatised to elevated levels of NH_3, at 667 mg l^{-1} NH_3 with no apparent signs of inhibition. The final NH_3 value of 1000 mg l^{-1} which was measured in flask 10 at the end of the experiment had obviously inhibited methane production to a degree, as methane production dropped quite sharply after the initial peak, but there were still viable methanogens present, indicating that they had adapted to this high level of NH_3.

The total volume of methane produced by flask 10 (7.4 l) was significantly greater than that produced by the control flask (4.6 l), and the maximum methane production rate of 1.6 l wk^{-1} was over twice that of the control flask, see Figures 3.6 and 3.7. It can be concluded that, despite the high concentrations of NH_3 generated, 15% total solids chicken manure can be successfully co-digested with cattle slurry. As has been mentioned in Section 3.3, in order to add chicken manure to a digester using a pump, auger or other conventional slurry transfer device, it would have to be diluted to at

least 15% total solids. Therefore, if it can be demonstrated that 15% solids chicken manure can be co-digested with cattle slurry in the 18 litre laboratory pilot plant, a new disposal route for chicken manure may become available.

3.6.6 Selection of waste most suitable for investigation using 18 litre pilot plant

Although sugar beet processing effluent and potato processing effluent are wastes which can be difficult to treat, there are UASB (Upflow Anaerobic Sludge Blanket) and anaerobic expanded bed reactor systems available which can remove most of the organic material from these effluents (Rockey, 1985). The best disposal method for chocolate manufacturing wash water seems to be disposal to sewer.

However, as has been mentioned in Section 3.3, apart from land spreading, there is currently no proven treatment method available for reducing the polluting potential of chicken manure. Also, it has been noted that the costs associated with diluting chicken manure to 7.5% total solids, and the volumes of wastes generated, would be likely to make a process operating on this feedstock un-economical. Therefore, it is proposed to study the co-digestion of 15% total solids chicken manure and cattle slurry on the 18 litre anaerobic digestion pilot plants.

3.7 Preliminary Conclusions

The first batch digestion trial showed that additions of sugar beet processing effluent, potato processing effluent and various dilutions of chicken manure enhanced the methane production rate, and the total volume of methane produced, in batch cattle slurry digesters. Addition of high loadings of chocolate manufacturing effluent

caused digester failure. 15% solids chicken manure was selected as the most suitable waste for co-digestion trials on the 18 litre pilot plant laboratory digesters, due to its ability to enhance methane production rates and also the requirement of the UK poultry industry to find alternative disposal routes for this material.

Chapter 4

Anaerobic digestion pilot plant trial 1: co-digestion of cattle slurry and chicken manure

4.1 Pilot plant operating history

The 2 anaerobic digester pilot plants were commissioned in November 1995, and filled with digesting cattle slurry, taken from a local farm digester, in early December 1995. Digestion of cattle slurry on a continuous basis was commenced at the beginning of February 1996. The digesters were operated on a 28 day retention time, and, after a number of blockage problems and heating unit failures steady state operation was achieved. As co-digestion trials were about to commence, the mixer units failed, due to a failure in the shaft bearings. These bearings were understood to be sealed units, but obviously this was not the case (see Section 2.10.2.6).

It was decided that it was of little use to include the results of the first 3 months of operation on cattle slurry (while the mixers were still in operation) in this chapter as the system operating conditions would be different for the co-digestion work as the system would be mixed by hand instead of by a motor. Therefore, the digesters were operated for another 28 day retention time on cattle slurry, which is labelled as retention time 1 in the results section, see Table 4.1, with mixing conducted by hand 3 times per day for 1 minute each time,. At the end of this retention time, co-digestion trials with various ratios of cattle slurry and chicken manure commenced and ran for a period of 6 months.

The digesters were shut down at the start of November 1996. Examination of the plant after decommissioning revealed that both slurry removal ball valves, at the base of the digesters, were leaking due to abrasion of the valve seat, caused by grit in the chicken manure. The abrasive nature of chicken manure should be taken into account when designing full scale anaerobic treatment systems for this material.

4.2 Digester operating regime

Both digesters were initially operated on 8% total solids (TS) cattle slurry at an estimated loading rate of 2.92 kg volatile solids (VS) $m^{-3}d^{-1}$. The digesters had a working volume of 18 litres and received 0.9 l of feed once a day, five days per week, giving a retention time of 28 days. The digesters were maintained at 35 ^{o}C ($\pm$ 0.5 ^{o}C) and mixed by hand 3 times per day for 1 minute each time.

Most commercial cattle slurry digesters are operated on a 21 day retention time (Cheshire, 1997). However it has been shown that chicken manure digesters produce a more stable digestate if operated at longer retention times (Aubart and Fauchille, 1983). 28 days was chosen as a compromise between the need to extend the retention time and the need to complete the experimental work within the required time period.

Chicken manure, at 15% TS was used as the co-digestate. A ratio of 70% wet weight cattle slurry to 30% wet weight slurried chicken manure gave a total feed solids content for the first stage of the co-digestion trials, of around 10%. It has been demonstrated that it is difficult to mix

systems above 10% TS, hence the need to attempt to maintain the feed total solids level below this value (Bujawlski, 1986).

The initial ratio of 70/30 also ensured an increase in the estimated volatile solids loading to the digester of about 24% to 3.64 kg VS $m^{-3}d^{-1}$. Feed ammonium (NH_4^+) also increased from around 800 mg l^{-1} to around 3000 mg l^{-1}. After 2 retention times running on a 70/30 mixture, intermittent shock loadings of neat chicken manure, diluted to 15% total solids, were applied to both digesters over a 2 week period to assess the effect that this would have on methane production. Digester 1 was fed neat chicken manure every second day for 2 weeks, with the 70/30 mixture being fed on the other days. Digester 2 was fed on the neat chicken manure for 3 days and then the 70/30 mixture for 2 days, again for 2 weeks.

At the end of this period the feeding was suspended to allow the high levels of (volatile fatty acid) VFA produced during the shock-loadings, see Figures 4.21 and 4.22, to be removed by the methanogens. After 3 weeks, feeding of the 70/30 mixture was resumed for a further retention time. Due to drying and decomposition of the chicken manure in the battery sheds, the estimated volumetric loading rate was lower than the previous runs on 70/30 mixtures, about 3.5 kg VS $m^{-3}d^{-1}$.

At the end of this retention time, the digesters were not fed for a week, as methane production was low, and it was decided that a week of no feeding may allow the system to stabilise. Feeding was then re-commenced with 50/50 mixture being fed to digester 1 and a 25/75 mixture to digester 2. This increased the estimated volumetric loading rate for digester 1 to around 3.8 kg

VS $m^{-3}d^{-1}$, and that to digester 2 to just under 4 kg VS $m^{-3}d^{-1}$. The digesters were operated for one retention time at these loadings.

For the 6th and final retention time, the feed to digester 1 was changed to neat cattle slurry at 8% total solids, giving an estimated volumetric loading rate of 2.92 kg VS $m^{-3}d^{-1}$. The feed to digester 2 was altered to a 10/90 mixture, giving an estimated volumetric loading rate of just over 4 kg VS $m^{-3}d^{-1}$.

4.3 Variation in feedstock quality

One of the main problems associated with running laboratory scale anaerobic digesters on animal wastes over an extended period of time is the need for a constant supply of fresh feedstock of reasonably uniform consistency. Some authors have tried to overcome this problem by drying wastes and grinding the dried material into a powder which can be stored without the need for refrigeration facilities and reconstituted when required. Others have extensively filtered and sieved slurries to produce a consistent, low solids, material. However, the more pre-treatment stages a slurry or manure is put through, the less likely it is that the operational performance of the laboratory digester can be correlated with the performance of a full scale digestion system on a farm site , where extensive pre-treatment of slurries is neither practical or technologically possible. Also, over-rigorous standardisation of manures and slurries can mean that seasonal variations in the quality of the waste can be overlooked, which again can lead to the results of a laboratory digester bearing little resemblance to those obtained from a full scale system.

Hence, throughout this project, slurry and manure pre-treatment has been kept to a minimum. Of course it was necessary to have some control over the consistency of the waste, hence the need to

remove long straw and to macerate the cattle slurry to break up the lumps of solids material which were present.

The chicken manure was found to be quite non-homogenous in nature, literally due to 'wet lumps' and 'dry lumps' of material being present in samples. This is graphically illustrated by the values recorded in Table 4.1.

6 samples of chicken manure were randomly taken from a 5 kg sample and analysed for total, fixed and volatile solids. Samples 1, 2 and 4 were quite similar to each other but 3, 5 and 6 are quite different. Sample 6 had a TS value of almost twice that of samples 1, 2 and 4. Therefore, while the mean TS content of the 5 kg sample was found to be around 30%, parts of the sample had values of up to 43.7%.

Table 4.1 Variation in total, fixed and volatile solids of 6 individual 30g samples of chicken manure taken from the same 5 kg sample.

Sample	% TS	% VS	% FS
1	24.64	14.69	9.96
2	25.26	14.95	10.31
3	30.23	17.45	12.78
4	24.02	14.05	9.97
5	32.68	19.56	13.12
6	43.72	22.66	21.07

Due to this variation in TS, VS and FS levels within one 5 kg sample, attempts were made to homogenise the chicken manure using a commercial blender. However the manure tended to

form a paste inside the blender, in which lumps of material remained, no amount of further blending was successful in homogenising the mixture once this non-homogenous paste had formed. Therefore it was expected that the quality of the chicken manure added to the digester would vary quite considerably and that it would therefore be difficult to control the volatile solids loading on the digesters, without resorting to excessive homogenisation measures such as drying and crushing the chicken manure. It was decided to measure the TS, VS and FS of a sample of each days digester feedstock, to ascertain the exact amount of VS added to the digester each day.

The manure was diluted to 15% TS before digestion (see Section 3.1.2 for reasons for diluting the chicken manure to 15% TS). In order to demonstrate that an anaerobic digester operating on cattle slurry and chicken manure could be successfully operated over a period of time it was considered necessary to take fresh material from the sites where the wastes were being produced, on a regular basis, over the course of the year, in order to assess the effects of any changes in the slurry and manure composition on digester performance. The work described in this report ran from April to November.

Figures 4.1 and 4.2 and 4.3 (**note**: see pages 115 - 133 for Figures 4.1 - 4.35) show the variation in total solids, volatile solids and the volatile solids to total solids ratio (VS/TS ratio) of the chicken manure and cattle slurry used during the course of the project. Cattle slurry TS and VS remained reasonably constant, apart from a peak in VS in the middle of July, (week 13), whereas the mean total solids content of the chicken manure increased by over 60% between week 5 and week 20 (May to September). The volatile solids content remained constant at about 20% over the course of the project, but the necessity of keeping the total solids content at the 15% level had the effect of reducing the volatile solids

concentration of the diluted manure over time, see Figure 4.4. This large increase in dry matter was most likely caused by the drying effect of the forced air ventilation systems used in the battery sheds. It was also noted that, as the summer progressed, the manure heaps in the sheds began to compost. Heap temperatures of up to 60 ^{o}C and strong ammonia emissions were observed.

The ammonium (NH_4^+) content of the chicken manure, collected over weeks 5 - 13 (average TS of 29 %) of the experiment, averaged 12, 000 mg kg^{-1} whereas the manure collected over weeks 20 -28 (average TS 43 %) had an average ammonium concentration of 7000 mg kg^{-1}. These values are similar to those reported by Webb and Hawkes for poultry manure (Webb and Hawkes, 1985) which were in the range 4,900 to 21,300 mg NH_4^+ kg^{-1}. In contrast to the low ammonium values noted in the samples with the highest solids content, the highest ammonium values reported by these authors were in the driest samples (47.3% TS). The VS/TS values recorded by these authors were in the range 0.6 - 0.71. The apparent composting of the waste, which was observed , and the intensive drying provided by the forced air ventilation system in the battery sheds may explain these differences. Also the battery sheds from which these authors obtained the manure were cleaned weekly, whereas the sheds from which manure was obtained in the current work were cleared only twice a year. Hence some of the manure could have been up to 6 months old.

4.4 Estimated and actual digester loading rates

Table 4.2 summarises the feedstock composition and the estimated and mean actual volatile solids loading rate for each retention time. Figures 4.5 and 4.6 show the estimated and mean

actual volatile solids loading rates for each week of operation. The estimated values were determined by sampling the raw manure after collection. Attempts to obtain as representative a sample as possible from the 10 kg raw manure sample, for this analysis, were made by taking portions of manure from throughout the sample and mixing them together in a container, but this mixing was carried out by hand as a blender could not accomplish the task, hence it was difficult to obtain a uniform sample.

Table 4.2 Mean estimated and actual loading rates for digesters 1 and 2.

Retention time	Week	Feedstock/ Event	Digester 1: estimated kg VS m^3 d^{-1}	Digester 1: mean actual kg VS m^3 d^{-1}	Digester 2: estimated kg VS m^3 d^{-1}	Digester 2: mean actual kg VS m^3 d^{-1}
1	1 - 4	100% cattle slurry	2.92	3.04	2.92	3.08
2	5 - 8	70% cattle / 30% chicken manure	3.64	3.86	3.64	3.85
3	9 - 12	70 / 30	3.64	3.81	3.64	3.78
	13 - 14	Shock loadings	4.6	4.2	4.6	4.1
	15 - 17	Cease feeding	-	-	-	-
4	18 - 21	70 / 30	3.5	3.68	3.5	3.78
	22	Cease feeding	-	-	-	-
5	23 - 26	Dig 1: 50 / 50 Dig 2: 25 / 75	3.8	3.97	3.95	4.44
6	27 - 30	Dig. 1: 100% cattle Dig. 2: 10 / 90	2.92	2.93	4.1	4.75

As the amounts of material to be added to the digestion system and the working volume of the digester were known, the volatile solids loading rate could be estimated. The mean values for each retention time tend to smooth out some of the variation which were more obvious in the mean weekly figures. For the first 2 weeks in digesters 1 and 2, the actual loading rate (2.85 - 2.92 kg VS m^{-3} d^{-1}) was similar to the estimated rate of 2.92 kg VS m^{-3} d^{-1}. However there was an increase to 3.1 - 3.25 kg VS m^{-3} d^{-1} in both systems for the next 2 weeks , due to the non - uniformity of the cattle slurry mixture.

The increase over the estimated value, for the cattle slurry/chicken manure mixtures, shows a similar pattern over the next 2 retention times, with values up to 10% greater than the estimated value being measured. The feedstock added during weeks 13 and 14, when shock loadings were applied to the systems, was estimated to have the same volatile solids concentration for each week, and while the actual values for digester 2 were almost the same, those for digester 1 differed by 20%. During the next retention time the variation was similar , and the general trend was that the variation was greater as the % of chicken manure in the feedstock increased. The difficulty in controlling feedstock volatile solids levels could be a problem in designing full scale digestion systems. Regular cleaning of battery sheds should overcome this problem as the manure would not have sufficient time to dry by any significant degree.

4.5 Effluent and feedstock total, fixed and volatile solids

Figures 4.7 to 4.12 show mean total, fixed and volatile solids levels in the feedstock and effluent for digesters 1 and 2 over the 30 week period described Table 4.1. TS levels increased only

slightly in the effluent from both digesters over the first 3 retention times, indicating that mixing by hand 3 times per day for one minute was sufficient to keep the systems relatively well mixed, when the feed TS remained around 10%. Some solids breakthrough did occur during the last week of the shock loading period (weeks 13 and 14) on digester 2, when the feed TS was around 15% for 3 of the 5 feed times. However, after the 3 week period during which feeding was suspended, TS levels in the effluent from both systems began to rise, and closely followed the rise in feed TS. There was clear evidence that solids build up was occurring in digester 1 as the effluent total solids level was actually greater than the influent total solids level during the first 2 weeks of the final retention time (when the feedstock was changed to 8% total solids cattle slurry). The solids appeared to be washed out by the lower solids material being added to the digester, indicating the problems associated with digestion of high solids manures. The TS level in the effluent from digester 2, while also showing a tendency to follow closely the rise in feed TS during the 4th and 5th retention times, fell away sharply during the final retention time, which was surprising considering that the feed solids value during this 4 week period was around 14% TS. Figures 4.13 and 4.14 show mean volatile solids removal. In digester 2, volatile solids removal efficiency increased with increasing volatile solids loading rate, up to the end of the 3rd retention time, when the applied shock loading caused an increase in effluent volatile solids. The same general trend was also observed in digester 1, apart from a drop in removal efficiency during weeks 9, 10 and 11. After the 3 week break from feeding, the volatile solids removal in digester 1 returned to the levels of the 4th retention time, and to lower levels in digester 2. Volatile solids removal dropped off to very low levels in digester 1 towards the end of the project, indicating that very little mixing was occurring, possibly due to crust formation on the surface of the liquid in the reactor. It is possible that the crust formation, which may have occurred during the break from feeding, significantly increased the dead volume of both

systems, and hence meant a shorter retention time for the solids. On dismantling at the end of the project, digester 1 was found to have substantial crusting, and clogging of the heating coil, although little crusting had occurred in digester 2, for reasons which are not clear.

4.6 Digester monitoring and performance over weeks 1 - 17

Figures 4.15 and 4.16 show the variation in methane production per kg VS added with volatile solids loading rate, for both digesters. The trend for the former to increase as the latter increased, has been previously noted by Hawkes and Horton (1983) for the digestion of sewage sludge. This trend was apparent in both systems until week 8. Then there was a fall in methane production per kg VS added in week 9 in both systems, and while there was a slight rise in the parameter in both systems during week 10, and in week 11 in digester 2, the parameter did not follow volatile solids loading trend for weeks 12, 13 and 14. The change in feed composition from 100% cattle slurry to the 70/30 cattle slurry/chicken manure (in week 5) did not initially seem to have affected the operation of the digestion system negatively. Figures 4.17 and 4.18 show effluent pH for both systems. The pH values during the first retention time were around 7.7. Although this was slightly above the recommended pH range for sewage sludge anaerobic digesters (Standard Methods, 1992) 6.8 - 7.6, it was within the range reported by other authors for the anaerobic digestion of cattle slurry (Angelidaki *et al.*, 1993) that is between 7.6 and 8.1. The change of feed to the digesters caused a gradual rise in effluent pH in both systems to 7.96 by week 10 in digester 1 and 7.92 in digester 2 by week 8.

Digester effluent alkalinity rose steadily from an initial mean value of around 13,000 mg l^{-1} $CaCO_3$ in both systems, to around 20,000 mg l^{-1} by week 12 (Figures 4.19 and 4.20). The high alkalinity values associated with chicken manure have been noted by Webb and Hawkes (1985),

who noted levels of around 21,000 mg l^{-1} $CaCO_3$ in the effluent from laboratory digester operating on 10% total solids chicken manure. It is interesting to note that the drop in alkalinity noted for digester 1 in week 13, was not accompanied by a drop in pH, while the rise in alkalinity noted in digester 2 over weeks 13 and 14 was accompanied by a drop in pH. This suggests difficulties with pH measurement in high solids materials, as one would expect alkalinity and pH to reflect each other quite closely. The high alkalinity values noted for digester 2 over weeks 13 and 14 were more than likely due to the sharp increase in the feed total solids concentration associated with the application of the shock loads.

4.7 The predicted and observed effects of an organic shock load on an anaerobic digester

The application of a shock-loading of volatile solids to a digestion system generally has the effect of initially decreasing the alkalinity and pH and decreasing biogas methane concentration (Callaghan *et al.*, 1997). However the degree to which these parameters are affected is determined by the rate at which the acidogenic bacteria in the system can convert those volatile solids to volatile fatty acids. A shock loading of glucose to an anaerobic digestion system can produce digester failure because of the speed at which glucose can be converted to acetate (Callaghan *et al.*, 1996). The conversion of high solids chicken manure to volatile acids is a slow process. Authors who have attempted digestion of chicken manures of 10 - 12% TS levels have found retention times of up to 46 days were required to convert a significant amount of the volatile solids to methane (Aubart and Fauchille, 1983), hence a build up of volatile fatty acids would not be expected to occur as quickly in a digester operating on chicken manure as would be expected in a digester operating on a more readily degradable material. Mean weekly effluent VFA concentrations, Figures 4.21 and 4.22, support this theory. It is clear that although total VFA levels in both digesters rose in the first week of shock loading (week 13), a second week of

feeding the same material (week 14) produced a much larger increase in VFA, from a mean effluent VFA concentration of 6,000 mg l^{-1} for digesters 1 and 2 in week 13, to 12,000 mg l^{-1} VFA for digester 1 and 14,000 mg l^{-1} for digester 2 in week 14.

Switzenbaum *et al.*, (1990) have concluded, from the work of a number of authors, that the VFA:Total Alkalinity ratio is a useful tool for monitoring digester stability. It is generally accepted that a VFA:TAlk ratio of between 0.1 and 0.35 indicates a stable digestion system. Much of the work on VFA:TAlk ratios has been carried out on sewage sludge digesters (Metcalf and Eddy, 1994) but, as can be seen from Figures 21a and 22a, the VFA:TAlk ratio during weeks 1-4 was between 0.15 and 0.2 for both digesters, indicating that stable cattle slurry digesters also have VFA:TAlk ratios in the 0.1 - 0.35 range. The introduction of chicken manure to both systems initially had the effect of depressing the ratio, due to the increased alkalinity of the feedstock containing chicken manure, and the drop in VFA caused by the partial change in feedstock. Once significant degradation of chicken manure began, the VFA:TAlk ratio rose sharply (in week 6) to 0.3 in digester 1 and 0.33 in digester 2. Over weeks 7 - 10 the ratio gradually decreased in both digesters, and remained around 0.1 - 0.13 during weeks 10 - 12. The drop in methane productivity recorded in both systems in week 9 was not accompanied by a rise in VFA:TAlk ratio, as the inhibition which seemed to be occurring did not cause an increase in VFA concentrations. The shock loadings with chicken manure during weeks 13 and 14 caused a rapid increase in VFA:TAlk ratio, caused by the build up of VFA in both digesters. The sharp rise in VFA:TAlk ratio in digester 2, to 0.27 in week 13 and 0.48 in week 14 was mirrored by the sharp drop in methane productivity during weeks 13 and 14. In this case inhibition of methanogenesis by VFA build up seemed to be the reason for the drop in productivity. VFA build up and a corresponding rise in VFA:TAlk ratio also occurred in digester 1 during weeks 13

and 14, however mean methane productivity rose slightly during week 13 (from 0.086 m^3 CH_4 kg VS^{-1} added in week 12 to 0.092 m^3 CH_4 kg VS^{-1} added in week 13 and 0.11 m^3 CH_4 kg VS^{-1} added in week 14). It is not clear why the methane productivity of the system began to rise in digester 1 during weeks 13 and 14, but certainly the rising VFA:TAlk ratio did not correspond to a fall in methane productivity. Perhaps the ratio is less useful as a tool for controlling a digester in high alkalinity/high VFA systems.

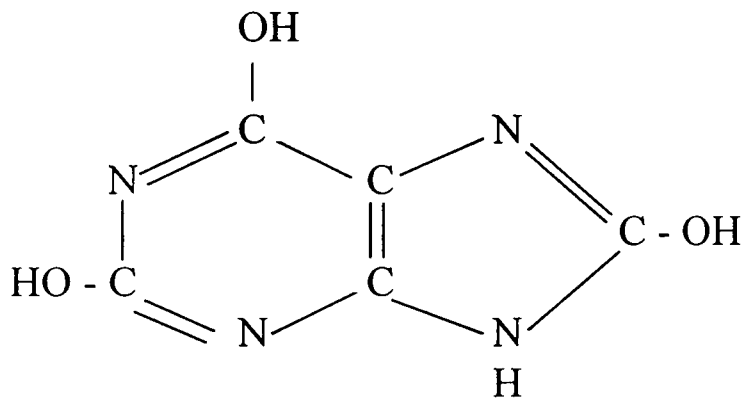
4.8 Evidence of incomplete degradation of chicken manure

Mean daily methane production did not fall rapidly when feeding ceased at the end of week 14, suggesting that significant amounts of volatile fatty acids were available to the methanogens during that week (Figures 4.23 and 4.24). Figures 4.21 and 4.22 confirm that large amounts of VFA were present in the digesters in week 14. Also it can be seen from Figures 4.25 and 4.26 that biogas methane concentration rose slightly in both digesters in the week immediately after cessation of feeding, then rapidly in the following week to values in excess of 70%. This indicates that significant acidogenesis and hence carbon dioxide production (indicating on-going breakdown of chicken manure) continued for a full week after feeding ceased, suggesting that a retention time of longer than 28 days would be necessary to maximise methane production per kg VS added, if neat shock loads of chicken manure were to be added to the system at regular intervals.

4.9 Inhibition of methanogenesis by NH_3 and NH_4^+

A full discussion of the inhibition of methanogenesis by NH_3 and NH_4^+ is given in Section 1.3.3.4. Figures 4.27, 4.28, 4.29 and 4.30 show NH_4^+ and NH_3 levels in the effluent from digesters 1 and 2. There was a steady rise in both parameters after the addition of chicken

manure commenced. Maximum NH_4^+ concentrations of 7,783 mg l^{-1} in digester 1 and 7,847 mg l^{-1} in digester 2 occurred during week 12. Feed NH_4^+ levels were in the range 2,400-3000 mg l^{-1} during the first 2 retention times. By the end of the first retention time one would expect NH_4^+ levels in the digester to be around these values, assuming adequate mixing. Levels in both systems were actually around 3,900 mg l^{-1} NH_4^+. The extra NH_4^+ most likely came from the breakdown of uric acid, the major nitrogenous waste excreted by birds and protein, elevated levels of which are found in poultry manure due to the high protein diet fed to the birds (ETSU, 1994). Uric acid has the following chemical structure:



Uric acid is de-aminated in anaerobic systems by bacterial action to yield NH_3 (Hawkes, 1981). NH_4^+ and NH_3 concentrations are related as follows:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

Hence, much of the extra NH_4^+ measured can be accounted for in this way. Protein degradation under anaerobic conditions also yields NH_3.

4.10 The effect of high NH_3 levels on methane production per kg VS added

NH_3 concentrations peaked in digester 1 during week 11, at 677 mg l^{-1} in digester 1 and during week 12 in digester 2 (612 mg l^{-1}). Maximum methane production per kg VS added was achieved in week 7 in digester 1 (0.121 m^3 kg VS added) and in week 8 in digester 2 (0.125 m^3

kg VS added) (Figures 4.15 and 4.16). The mean NH_3 concentration for digester 1 for week 7 was 280 mg l^{-1} (± 40), and for digester 2 for week 8 was 391 mg l^{-1} (±100). There was a slight decrease in methane productivity during week 8 for digester 1, possibly caused by the drop in volatile solids loading. The mean NH_3 for this week was 441 mg l^{-1} (±100). However, a sharp drop in methane productivity is obvious during week 9, to 0.095 m^3 kg VS^{-1} added, the mean NH_3 concentration for this week was 573 (±20) mg l^{-1}. A sharp drop in the methane productivity of digester 2 also occurred in week 9, again to a value of 0.095 m^3 kg VS^{-1}. The mean NH_3 concentration was 499 mg l^{-1} (± 30). The decrease in methane productivity observed in both systems suggested that significant inhibition of methanogenesis occurred above 550 mg l^{-1} NH_3. This is quite a lot higher than the upper limit of 225 mg l^{-1} NH_3 proposed by Webb and Hawkes (1985) but lower than values suggested by Pechan *et al.*(1987), who noted no inhibition of methanogenesis at NH_3 values up to 665 mg l^{-1}.

4.11 Adaptation of methanogens to high NH_3 levels

The degree to which methanogenic populations are affected by NH_3 concentrations seems to be governed by how acclimatised the bacteria are to a particular concentration, or range of concentrations. Although Webb and Hawkes reported significant inhibition of methanogenesis at NH_3 concentrations above 235 mg l^{-1}, they found that, after a period of adaptation, methaongenesis was relatively un-affected at NH_3 concentrations as high as 370 mg l^{-1}(1985). Koster and Lettinga (1988) found that sludge from a UASB reactor treating potato juice, which had a specific methanogenic activity of 0.73 g COD equivalent of methane produced per g volatile sludge solids at about 64 mg l^{-1} NH_3, completely failed to produce methane at 109 mg l^{-1} NH_3. However, after 2800 hours in contact with this NH_3 concentration, methanogenic activity returned, with a maximum specific methanogenic activity of 0.46 being observed. A number of

samples of the sludge were exposed to increasing levels of NH_3, up to a maximum of 447 mg l^{-1}. At this point specific methanogenic activity had declined to 0.04, and above this methanogenic activity ceased. Hence, although the methanogens present adapted to the higher NH_3 concentrations, their ability to produce a given unit of methane from a given amount of nutrients declined as NH_3 concentrations increased. Alternatively it is feasible that not only the methanogens were inhibited by increasing NH_3 concentrations, the acidogens may also have been inhibited, and so a decrease in the overall productivity of the system, rather than just that of the methanogens may have been responsible for the effects of increasing NH_3 concentrations noted by Koster and Lettinga. Reduced system productivity at high NH_3 was observed in both systems during weeks 10 - 14 of the current work. There was a slight increase in methane productivity in digester 1 during weeks 13 and 14, but in digester 2 the trend continued downwards. The mean NH_3 concentrations in both systems dropped to around 400 mg l^{-1} over this period, but no sudden rise in methane productivity was observed, suggesting that the activity of the methanogenic population, or of the bacterial system as a whole, was severely affected by the high NH_3 levels.

Poggi-Varaldo *et al.*, (1991) showed that the growth rate of acetoclastic methanogens was halved above NH_3 levels of 100 mg l^{-1}, see Figure 4.31. Therefore, a sharp increase in system NH_3 levels should be followed by an increase in VFA concentration. Figures 4.21 and 4.22 show mean VFA levels in the effluent from each digester. In both systems there was a sharp rise in mean effluent VFA concentrations during week 6. Mean effluent NH_3 levels rose from around 50 mg l^{-1} in both systems in the weeks before the addition of chicken manure, to around 100 mg l^{-1} in week 5, the week immediately after the commencement of addition of chicken manure and to over 200 mg l^{-1} during week 6. Some of this increase may have been due to the organic shock

loading to the system caused by a 25% increase in volatile solids loading, due to the addition of the chicken manure. However, if this were so one would expect to see further increases in effluent VFA as the volatile solids loading continued to increase until week 7. In fact a gradual and steady decrease in effluent VFA concentrations was observed over weeks 7 -12. This suggests that either the methanogens gradually adapted to the high NH_3 levels present and hence began to metabolise the "pool" of VFA which built up due to NH_3 inhibition, or VFA production was gradually inhibited by rising NH_3 levels, which eventually peaked at 600 - 700 mg l^{-1} between weeks 10 and 12.

McInerney and Bryant (1981) have reported that acetate utilising methanogens are, as far as can be ascertained, exclusively rod shaped. Poggi-Varaldo *et al.*(1991), as has been noted above, have shown that the growth rate of acetoclastic methanogens was severely reduced above NH_3 concentrations of 100 mg l^{-1}. Therefore increasing NH_3 levels should lead to VFA build up and a reduction in viable numbers of rod shaped methanogens. Microbiological analysis of both pilot plant digesters, using a UV microscope, showed that initially the ratio of rod shaped methanogens to spheres was around 1:2. Analysis after 2 months of addition of chicken manure revealed that very few rod shaped methanogens were present, indicating that high NH_3 levels had severely reduced the viable numbers of these bacteria. It was also noted that the number of spheres present was similar to samples analysed at the beginning of the experiment. This indicates that VFA production must also have been inhibited by the NH_3 concentrations present. If VFA production had continued at a similar rate to what it was during weeks 1- 4, significant VFA build-up would have been expected as the numbers of rod shaped methanogens available to metabolise VFA were reduced over weeks 4 - 12..

It can be concluded that the inhibition of methane production noted during weeks 7 - 12 was due to inhibition of methanogenic and acidogenic bacteria.

4.12 Redox potential as a parameter for monitoring the status of an anaerobic digester

Redox potential was measured in both digesters throughout the project. The initial redox potentials were found to be -486 milli Volts (mV), in digester 1 and -535 mV in digester 2.

There was no apparent explanation for this initial difference in redox potential, which seemed to be a function of the probes, as exchanging the meters yielded the same values for the relevant digesters, and exchanging the probes gave the opposite value for each digester. Figures 4.32 and 4.33 show the mean weekly redox potential for each digester. There was no real change in the baseline redox values over the course of the project. The baseline value stayed around -486 mV in digester 1 and around -535 mV in digester 2. The sudden rises in redox on both graphs can be attributed to air entering the system during removal of effluent from the reactors. Redox, therefore, does not seem to be of much help in monitoring the operational status of an anaerobic digester, apart from indicating the ingress of air when feeding or discharging effluent. Switzenbaum *et al.* (1990) have noted that although some authors have suggested there is a link between redox potential and volatile fatty acid accumulation, in a multi-redox component system such as an anaerobic digester, it is impossible to predict which redox couples are being measured by the probe. Certainly no relationship between redox potential and VFA concentration was observed during the current work.

4.13 Hydrogen sulphide levels in the biogas

It has been reported previously that a farm anaerobic digester operating on chicken manure produced biogas with an average hydrogen sulphide (H_2S) content of 3,200 - 3,800 ppm, with

occasional peaks of 4,500 ppm being observed (ETSU, 1994). Current UK Health and Safety guidelines require H_2S levels to be reduced to 15 ppm before combustion or discharge to the atmosphere, hence monitoring of biogas H_2S levels was deemed to be necessary (ETSU, 1997). Several farm digester operators have noted that a digester which is overloaded generally has elevated H_2S concentrations in the biogas (Windridge, 1997, Maltin 1997). Hence it is possible that elevated H_2S levels may provide a warning of the onset of digester instability, although there is nothing in the literature to support this assumption. Figures 4.34 and 4.35 show the mean weekly biogas H_2S concentration. The mean concentration in the gas from both digesters was around 700 ppm, for the 4 weeks of operation on cattle slurry, and when chicken manure was added to the feed, H_2S levels quickly rose to a maximum of 5000 ppm in digester 1 and 4500 ppm in digester 2. It is possible that the initial rise in H_2S was a result of extra hydrogen becoming available due to excess fatty acid production caused by the increase in volatile solids loading. Hilton and Archer (1988) have noted that sulphate reducing bacteria compete with methanogens for the substrates acetic acid and hydrogen. An excess of both, caused by a shock loading, could have encouraged the growth of sulphate reducing bacteria and hence an increase H_2S in the biogas, however no relationship was observed between biogas H_2S levels and VFA concentrations.

The rapid rise in biogas H_2S levels noted during weeks 5 - 8 in both digesters was caused by the addition of chicken manure, which provided additional sulphate in the system.

H_2S is formed in the following manner (Metcalf and Eddy, 1991):

$$\text{Organic matter} + SO_4^{2-} \xrightarrow{\text{bacteria}} S^{2-} + H_2O + CO_2$$

$$S^{2-} + 2H^{+} \longrightarrow H_2S$$

Protein in the chicken manure could also have porvided an additional source of sulphur in the system, however it is unlikely that this sulphur would be converted to sulphate under anaerobic conditions. It can therefore be concluded that it is more likely that the rapid increase in H_2S in the biogas was due to the presence of sulphate in the chicken manure as opposed to hydrogen production caused by the increase in organic loading.

4.14 A possible link between the decline in H_2S levels and the rise in NH_3 concentrations

The sharp drop in H_2S noted in both systems seems to be linked to rising NH_3 levels. H_2S levels remained high in the biogas during weeks 8, 9 and 10 in digester 1, but fell rapidly in week 11 as effluent NH_3 peaked. H_2S levels in the biogas from digester 2 peaked in week 8 but fell rapidly during weeks 9 and 10, again as effluent NH_3 reached its maximum in week 11. It would seem that the extreme NH_3 concentrations may in some way have inhibited the sulphate reducing bacteria (SRB). However, on closer examination, it is apparent that H_2S levels in the biogas from digester 1 did not begin to fall until the NH_3 concentration reached 677 mg l^{-1}, whereas they had begun to fall in digester 2 when the NH_3 concentration exceeded 390 mg l^{-1} and also, close observation of Figures 4.27, 4.28, 4.29, 4.30, 4.34 and 4.35, reveals that between weeks 5 and 11 H_2S levels in the biogas and NH_3 concentrations in the effluent show very similar increasing trends. Also, there is no evidence in the literature to support the assumption that high NH_3 concentrations inhibit SRB, and as biogas H_2S levels seem to be of little use as a control parameter for animal manure digestion, there seems little point in investigating NH_3 inhibition of SRB.

4.15 Digester monitoring and performance during weeks 15 - 17

After 2 weeks of adding shock loads of 15% TS chicken manure to both digesters, it was observed that effluent VFA concentrations had risen sharply and methane production per kg VS added had also declined. Standard operating practise when a digester becomes overloaded is to stop feeding for a number of weeks until system VFA concentrations return to levels which they were at before the system upset (Parkin and Owen, 1986). Hence it was decided to suspend feeding during weeks 15 - 17.

During this period, mean daily methane production declined only slightly in week 15 (indicating, as has been noted earlier incomplete degradation of chicken manure added in earlier weeks), but fell sharply in weeks 16 and 17 in both systems, to around 2 litres day^{-1} in week 16 and 1 litre day^{-1} in week 17, see Figures 4.23 and 4.24. The mean biogas methane concentration rose to quite high levels between weeks 15 and 17, peaking at 73% CH_4 for digester 1, in week 16 and 83% CH_4 for digester 2 in week 17, see Figures 4.25 and 4.26. CO_2 in the biogas comes from 2 major sources, the production of VFA by the acidogenic bacteria (see Section 1.2) and the cleavage of acetic acid (CH_3COOH) to produce methane. This reaction can be described by the following equation:

$$CH_3COOH \longrightarrow CH_4 + CO_2$$

As no new fresh feed material was added during weeks 15 - 17 acidogenic activity decreased in week 17, leaving the above reaction as the only source of biogas CO_2 levels during that week. As has been noted in Section 4.8, biogas CO_2 levels did not drop immediately after feeding ceased due to the ongoing acetogenic activity associated with breakdown of residual chicken manure during weeks 15 and 16.

4.16 Digester monitoring during weeks 18 - 21

After 3 weeks, effluent VFA concentrations were found to have returned to low levels (VFA levels at the start of week 18, were around 2000 mg l^{-1} in both digesters, see Figures 4.21 and 4.22.) and feeding of a mixture of 70% cattle slurry / 30% chicken manure recommenced at the start of week 18, see Table 4.1 for loading rates. This caused a rapid increase in biogas CO_2 levels, as the acidogens began to convert this material to VFA.

As can be seen from Figures 4.15 and 4.16, methane production per kg of volatile solids added never recovered to previous levels once feeding was recommenced in week 18. This was unusual as the mean loading rate at which the reactors were being operated, 3.5 kg VS m^{-3} d^{-1}, was only slightly lower than the mean loading rate used during weeks 5 - 12, which was 3.6 kg VS m^{-3} d^{-1}. Also the hydraulic retention time in digester 1 appeared to be the same as during weeks 5 - 12, as effluent volatile solids levels during weeks 18 - 21 remained between 4 and 5 %. Effluent volatile solids did gradually increase in digester 2 to over 6% indicating poor mixing. It was also noted that methane productivity, compared to digester 1 from the same period, was correspondingly lower in digester 2 due to a greater proportion of the feed volatile solids passing through the system un-digested see Figures 4.15 and 4.16. Even taking into account the shorter retention time in digester 2, it was puzzling that methane productivity in both systems did not return to near previous levels. The acidogenic bacteria continued to produce large amounts of VFA during this period but the methanogens were unable to convert the VFA to methane, hence the VFA build up seen in Figures 4.21 and 4.22, during weeks 18 - 20. There was a concurrent steady decline in pH and alkalinity in digester 1, with both parameters reaching minima of 7.6 and 17,500 mg l^{-1} in week 20, see Figures 4.17 and 4.19. Digester 2 did not exhibit a drop in mean effluent pH, or alkalinity, despite having similar VFA levels to digester 1. This was due to

the breakthrough of feed solids into the effluent of digester 2, see Figure 4.8, which shows mean feed and effluent total solids were almost identical during week 21. This occurred due to poor mixing in the system. Effluent total solids in digester 1 remained relatively constant during weeks 18 - 21.

The slight drop in mean VFA:TAlk noted in week 21 was caused by the fall in effluent VFA. It is not clear why this drop occurred, and no corresponding rise in mean effluent pH was noted during week 21, see Figure 4.17. The VFA result for week 21 was based on only one sample, due to damage during freezing of the other samples. It is possible that the VFA reading for week 21 was incorrect. There is no other apparent reason for the drop in effluent VFA during that week.

Both systems experienced a rapid rise in mean VFA:TAlk ratio during weeks 18 - 20, see Figures 21a and 22a. The drop in VFA:TAlk noted during week 21 in digester 2 seemed to be due to the breakthrough of feed solids in the effluent during that week. This had the effect of diluting the effluent with un-digested material. The drop in VFA:TAlk during week 21 in digester 1 seemed to have been due to an error in VFA analysis.

It is interesting to note that NH_4^+ and NH_3 levels in digesters 1 and 2 fell sharply during this 4 week period. This appeared to be due to a drop in feed NH_4^+ levels to around 1500 mg l^{-1}. It seems the NH_3 levels observed in digesters 1 and 2 during weeks 18 and 19, around 400 mg $^{-}1$, were sufficient to inhibit methanogenesis but not acidogenesis. This was different from the inhibition by extremely high levels of NH_3 noted during weeks 10, 11 and 12 which seemed to have inhibited both groups of bacteria. The VFA build up noted in both systems may have been

due to the inhibition of acetoclastic methanogens by NH_3 described in Section 4.11. Although the addition of fresh cattle slurry would be expected to re-seed the digester with these methanogens, the ammonia (NH_3)concentrations present were sufficient to maintain the population at low levels.

4.17 Digester monitoring during weeks 22 to 26

Due to the VFA build up observed during weeks 18 - 20 and the declining methane productivity rate see Figures 4.21, 4.22, 4.15 and 4.16 it was decided to stop feeding the digester until the VFA levels had dropped to lower levels. Some drop in effluent VFA did occur during week 22, so it was decided to recommence feeding of cattle slurry and chicken manure mixtures, see Table 4.1. To study whether the systems could be adapted to higher proportions of chicken manure in the feed, the ratio of chicken manure to cattle slurry was increased to 50/50 for digester 1 and 25/75 for digester 2.

The high total solids content (10.5 - 12.5% TS) see Figure 4.7 of the feed to digester 1 proved difficult to mix into the digester, and by week 26, the 4th week of feeding a mixture of 50% cattle slurry and 50% chicken manure, the total solids reduction being achieved by the digester was reduced to 11%. Figure 4.13 shows that volatile solids removal followed a similar pattern, dropping to 13% by week 26. This highlights the difficulty of operating anaerobic digesters on high solids wastes and partially explains the poor methane productivity noted during weeks 23 - 26.

Digester 2 was fed a mixture of 25% cattle slurry / 75% chicken manure over this period, and although feed total solids was slightly higher than the feed to digester 1, volatile solids removal remained between 26 and 34%, indicating better mixing in this system. NH_4^+ levels were slightly higher in digester 2 (3,300 - 4,500 mg l^{-1}) than in digester 1 (3,000 - 4000 mg l^{-1}), due to the slightly greater proportion on chicken manure added to digester 2. NH_3 levels were slightly higher in digester 1 (200 - 450 mg l^{-1}) than in digester 2 (280 - 320 mg l^{-1}) due to higher pH in the former system. There was, however, a clear difference in methane productivity for each system, which stayed around 0.04 m^3 CH_4 kg VS^{-1} for digester 1, but rose from 0.04 in week 23 to 0.059 m^3 CH_4 kg VS^{-1} for digester 2 by week 26. This difference can most likely be attributed to the better destruction of volatile solids in digester 2, and highlights an important point which was noted during the addition of the mixtures to the digesters, namely than although the feed to digester 2 had a higher total solids concentration, it flowed much easier that the feed to digester 1, and hence could be mixed more easily into the bulk digester contents. Although no viscosity measurements have been undertaken, it would seem that a sample of chicken manure of a given total solids concentration, has a lower viscosity than a sample of cattle slurry of similar total solids. The average volatile solids removal rate for digester 2 was around 30% during weeks 23 - 26 and was less than 20% for digester 1, indicating a lot of the solid material was short circuiting in digester 1.

The high VFA values noted in the effluent during weeks 23 - 26 (see Figures 4.21 and 4.22) can be, in part, attributed to the high solids levels of the material leaving the reactors, indicating that only partial degradation of chicken manure had taken place, and may also be in part due to low levels of acetoclastic methanogens present. It can be concluded that for these high solids

mixtures to be digested more successfully longer solids retention times and lower organic loading rates would be necessary.

Mean biogas H_2S concentrations in digester 1 rose from 1,000 ppm to just over 2,000 ppm over this 4 week period, and from a similar baseline to over 3,500 ppm in digester 2, see Figures 4.34 and 4.35. Again this occurrence seems to be linked to increasing the amount of chicken manure present, and hence the amount of available sulphate.

Mean biogas CH_4 fell initially to around 57% in digester 1 during the first week of feeding the 50 / 50 mixture, but gradually recovered to 64% methane by the end of the 4 week period. The initial methane concentration in digester 2 was not affected during the first week of feeding the 25 / 75 mixture, but fell rapidly to 57% during the second week, and then rose gradually to 64% by the end of the 4th week. These patterns would seem to indicate that, initially, the substrate to digester 1 was found to be more degradable by the acidogenic population present, hence the increase in biogas CO_2 in week 23, whereas it took an extra week for the acidogens in digester 2 to produce significant quantities of volatile fatty acids, and concurrently CO_2, from the feed which contained a higher proportion of chicken manure. Again, this concurs with observations made by authors concerning the slow degradation of chicken manure in anaerobic reactors (Aubart and Fauchille, 1983).

The VFA:TAlk values noted during weeks 23 - 25 indicated system instability, but again the effect of un-digested feedstock in the effluent during week 26 had the effect of diluting the VFA:TAlk ratio with un-digested material.

4.18 Digester monitoring weeks 27 - 30

As methane productivity had been declining in digester 1 over weeks 23 - 26 (see Figure 4.15) it was decided change the feed to 100% cattle slurry at the beginning of week 27, to determine if this would have the effect of improving methane productivity. Mean effluent alkalinity and pH fell sharply over this period, but effluent VFA remained reasonably constant at around 6000 mg l^{-1}. The drop in pH can be explained by the reduced alkalinity available from the feed material, as the cattle slurry had a mean alkalinity of around 13, 000 mg l^{-1} and chicken manure had a mean alkalinity of around 30,000 mg l^{-1}. Also it will be noted, that although the digester was now being operated at an organic loading rate similar and to, and on the same material as, that at which it was being operated on during the first 4 weeks of the experiment (see Table 4.1), the effluent VFA was substantially higher than it had been during weeks 1 - 4. Also from Figure 4.13 it can be seen that the volatile solids removal was virtually 0 for weeks 27, 28 and 30, indicating that solids build up had occurred in the reactor, causing a reduction in reactor working volume. Therefore the reactor could no longer be assumed to have an 18 litre working volume, and hence the organic loading rate may have been a lot greater than 2.92 kg VS m^{-3} d^{-1}.

Biogas methane concentration, see Figure 4.23, also rose substantially during this period, although methane productivity did not, see Figure 4.15. The rise in biogas methane levels indicated reduced CO_2 production, due to either low rates of acidogenesis or acetoclastic methanogenesis. Microbiological analysis of the effluent from digester 1 indicated the presence of some rod shaped acetoclastic methanogens in the digester effluent. The low rates of acidogenesis and methanogenesis observed may have been due in part to the low residence time of solids in the digester. On dismantling digester 1 after the experiment, a lot of crusted material was found on the heating coil and digester probes, this would have contributed substantially to

reducing the volume of the digester. This crusting obviously only occurred towards the end of the digestion trials, weeks 22 - 30, as there had been no large increase in effluent total solids or decrease in volatile solids removal during weeks 1 - 21.

The rapid increase in the VFA:Talk ratio noted during weeks 27 - 30 was due to the drop in effluent alkalinity, mean effluent VFA rose only slightly over the 4 week period, see Figures 4.19, 4.21 and 4.21a. Methane productivity remained very low over this period, see Figure 4.15, despite the fact that the feedstock consisted of cattle slurry only.

4.19 The effect of increasing the chicken manure loading to digester 2

The increase in the chicken manure content of the feed to digester 2, from 25 / 75 to 10 / 90 at the beginning of week 27 initially had the effect of depressing methane productivity, see Figure 4.16. Increasing the volatile solids loading rate, from 4.5 kg VS m^3 d^{-1} in week 26 to almost 5 kg VS m^3 d^{-1} in week 27, also reduced the pH, from 7.88 to 7.63, but the high alkalinity of the feed ensured that a pH drop similar to that which occurred in digester 1 did not occur, even though mean effluent VFA levels were similar, see Figures 4.21 and 4.22. The high alkalinity also ensured the VFA:TAlk ratio remained below the threshold value of 0.3, see Figure 22a. The difference in performance between the 2 digesters during weeks 27 - 30 was certainly in part due to the fact that digester 1 was not very well buffered and hence the environment within the digester changed quite rapidly over the 4 week period, whereas the high alkalinity of the feedstock to digester 2 ensured a well buffered system and a more stable environment for bacterial growth.

Methane productivity continued to increase over weeks 27 - 30 in digester 2, from 0.04 m^3 CH_4 kg VS^{-1} in week 27 to 0.079 m^3 CH_4 kg VS^{-1} in week 30, indicating that the digestion system had become adapted to the chicken manure feedstock. Microbiological analysis of the effluent from digester 2 (see page 66 for method description) indicated that very few rod shaped methanogens, were present. However, there was no increase in biogas CO_2, which would be expected from a system operating with reduced acetoclastic methanogens levels, as these bacteria are CO_2 producers. It seems that other acetoclastic species were present, which were not rod shaped, but it is not clear why these species were not present in digester 1, it is possible that the sharp drop in pH which occured in digester 1 over this period limited their growth. The system NH_3 levels were similar in both digesters over this period, and indeed dropped sharply in digester 1 as the pH dropped.

Mean volatile solids removal rose from 30% in week 27 to over 40% in week 30, and total solids dropped from just under 12% to around 5 % over this period, indicating that no solids short circuiting had occurred. The increased residence time of the solids in the digester, compared to digester 1, accounted in part for the increased methane productivity observed during weeks 27 - 30 in digester 2.

On a qualitative level an observation can be made that the microbiological population in both digesters became adapted to a feedstock containing chicken manure over weeks 18 - 26, and that a sudden change to a cattle slurry feedstock in week 27 meant the microbiological fauna in digester was not able to readily adapt to metabolising the new feed material. The microbiological population in digester 2, which had also become adapted to high chicken manure levels, continued to flourish as the proportion of chicken manure was increased, hence the

increase in methane productivity over weeks 27 - 30 in digester 2 was in part due to the presence of a bacterial population which had become adapted to the anaerobic degradation of chicken manure. This adaptation would be difficult to measure quantitatively without detailed microbiological analysis of all the different groups of bacteria involved in the anaerobic digestion process in digester 2.

4.20 Preliminary conclusions

* Addition of high solids chicken manure to an anaerobic digester operating on cattle slurry, initially had the effect of increasing methane production per kg VS added.

* However, as ammonia(NH_3) levels increased in the digestion system, methane productivity was inhibited. It is likely that this was due to inhibition of acetoclastic methanogens.

* Hydrogen sulphide levels in the biogas began to increase on commencement of the addition of chicken manure to the system.

* As the proportion of chicken manure was increased in the feedstock to digester 2, the system gradually became more adapted to the degradation of high solids chicken manure.

Figure 4.1 Variation in total and volatile solids in cattle slurry samples collected over 30 week period.

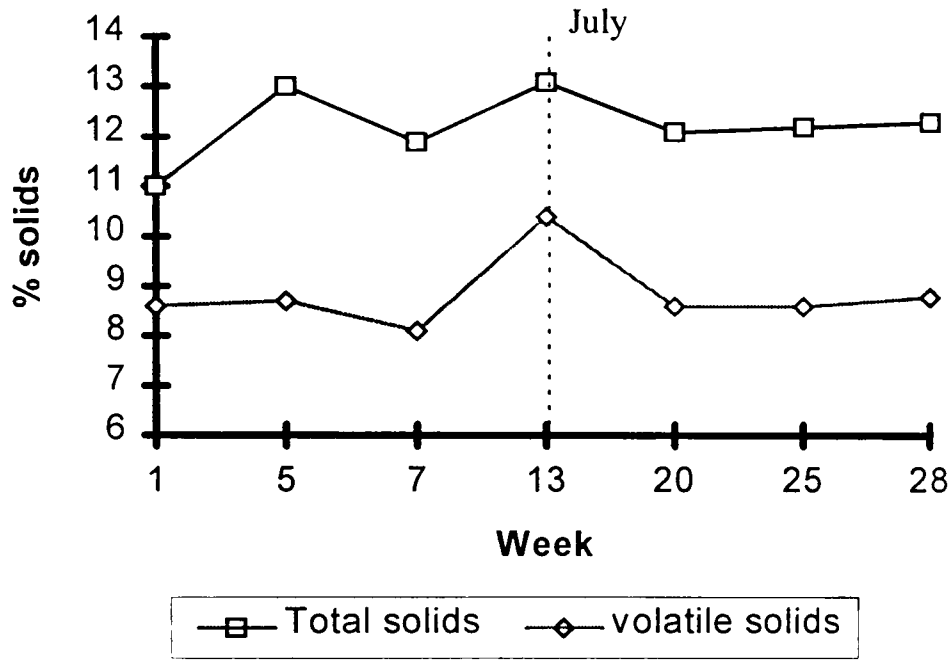


Figure 4.2 Variation in total and volatile solids of chicken manure samples collectd over 30 week period.

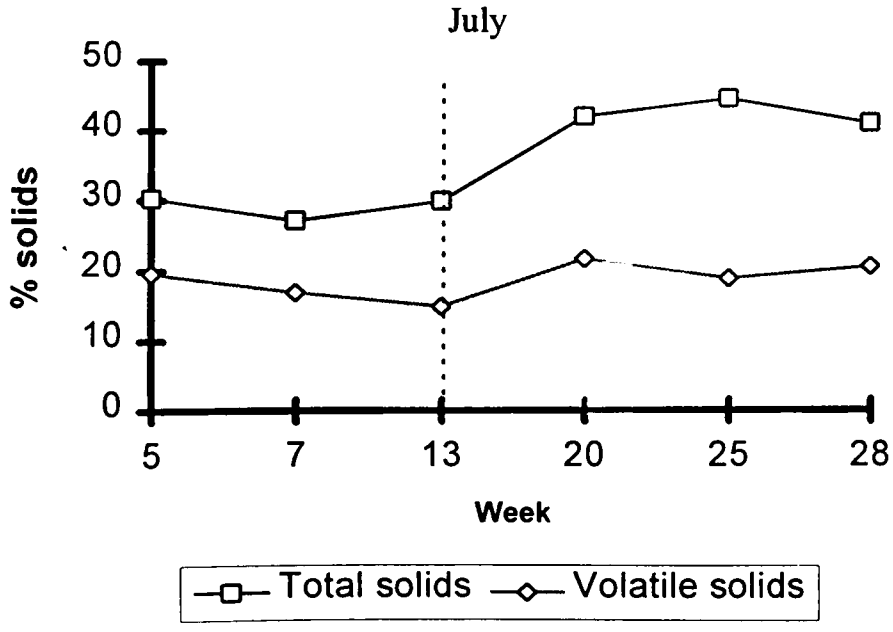


Figure 4.3 Variation in digester feedstock VM/DM ratio.

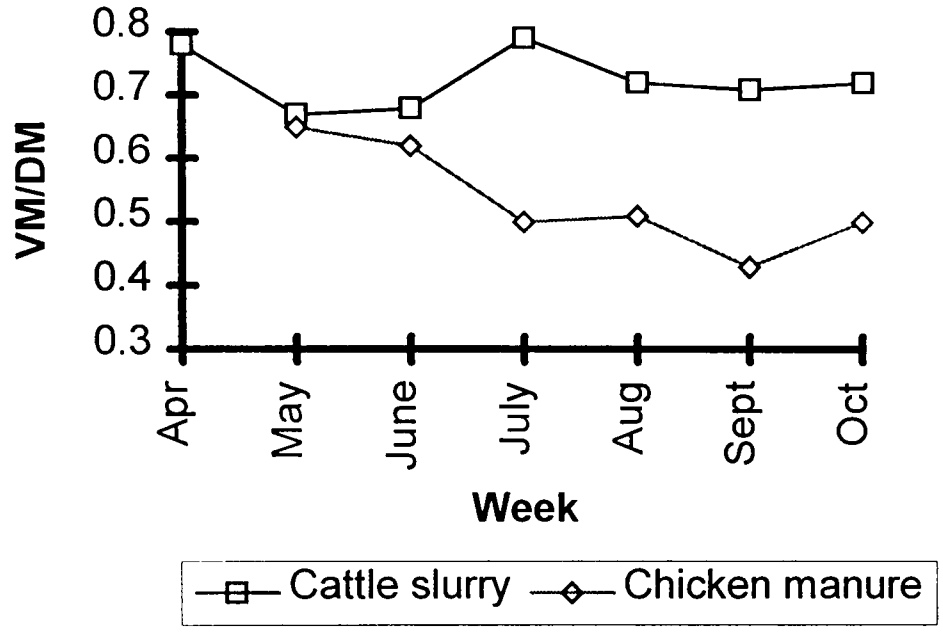


Figure 4.4 Decrease in volatile solids content of chicken manure samples diluted to 15% total solids over period of digester operation.

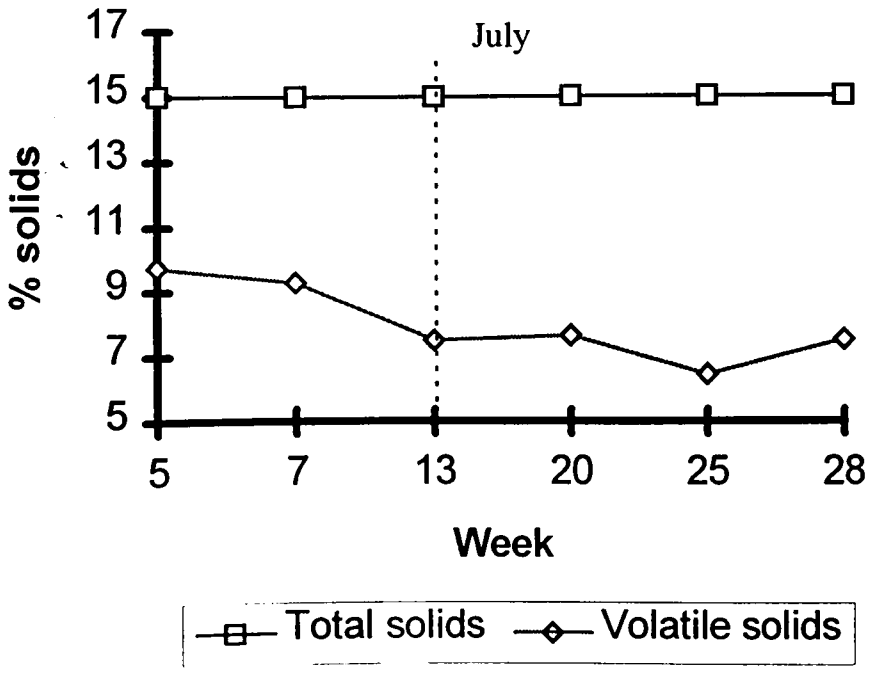


Figure 4.5 Digester 1: mean estimated and actual volatile solids loading rate for each week.

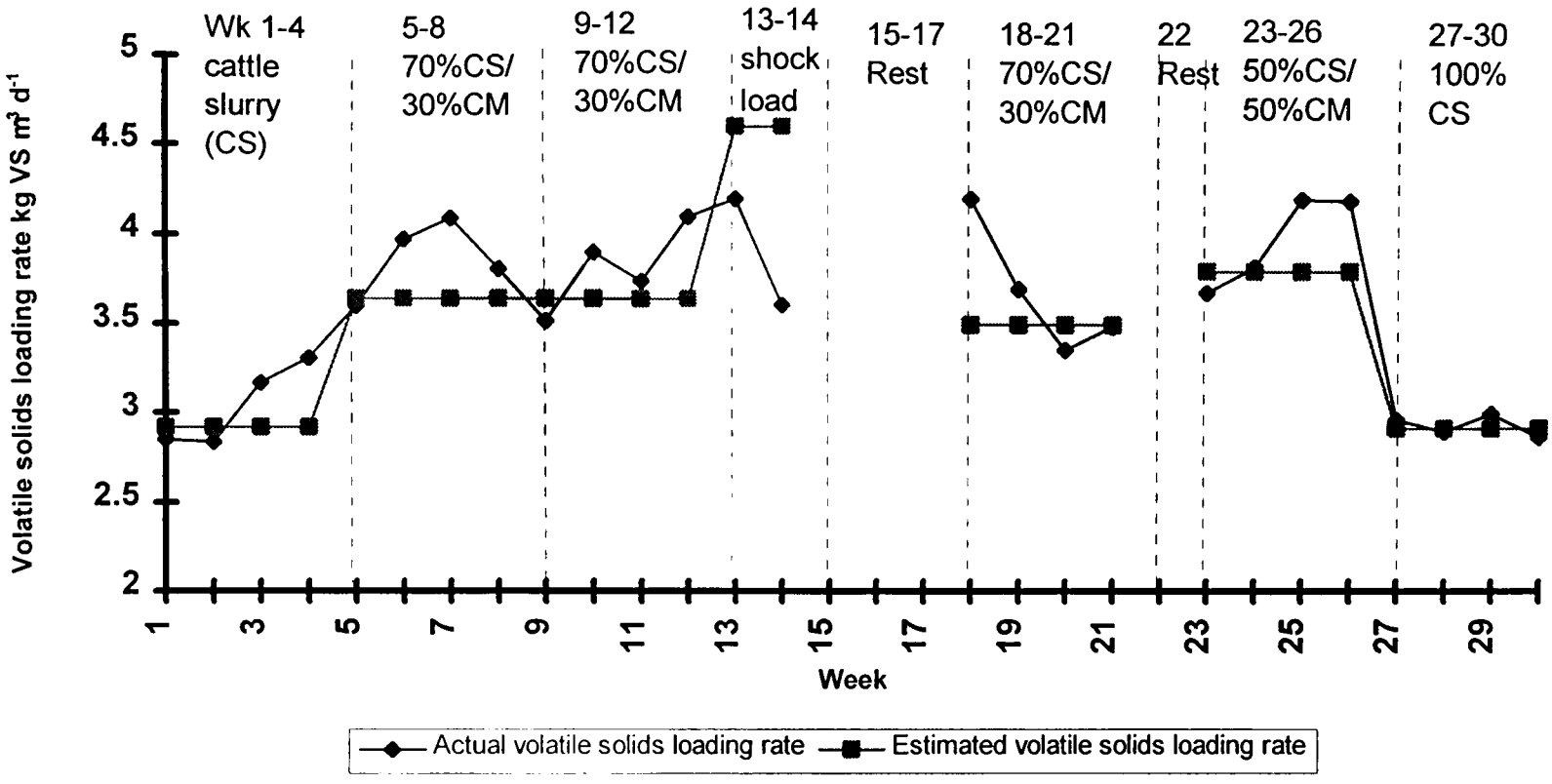


Figure 4.6 Digester 2: mean estimated and actual volatile solids loading rate for each week.

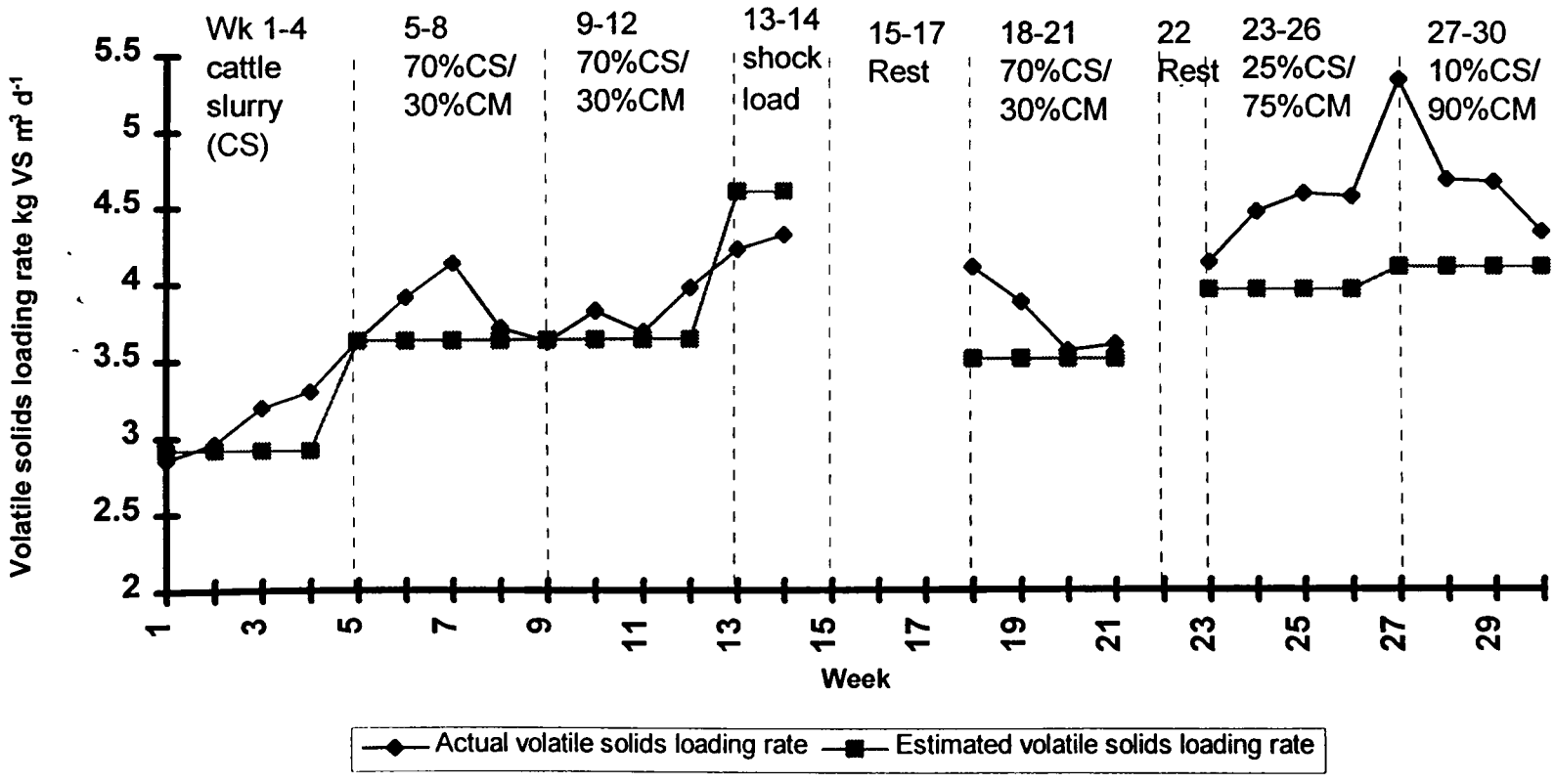


Figure 4.7 Digester 1: daily mean feed and effluent total solids for each week.

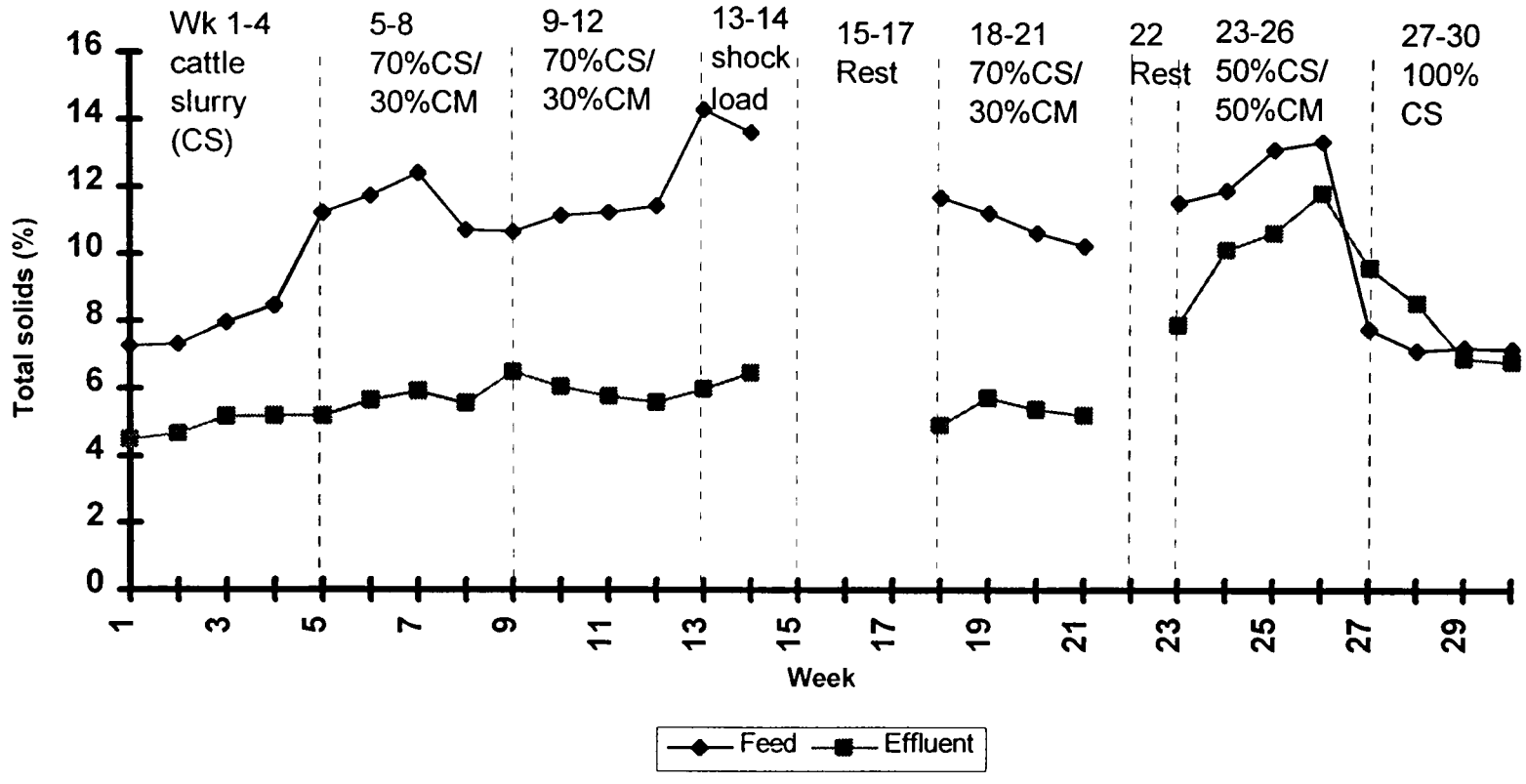


Figure 4.8 Digester 2: daily mean feed and effluent total solids for each week.

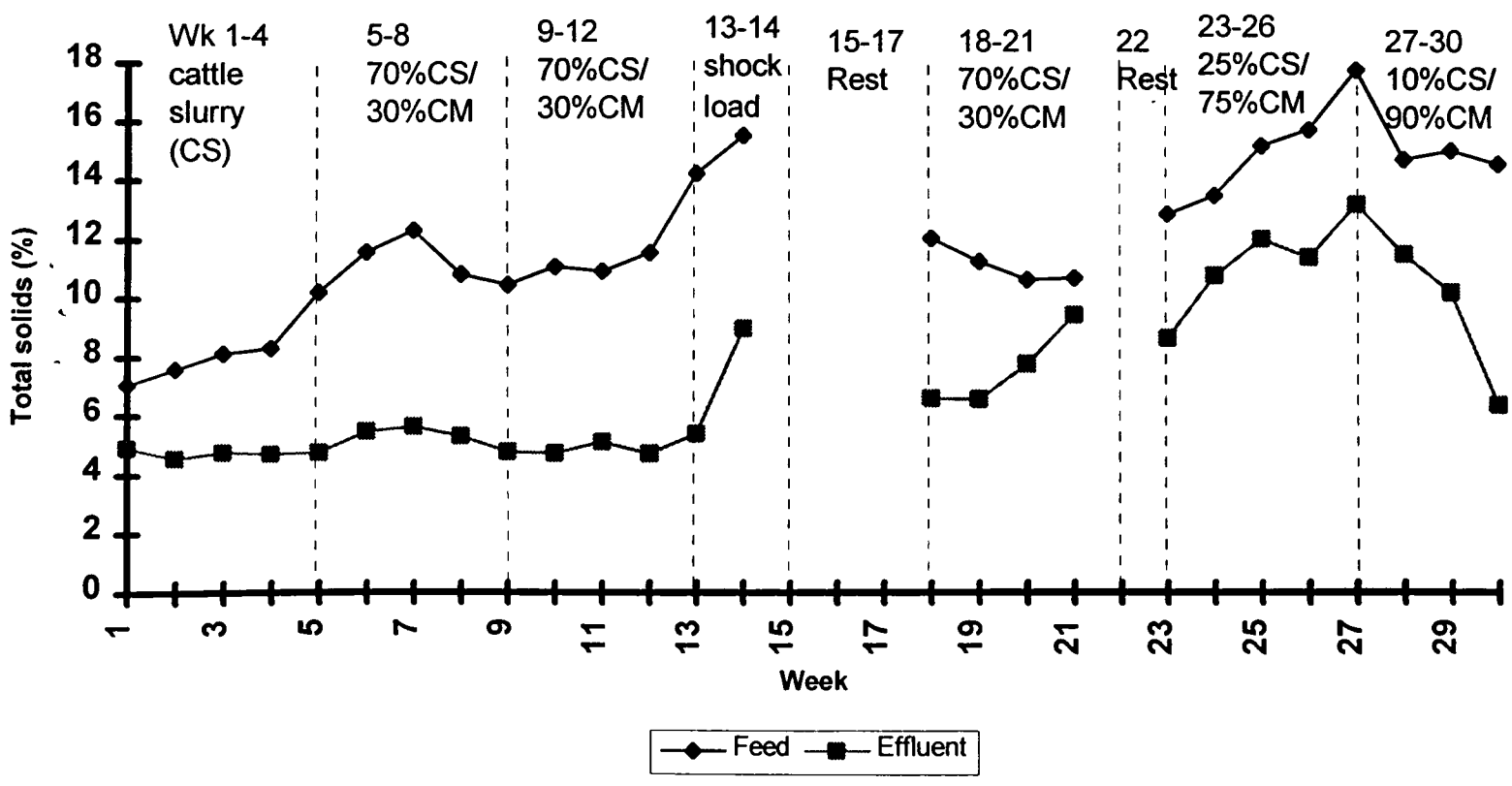


Figure 4.9 Digester 1: daily mean feed and effluent volatile solids for each week.

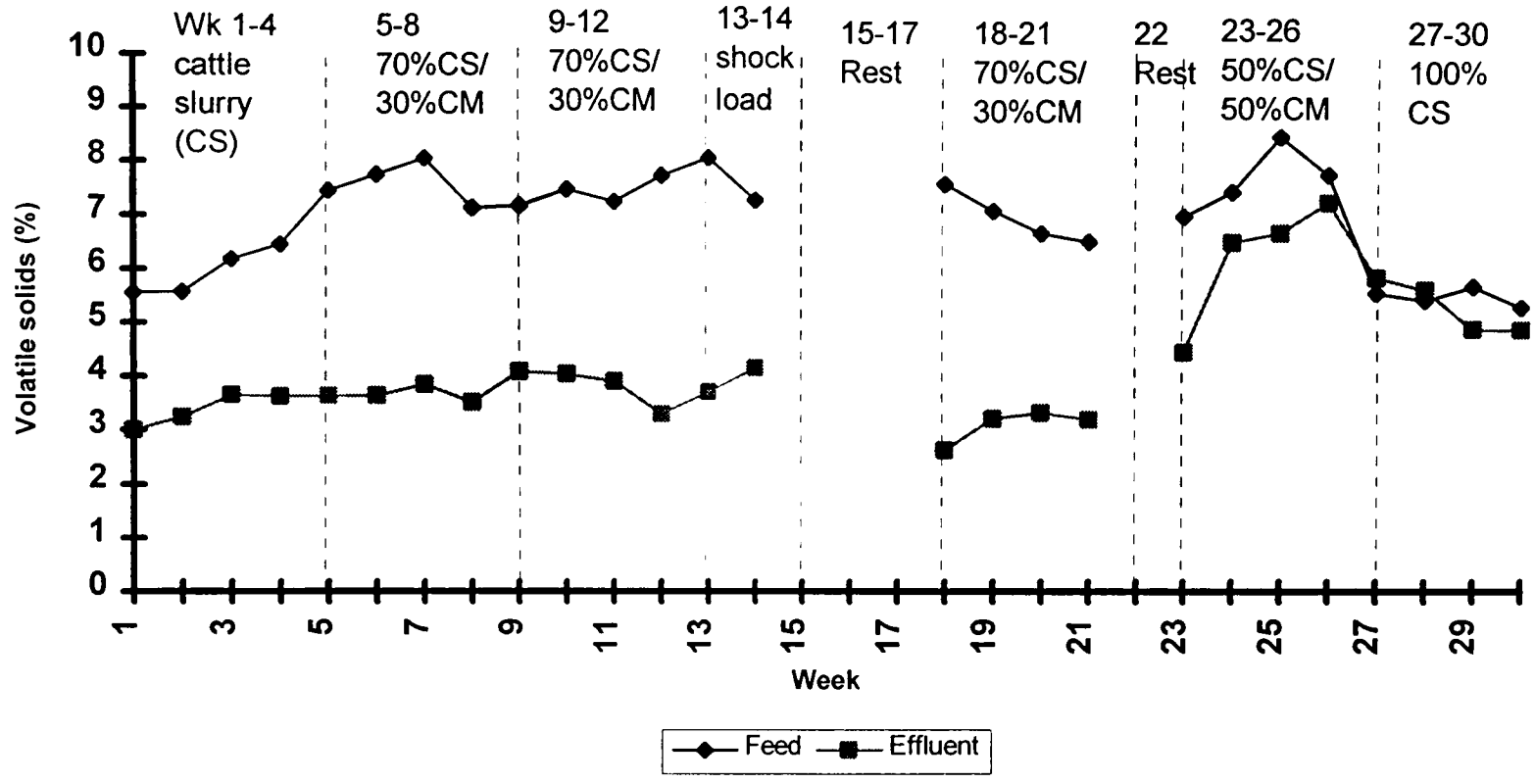


Figure 4.10 Digester 2: mean daily feed and effluent volatile solids for each week.

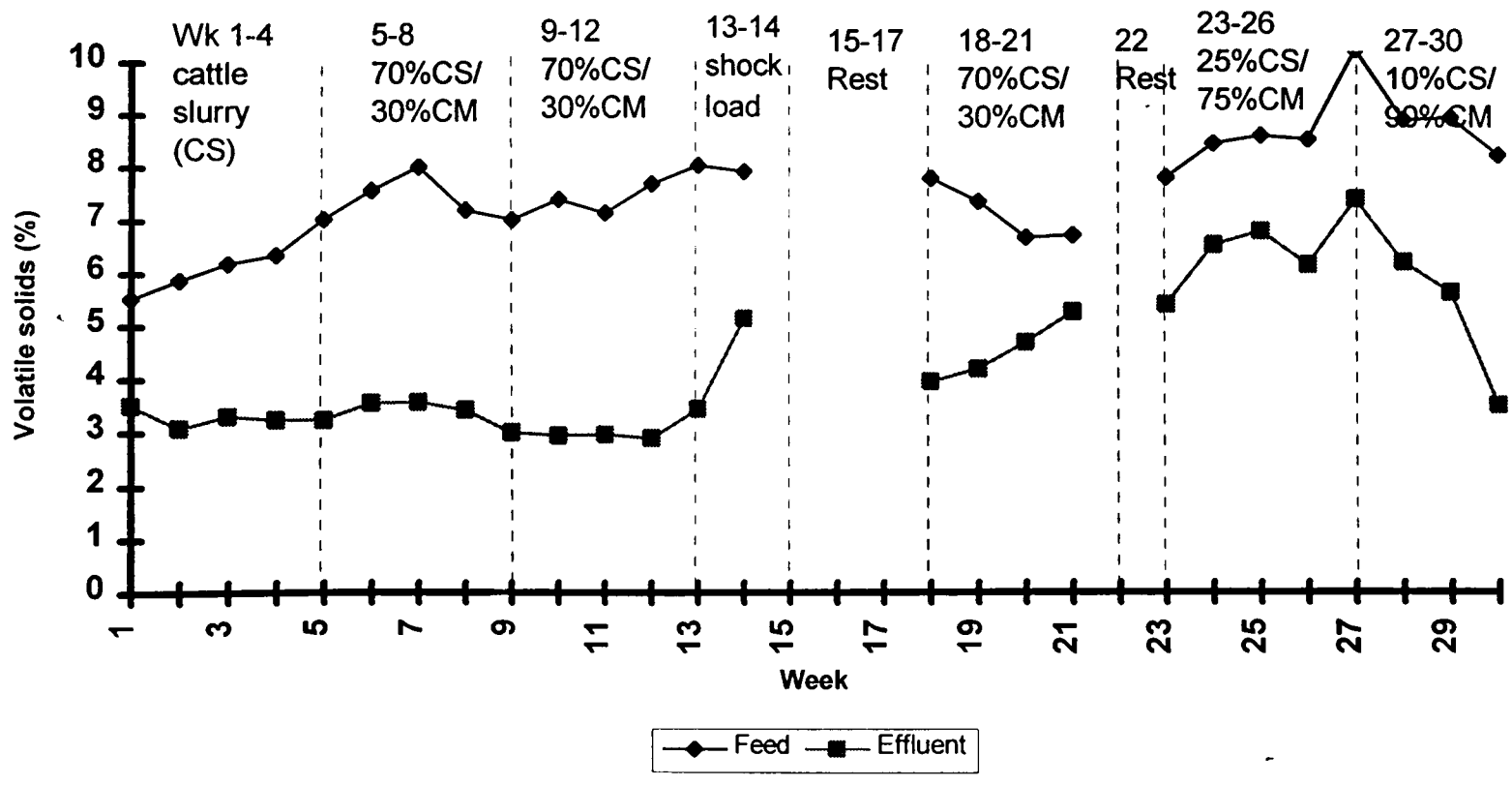


Figure 4.11 Digester 1: mean daily feed and effluent fixed solids for each week.

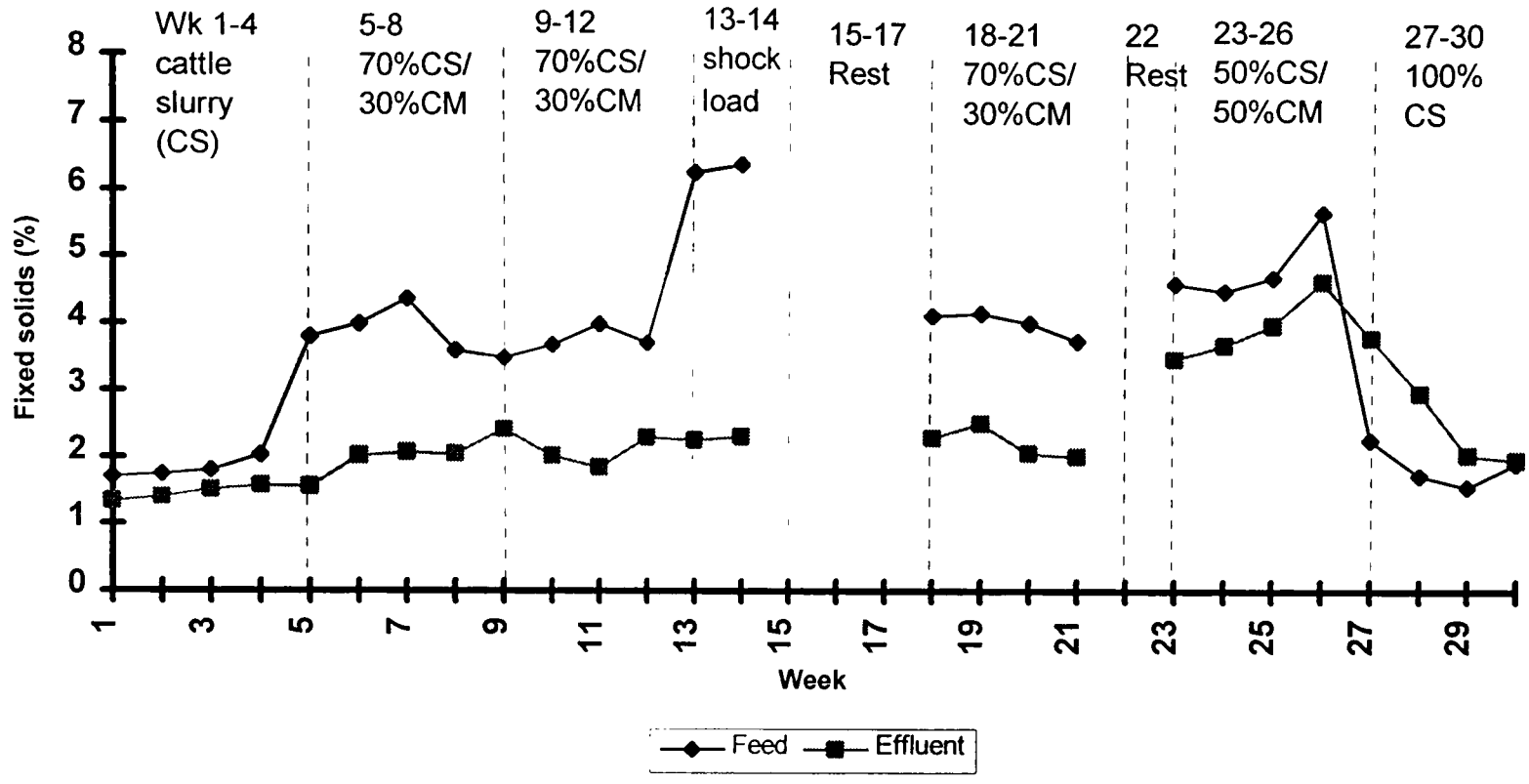


Figure 4.12 Digester 2: mean daily feed and effluent fixed solids for each week.

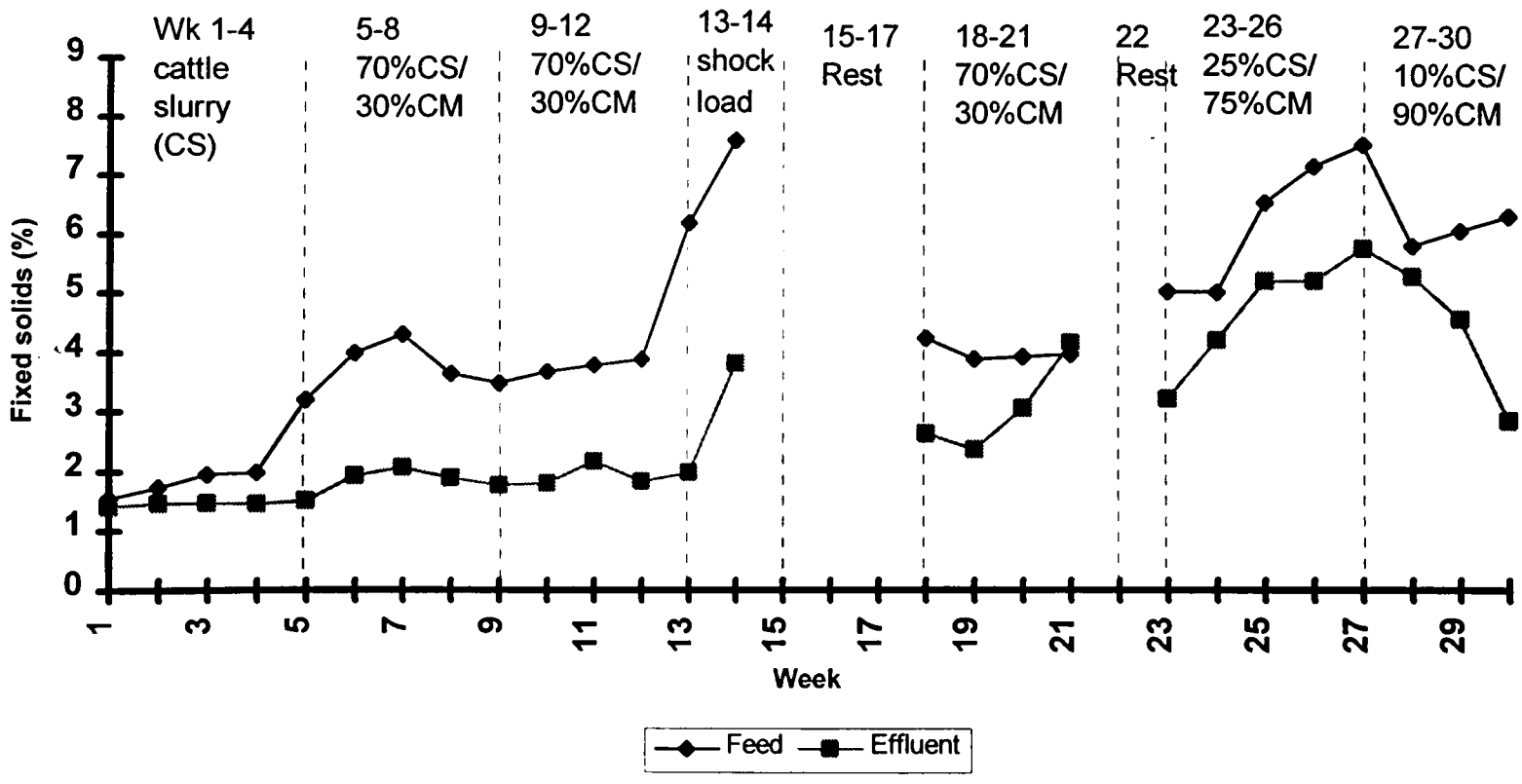


Figure 4.13 Digester 1: mean daily % volatile solids removal for each week.

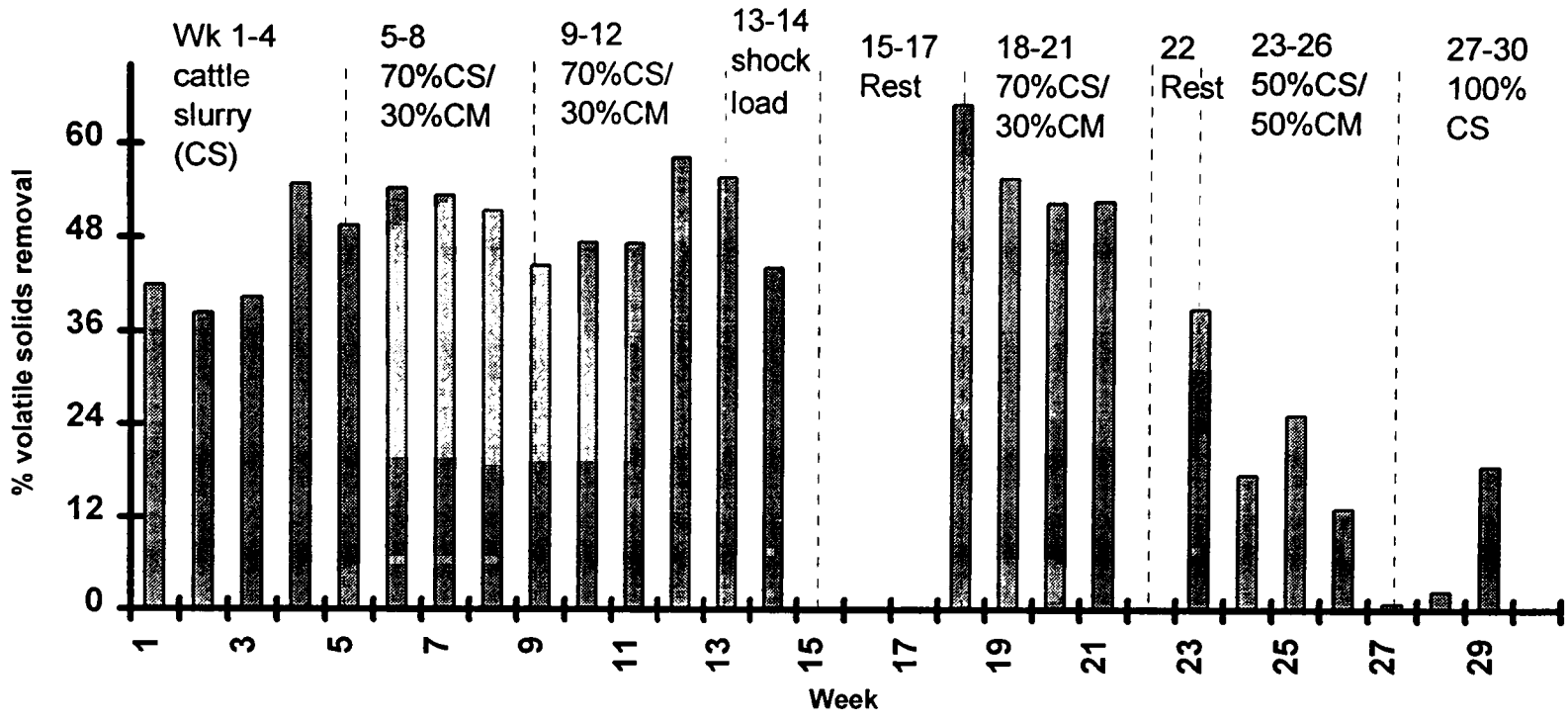


Figure 4.14 Digester 2: mean % daily volatile solids removal for each week.

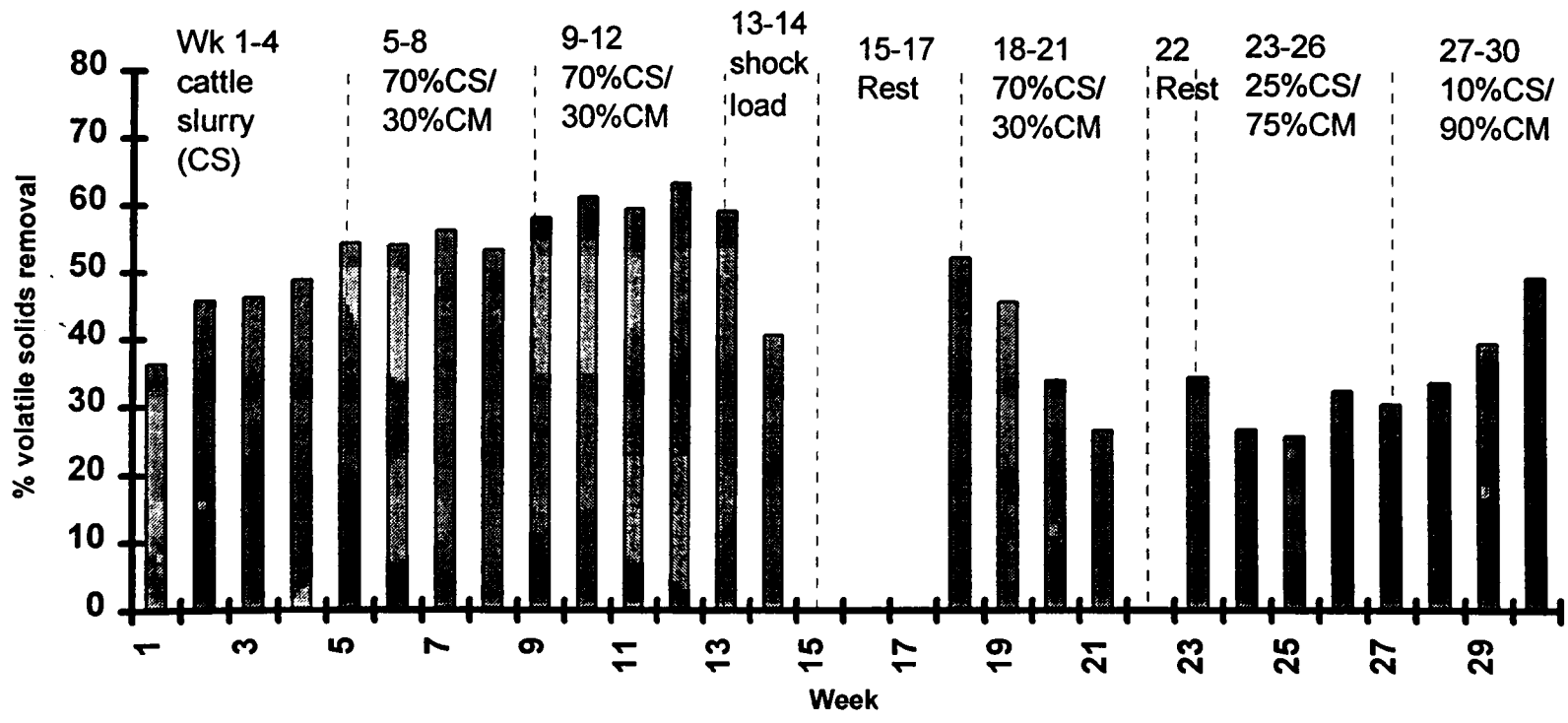


Figure 4.15 Digester 1: variation in mean methane production per kg VS added and volatile solids loading rate.

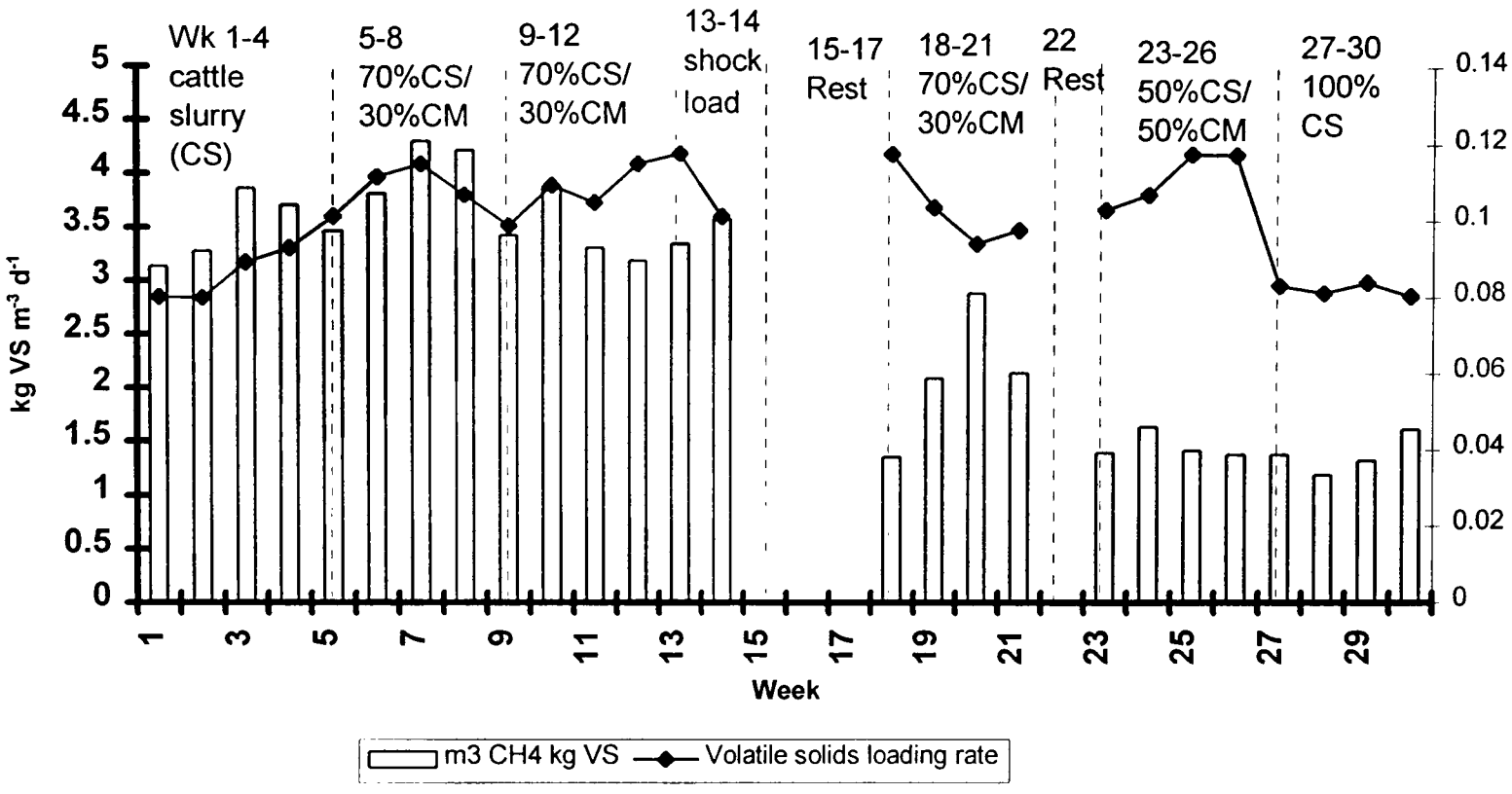


Figure 4.16 Digester 2: variation in mean methane production per kg VS added and volatile solids loading rate.

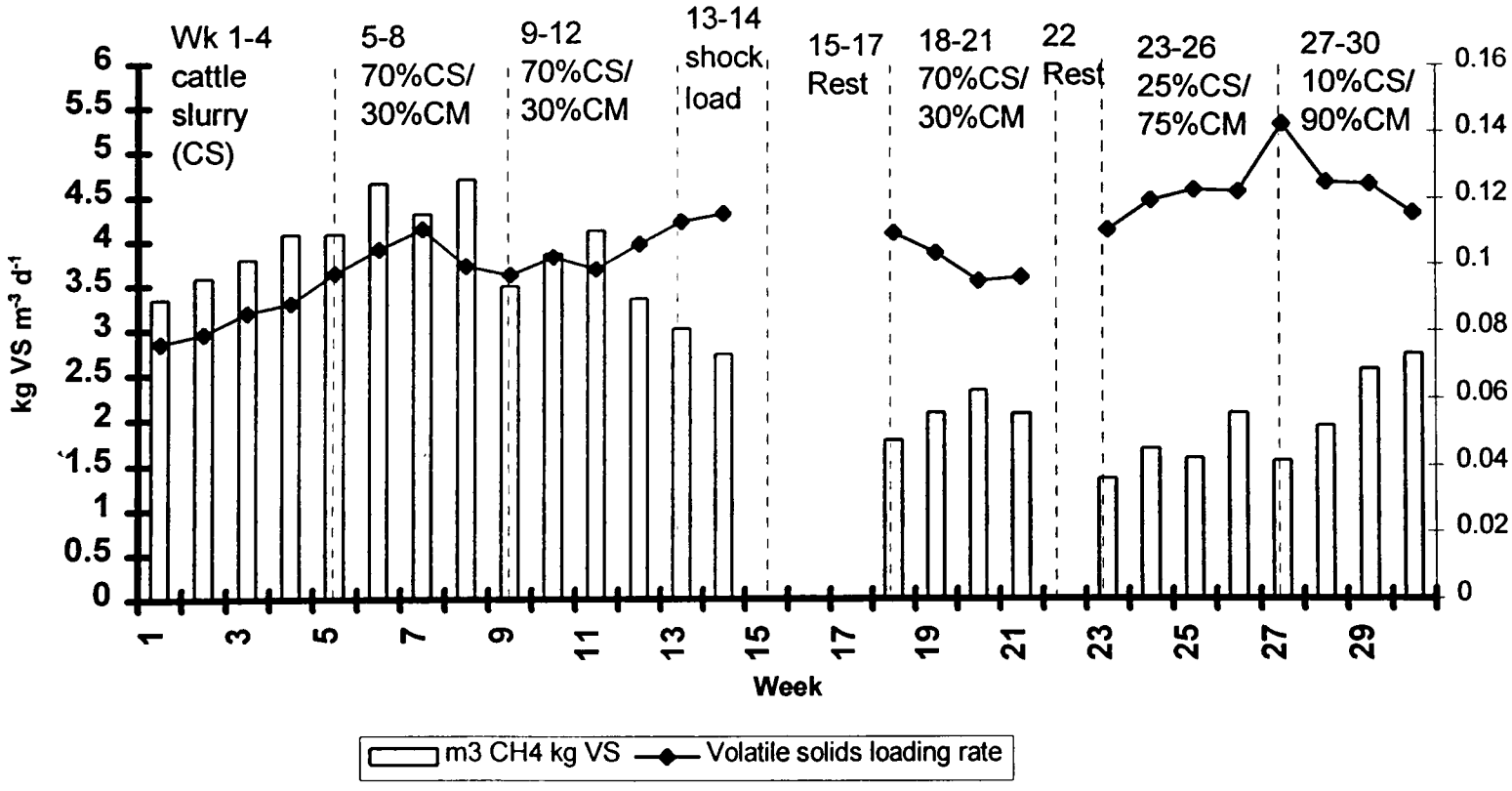


Figure 4.17 Digester 1: mean pH for each week.

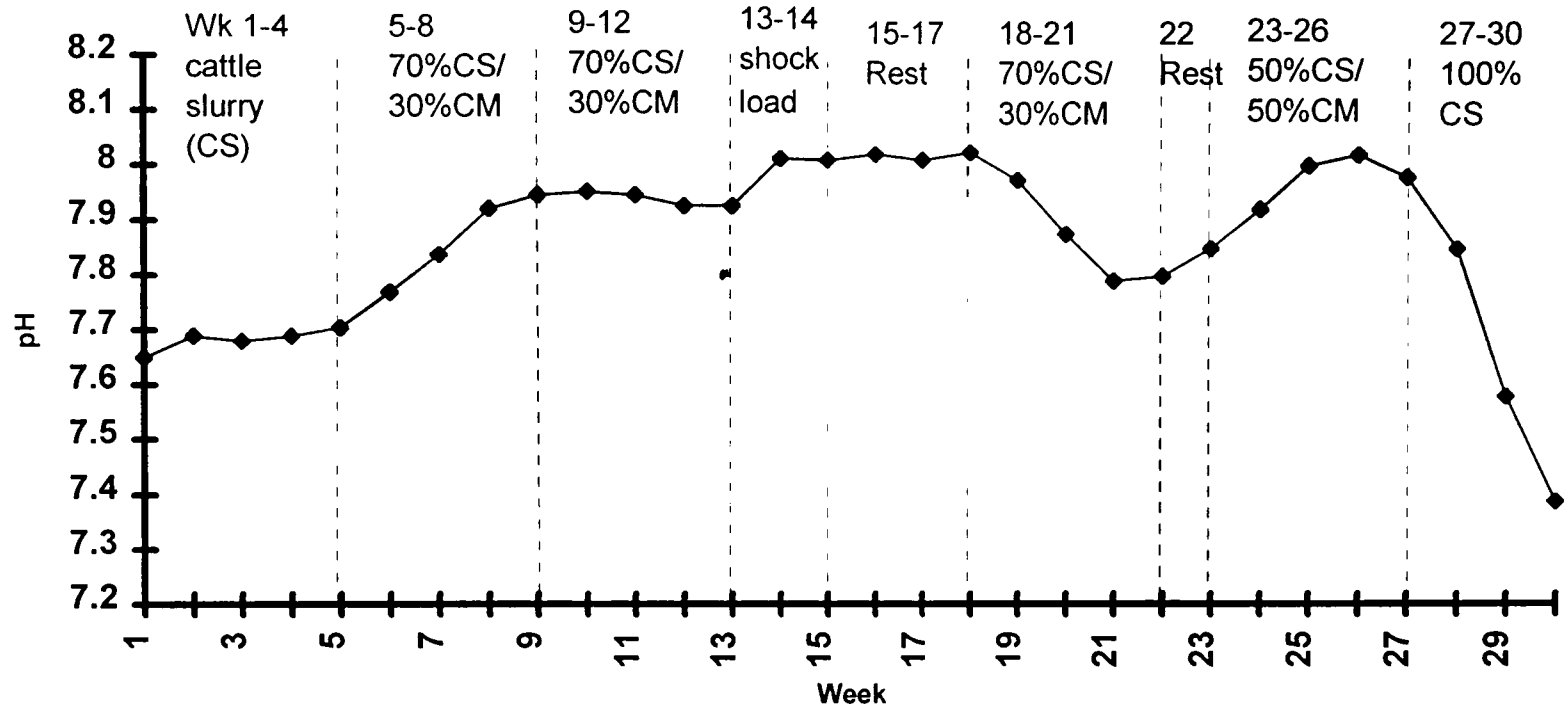


Figure 4.18 Digester 2: mean pH for each week.

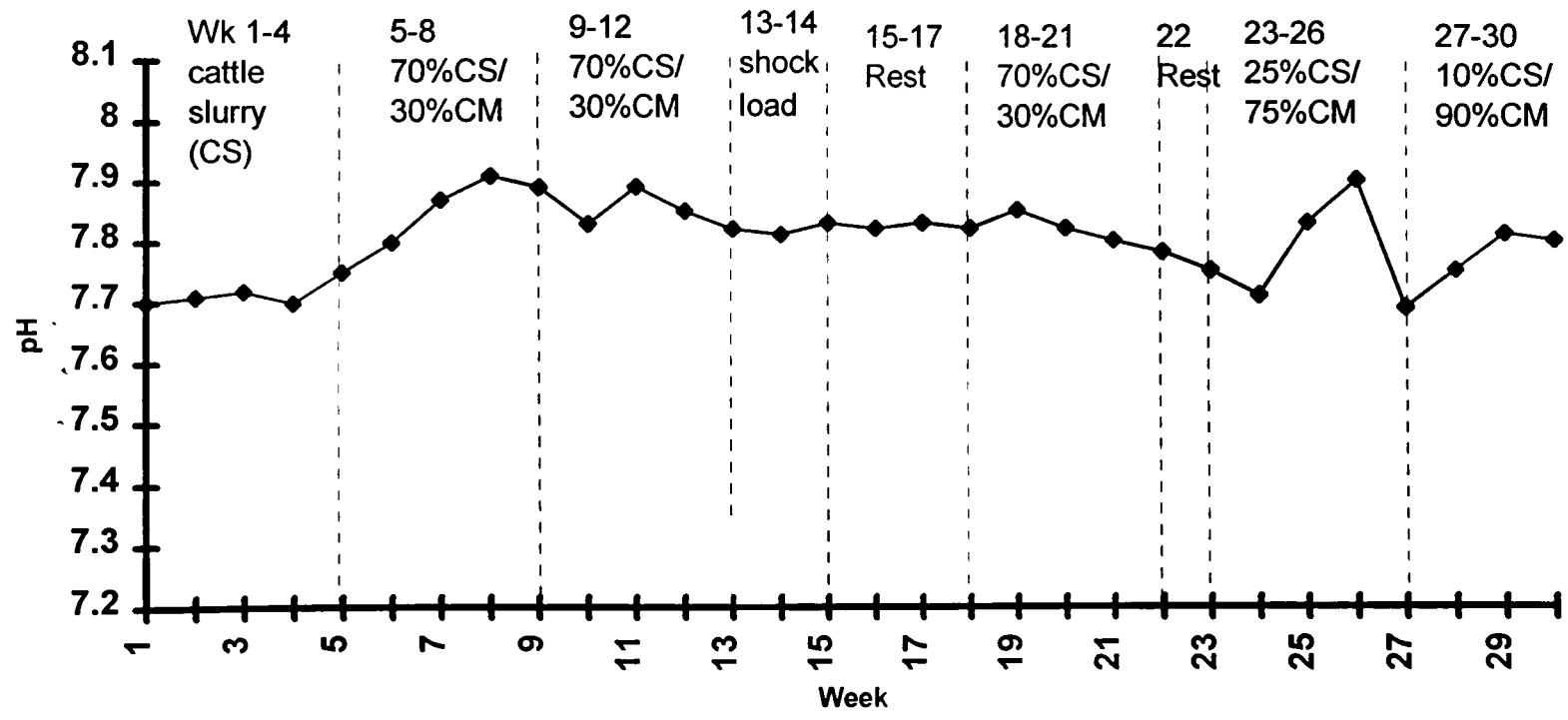


Figure 4.19 Digester 1: mean daily alkalinity for each week.

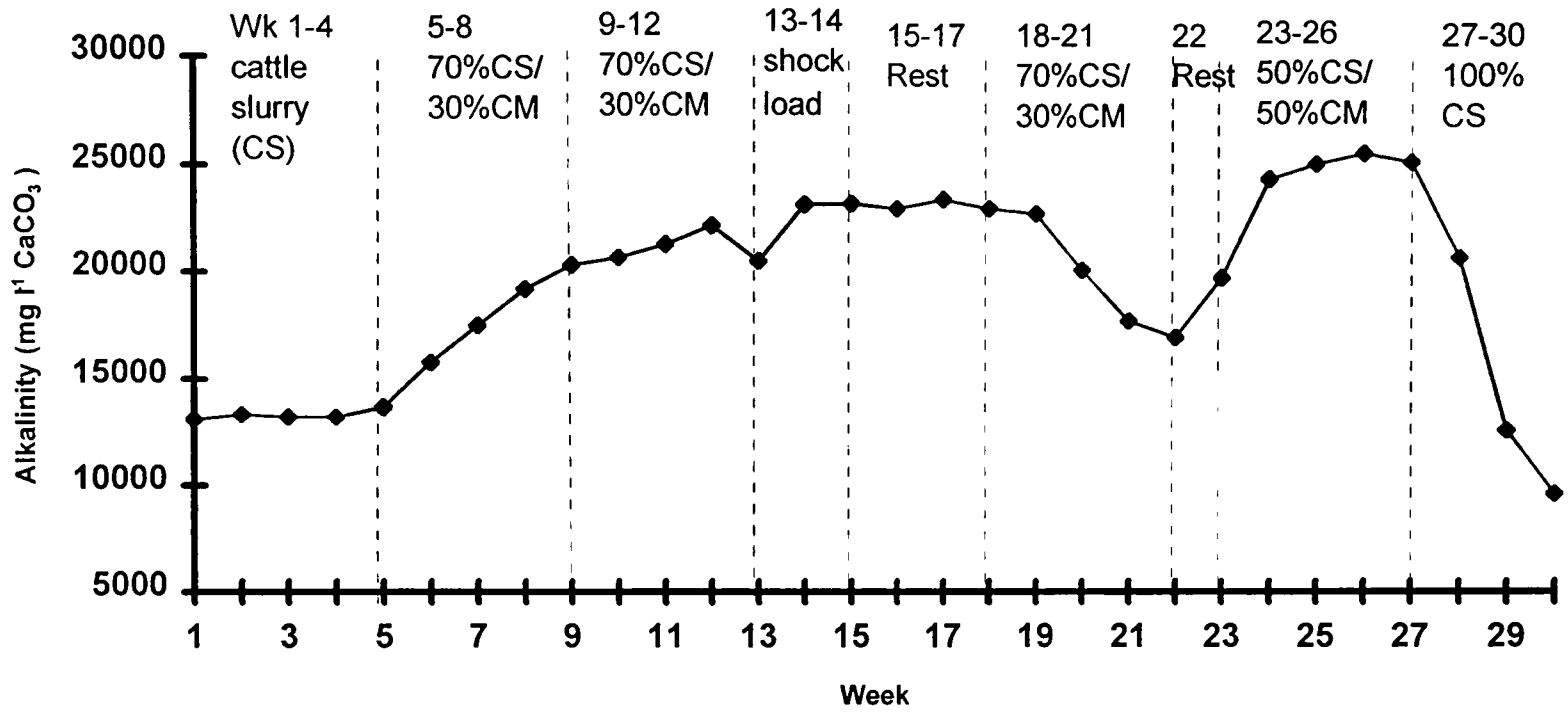


Figure 4.20 Digester 2: mean daily alkalinity for each week

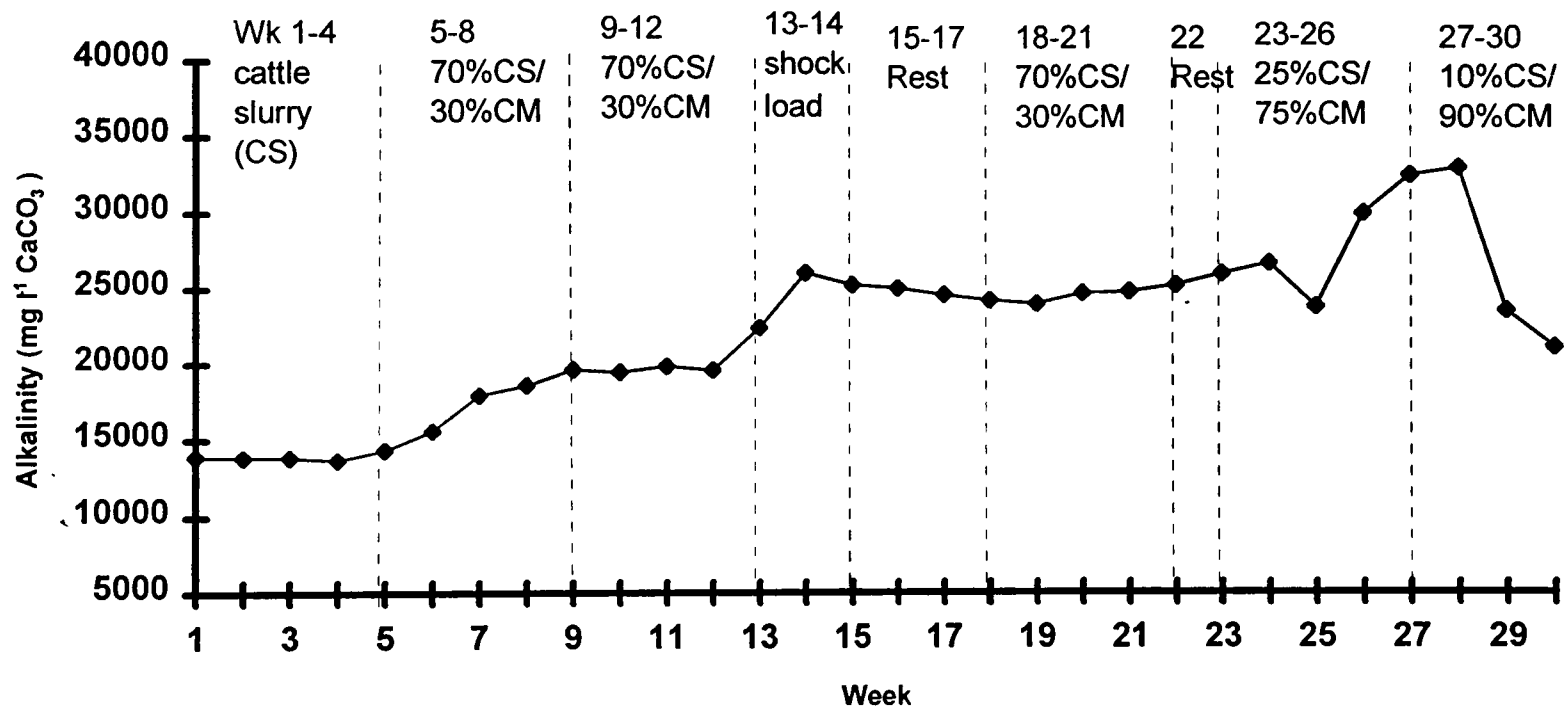


Figure 4.21 Digester 1 mean effluent VFA for each week.

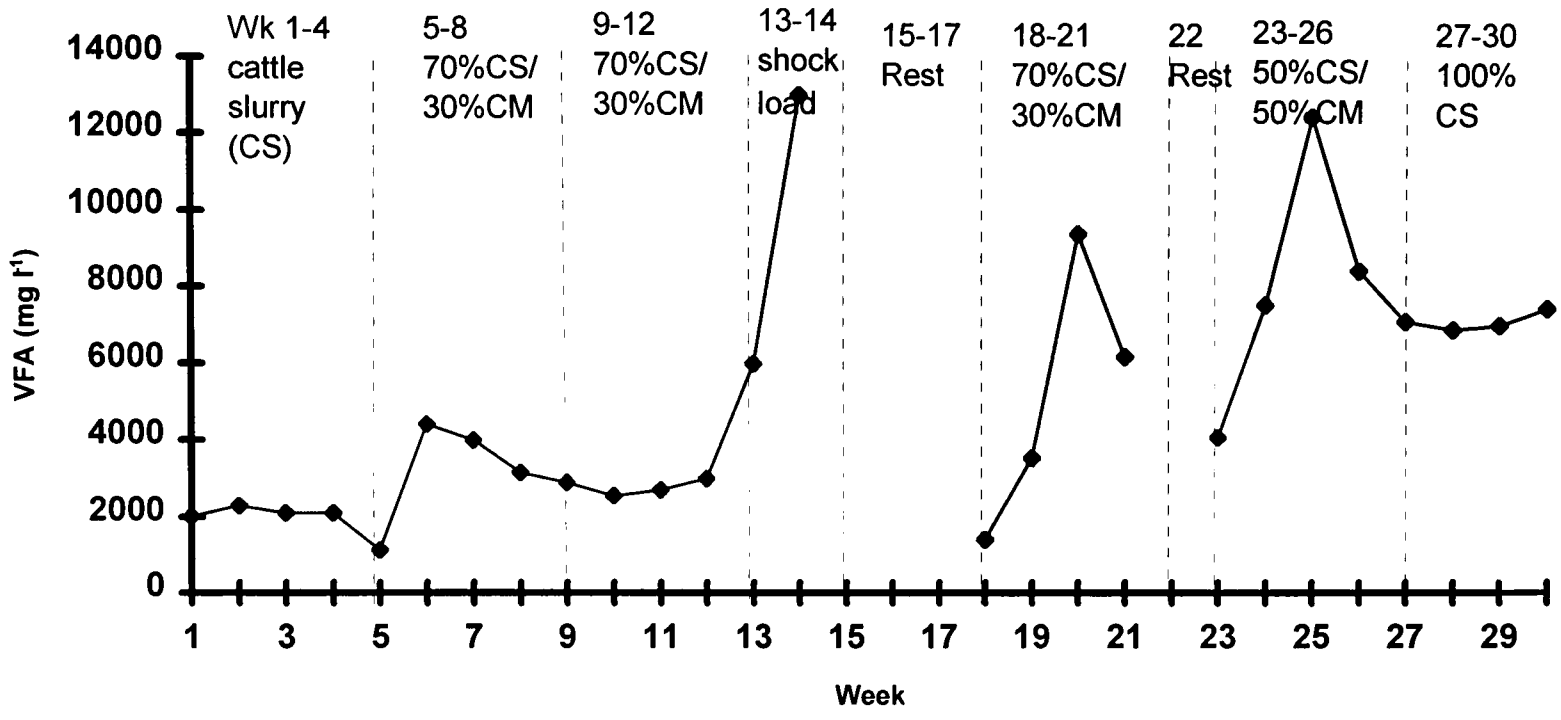


Figure 4.22 Digester 2 mean effluent VFA for each week.

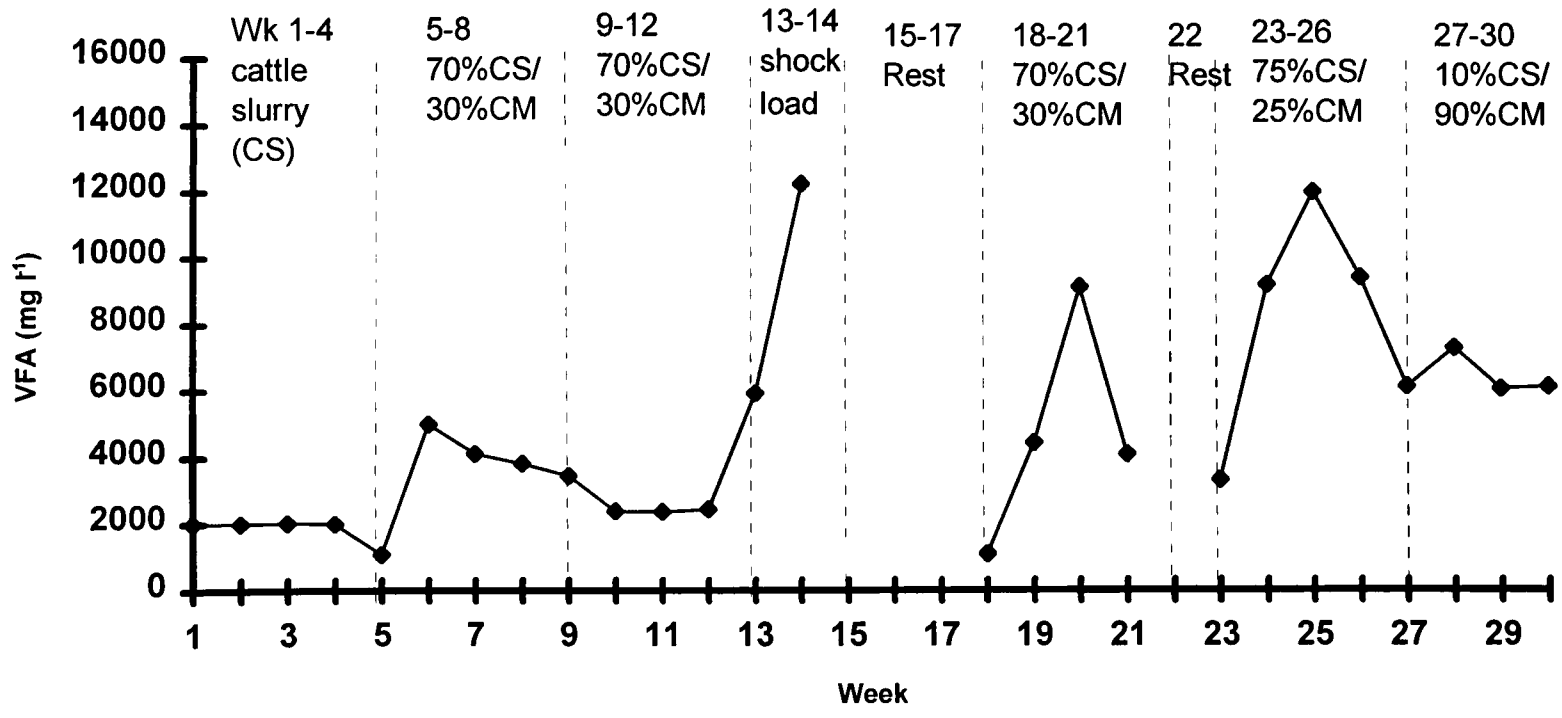


Figure 4.21(a) Digester 1: mean effluent VFA:Total Alkalinity for each week.

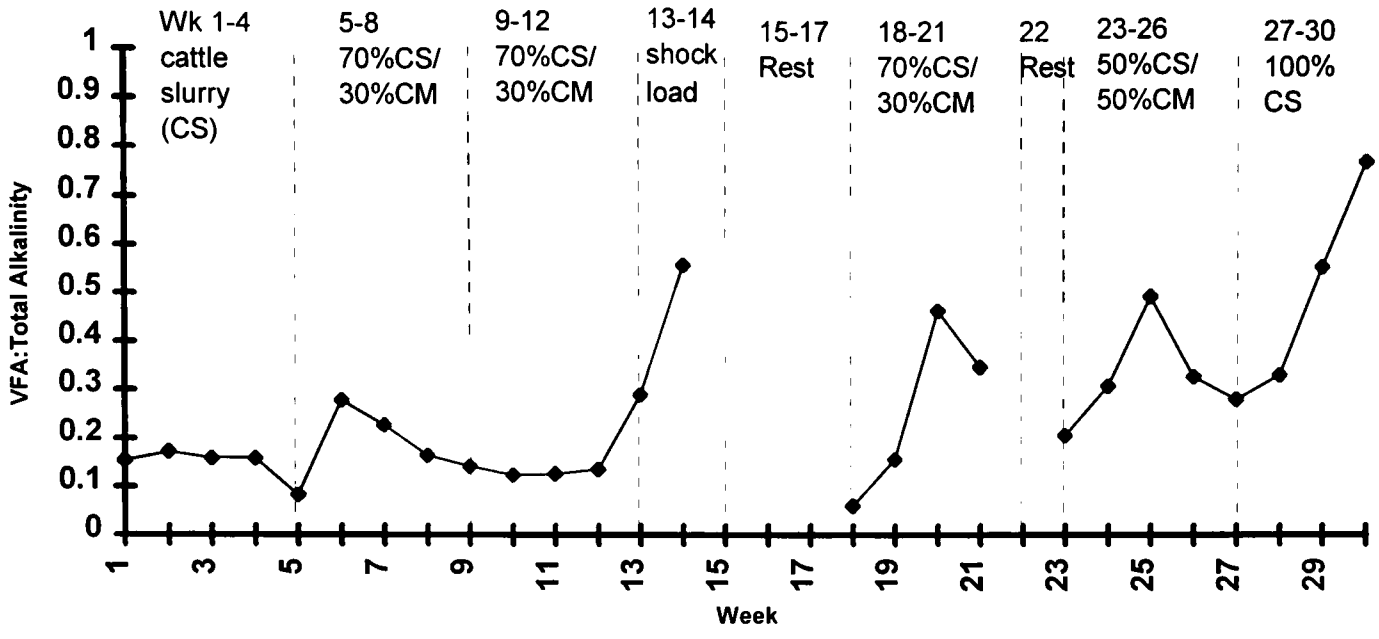


Figure 22a Digester 2: mean effluent VFA:Total Alkalinity for each week.

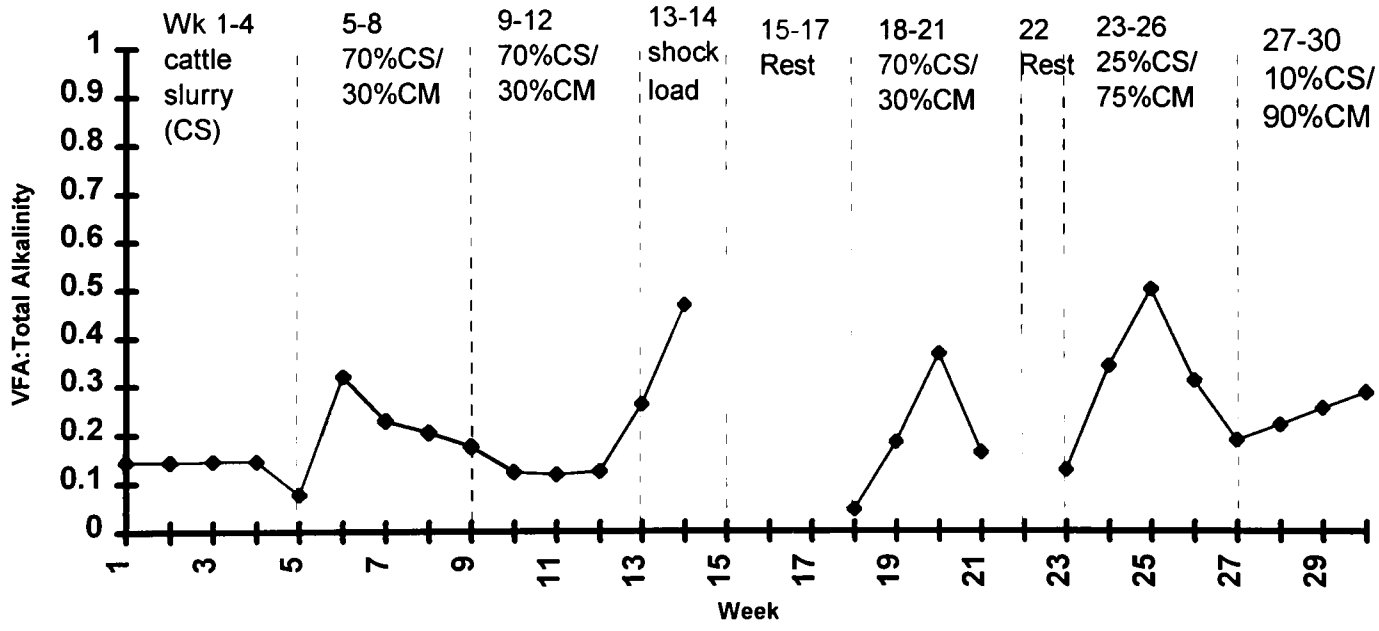


Figure 4.23 Digester 1: mean daily methane production for each week.

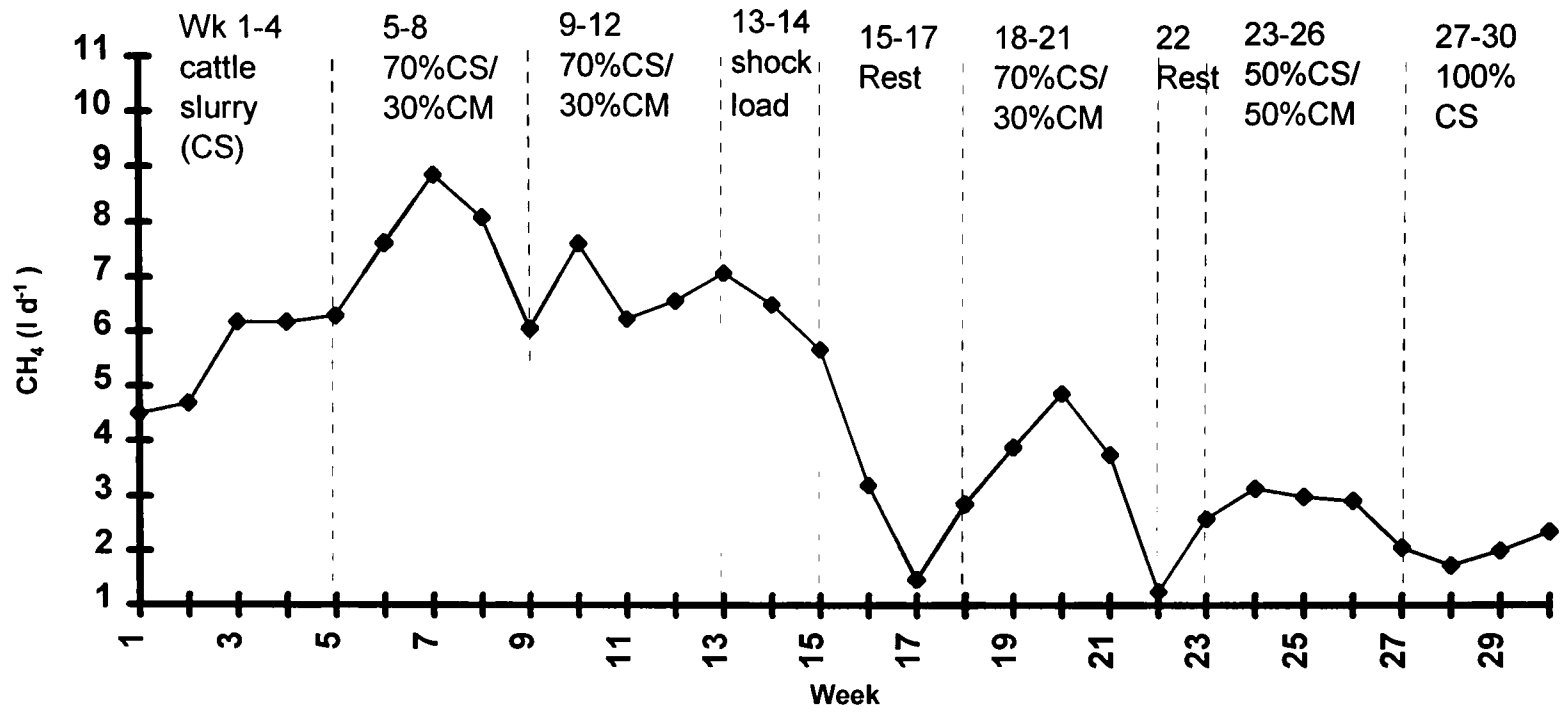


Figure 4.24 Digester 2: mean daily methane production for each week.

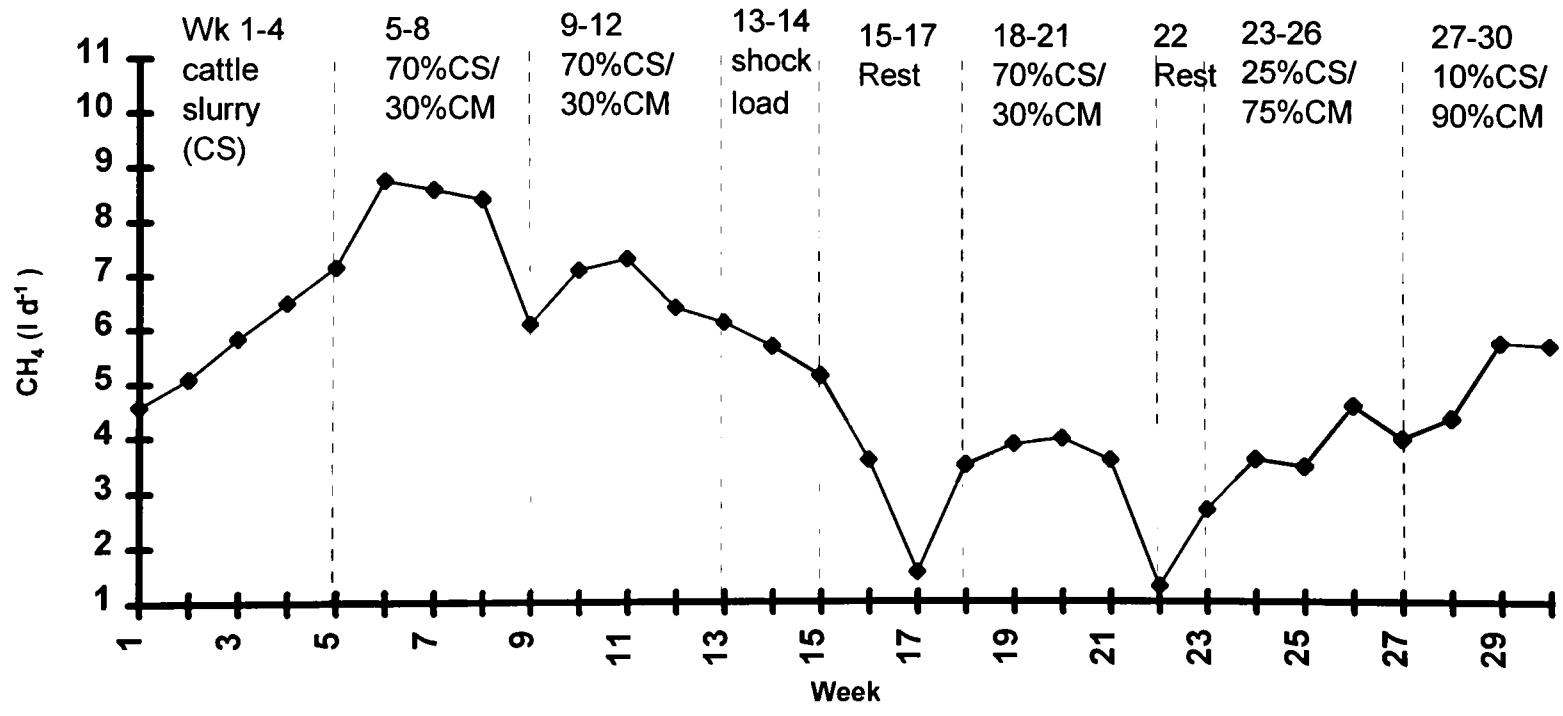


Figure 4.25 Digester 1: mean biogas methane concentration for each week.

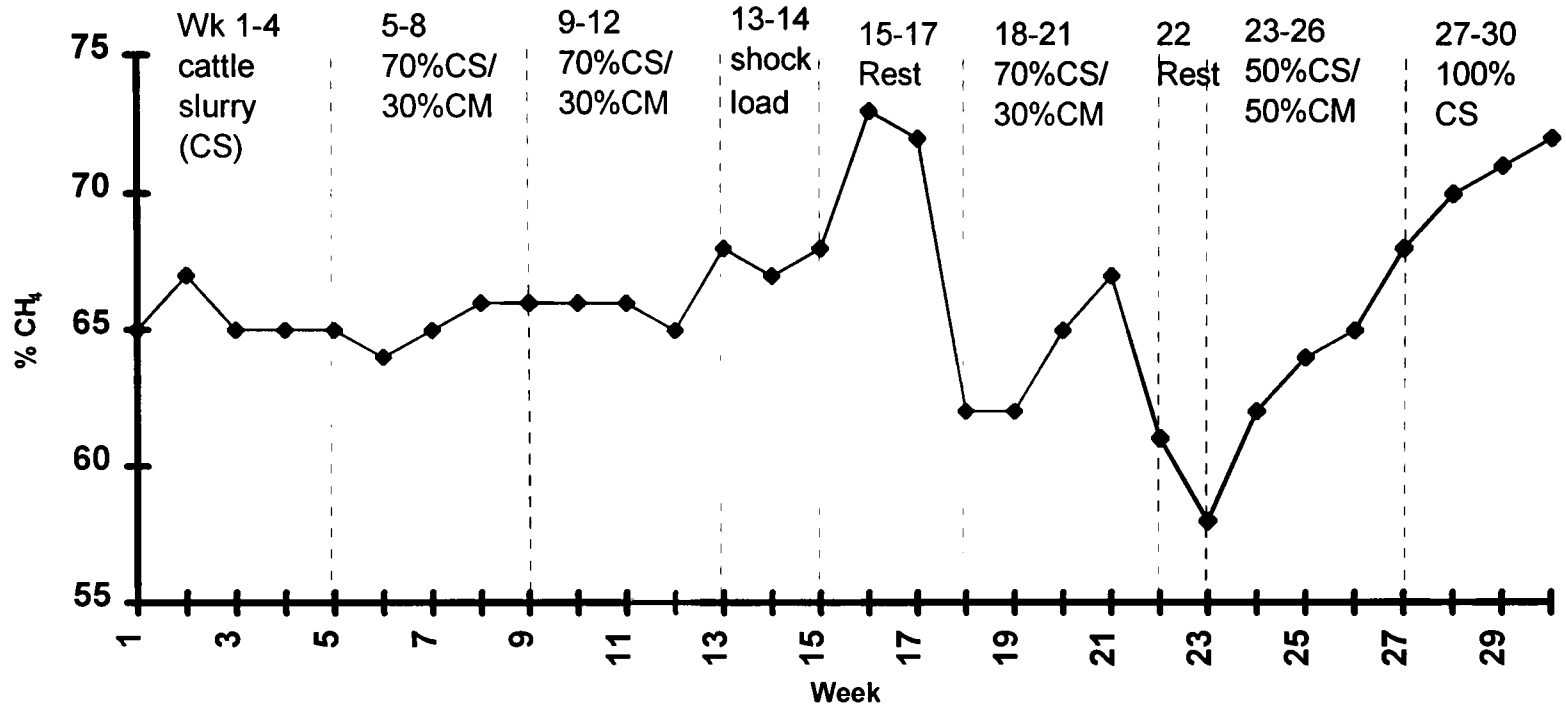


Figure 4.26 Digester 2: mean biogas methane concentration for each week.

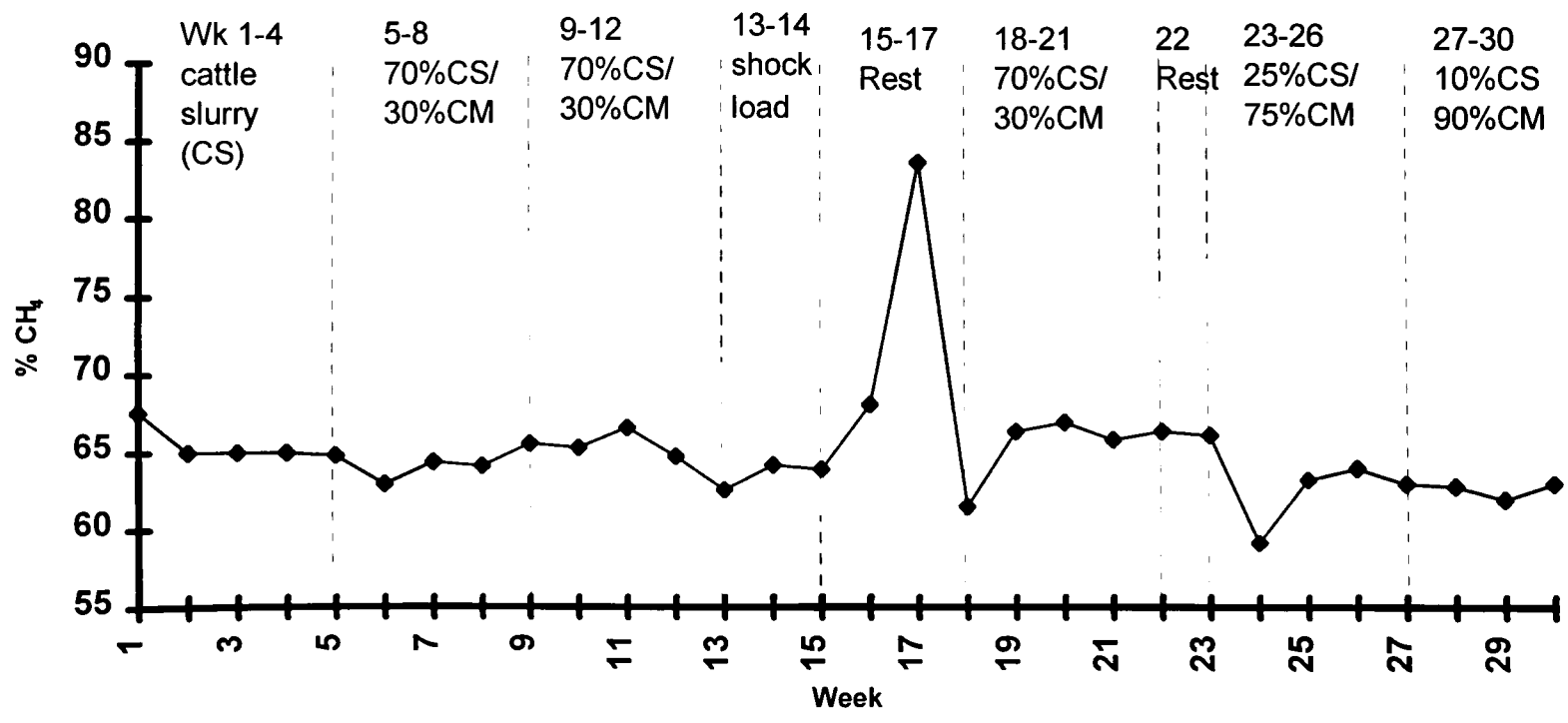


Figure 4.27 Digester 1: mean ammonia concentration for each week.

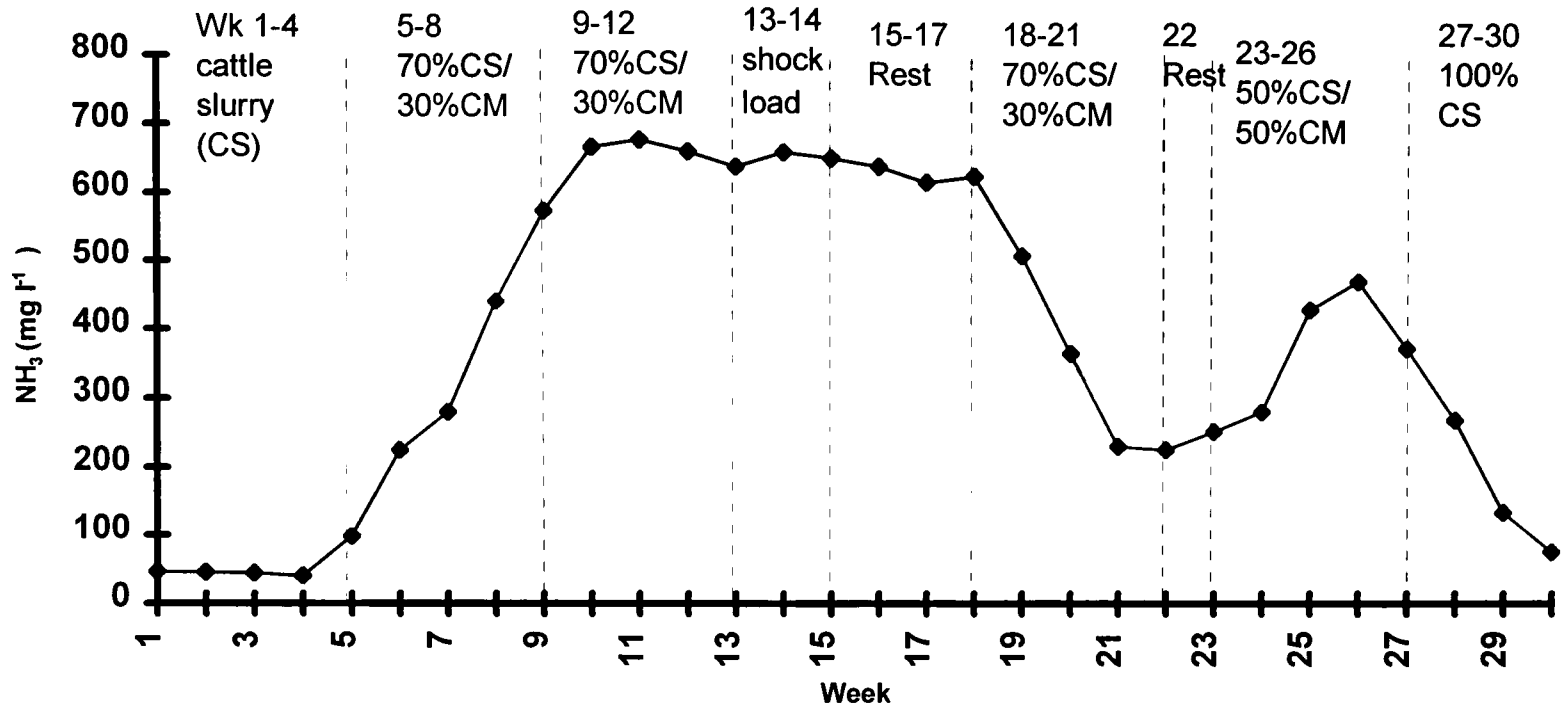


Figure 4.28 Digester1: mean ammonium concentration for each week.

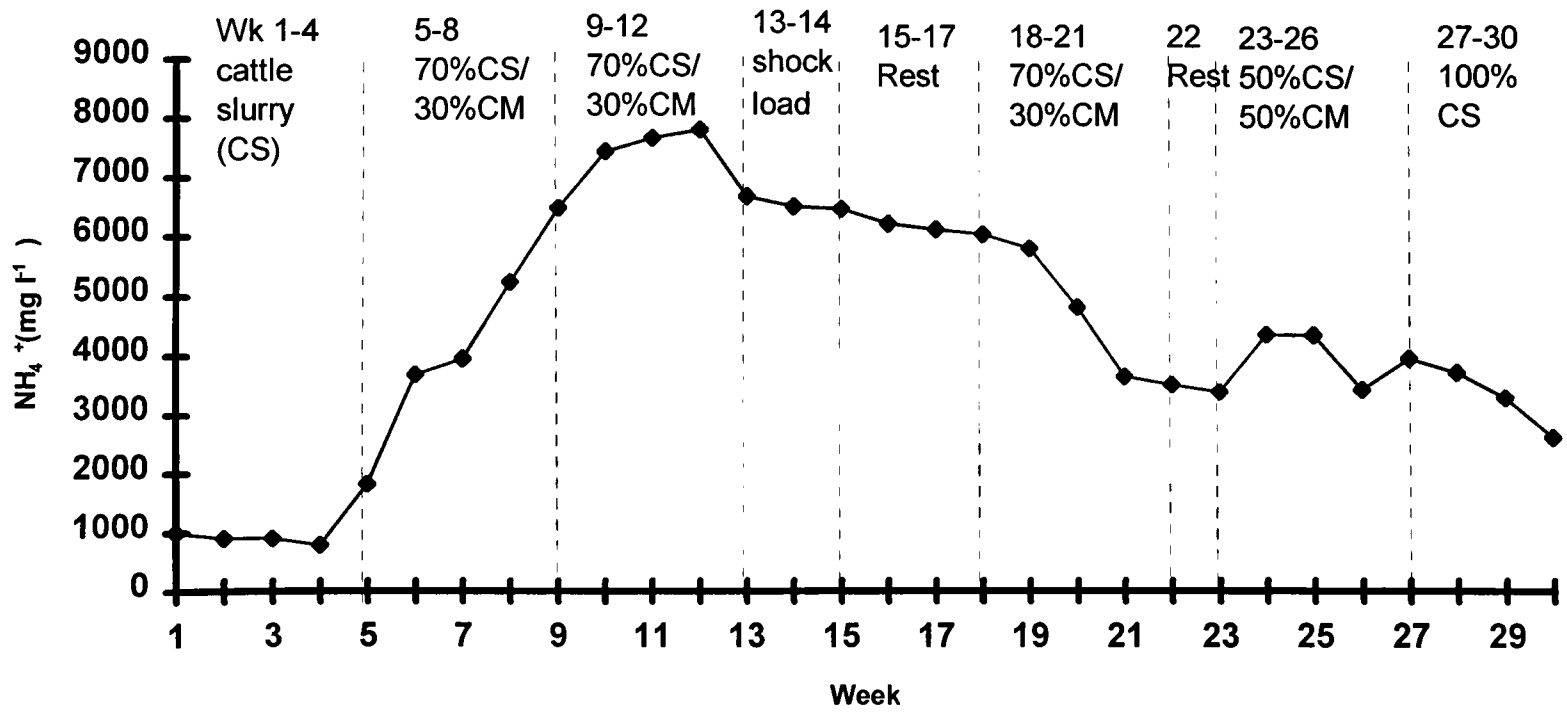


Figure 4.29 Digester 2: Mean ammonia concentration for each week.

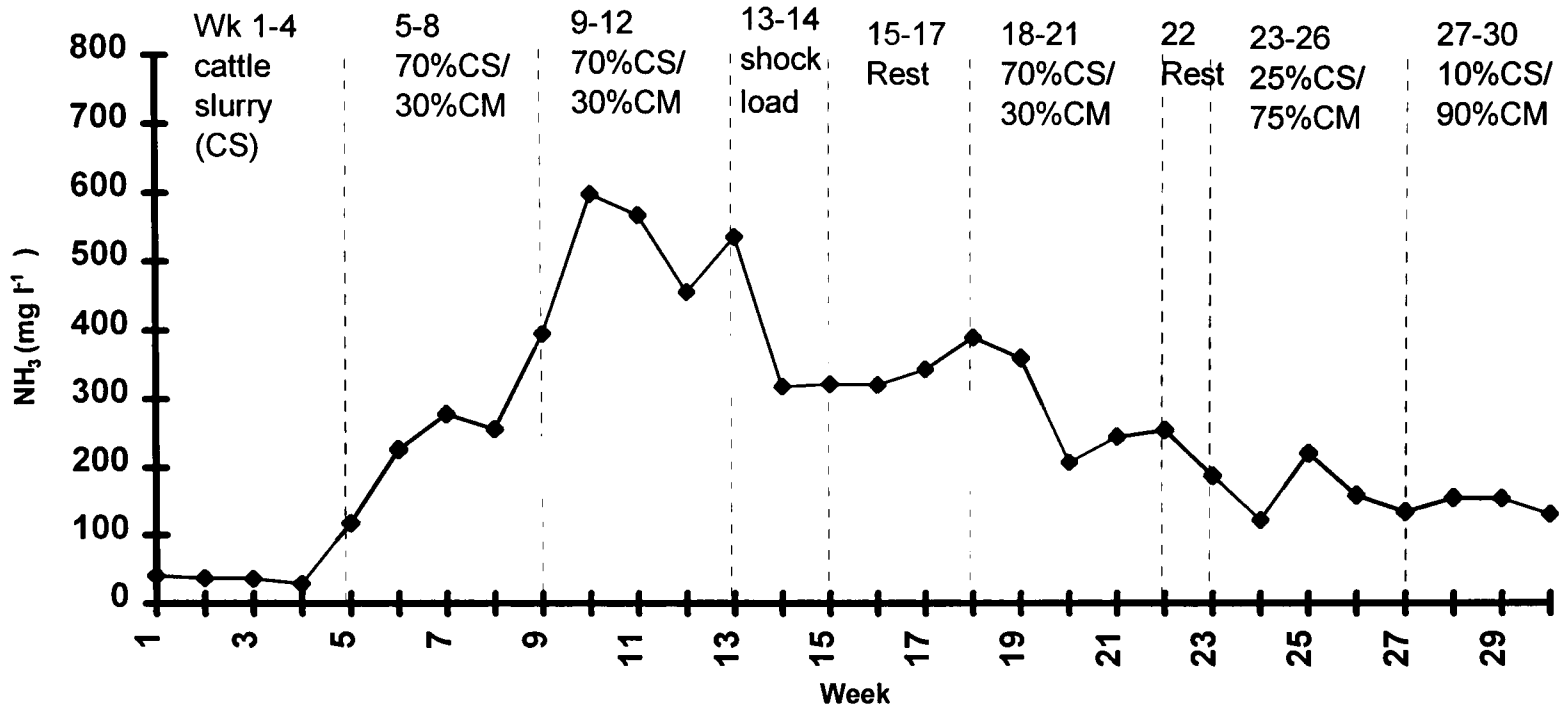


Figure 4.30 Digester 2: Mean ammonium concentration for each week.

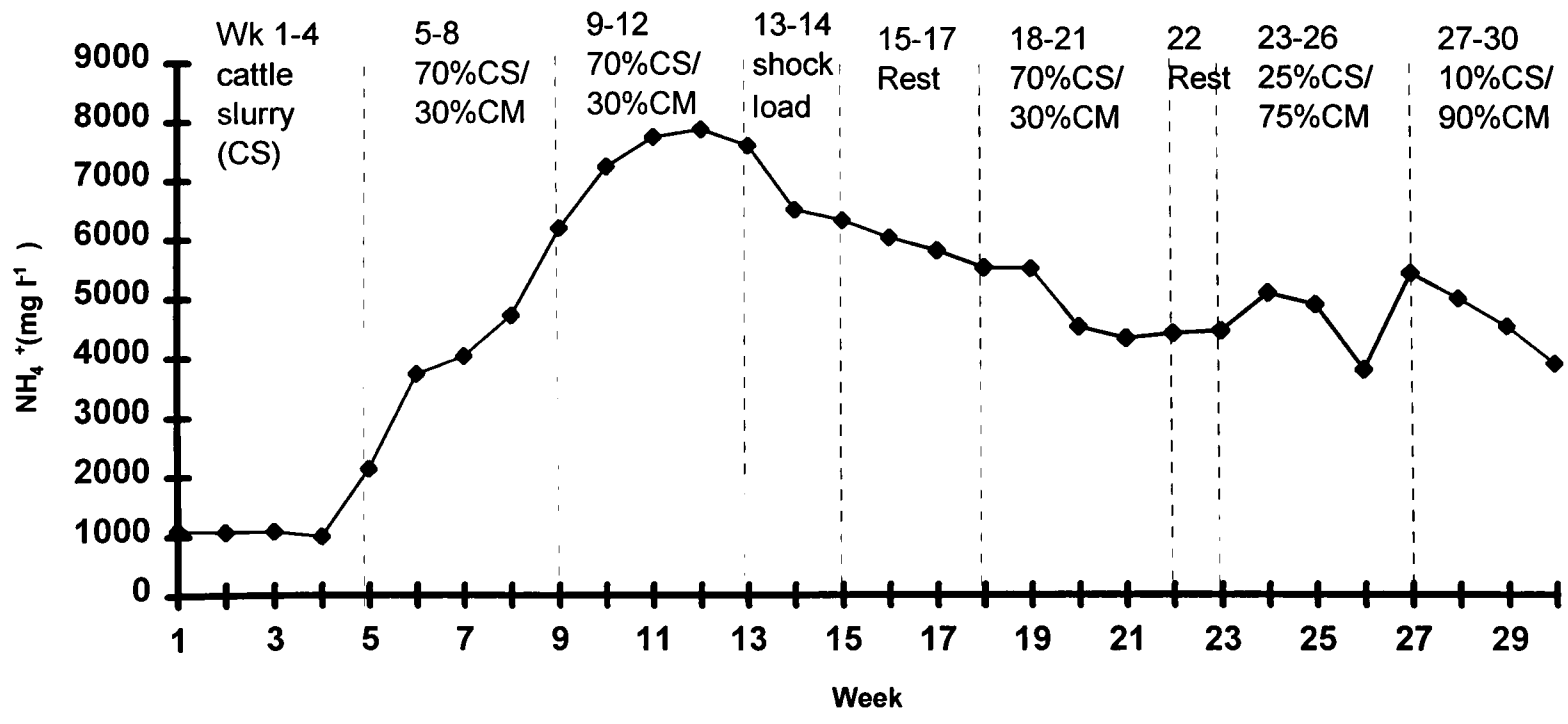


Figure 4.31 Inhibition of growth rate of acetoclastic methanogens (after Poggi-Varaldo *et al.*, 1991).

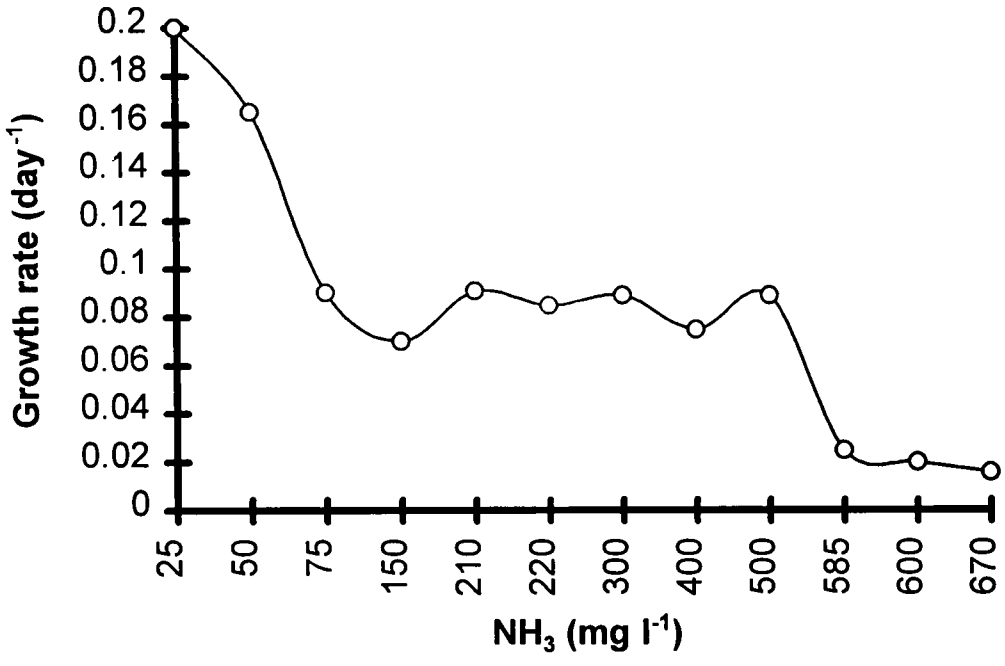


Figure 4.32 Digester 1: mean redox potential for each week. The redox values found in anaerobic systems are negative, for ease of graphical representation, all redox values have been multiplied by minus 1, so 480 on the figures actually corresponds to -480 mV, and so on.

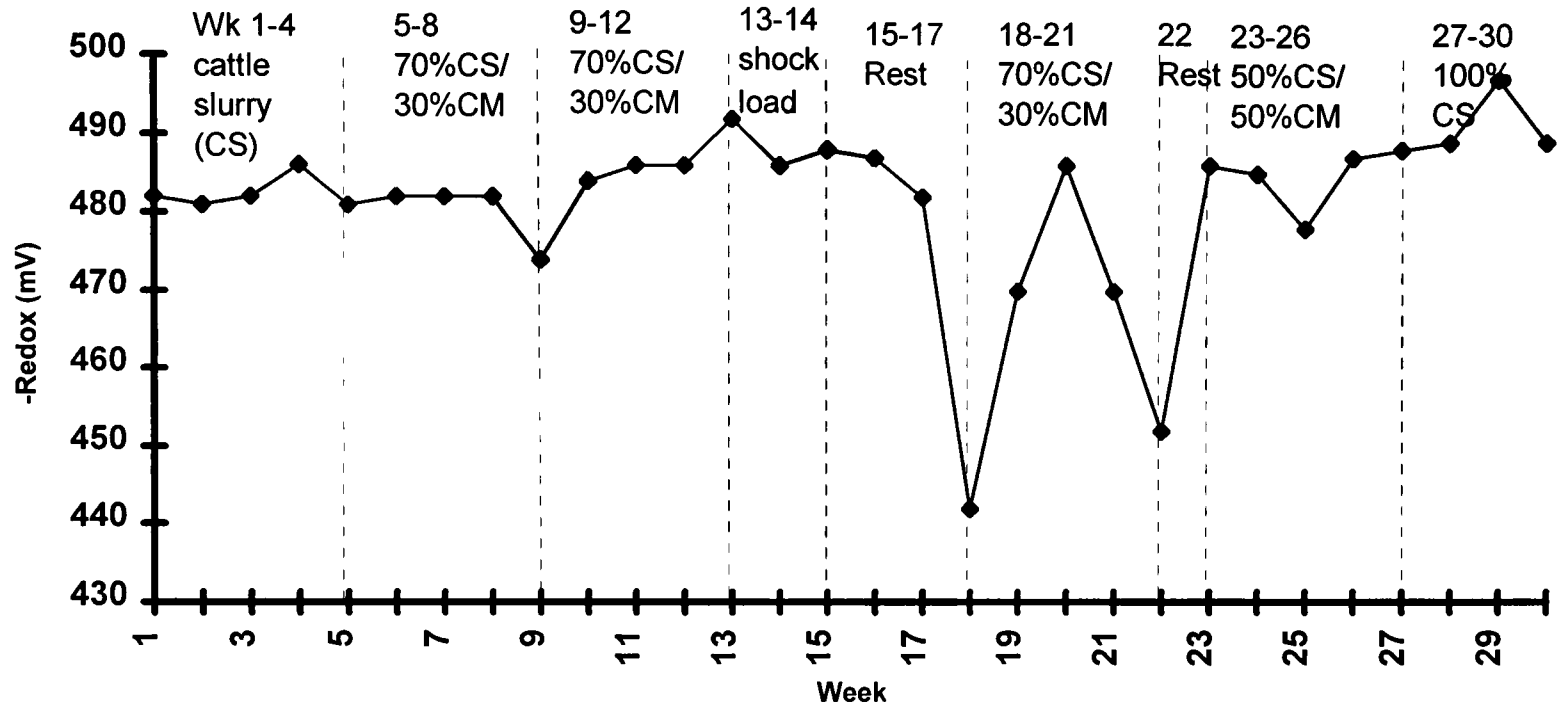


Figure 4.33 Digester 2: mean redox potential for each week.

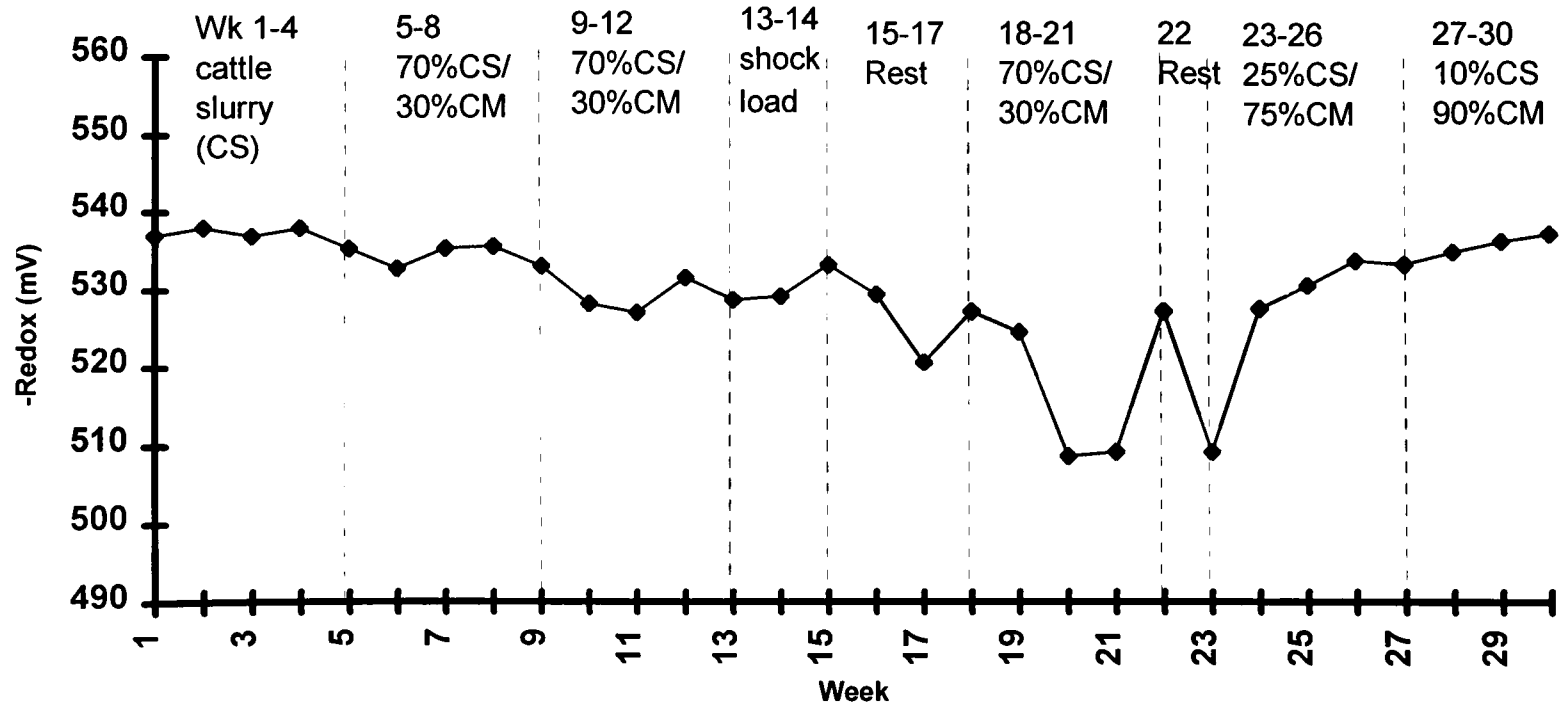


Figure 4.34 Digester 1: mean biogas hydrogen sulphide concentration for each week.

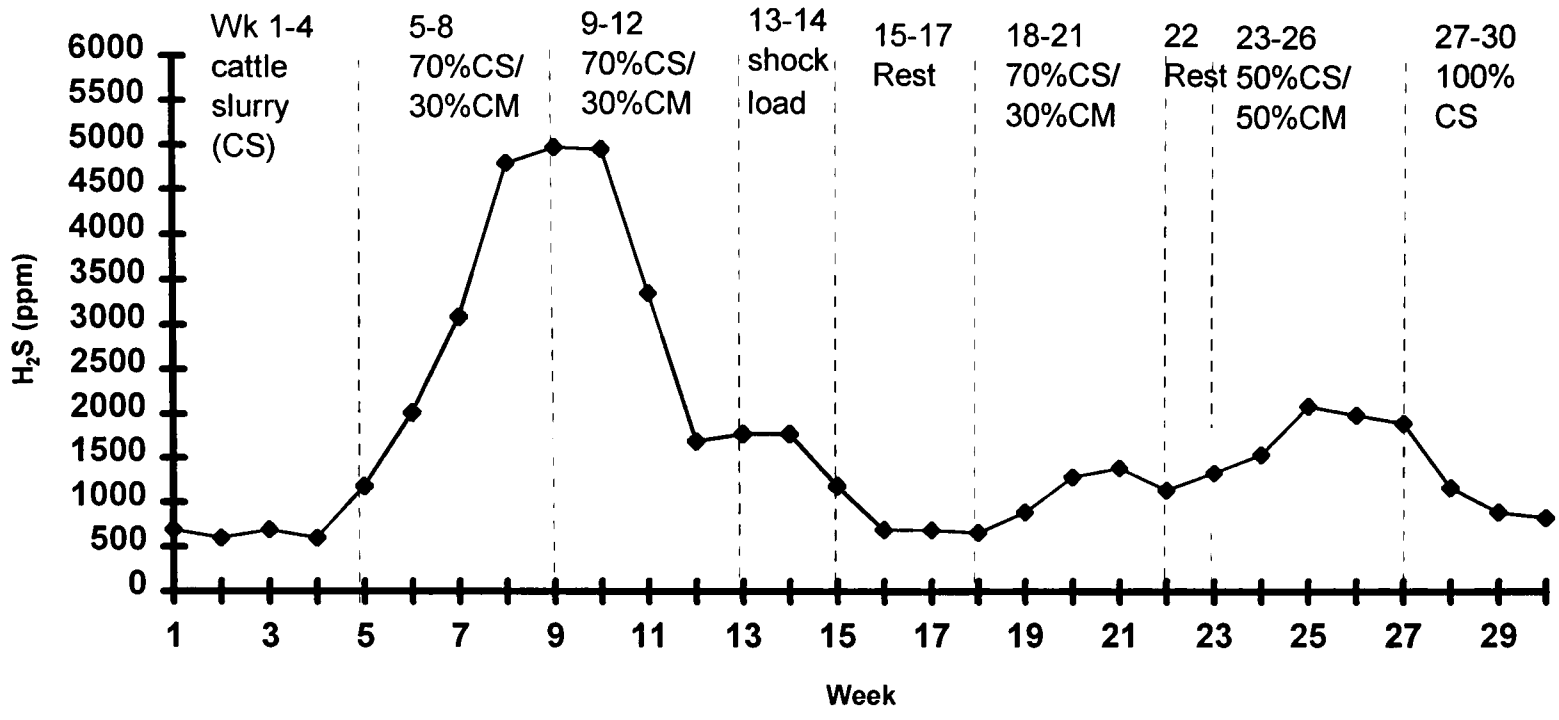
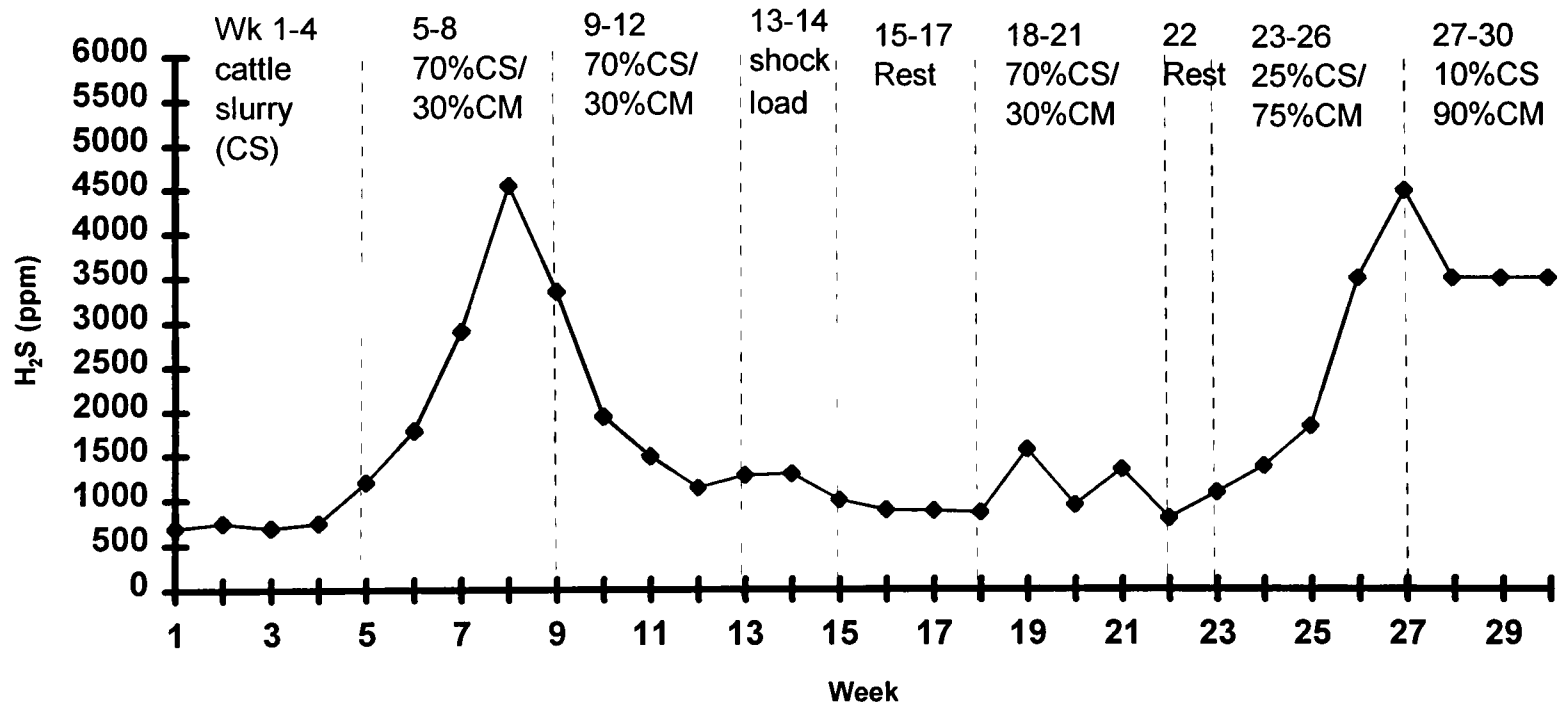


Figure 4.35 Digester 2: mean biogas hydrogen sulphide concentration for each week.



Chapter 5

Batch co-digestion of agricultural and industrial wastes - trial 2

5.1 Selection of wastes for co-digestion

The wastes chosen as co-digestates for the second waste selection trials were silage effluent, sludge from a brewery effluent treatment plant, fish offal, dissolved air floatation (DAF) sludge from a dairy wastewater treatment plant, and fruit and vegetable waste (FVW). All these wastes are difficult to dispose of by conventional means, or the traditional disposal routes are being restricted.

5.1.1 Silage effluent

Silage effluent, produced by the anaerobic fermentation of grass to make cattle feed which can be stored over the winter months, is the cause of a number of pollution incidents in rivers every year (The Environment Agency, 1995). Typically, this waste is produced during the summer months (the silage making season) and is usually disposed of by spreading on land. Occasionally, careless spreading near water-

courses, or failure of effluent collection systems, can cause silage effluent to enter water courses, causing severe oxygen depletion. Typical silage effluent COD values can be up to 1,000,000 mg l^{-1} (Hobson and Robertson, 1977). The effluent used in the current work, was quite dilute, due to recent rainfall, and had a COD of only 4,000 mg l^{-1}, however this effluent would still have substantial polluting potential if it were to enter a watercourse. The silage effluent used in this work was obtained from Southlands Farms Ltd, Birmingham.

5.1.2 Brewery sludge

Whitbread brewery at Magor produces an average of 5,500 m^3 d^{-1} of aqueous organic effluent, about 1% of which (54.7 m^3 d^{-1}) is converted to a biological sludge by the brewery's dedicated effluent treatment plant (Bechtel, 1988). The effluent treatment plant consists of screens and a settling tank, followed by high rate trickling filters. The sludge is currently disposed of to farm-land using a tractor and bowser system. However this disposal route is becoming severely restricted due to the run-off pollution of some local water-courses and the high local annual rainfall which makes access to local agricultural land difficult for much of the year (Walsh, 1997).

5.1.3 Fish offal

The fish offal used in this work was obtained from a small freshwater rainbow trout farm, typically producing 50 kg of fish for the hotel and restaurant market every week. Typical offal production rates are around 10 kg wk^{-1}. The offal consists of fish heads, tails and viscera. No information is available concerning the amount of fish offal produced by fresh water fish farms in the UK, but anecdotal evidence suggests that

substantial quantities are produced every year (Bull, 1997). Current disposal routes are land spreading or landfill, both of which are severely restricted due to associated odour problems. Much larger quantities of fish offal are produced by the processing of saltwater species. Again no published data is available, but anecdotal evidence from the west coast of Scotland suggests that there is an urgent requirement to find a disposal alternative to land spreading or landfill. (Cousins, 1994).

5.1.4 DAF sludge

Dissolved air floatation (DAF) units are commonly used for removing fine particulate matter from effluent streams (Metcalf and Eddy, 1991). The system works by dissolving air in a portion of the effluent stream under several atmospheres of pressure, then re-mixing this portion with the main effluent stream and then releasing the effluent through a nozzle into a tank at atmospheric pressure. The sudden pressure change causes the air to form small bubbles which attach to particles within the effluent and carry them to the surface where the particles form a scum, which is then skimmed off. Flocculating agents such as ferric sulphate are often used to maximise solids removal and pH adjustment using sodium hydroxide and sulphuric acid is often necessary to provide the optimum environment for flocculation to take place.

This particular sludge came from the wastewater plant of a yoghurt manufacturing facility. The DAF unit was used to reduce the effluent solids load before activated sludge treatment. Typical effluent flows to the DAF plant were around 200 m^3 d^{-1}, and typical sludge production was around 3 $m^3 d^{-1}$.

5.1.5 Fruit and vegetable waste (FVW)

It has been estimated that as much as 75 % of the dry weight of household MSW (Municipal Solid Waste) is biodegradable, and that significant proportion of this material is fruit and vegetable waste (Nyns and Gendebien, 1994). A proposed European Community (EC) directive on landfill will require that all degradable wastes to be disposed of to landfill must be treated to reduce the total organic carbon (TOC) content to at least 10% (The ENDS Report, 1996*c*). Methods under consideration for reducing the organic fraction of MSW include 2 phase anaerobic digestion (The ENDS Report, 1997*d*), incineration, composting (The ENDS Report 1997*e*) and landfills operated as flushing bioreactors (The ENDS Report, 1996*c*) 2 phase anaerobic digestion and composting would require separation of the MSW into organic and non-organic fractions. There are a number of separators on the market for effecting this, the most efficient being the DANO revolving drum process (Andrews, 1996). However even this process cannot remove small particles of glass and metal, and hence the composted or digested solids produced would not be suitable for spreading on agricultural land or use as a soil conditioner. Source separation of the waste is a much more efficient way of ensuring that the waste contains only organic food waste. This would involve households having a number of dustbins, with one dedicated to organic food waste. The waste used in this work was collected from the kitchen of a student residence over a period of weeks.

5.2 Analysis of wastes

The wastes chosen for co-digestion were analysed for total, fixed and volatile solids, NH_4^+ and pH, see Table 5.1. Additional analysis was also carried out on the DAF

sludge by another laboratory, and the different types of wastes which made up the kitchen waste were recorded as they were produced. As all the wastes, except for silage effluent contained significant amounts of particulate material, it was decided to use volatile solids analysis as a more reliable method of estimating organic loading than COD.

The silage effluent, as has been noted earlier, was quite dilute, and not a very good example of this type of effluent.

The brewery sludge, as it consisted largely of biomass from the trickling filters, may, like many sludges which consist largely of biomass, be difficult to digest anaerobically (Parkin and Owen, 1986). The organic matter content of the sludge, as a percentage of sludge total solids, was found to be the same as cattle slurry. The sludge was the only waste, apart from cattle slurry, that had significant quantities of NH_4^+ present.

The fish offal was found to consist largely of volatile matter, having a VS/TS ratio of 0.98 and to be very high in total solids, see Table 5.1. Hence tightly controlled addition of this material to a working digester would be necessary to ensure digester imbalance did not occur.

The DAF sludge was found to have a pH of 5.5, due to the optimum pH range of the DAF unit being 5 - 6. The organic content of the material was found to be slightly higher (VS/TS ratio of 0.76) than the brewery sludge or cattle slurry. Further analysis

by an external laboratory (ADAS, Wolverhampton)revealed that the sludge consisted of about 32% milk fat.

Each item of of the fruit and vegetable waste was weighed before being placed in the bin, and so a profile of the waste composition, based on wet weight, was constructed, see Table 5.2.

Table 5.1 Composition of wastes selected for batch co-digestion trials - part 2

Waste type	pH	NH_4^+ mg/l	Total solids %	Fixed solids %	Volatile solids %	VS/TS
Cattle slurry	8.1	1040 0	10.0	3.0	7.0	0.7
Silage effluent	7.1	< 10	0.5	0.2	0.3	0.6
DAF sludge	5.5	< 10	5.0	1.2	3.8	0.76
Fish offal	6.7	< 10	49	0.9	48.1	0.98
FVW	4.2	< 10	16.7	1.1	15.6	0.93
Brewery sludge	8.0	1000	4.1	1.2	2.9	0.70

Table 5.2 Composition of FVW collected for co-digestion trials

Waste fraction	% (wet weight/weight)
Banana skins	7.5
Orange skins	13.2
Grapefruit skins	7.5
Brussels sprouts	17
Rice	3.9
Kiwi fruit skins	13.2
Grapefruit pieces	7.5
Potato skins	24.5
Broccoli stalks	5.7

5.3 Waste selection trials

12 one litre flasks fitted with baffles were used as digesters for these trials. See Section 2.10.1 for a full description of the apparatus. 700 g of waste mixture was placed in each flask, as specified in Table 5.3. The flasks were maintained at 35^0 C in an incubator, and mixed by hand once a day. Each flask was analysed for pH, NH_4^+, total, fixed and volatile solids before being placed in the incubator, see Tables 5.4 and 5.5. The experiment lasted for 11 weeks. Biogas production was recorded weekly and biogas analysis for methane and carbon dioxide was also carried out weekly. After 11 weeks biogas production had become negligible and the experiment was terminated. Samples from each flask were again analysed for pH, NH_4^+, total, fixed and volatile solids, see Tables 5.4 and 5.5. A full description of the analytical methods can be found in Chapter 2, Sections 2.1 - 2.5.

The volatile solids (VS) loading figures in Table 5.2 were used to compare the different waste loadings on the flasks and were calculated in the following manner, using the flasks receiving additions of brewery sludge as an example. The total weight of material present in each flask was 700 g, this was approximately equal to 0.7 l of material and was taken to be the working volume of the flask. 140 g (20% by weight) of this material was brewery sludge, which had a volatile solids content of 2.9%. 140g of brewery sludge, contained 4.06g of VS or 0.0046 kg of VS. The working volume of the flask was 0.0007 m^3 so the VS loading, as brewery sludge, was 0.0046 kg VS added to 0.0007 m^3, which was 6.6 kg VS m^{-3}. The VS loadings for the other flasks were calculated in a similar manner.

To initially test the suitability of a waste for co-digestion it was decided to limit the fraction of waste present to 20% of the volume of the flask, or a volatile solids loading about equal to the loading the cattle slurry controls received. The loading on the flasks receiving silage effluent, DAF sludge and brewery sludge was therefore lower than the cattle slurry control, and due to difficulties in obtaining homogenous samples, the loadings of FVW and fish offal were slightly higher than the control.

Table 5.3 Contents of each flask and VS loadings

Flask	70% of flask contents (by weight)	20% of flask contents (by weight)	10% of flask contents (by weight)	VS loading kg VS m^{-3}
1	Cattle slurry	Cattle slurry	Digester inoculum	14
2	Cattle slurry	Cattle slurry	Digester inoculum	14
3	Cattle slurry	Silage effluent	Digester inoculum	1.7
4	Cattle slurry	Silage effluent	Digester inoculum	1.7
5	Cattle slurry	Brewery sludge	Digester inoculum	6.6
6	Cattle slurry	Brewery sludge	Digester inoculum	6.6
7	Cattle slurry	**3.6% Fish offal**	Digester inoculum	17.1
8	Cattle slurry	**3.6% Fish offal**	Digester inoculum	17.1
9	Cattle slurry	DAF sludge	Digester inoculum	7.6
10	Cattle slurry	DAF sludge	Digester inoculum	7.6
11	Cattle slurry	**11% FVW**	Digester inoculum	17.1
12	Cattle slurry	**11% FVW**	Digester inoculum	17.1

Table 5.4 % total solids and % volatile solids of flask contents and % reduction in both parameters over the course of the experiment

Flask	%TS initial	%TS final	%TS reduct.	%VS initial	%VS final	%VS reduct.
1	10.1	7.6	24.8	7.1	4.9	30.9
2	10	6.7	33	6.4	4.4	31.2
3	8	5.8	27.5	5.5	3.7	32.7
4	7.9	5.4	31.6	5.4	3.4	37
5	8.8	6.7	23.9	6.1	4.3	29.5
6	9	5.8	35.5	6.3	3.9	38.1
7	12.3	7.4	39.8	9.4	4.9	47.9
8	12.3	7.4	39.8	9.2	4.9	46.7
9	8.7	5.2	40	6.2	3.4	45.2
10	8.8	5.5	37.5	6.2	3.4	45.2
11	11.2	6.5	42	8.5	4.2	50.6
12	11.1	6.3	43	8.4	3.9	53.6

Table 5.5 pH, NH_4^+, and NH_3 at the beginning and end of the experiment

Flask	pH initial	pH final	NH_4^+ (mg l^{-1}) initial	NH_4^+ (mg l^{-1}) final	NH_3 (mg l^{-1}) initial	NH_3 (mg l^{-1}) final
1	8.1	8	1037	1848	36	100
2	8.1	8	1076	1943	37	105
3	8.1	7.9	1089	1693	37	91
4	8.1	7.9	1102	1820	38	99
5	8.1	8	1150	1702	40	114
6	8	8	1099	2011	39	135
7	7.7	8	1179	2157	41	145
8	7.7	8	993	1762	35	118
9	7.8	7.9	1038	2021	45	109
10	7.8	7.9	1032	1891	45	102
11	7.7	7.9	1070	2110	37	114
12	7.6	7.9	1105	2087	31	113

Figure 5.1 Weekly methane production: digesters 3 and 4 (silage effluent/cattle slurry) compared to cattle slurry control.

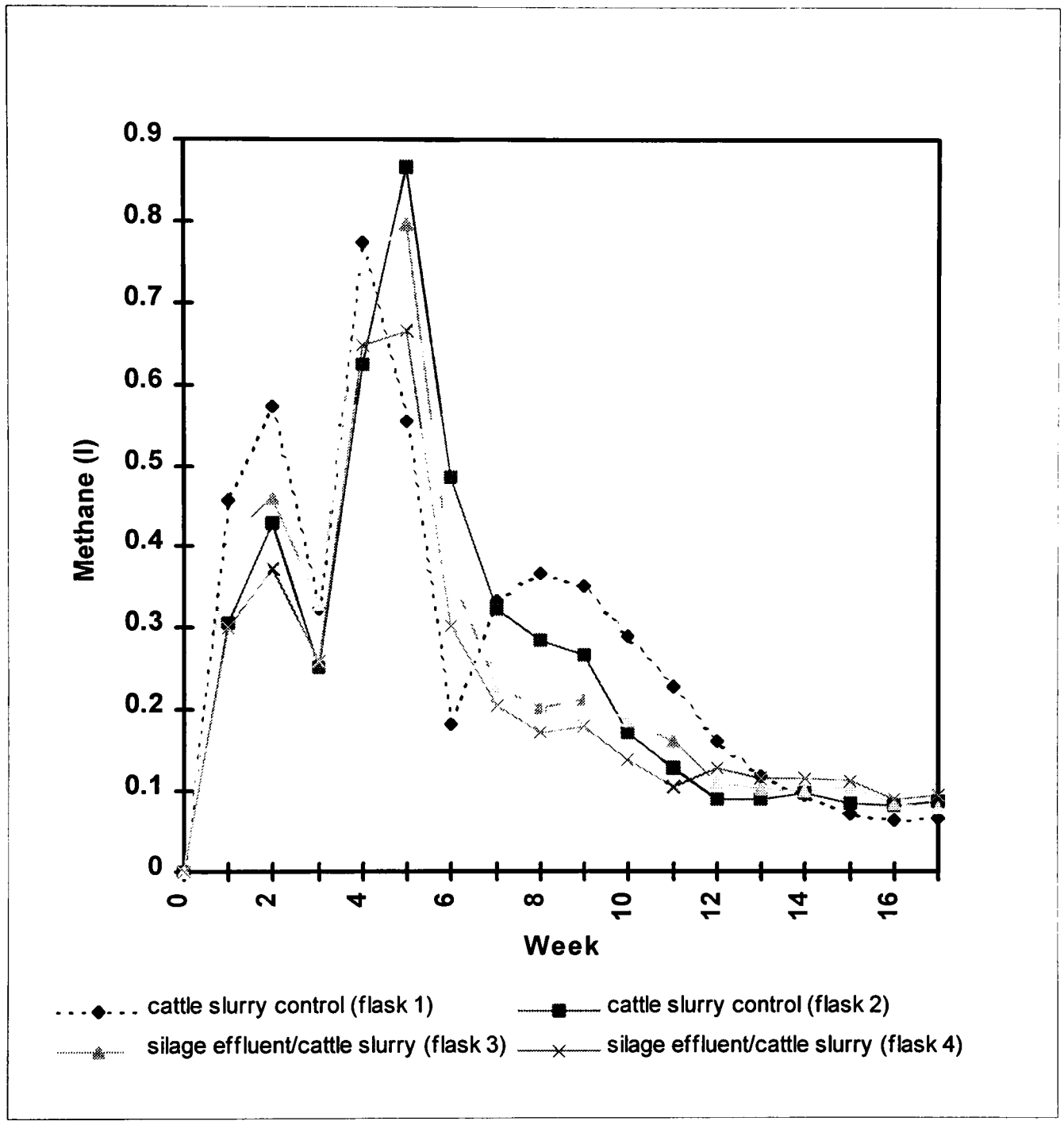


Figure 5.2 Weekly methane production: digesters 5 and 6 (brewery sludge/cattle slurry) compared to cattle slurry control.

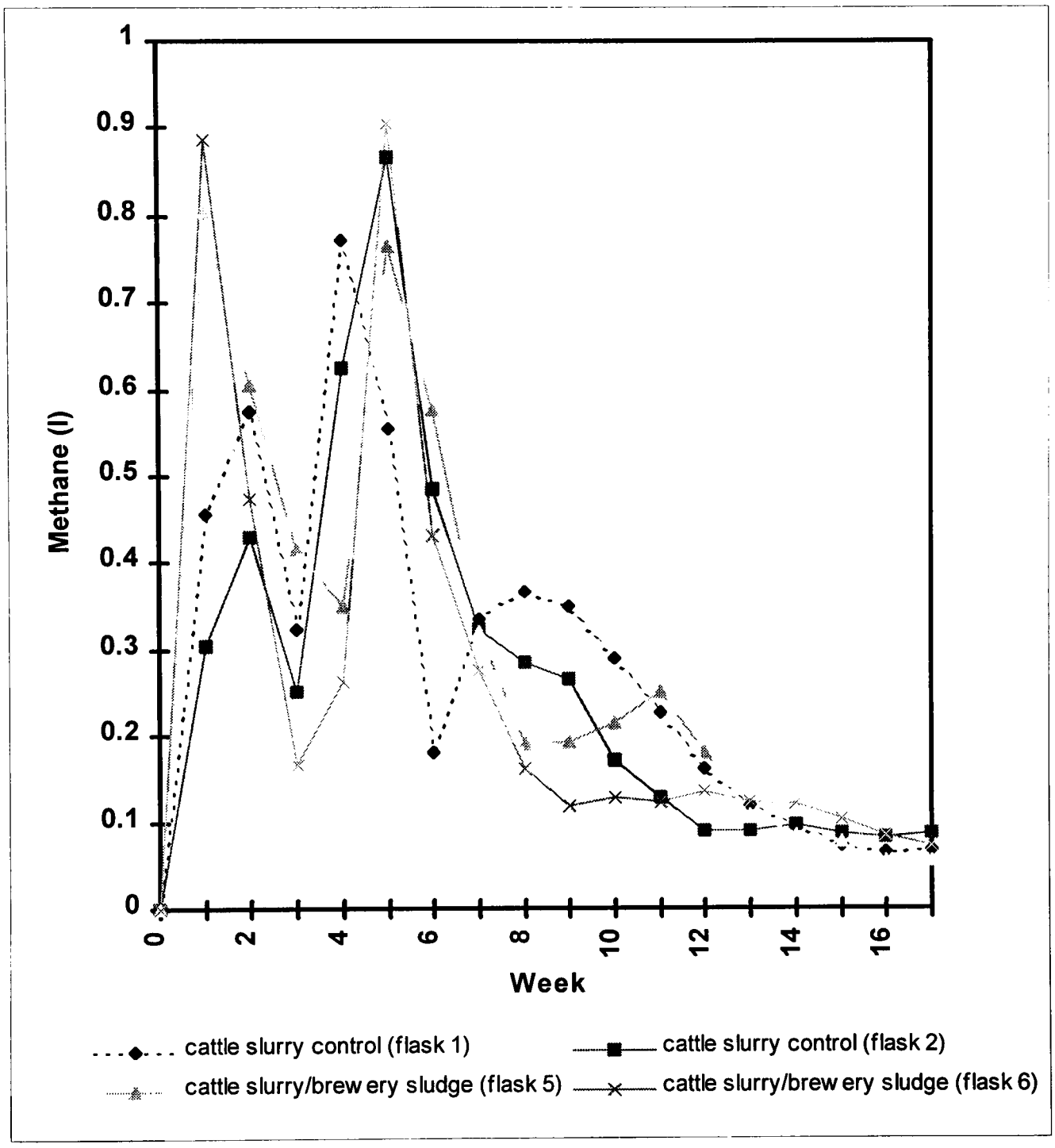


Figure 5.3 Weekly methane production: digesters 7 and 8 (fish offal/cattle slurry) compared to cattle slurry control.

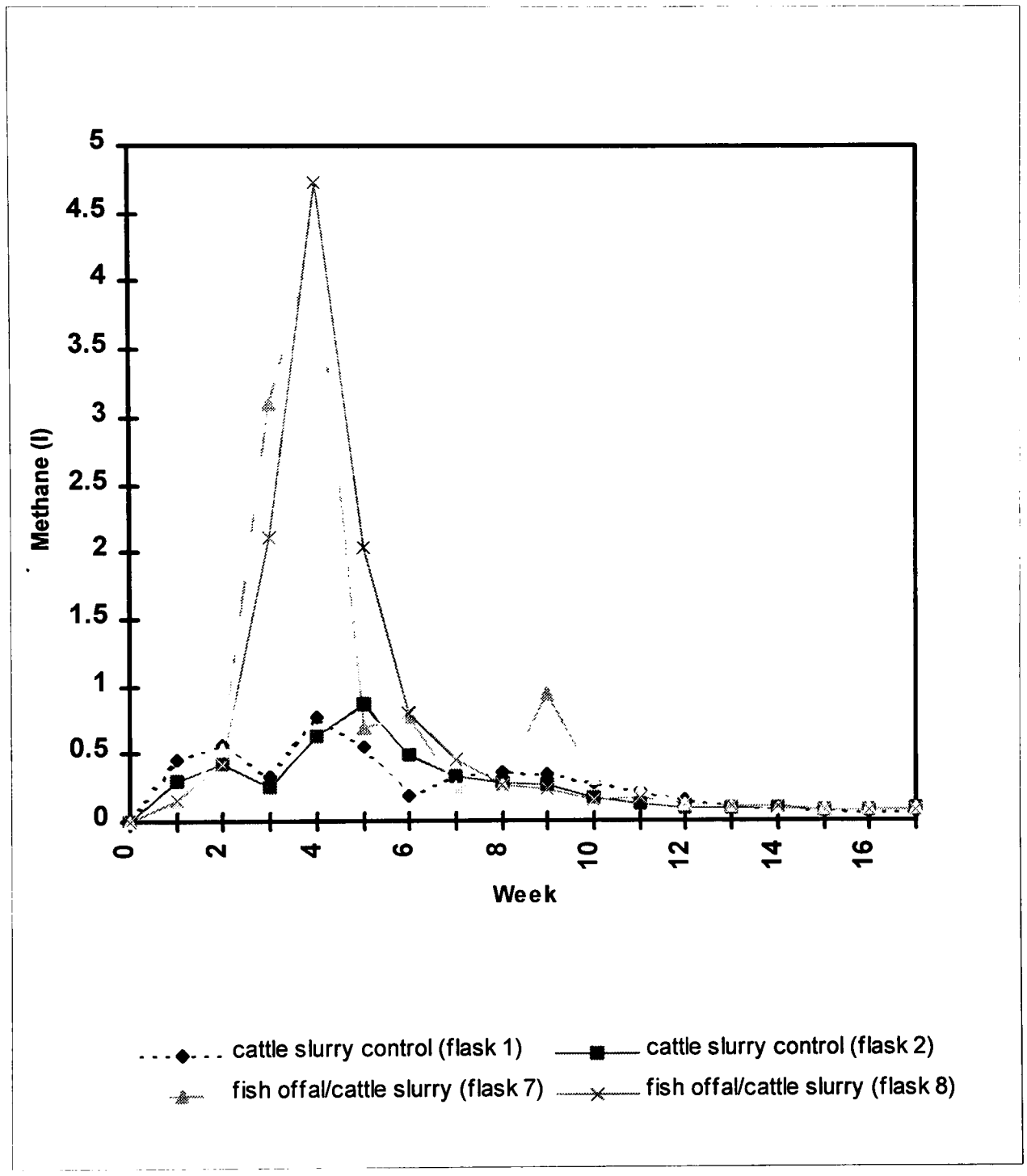


Figure 5.4 Weekly methane production: digesters 9 and 10 (DAF sludge/cattle slurry) compared to cattle slurry control.

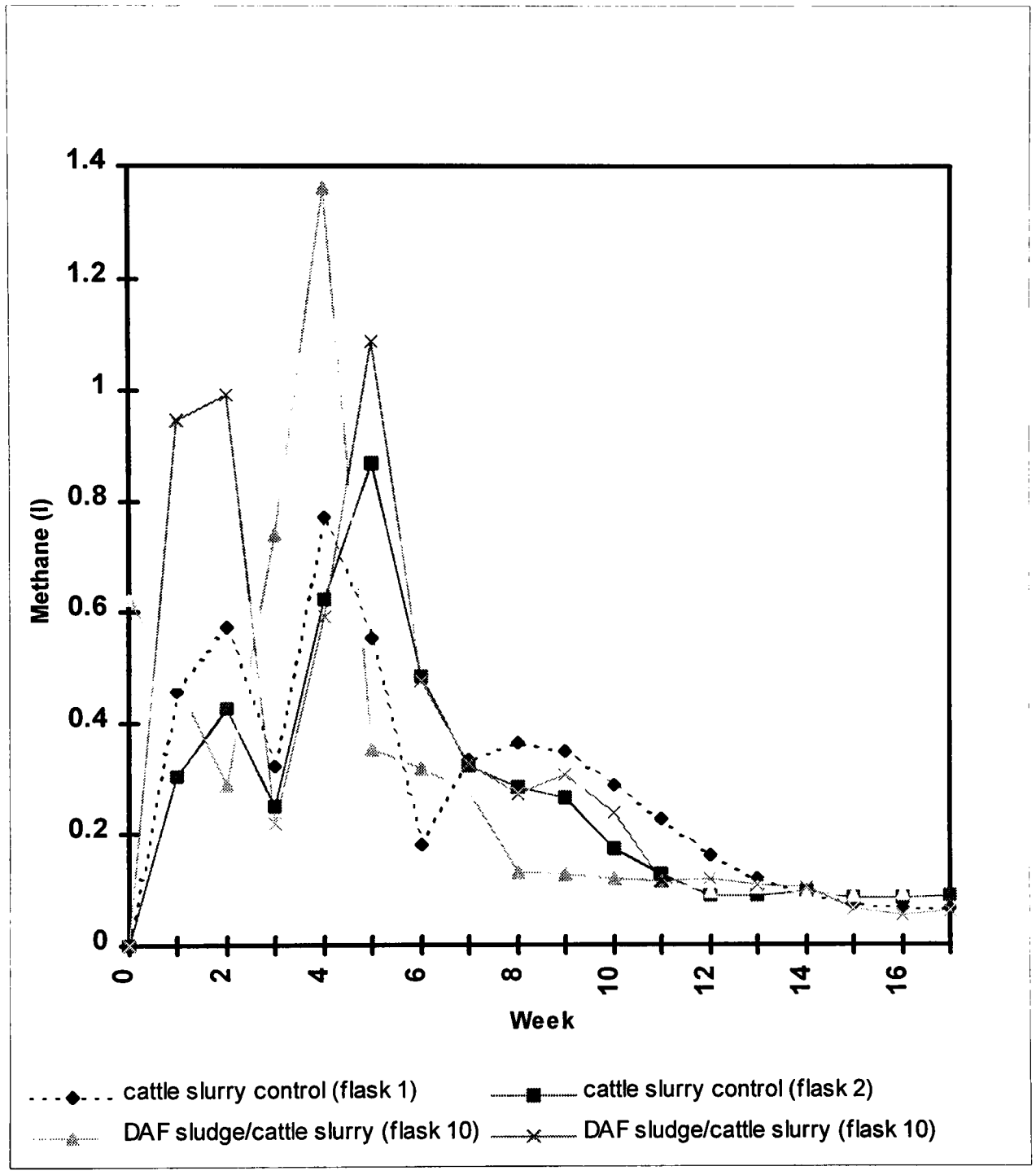


Figure 5.5 Weekly methane production: digesters 11 and 12 (OFMSW/cattle slurry) compared to cattle slurry control.

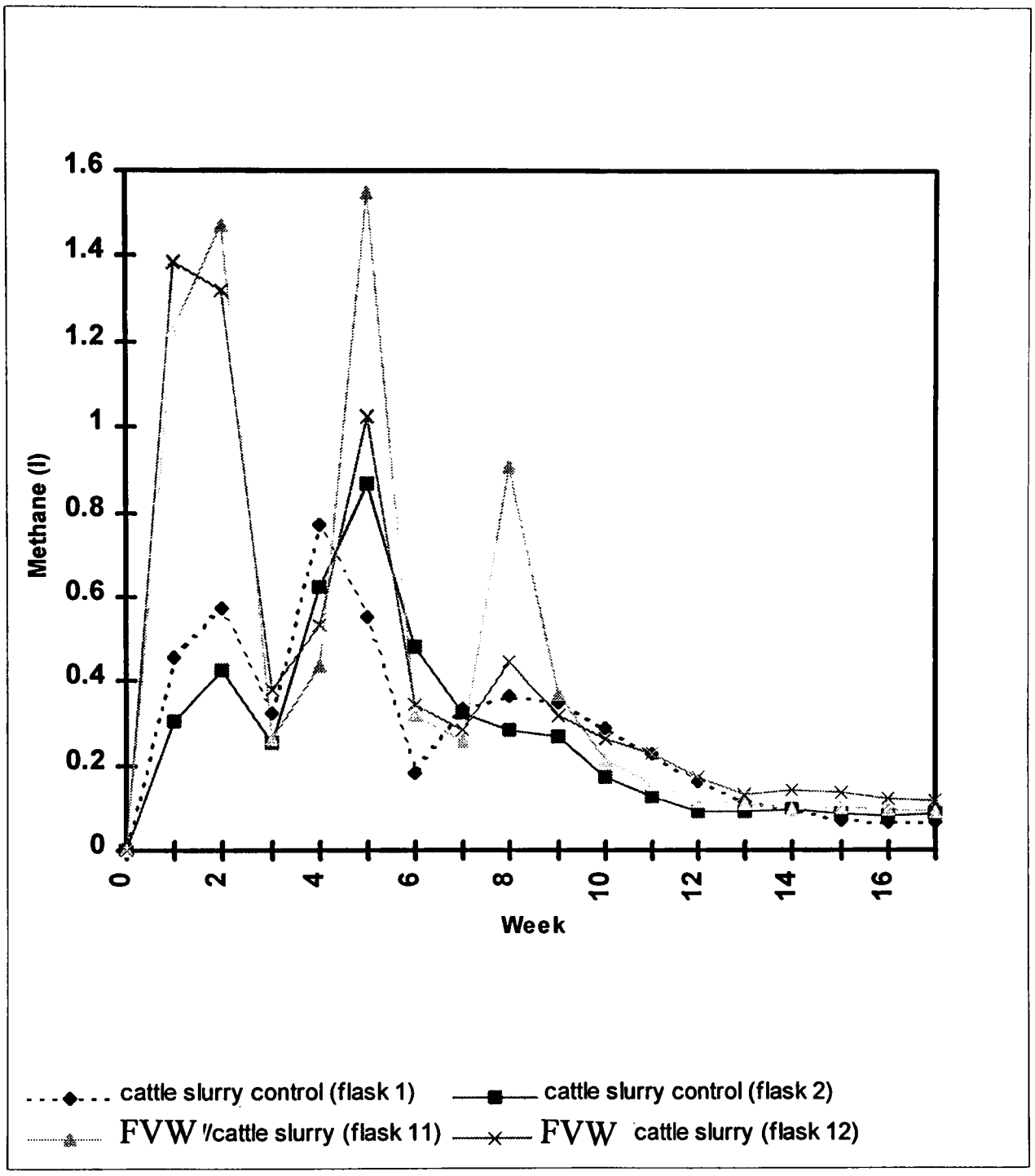


Figure 5.6 % volatile solids reduction for each flask over 22 week digestion period

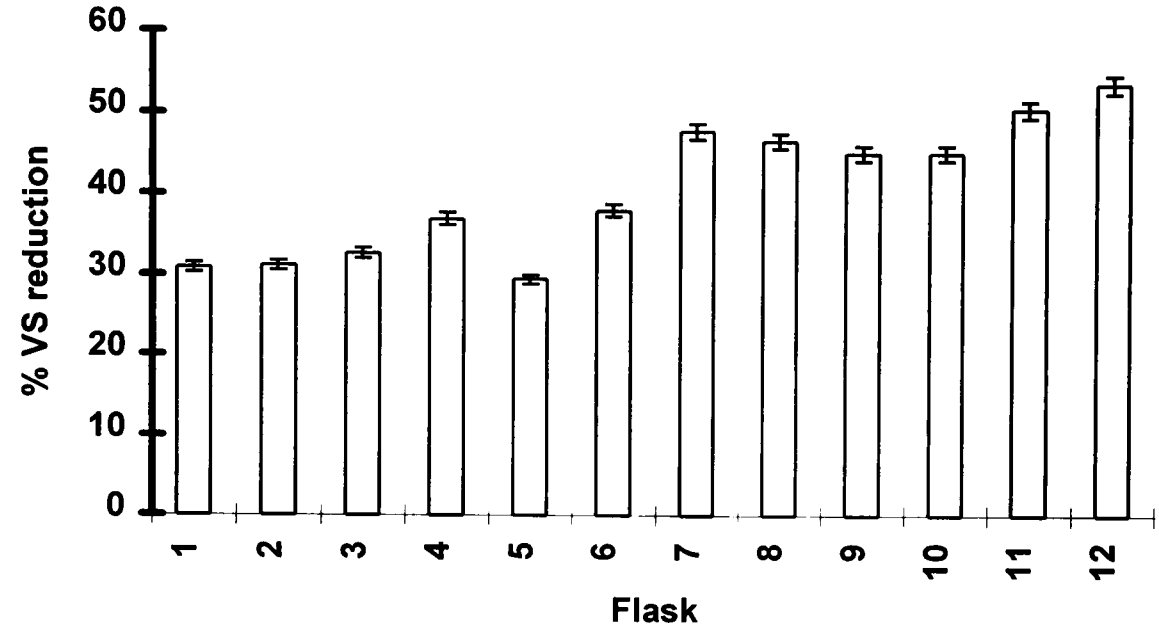


Figure 5.7 Maximum methane production rate for each flask

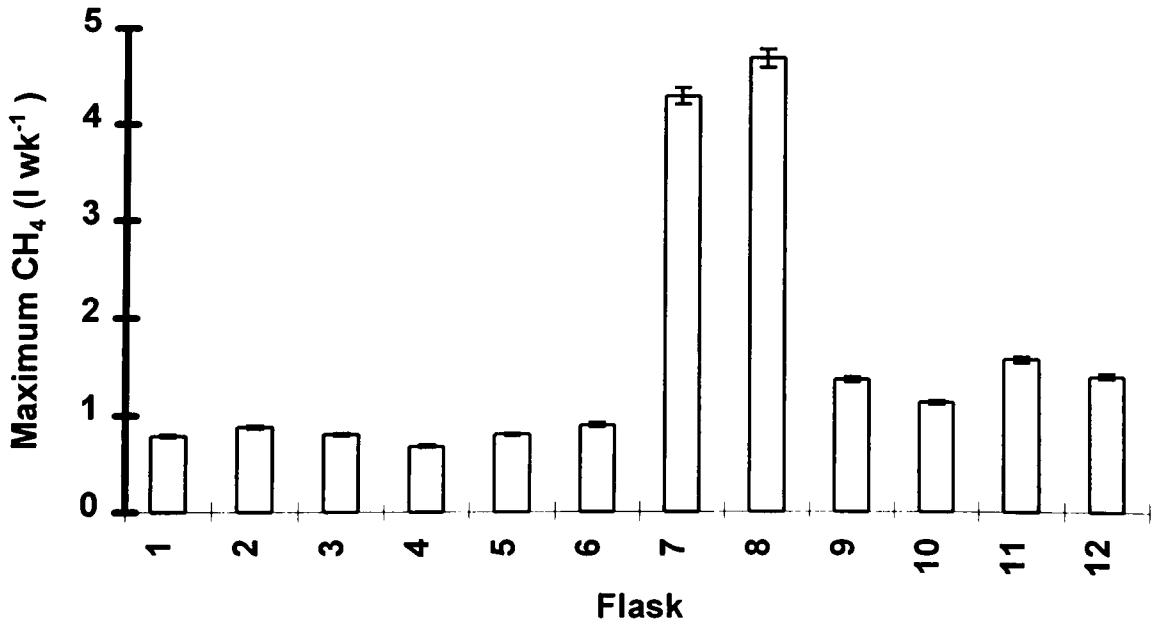
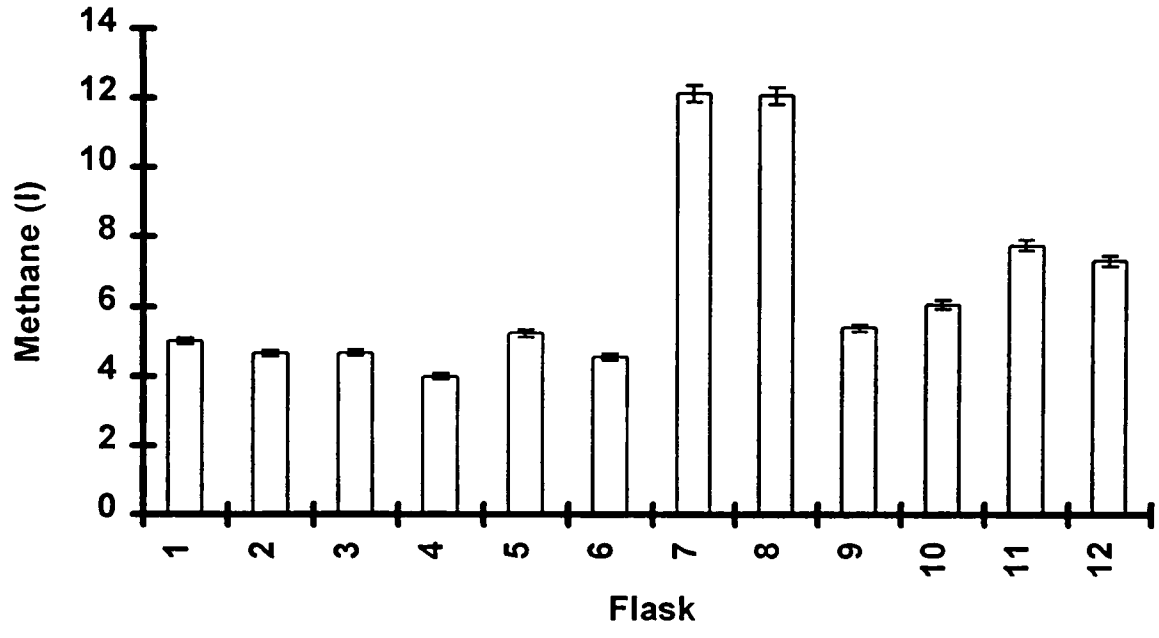


Figure 5.8 Total methane production from each flask over 17 week digestion period



5.4 Criteria used for assessing performance of the co-digestion mixtures

Figures 5.1 to 5.5 show weekly methane production from each flask over the 17 week period of the experiment. The maximum methane production rate, the total methane volume produced over the course of the experiment and the reduction in volatile solids levels were determined for each flask and are displayed in Figures 5.6 to 5.8.

As all the cattle slurry used in the experiment was from the same homogenised sample, it could be assumed that the methane production potential of the cattle slurry in each flask was roughly the same, and therefore any great differences in methane

production rates or total methane volumes between any flask and the control flask, was assumed to be due to the addition of the other waste. Using these criteria it was then possible to determine which wastes made the greatest contribution to enhancing methane production.

5.4.1 General comments

It will be noted that methane production began much earlier in this experiment than in the first batch experiment, which is described in Chapter 3, see Figures 3.1 - 3.4. This was due to a combination of using an inocolum from a cattle slurry laboratory digester, which could be expected to be more thoroughly mixed and heated than a farm digester and hence have a higher concentration of methanogens. Also the mixture of cattle slurry used in this experiment, was actually a 50/50 mix of raw and digested slurry. The experiment was terminated after 17 weeks in this work, whereas it was allowed to run for 22 weeks in the experiment described in Chapter 3. Again this was due to the early onset of methane production. Total methane produced over the course of the experiment was similar, 5.02 and 4.7 litres for digester 1 and 2 respectively, compared to 4.6 litres in the first experiment.

5.4.2 Silage effluent

Hobson and Robertson (1977) noted that silage effluent, which can contain soluble sugars, lactic acid and other products of anaerobic fermentation of grass, can have COD values of up to 1,000,000 mg l^{-1}. The effluent used in this work, as has been previously noted, had a COD of just over 4000 mg l^{-1}. Hence the organic loading on flasks 3 and 4 was quite low, only 1.7 kg VS m^{-3}, see Table 5.2. Despite this, total

methane produced, % volatile solids reduction and maximum methane production rate were all similar to the control digester values, see Figures 5.6 - 5.8, indicating that the volatile material present was readily degradable. One would expect that flasks receiving lower loadings of volatile solids than the control digesters would have produced correspondingly less methane, that they did not indicated that a large proportion of the organic fraction of the silage effluent was converted to methane. It can be concluded that silage effluent is certainly suitable for co-digestion with cattle slurry, but higher strength effluent than that used in this work would be needed to increase methane production by a significant amount

5.4.3 Brewery sludge

This material consisted mostly of biomass from the high-rate trickling filters (Walsh, 1997). Pavlostathis and Gosset (1988) have pointed out that a number of studies have shown that sludges containing a significant fraction of biological solids are much less digestible than primary settled sewage sludge (the fraction of sewage which is settled out after the material has entered a sewage works, and before any biological treatment takes place). Gossett and Belser (1982) reported destruction rates of between 20 and 50% VS for a biological sludge from a sewage works, whereas digestion of primary settled sewage sludge typically achieves a reduction in VS of 40 -60% (Haug 1978).

Destruction of volatile solids in those flasks receiving additions of brewery sludge, flasks 5 and 6, was similar to that observed in the control digesters, see Figure 5.6. Total methane produced was also similar to the control digesters, as were maximum methane production rates, see Figures 5.7 and 5.8. The one difference of note was

that digesters 5 and 6 produced 0.8 and 0.9 l CH_4 in week 1, compared to 0.45 and 0.3 l CH_4 in week 1 for the control digesters. After week 1 the methane production pattern for digesters 5 and 6 was very similar to that of the control digesters, so the increased methane production rate seen in week 1 must have been due to nutrients contained in the brewery sludge. The sudden increase in methane production was surprising as one would have expected a sludge which was biological in origin would not have a lot of readily degradable material. It is possible that the freezing of the sludge sample after collection from the brewery site caused some of the bacterial cell mass present to rupture, releasing readily degradable cell contents into the sludge. Autoclaving of bacterial sludges, which could also be expected to cause cell rupture, has been shown to increase their degradability (Pavlostathis and Gossett, 1986). Hence without the freezing process it is likely that the increased methane production rate observed in week 1 would not have occurred.

The VS loading on flasks 5 and 6 was less than half that applied to the control digesters (6.6 kg VS m^{-3} compared to 14 kg VS m^{-3} respectively), however as has been noted above, total methane production was similar for both sets of flasks. This indicates that a large proportion of the biological sludge was degraded and that no inhibition of the process took place. Therefore, it can be concluded that this material could be disposed of by co-digestion with cattle slurry, although methane production rates would not be increased by any significant amount if it were added to an anaerobic digestion system.

5.4.4 Fish offal

The fish offal used was obtained from a fish farm producing rainbow trout. An analysis of brown trout, which are closely related, indicates that whole brown trout consist of 3.76% nitrogen, 4.5 % fat, 23.5% protein and no carbohydrate (McCance and Widdowson, 1978). As the offal used consisted of flesh and viscera it can be assumed to have approximately the same constituents as a whole fish. The majority of the solid material present was protein. Pavlostathis and Gossett, (1988) have shown that in a sludge consisting predominantly of protein, protein hydrolysis is the rate limiting step in the anaerobic digestion process. Figure 5.3 shows weekly methane production for those flasks receiving additions of fish offal, flasks 7 and 8. Methane production rates for week 1 for both flasks were actually slightly less than those of the control digesters. This was interesting, as other flasks receiving additions of readily degradeable material, such as flasks 9, 10, 11 and 12, had much higher methane production rates in week 1 than the control digesters. The methane production profile for flasks 7 and 8 for weeks 1 and 2 suggests some inhibition of methane porduction, or inhibition of the conversion of the components of fish offal to volatile fatty acids. This may pose a problem for continuous co-digestion of cattle slurry and fish offal. If one addition of fish offal to a batch digester caused some inhibition of methane production, then perhaps repeated addition could cause significant inhibition.

However, maximum methane production rates were over 5 times the values measured for the control digesters (4.3 and 4.7 l wk^{-1} compared to 0.79 and 0.88 l wk^{-1}) and total

methane production was over twice that of the control digesters (see Figure 5.8), despite the fact that the VS loading on flasks 7 and 8 was only 21% greater than the VS load on the control flasks (17 kg VS m^{-3} compared to the control value of 14 kg VS m^{-3}). % VS removal was also higher in these flasks than in the control digesters (see Figure 5.6), at just over 45% compared to control values of 30%. Despite the much higher initial VS loading the final VS values for flasks 7 and 8 and the control digesters were very similar, 4.9% compared to 4.9% and 4.4% for the control digesters(see Table 5.3). This, coupled with the strong increase in methane production rate, indicates that the majority of the fish offal present was converted to methane.

Protein hydrolysis in biological systems produces ammonium ions (NH_4^+) (Hawkes, 1981). Elevated ammonium levels were noted in flasks 7 and 8, and both were significantly higher than the control digester values (2011 and 2157 mg l^{-1} compared to control values of 1848 and 1943 mg l^{-1}). Ammonia (NH_3) levels were also elevated 135 and 145 mg l^{-1} for flasks 7 and 8 compared to 100 and 105 mg l^{-1} NH_3 for the control digesters. Webb and Hawkes (1985) suggested that significant inhibition of methanogenesis occurred at NH_3 concentrations greater than 138 mg l^{-1}, and other authors have proposed similar values. The NH_3 values measured this work were at the bottom end of this scale. However, monitoring of NH_3 levels would be necessary on large scale systems receiving additions of fish offal.

It can be concluded that the addition of fish offal, in controlled manner, to cattle slurry digester could significantly enhance methane production.

5.4.5 DAF sludge

This sludge was found to have a total solids content of 5%, of which 31% was milk fat. The other organic materials present were likely to be milk protein and some biomass from the yoghurt manufacturing process. Callaghan *et al* (1997) have noted that addition of waste milk to batch cattle slurry digesters significantly increased methane production rates. A slight increase in methane production rates was noted in this experiment (see Figure 5.7). Methane production in week 1 was significantly higher than the control values (see Figure 5.4), probably due to the presence of soluble milk sugars such as lactose. Methane production then returned to levels similar to the control digesters until week 3 when a rapid increase in methane production rates was noted.

Total methane production and % VS removal were significantly higher than the values recorded for the control digesters (see Figures 5.6 and 5.7). The % VS remaining in flasks 9 and10 at the end of the experiment (see Table 5.3) was significantly less than the levels measured in the control digesters (3.4% VS compared to 4.4 and 4.9 %VS for the control digesters), indicating that most of the DAF sludge was converted to CH_4.

A qualitative observation was made that the biogas from flasks 9 and 10 had no detectable H_2S odour, whereas all the other flasks produced strong H_2S odours. This

was possibly due to the presence of ferric salts in the DAF sludge, which react with sulphide and sulphate present to form ferric sulphate and ferric sulphide.

The addition of this DAF sludge to a cattle slurry digester would enhance methane production rates and also possibly reduce H_2S levels in the biogas.

5.4.6 Fruit and vegetable waste (FVW)

The FVW used for this work consisted of fruit and vegetables with some rice. 80 - 90 % of most fruit and vegetables consists of water, with the remainder being sugars, carbohydrates, protein and some fats (Paul and Southgate, 1978). Fruit and vegetable wastes are readily degraded by anaerobic bacteria (Poggii-Varaldo *et al.*, 1988), but often require the addition of water to allow mixing within the digestion vessels.

From Figure 5.5 it can be seen that methane production rates in week 1 were around 3 times those of the control digesters, most likely due to the conversion of soluble sugars to methane. Once this material had been used up there was a drop in methane production until week 4, when methane production rates again rose sharply, most likely due to the availability of sugars from the hydrolysis of starch and possibly protein hydrolysis.

Total methane produced and % volatile solids reduction were significantly higher than the control digester values (see Figures 5.6 and 5.8), and volatile solids levels in flasks 11 and 12 at the end of the experiment were significantly lower than those in the

control flasks (4.2 and 3.9 % VS compared to 4.9 and 4.4% VS in the control flasks), indicating that most of the FVW had been metabolised.

The above results indicate that the addition of the organic fraction of FVW would enhance methane production from cattle slurry anaerobic digesters.

5.5 Preliminary conclusions

Fish offal and fruit and vegetable waste were found to enhance methane production rates and total methane produced by the greatest margin. It was decided to study the co-digestion of both these wastes with cattle slurry using the 18 litre anaerobic digestion pilot plants.

Chapter 6

Anaerobic digestion pilot plant trial 2: co-digestion of cattle slurry and fruit and vegetable waste (FVW).

6.1 Pilot plant operating history

The digester was filled with a mixture of digesting cattle slurry, taken from a local farm anaerobic digester and fresh cattle slurry, also obtained from the same farm. The mixing system was controlled by timers, and was set to mix the digester at 60 rpm for 12 hours out of every 24 hours, by running the motor for 3 hours followed by 3 hours resting. This cycle was repeated 4 times in 24 hours. The system was allowed to operate as a batch digester for one month to allow the methanogens to recover from being removed from the anaerobic environment of the farm digester. Feeding of cattle slurry was commenced at the end of this period. The digesters were fed once a day, 5 days per week. Each retention time lasted 21 days, including weekends.

After 2 retention times, feeding of various mixtures of cattle slurry and FVW commenced. The digesters were operated for a further 5 retention times, and shut down at the end of this period. No mechanical or electrical failures occurred during the operating period.

6.2 Digester operating regime

The digester was initially operated on a feedstock of 10% total solids (TS) cattle slurry, at an estimated loading rate of 5.2 kg VS m^3 d^{-1}. The digester had a working volume of 18 litres, and received 1.2 litres of cattle slurry once a day, 5 days per week, giving a retention time of 21 days. This retention time is typical of many cattle slurry digesters (Cheshire, 1997). Due to the rapid onset of digestion noted during the batch digestion of cattle slurry and FVW, which is described in Chapter 5, it was decided that the 21 day retention time would be sufficient to accomplish significant degradation of the FVW.

The fruit and vegetable waste (FVW) used as the co-digestate was collected from a specially designated bin in the kitchen of a student residence. Each different type of waste was weighed before being placed in the bin. The bin was emptied once a week and the contents were macerated in a Magimix food blender (Magimix SA, France) and stored at -10°C. During the operation of the pilot plant digester, a quantity of FVW, sufficient for one weeks operation was thawed out at the beginning of each week. The relative portions of different wastes in the FVW are described in Table 5.2.

Initially, the digester was operated for 2 retention times (RT 1 and 2) on cattle slurry, at a loading rate of 5.2 kg VS m^3 d^{-1}, see Figure 6.1 (**note**: see pages 179 - 186 for Figures). At the end of this period co-digestion commenced. The initial co-digestion ratio was 80 % wet weight cattle slurry and 20% FVW. This increased the volatile solids loading rate by about 15%, from 5.2 to about 6.0 kg VS m^3 d^{-1}. The digester was operated for 2 retention times (RT 3 and 4) at this loading rate. At the end of this period the FVW fraction was increased to 40% wet weight, which increased the volatile solids loading rate by 25% to 7.2 kg VS m^3 d^{-1} (RT 5) This increased

loading rate caused foaming problems, which were eventually overcome by reducing the loading rate to around 6.3 kg VS m^3 d^{-1} for the next retention time(RT 6) and reducing the working volume of the digester from 18 litres to 12.89 litres, to create more headspace volume in which the foam could build up without blocking the gas outlet ports. The volumes of liquid added to and removed from the digester were adjusted accordingly to ensure the retention time remained constant. At the beginning of retention time 7 (RT 7)the fraction of FVW was increased to 50%, this increased the volatile solids loading rate to around 7.1 kg VS m^3 d^{-1}. The digester was shut down at the end of retention time 7.

6.3 Variations in feedstock quality during the experiment

Figures 6.2 and 6.3 show the variation in total and volatile solids and VS/TS ratio of cattle slurry and FVW over the course of the experiment. The quality of the cattle slurry remained reasonably constant over this time although a slight drop in slurry volatile solids did occur towards the end of the experiment.

The samples of FVW collected all had a VS/DS ratio of around 0.93 and all except one had a total solids level of around 15.5%. It is not clear why one sample had a much higher TS value than the others, but the VS/TS ratio of this sample remained at 0.93.

Figure 6.1 shows the estimated and actual volatile solids loading rates over the course of the experiment. The estimated loading rates were calculated by determining the volatile solids content of the FVW and cattle slurry samples being used. Knowing the amounts of each which were to be added to the digester, and the digester working volume, the volatile solids loading rate could be estimated. The measured values were determined by measuring the volatile solid levels

of the digester immediately before it was added to the digester. This value was measured each day, 5 days per week , and a mean value was determined for each week. The mean volatile solids loading rate for that week was then calculated from this value.

Despite a drop in week 6, which may have been due to sampling error, the estimated and actual values were quite close throughout the course of the experiment, indicating that the waste samples were reasonably homogenous. This contrasts sharply with the work on chicken manure described in Chapter 4, which found that the non-homogeneity of chicken manure samples meant that there was often a difference of up to 10% between the estimated and measured volatile solids loading levels (see Section 4.4).

6.4 Digester monitoring and performance

Total and volatile solids of the digester feedstock and effluent were monitored on a daily basis. The digester effluent was also monitored daily for pH, alkalinity, total VFA and NH_4^+. These parameters were used to determine the status of the digestion system and to determine how it coped with the addition of FVW.

6.5 Weeks 1-6; operation on cattle slurry

The digester was operated using cattle slurry as a feedstock for the first 2 retention times (weeks 1-6) at a volatile solids loading rate of 5.2 kg VS m^3 d^{-1}. This value was slightly higher than the loading rates at which farm based cattle slurry digesters are operated, which are typically in the range of 2.25 to 4.5 kg VS m^3 d^{-1} (Linke, 1997). The mean methane productivity for the reactor was around 0.23 m^3 CH_4 per kg VS added, see Figure 6.4. Hawkes and Horton, (1983) demonstrated that methane productivity, measured as m^3 CH_4 produced per kg VS added to the

reactor, tended to increase with increasing volatile solids loading rate. Linke (1997) has recorded methane productivity values of around 0.2 m^3 CH_4 per kg VS added on cattle slurry reactors. operating at 4.5 kg VS m^3 d^{-1}. Based on Hawkes Hawkes work it could reasonably be assumed that a reactor operating at slightly higher VS loading rate would also have a slightly higher methane productivity value.

Volatile solids removal over weeks 1-6 remained around 52%, see Figure 6.5. Effluent volatile solids and total solids also remained reasonably constant during this period, as did effluent VS/TS ratios, see Figures 6.6, 6.7 and 6.8, indicating that the system was sufficiently mixed.

Biogas methane concentrations dropped slightly after digester start up, but remained between 68 and 70 % between weeks 3 and 6, see Figure 6.9. These values are slightly higher than other values recorded for cattle slurry digesters, which range between 60% CH_4 (Sarapatka, 1994) and 65% (Erdman, 1985). Daily methane production stabilised after the first 2 weeks at around 15 litres d^{-1} , see Figure 6.10.

Digester alkalinity initially was around 15,000 mg l^{-1} $CaCO_3$, and rose sharply to around 16,000 mg l^{-1} in week 2 and 17,300 mg l^{-1} in week 3, before returning to around 15,000 mg l^{-1} during weeks 4 and 5, see Figure 6.11. It is not clear why this increase in alkalinity occurred, it may have been due to the slight increase in biogas CO_2 observed during weeks 3 and 4. Alkalinity values of around 11,000 mg l^{-1} have been recorded for cattle slurry digesters by Chayovan *et al.*, (1988). Total alkalinity is a measurement of the acid neutralising potential of a waste, it is expressed as mg l^{-1} $CaCO_3$ and is measured by titrating a sample of waste with dilute acid to pH 4.5. Hence it is the sum of all titratable bases and can be expected to vary from slurry to slurry,

depending on the type of cattle feed and farm soil conditions. Farms with alkaline soils (such as the farm from which the slurry used in the current work was obtained) would be expected to produce slurries with higher alkalinity values.

Total VFA (volatile fatty acid) concentrations increased from 1800 mg l^{-1} to 2700 mg l^{-1} in week 2, most likely due to increased acidogenic activity caused by adding fresh slurry, see Figure 6.12. Effluent VFA levels stabilised at around 2000 mg l^{-1} during weeks 4-6, similar to values recorded by Hall *et al.*, (1985) who noted effluent VFA concentrations of 1433 to 2643 mg l^{-1} for a cattle slurry digester.

Digester pH was stable at around 7.7 during weeks 1-6, see Figure 6.13. This was similar to pH values record for cattle slurry digesters by Scharer *et al.* (1981), (pH 7.4 to 7.7) and Chayovan *et al.*, (1988) 7.4.

The VFA to Total alkalinity ratio (VFA:TAlk) is used to monitor the operational stability of a digestion system. It is generally one of the first parameters to register the onset of inhibitory changes in an anaerobic system (Hickey and Switzenbaum, 1991). In a review of anaerobic digester control parameters Switzenbaum *et al.* (1990) noted that the operating range for a healthy digester for this parameter was between 0.1 and 0.35. Parkin and Owen (1986) suggested that a digestion system could be considered unstable and liable to failure if this parameter rose above 0.3 to 0.4. Monroy *et al.*, (1994) operated an upflow anaerobic filter on wastewater from ice-cream manufacture over a 2 year period and found that sudden drops in methane productivity coincided with sudden increases in VFA:TAlk above 0.3-0.4.

Much of the work to determine what the normal VFA:TAlk range should be was done on sewage sludge digestion systems. However the 0.1 - 0.35 range seems to be applicable to other systems such as the filter operating on ice-cream wastewater, and can be assumed to be applicable to cattle slurry systems also. While no typical range of VFA:TAlk values has been suggested for cattle slurry systems, values calculated from data published by other authors indicate VFA:TAlk ratios of 0.12 are typical for a stable cattle slurry digester (Hall *et al.*, 1985).

Values of 0.13 for VFA:TAlk were recorded during weeks 2-6, see Figure 6.14, when all other parameters were considered to be indicating stable digester operation, therefore it can be concluded that a VFA:TAlk ratio of around 0.13 is typical of a stable cattle slurry digestion system..

From the above parameters, it can also be concluded that the digester was operating under steady-state, stable conditions during weeks 3-6.

6.6 Weeks 7-12 - digester operation on cattle slurry / FVW (80 / 20).

At the beginning of week 7 the digester feedstock composition was altered to 80% wet weight cattle slurry and 20% wet weight FVW. This had the effect of increasing the volatile solids loading rate by 11-17%, over weeks 7 - 12, and also changing the nature of a portion of the digester feedstock. Table 6.1 shows the approximate amounts of different materials which comprised the FVW. Using McCance and Widdowson's The Composition of Foods (Paul and Southgate, 1978) it was possible to determine the percentages of carbohydrate, protein, fats and sugars present in the FVW mixture. Table 6.2 shows the estimated amounts of carbohydrate, protein, fats and sugar present in the FVW sample, expressed as a percentage of total solids and

also shows the relative amounts of each in a cattle slurry sample for comparison purposes. It should be noted that up to 20% of the carbohydrate in the cattle slurry sample was lignin (which is not degradable under anaerobic conditions) , and a further 27% was hemi-cellulose,which is slightly degradable under anaerobic conditions (Hawkes, 1981).

Table 6.1 Estimation of carbohydrate, protein, fats and sugar levels in FVW samples from known values for the materials in the sample (all values from Paul and Southgate, 1978).

Item	% in FVW	% carb	% protein	% fats	% sugars	total carb %	total protein %	total fats %	total sugars %
bananna	7.5	11.4	0.7	0.2	9.6	0.855	0.0525	0.015	0.72
orange	13.2	6.4	0.6	0	6.4	0.8448	0.0792	0	0.8448
grapefruit	15	2.5	0.3	0	2.5	0.375	0.045	0	0.375
brussels	17	2.7	4	0	2.6	0.459	0.68	0	0.442
rice	3.9	86.8	6.5	1	0	3.3852	0.2535	0.039	0
kiwi fruit	13.2	2.5	0.2	0	2.6	0.33	0.0264	0	0.3432
potato	24.5	25	2.1	0.1	0.5	6.125	0.5145	0.0245	0.1225
brocoli	5.7	2.5	3.3	0	2.5	0.1425	0.1881	0	0.1425
Totals	100					12.5165	1.8392	0.0785	2.99

Table 6.2 Comparison of the relative percentages of carbohydrate, protein, fat and sugars in FVW sample and cattle slurry.

	carb.	protein	fat	sugar	Total solids*
for 100g FVW	12.5g	1.84g	0.08g	2.99g	15.5
as a % of TS	66.8	9.8	0.4	15.9	
for 100 of CS	5.35	0.54	0.58	0	8%
as a % of TS	66.9	6.75	7.25	0	

* The TS value was estimated from the total volatile solids (VS) content of 14.4% (12.5 + 1.84 + 0.08)and a VS/TS ratio of 0.93.

The values for cattle slurry are from Peck *et al.* (1985).

It will be noted that, using the estimates provided by Paul and Southgate, the figures obtained for carbohydrate, protein, fats and sugars add up to 14.4g per 100g of wet vegetable waste (this is 12.5 + 1.84 + 0.08, the carbohydrate value given is for total carbohydrate and includes sugars) or 14.4% total solids. If we assume that the VS/DS ratio is 0.93, as it was for all the samples of

FVW analysed during the experiment, see Figure 6.3, and that 14.4% represents the total organic fraction present, then the ash fraction of this material would be 1.1%, and the total solids value for a waste of the composition described in Table 6.1 would be 15.5 %. All but one of the waste samples used in the experiment actually had TS values of 15.5%, see Figure 6.3. This suggests that the estimates for carbohydrate, protein and fat content are quite accurate.

The addition of the feedstock containing FVW to the digester immediately caused a rapid increase in daily methane production, from an average of 15 litres d^{-1} in week 6 to 25 litres d^{-1} in week 7, see Figure 6.10. Biogas CO_2 also increased sharply in week 7, causing a corresponding drop in biogas CH_4 concentrations, from 70% CH_4 to 60% CH_4. This effect was in part due to the sugars present in the FVW. Marsili-Libelli and Beni (1996) noted that an organic shock loading of readily degradable material to an anaerobic system produced a rapid increase in biogas CO_2 concentrations due to the production of volatile fatty acids from the organic material. A similar rapid increase in biogas CO_2 following the addition of shock loadings of waste milk to batch digesters, has been observed by Callaghan *et al.* (1997). In bacterial anaerobic systems, sugars are fermented via the Embden-Meyerhof-Parnas pathway to pyruvate and from there to volatile fatty acids, CO_2 and H_2 (McInerney and Bryant, 1981). Biogas CO_2 remained slightly elevated over weeks 7 - 12 at around 37% CO_2.

Effluent VFA concentrations rose slightly in week 7 to around 2,300 mg l^{-1} and to just over 3,000 mg l^{-1} in week 8, before returning to 2,300 - 2,600 mg l^{-1} during weeks 9 - 12, see Figure 6.12. This suggests that no substantial build up of VFA was occurring, and that the methanogenic bacteria were not inhibited in any way by the addition of FVW, as the growth rate of the methanogens present increased to convert the excess VFA to methane. The VFA:TAlk ratio also

supports the assumption that the system was not negatively affected by the addition of FVW, see Figure 6.14. The ratio increased from 0.12 to 0.15 in week 7 and to 0.2 in week 8, and remained between 0.15 and 0.2 during weeks 9 - 12, well below the trigger value of 0.35.

Methane productivity, expressed as m^3 CH_4 produced per kg VS added to the digester, rose from 0.21 in week 6 to 0.34 m^3 CH_4 kg VS^{-1} in week 7, an increase of 62%, and remained between 0.35 and 0.4 during weeks 8 - 12. It is interesting to note that an increase in VS loading of between 11 and 17% produced such a large increase in methane productivity. This can be attributed to the fact that the FVW was much more degradable than the cattle slurry, as noted earlier in this section. An increase in volatile solid loading rate of between 11 and 17% VS greatly enhanced methane productivity.

6.7 Weeks 13 - 15; digester operation on cattle slurry / FVW (60 / 40)

At the beginning of week 13, the fraction of FVW present in the digester feedstock was increased to 40% wet weight, increasing the VS loading rate to between 7.2 and 7.4 kg VS m^3 d^{-1}, a 38 - 42% increase over the loading rate used in weeks 1-6. This shock loading had the effect of increasing daily methane production to an average of 39 litres d^{-1} during week 13, a 260% increase on the value of 15 litres d^{-1} observed for operation on cattle slurry during weeks 1 - 6, see Figure 6.10. Methane productivity, see Figure 6.4, also rose slightly, from 0.4 to 0.42 m^3 CH_4 kg VS^{-1} during week 13.

However the VFA:TAlk ratio also increased from 0.18 in week 12 to 0.34 in week 13 and continued to increase reaching 0.69 by week 15, see Figure 6.14. Methane productivity also declined sharply over this period, reaching 0.30 m^3 CH_4 kg VS^{-1} by week 15. Conventional

process indicators such as pH and biogas methane concentration also declined sharply over weeks 13 to 15, see Figures 6.9 and 6.13. Percentage volatile solids removal also declined sharply over this period. A lot of foaming also occurred in the digester, causing blockage of gas outlet ports. The foaming seemed to interfere with system mixing as effluent total and volatile solids levels increased sharply during week 15, see Figures 6.6 and 6.7, indicating that some of the feedstock solids were not remaining in the reactor for a full retention time. The most likely mechanism of interference with the mixing system was that the foam layer was forming a mat of FVW solids on the surface of the digester, some of which was being drawn into the effluent removal pipework during each feeding cycle. The foam layer was operating in a similar way to foam floatation mechanisms used in mineral ore processing to remove small particles from non-homogenous mixtures. It was noted that the effluent taken from the digester during week 15 did seem to contain a lot more FVW particles than usual. The increased volatile solids loading rate associated with increasing the FVW fraction of the digester feedstock to 40%, coupled with the foaming problems which this introduced, caused system instability.

6.8 Weeks 16 - 18; digester operation on cattle slurry / FVW (70/30)

Due to the system instability described above, it was decided to reduce the fraction of FVWin the feedstock to 30% wet weight. This reduced the volatile solids loading rate to between 6.2 and 6.4 kg VS m^3 d^{-1}, see Figure 6.1. One would have expected that a mixture of 70/30 cattle slurry / FVW would have given a VS loading rate of around 6.6 kg VS m^3 d^{-1}, as an 80/20 mixture gave a loading rate of around 6.2 kg VS m^3 d^{-1}. That it did not was due to a drop in the VS/TS ratio of the cattle slurry, from 0.79 to 0.74, see Figure 6.2. This may have been caused by the cattle feed-cake rations being reduced.

At this lower loading rate, which was only 5% higher than the loading rate used during weeks 7 - 12, methane productivity recovered slightly to 0.33 m^3 CH_4 kg VS^{-1} in week 16 and stayed between 0.3 and 0.34 m^3 CH_4 kg VS^{-1} during weeks 17 and 18. This was still below the values of 0.35 to 0.4 m^3 CH_4 kg VS^{-1} recorded during weeks 7 - 12 for the slightly lower volatile solids loading rate of 6.2 kg VS m^3 d^{-1}. The reduced productivity was probably due to the high VFA levels which persisted during weeks 16 and 17, see Figure 6.12. The VFA:TAlk ratio was 0.49 during week 16. It increased to 0.63 during week 17, before dropping to 0.42 in week 18, still outside the recommended operating limit of 0.35.

By the end of week 18 methane productivity had levelled off at 0.33 - 0.34 m^3 CH_4 kg VS^{-1} and no foaming problems were occurring, so it can be concluded the system had achieved a measure of stability by the end of week 18, albeit with a reduced methane productivity.

6.9 Weeks 19 - 21; digester operation on cattle slurry / FVW (50/50)

As the system had achieved a measure of stability over weeks 16 - 18 it was decided to assess the effect of sharply increasing the volatile solids loading rate to a value of around 7 kg VS m^3 d^{-1}. Due to the reduced volatile solids level of the cattle slurry and a slightly reduced volatile solids content in the FVW it was necessary to increase the fraction of FVW in the feedstock to 50% to achieve this VS increase.

The increased loading rate caused methane productivity to increase to 0.41 m^3 CH_4 kg VS^{-1} in week 19 and 0.46 m^3 CH_4 kg VS^{-1} in week 20, before dropping slightly to 0.44 m^3 CH_4 kg VS^{-1} in week 21, see Figure 6.4. The increase in methane productivity was surprising as the VFA:TAlk ratio was 0.49 in week 19, 0.60 in week 20 and 0.59 in week 21, see Figure 6.14, all well above

the recommended safe range of 0.35, and similar to the figures which coincided with falling methane productivity values during weeks 13 - 15.

A comparison of effluent total and volatile solids and the volatile solids removal rate for weeks 13 - 15 and 19 - 21, see Figures 6.5, 6.6 and 6.7, revealed that a significant amount of material was passing through the digester undegraded during week 15 (when methane productivity was at its lowest point during weeks 13 - 15, 0.30 m^3 CH_4 kg VS^{-1}). This was due to the foaming produced by the feedstock during this period. For reasons which were not clear no significant foaming occurred during weeks 19 - 21, even though the volatile solids loading rate was only slightly lower than that which caused foaming during weeks 13 - 15 and the fraction of FVW in the feedstock was slightly higher. A change in the composition of the FVW may have been responsible for the foaming problems noted during weeks 13 - 15, although no changes were noted during visual inspection of the sample, or from the monitoring record of what was placed in the FVW bin.

It can be concluded that system methane productivity was enhanced by increasing the fraction of FVW present in the feedstock to 50%, and that foaming, which had been associated with similar increases in feedstock composition and volatile solids loading rate earlier in the pilot plant run, did not occur to any significant degree.

One point which should be noted is the gradual decline in biogas methane concentration which occurred over weeks 18 - 21, from over 60% CH_4 in week 18, to 51 % CH_4 in week 19, 52 % CH_4 in week 20 and 49 % CH_4 in week 21. Although the amount of methane per kg VS added was increasing over this period, the calorific value of the biogas produced was declining. On a

large scale plant this could cause problems with boilers and power generation equipment running on the biogas.

6.10 Ammonium (NH_4^+) and ammonia (NH_3) levels over weeks 1 - 21

Ammonium (NH_4^+) levels in the effluent were monitored over the course of the experiment, although the addition of FVW was not expected to increase the nitrogen in the system to any great degree as the mixture was calculated to have a carbon to nitrogen ratio of only 42:1 (calculated using the nitrogen values from McCance and Widdowson (1978) for each material in the FVW sample). Nitrogenous compounds are converted to NH_4^+ under anaerobic conditions (Hobson and Wheatley, 1993), hence materials with high C:N ratios, such as chicken manure (which can have C:N values of 6.8 - 8.8 (*calculated from* Webb and Hawkes, 1985)), when added to an anaerobic digester, produce significant increases in system NH_4^+ (Aubert and Fauchille, 1983).

NH_3 values were calculated from NH_4^+ and pH values using an equation developed by Abeling, (1994). Figure 6.12 shows NH_3 and NH_4^+ levels over the course of the experiment. NH_4^+ levels varied between 2,200 and 2,300 mg l^{-1} during weeks 1- 6, with NH_3 levels remaining at around 80 mg l^{-1}. The addition of FVW in week 7 produced a small, but significant increase in effluent NH_4^+ levels, which increased to around 2,800 mg l^{-1} over weeks 7 - 12, (standard deviation of $\pm$28 mg l^{-1}). This increase was most likely due to the degradation of the FVW protein fraction. A further increase to around 3,000 mg l^{-1} was noted when the FVW fraction was increased to 40% of total feed weight over weeks 13 - 16, although the highest value for NH_4^+, 3143 mg l^{-1}, was recorded in week 17, indicating that there was a delayed reaction by the protein degrading bacteria to the

increase in FVW. A similar increase in effluent NH_4^+ concentrations was noted during weeks 19 - 21 when the FVW fraction was increased to 50% of feed weight.

Effluent NH_3 levels were reasonably low throughout the course of the experiment, through a combination of low NH_4^+ concentrations and low pH values (see Section 1.3.3.4 for a full discussion of the relationship between pH, NH_4^+ and NH_3 levels). A number of authors have agreed that NH_3 levels of between 138 and 220 mg l^{-1} can significantly inhibit methane production rates in anaerobic digestion systems which are un-acclimatised to high NH_3 levels (Webb and Hawkes, 1985). The highest value reached during the current work was 104 mg l^{-1} NH_3 during week 9 and for most of the experiment the NH_3 level remained between 40 and 80 mg l^{-1}. Therefore it can be assumed that no inhibition of the system by NH_4^+ and NH_3 occurred over the course of the experiment.

6.11 Hydrogen Sulphide levels (H_2S) levels in the biogas over weeks 1 - 21.

There is some anecdotal evidence to suggest that sharp increases in H_2S levels occur when digesters receive organic shock loadings (Maltin, 1995), however there is nothing in the literature to support this claim. Figure 6.16 shows H_2S levels in the biogas over weeks 1 - 21. The H_2S concentrations in the biogas rose sharply on commencement of feeding cattle slurry to the digester, and levelled off at around 1100 ppm during weeks 4 - 7. Commencement of addition of FVWcaused a further gradual increase in biogas H_2S to a maximum of 1800 ppm in week 10. Levels then fell sharply to around 1100 ppm during week 11 and remained in the 1000 - 1200 ppm range during weeks 12 and 13, before falling sharply to around 600 ppm during weeks 14 and 15. Levels then increased sharply to around 1600 ppm during week 16, before falling again

to 1000 ppm in weeks 17 and 18, and then rose steadily to a plateau of around 1200 ppm during weeks 20 and 21.

Apart from the increase in biogas H_2S levels noted in weeks 1-4, which coincided with the start-up of the digestion system and was most likely due to the presence of protein residues in the slurry, the changes in biogas H_2S concentration noted above did not coincide with any events or significant changes in the other process parameters. Some amino acids, which are the chemical units from which proteins are formed, contain sulphur molecules. Examples of these amino acids include methionine and cysteine (Conn *et al.*, 1987). The conversion of organic sulphur to sluphate is an aerobic process, and hence would not be expected to occur in an anaerobic system. However sulphate reducing bacteria, which produce sulphides in anaerobic systems, require a source of sulphate. The slight, but significant, increase in biogas H_2S noted during weeks 7 - 12 must have required an additional source of sulphate. It is possible that the FVW protein fraction had undergone some aerobic degradation while being collected, as the bin contents were emptied once a week. Therefore a fraction of the protein present in the FVW could have been oxidised with he resulting production of sulphate. Hence an increase in protein concentrations in the feedstock could lead to an increase in biogas H_2S concentrations. The addition of FVW to the feedstock, which was calculated to have a protein content of 9.8 % (expressed as a percentage of total solids) as compared to the protein content of the cattle slurry which was around 6.75% of total solids, see Table 6.2, provided such an increase. This explains the increase in biogas H_2S which occurred between weeks 7 and 10, but does not account for the sudden drop in biogas H_2S noted in week 11. As far as can be ascertained the feedstock consistency remained reasonably constant throughout this period. This sudden drop may have been due to inhibition of the H_2S producing bacteria present. It was not due to inhibition of protein degradation as effluent NH_4^+

levels remained constant over this period, see Figure 6.12. However there is no indication why the H_2S producers would have been inhibited. It can be concluded that H_2S levels in the biogas are of little practical use in controlling an anaerobic digestion process.

6.12 Methane production potential of FVW and actual methane production

Table 6.3 shows the theoretical methane production which would be expected if the FVW amounts added to the digester were completely converted to methane.

period	kg FVW	kg carbohy.	kg protein	kg fat	ch4 kg carbohyd.	Ch4 kg protein	ch4 kg fat	total m3 ch4/ mass FVW destroyed
wk1-6	0	0	0	0	0	0	0	0
wk 7-12	0.24	0.03	0.004416	0.000192	0.0130980.	0.00327	0.000205	0.01658
wk 13-15	0.48	0.06	0.008832	0.000384	0.026196	0.006558	0.000411	0.033162
wk 16-18	0.36	0.05	0.006624	0.000288	0.019647	0.004916	0.000308	0.024872
wk 19-21	0.6	0.08	0.01104	0.00048	0.032745	0.008194	0.000513	0.041453
1 kg FVW	1	0.13	0.0184	0.0008	0.054575	0.013657	0.000858	0.06908

Table 6.3 Amounts of FVW added to the digestion system during weeks 7 - 21 and theoretical methane yield, based on composition of FVW (calculated using values of 0.4 m^3 CH_4 kg^{-1} carbohydrate destroyed, 0.68 m^3 CH_4 kg^{-1} protein destroyed and 0.98 m^3 CH_4 kg^{-1} of fat destroyed from Peck *et al.*, 1985, at 273 K and 760 mm Hg. The methane values in the current work have been calculated at 298 K and 760 mm Hg, therefore the values from Peck *et al.*, were adjusted to 298 K).

From Table 6.3 it was possible to calculate the methane production potential per kg VS degraded for FVW, as 1 kg of FVW, which had an average volatile solids (VS) concentration of 14.4 % (0.144 kg VS) would produce 0.06908 m^3 CH_4, if completely degraded in the digester. Assuming that the mass of carbohydrate, lipid and protein present was equal to the mass of VS present, this was equal to a methane production potential of 0.479 m^3 CH_4 kg VS^{-1} degraded.

Similarly, using the figures provided for cattle slurry by Peck *et al.*, (1985), see Table 6.2, it was possible to calculate the methane production potential of cattle slurry. 1 kg of cattle slurry at 10% TS would contain 66.9g carbohydrate, 6.75g of fat and 7.25g of protein. If these amounts of these components were fully converted to methane they would produce 0.0377 m^3 CH_4. Again if it is assumed that the mass of carbohydrate, lipid and protein present is equal to the mass of VS present, 80.9g of VS, if fully degraded would produce 0.0411 m^3 CH_4. This gives a methane production potential of 0.508 m^3 CH_4 kg VS degraded.

Prior to the commencement of co-digestion, daily methane production was running at around 15 l CH_4 d^{-1}, see Figure 6.10 Mean volatile solids reduction was around 52% over weeks 2- 6, see Figure 6.5. Based on this % reduction in volatile solids, the theoretical methane production would be 0.26 m^3 CH_4 kg VS added. It was actually measured at 0.22 - 0.24 m^3 CH_4 kg VS^{-1} added, over this period. The slight discrepancy can be attributed to conversion of a portion of VS to cell mass and errors associated with the VS analysis technique. Also the mean addition of 91.8 g VS d^{-1}, 5 days per week to the digester, and a 52% reduction in VS, gives a theoretical daily methane production over a 7 day week of 17.1 l CH_4 d^{-1}, which compared reasonably closely with the measured range values of 14.2 - 16.1 l CH_4 d^{-1} over weeks 3- 6, with the mean value being 15.2 l CH_4 d^{-1}.

Daily methane production increased to 26 l CH_4 d^{-1} during weeks 7 and 8 and to 29 l CH_4 d^{-1} during week 9, and then stabilised around 30 l CH_4 d^{-1} over weeks 10 - 12, see Figure 6.10. The amount of cattle slurry being added to the digester was reduced by 20%, to 0.96 kg d^{-1}, and consequently the amount of cattle slurry volatile solids being added was reduced from 91.8g VS

d^{-1} to 73.4g VS d^{-1}. This meant that the contribution of cattle slurry to daily methane production would have dropped from around 15 litres CH_4 d^{-1} to 12.4 l CH_4 d^{-1}. The 0.24 kg of FVW added each day contributed 37.2 g VS to the total volatile solids loading, which would theoretically yield 17.8 litres of methane if completely converted to CH_4, and equates to 12.7 litres d^{-1} CH_4 if averaged over a 7 day week. If it is assumed that the contribution of the cattle slurry to daily methane production was reduced to 12.4 l CH_4 d^{-1} then the extra CH_4 produced, between 13.6 and 17.6 l d^{-1} must have come from the FVW.

The figures for volumes of methane produced per kg of carbohydrate, protein and lipid destroyed, quoted by Peck *et al.*, see Table 6.3, were based on cattle slurry and the predicted methane production figures for cattle slurry using these values were found to be quite close to the values which were measured during weeks 3 - 6. It can be concluded, however, that their values were not found to be useful for predicting methane production from FVW, most likely due to the very different nature of the materials which constitute FVW and cattle slurry.

Methane productivity increased to 0.35 m^3 CH_4 kg VS^{-1} in weeks 7 and 8 and then to 0.39 - 0.41 m^3 CH_4 kg VS^{-1} added in weeks 9 - 12. Increasing the fraction of FVW present to 40% of feedstock weight, had the effect of further increasing methane productivity to 0.42 m^3 CH_4 kg VS^{-1} in week 13, before returning to 0.4 m^3 CH_4 kg VS^{-1} in week 14 and then dropping quite sharply in weeks 15 and 16, due to the problems described in Section 6.7. After the system had been stabilised at a lower loading rate, the % of FVW in the feedstock was increased to 50% wet weight during weeks 19 - 21. This had the effect of increasing methane productivity to 0.41 m^3 CH_4 kg VS^{-1} in week 19, 0.46 m^3 CH_4 kg VS^{-1} in week 20 and 0.44 m^3 CH_4 kg VS^{-1} in week 21. Nand *et al.* (1991) in a study of the digestibility of canteen wastes, which consisted of rice, bread

and vegetables, found that methane production from a digester operating on this type of waste had methane productivties of up to 0.49 m^3 CH_4 kg VS^{-1} added, with a 65% reduction in volatile solids content. No information was given by the authors about the % of each material present in the mixture, but the methane productivity was certainly similar to the values noted in the current work. Mata-Alvarez *et al.*, (1989) reported methane productivity values of up to 0.51 m^3 CH_4 kg VS^{-1} for a 2 phase digester operating on a mixture of orange, cauliflower, cucumber, lettuce, tomato and water melon waste. Again no information was given on the exact quantities of each material present in the feedstock. Lane (1984) studied the digestion of fruit and vegetable wastes and measured methane production rates of up to 0.568 m^3 CH_4 kg VS^{-1} removed.

The current work involved adding 37.2g of VS as FVW to the digester each day , at an 80/20 ratio CS/FVW. This equates to 27.9 l d^{-1} of methane using Lane's figures if the FVW was completely degraded, or 13.9 l d^{-1} of methane if the material was 50% degraded and 19.5 l d^{-1} methane if the material was 70% degraded. The values of between 13.6 and 17.6 l d^{-1} observed during the current work match closely the figures obtained by Lane.

6.13 Preliminary conclusions

The addition of FVW to an anaerobic digester operating on cattle slurry significantly increased methane productivity, at loading rates of up to 7.3 kg VS m^{-3} d^{-1} and with feedstock fractions of FVW of up to 50%. Foaming problems were noted at cattle slurry/FVW ratios of 60/40, but these problems did not re-occur at the higher ratio of 50/50, for reasons which were not clear.

Figure 6.1 Estimated and measured volatile solids loading rate.

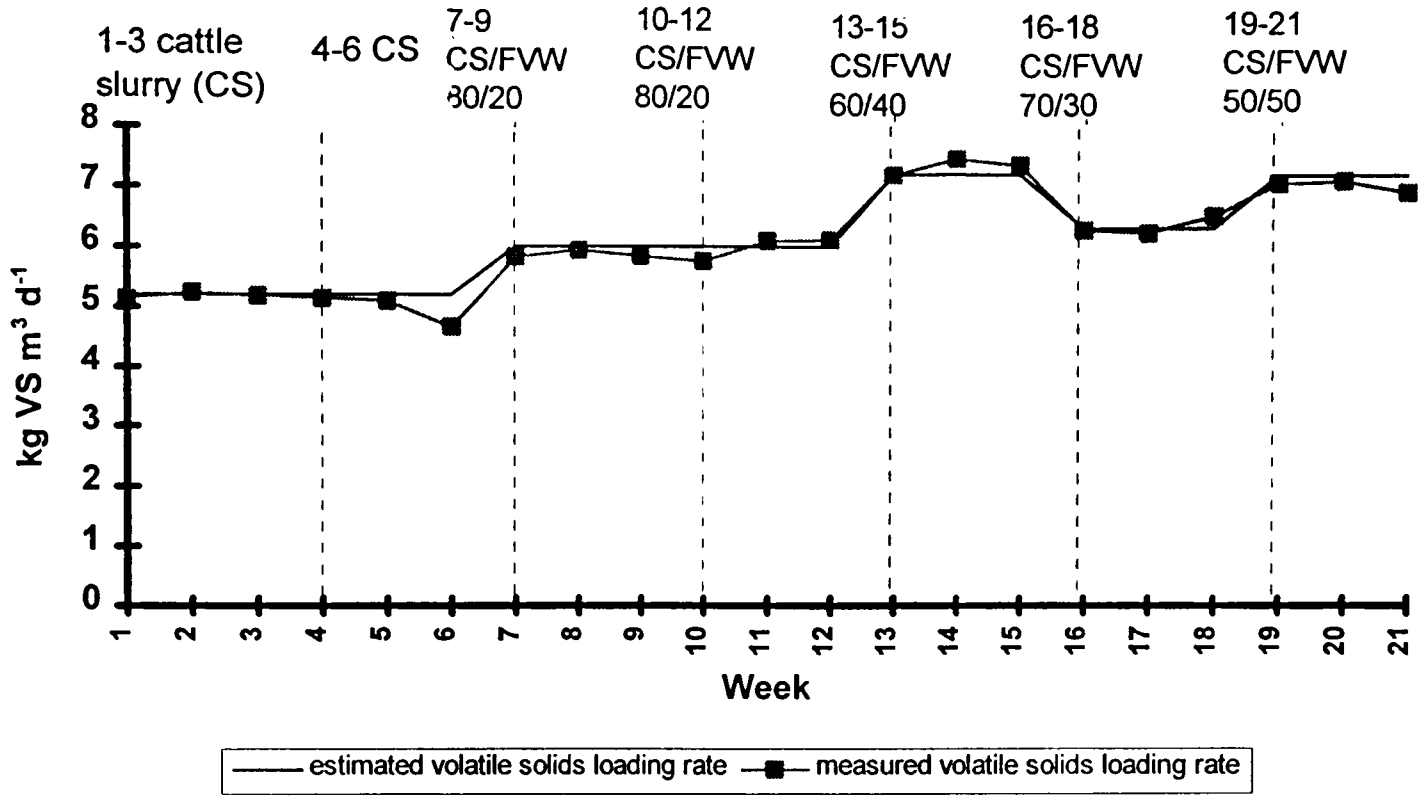


Figure 6.2 Variation in cattle slurry total and volatile solids and VM/DM ratio over the course of the experiment.

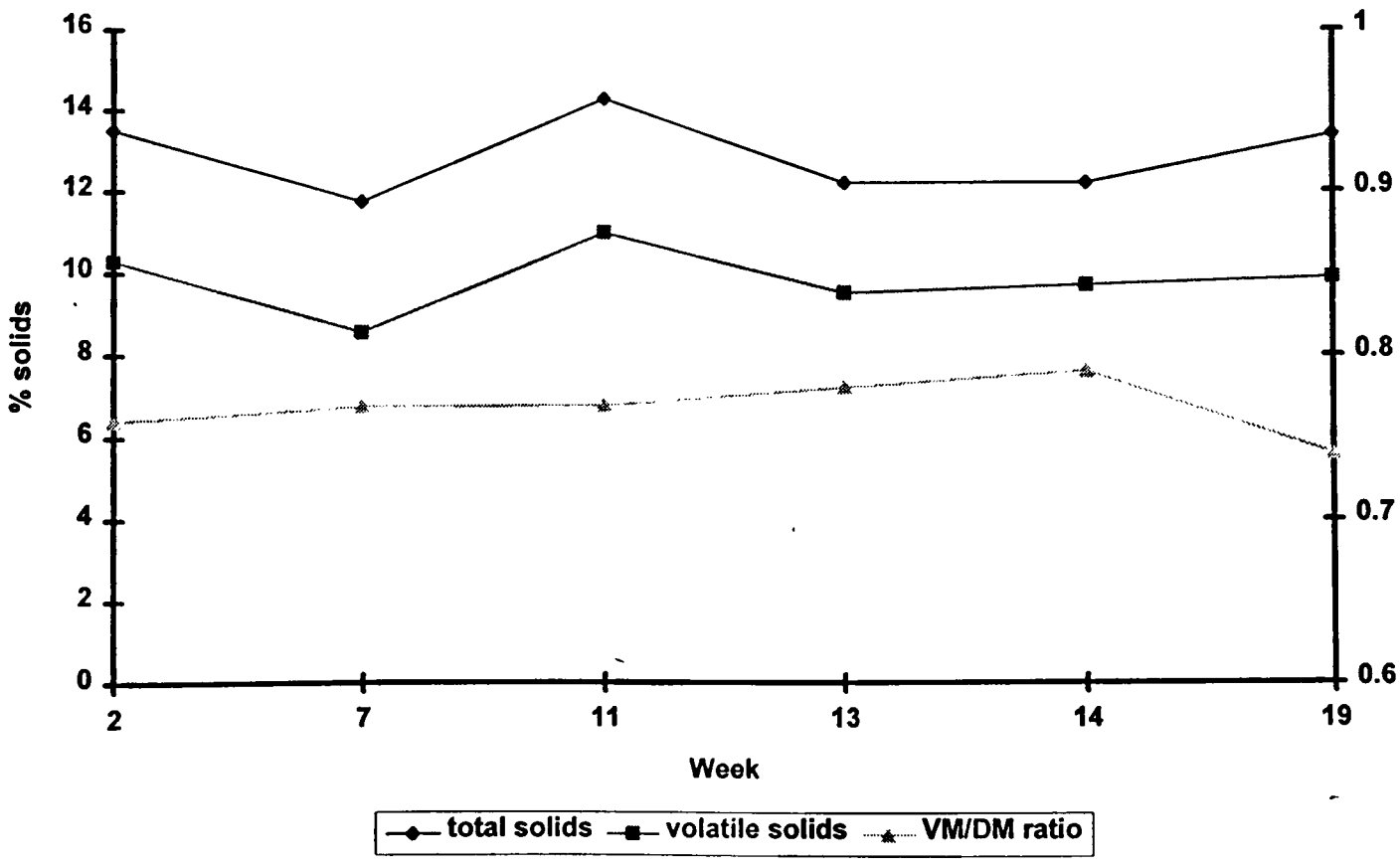


Figure 6.3 Variation in total and volatile solids and VM/DM ratio over the course of the experiment

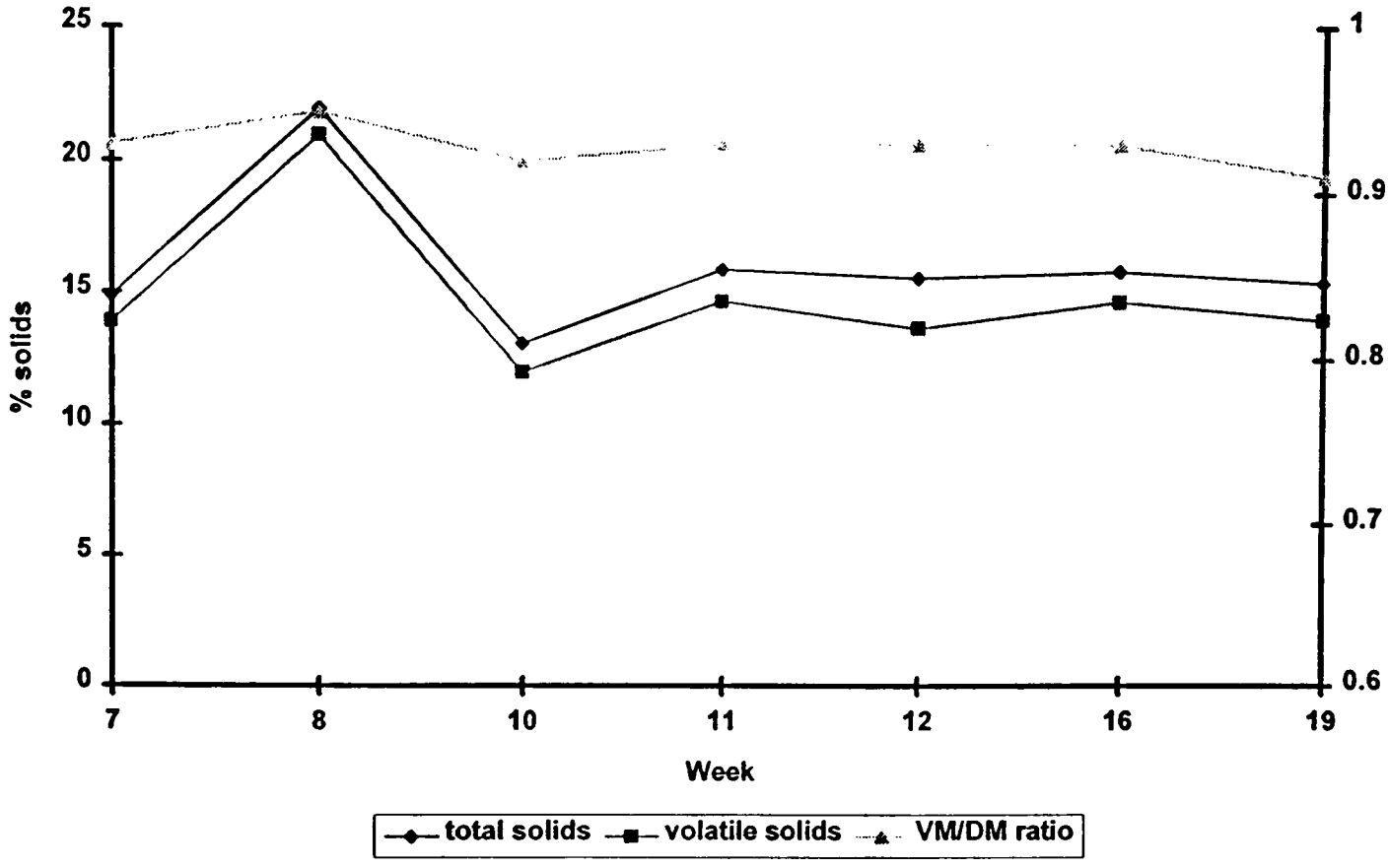


Figure 6.4 Mean daily volatile solids loading and methane production per kg volatile solids added for each week.

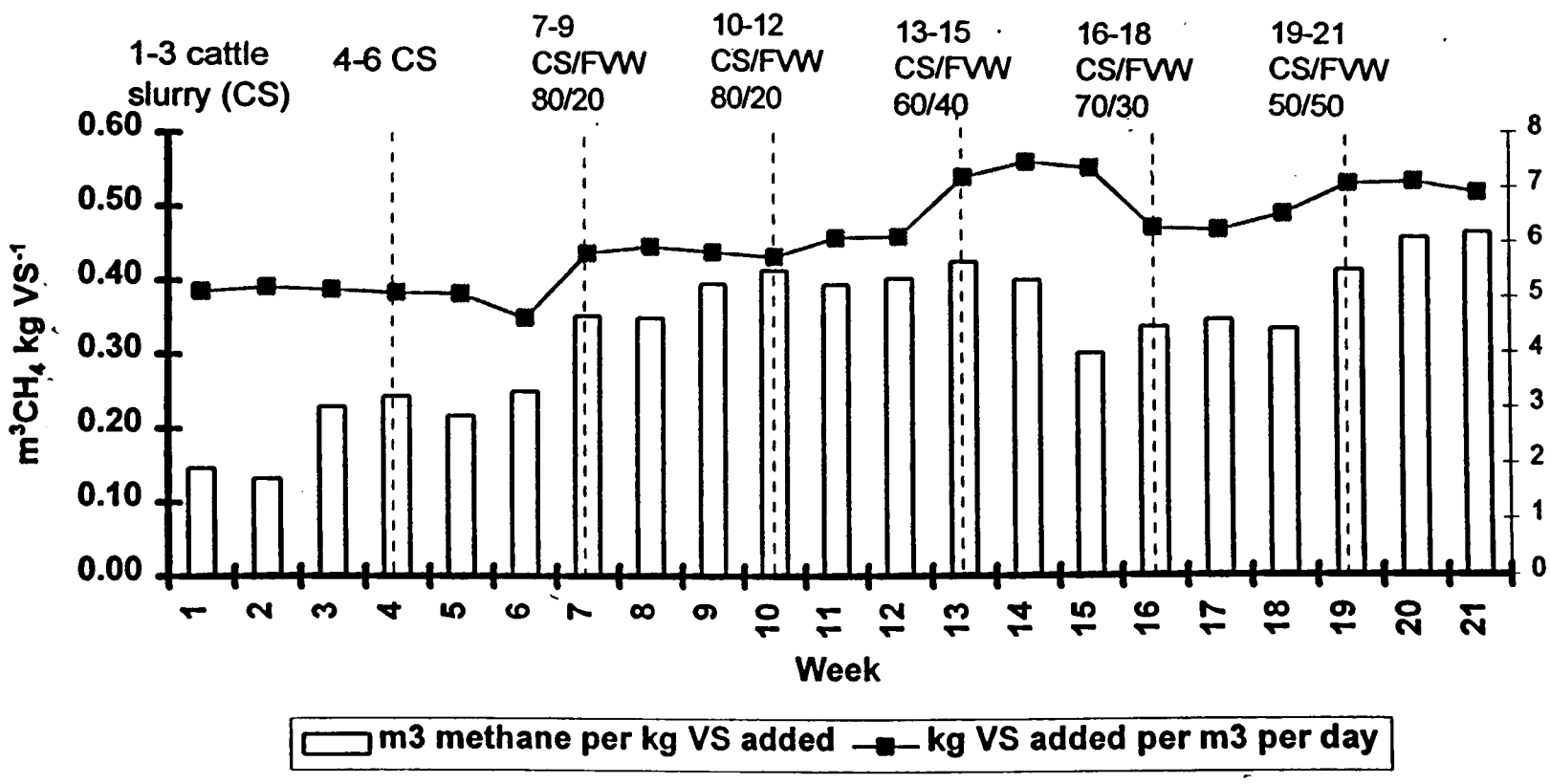


Figure 6.5 Mean daily % volatile solids removal for each week

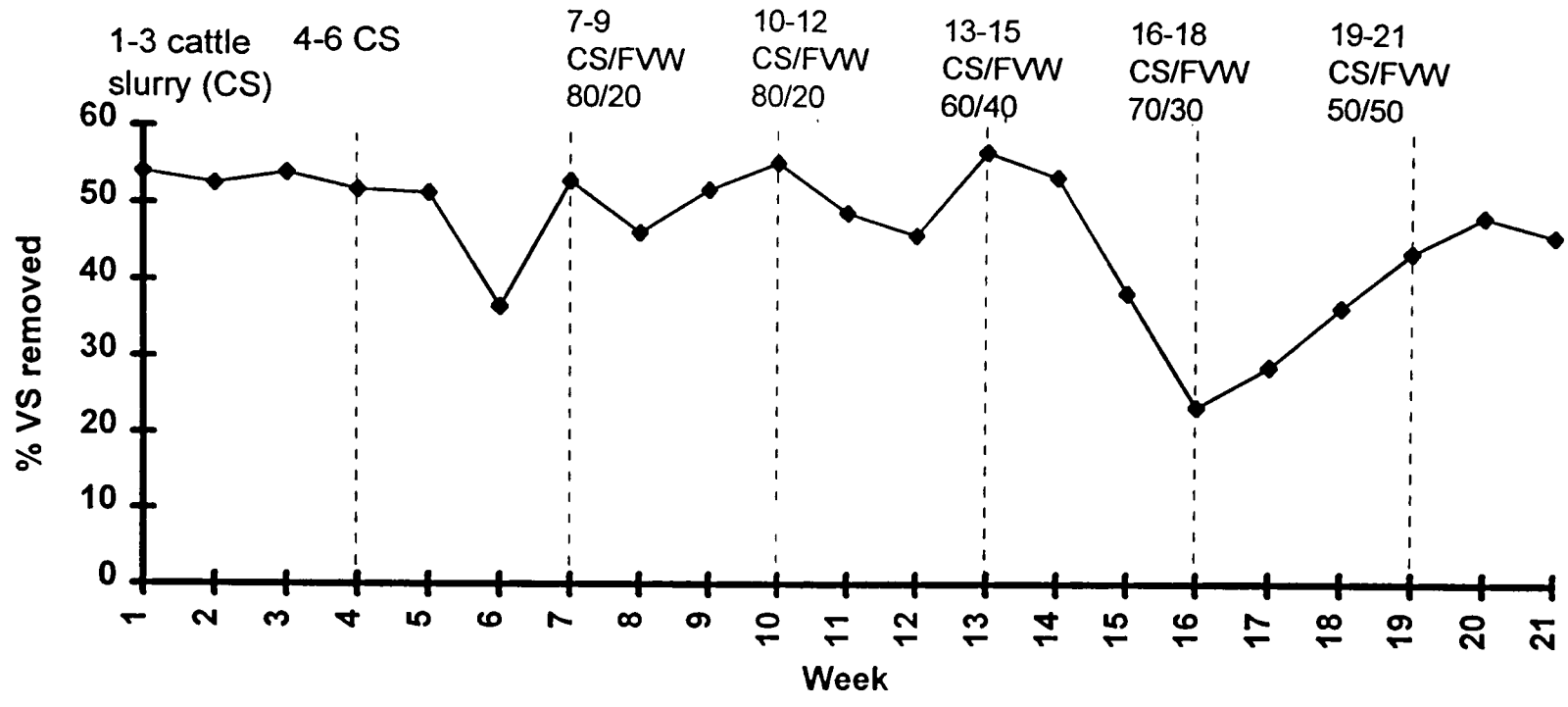


Figure 6.6 Mean daily feed and effluent total solids for each week.

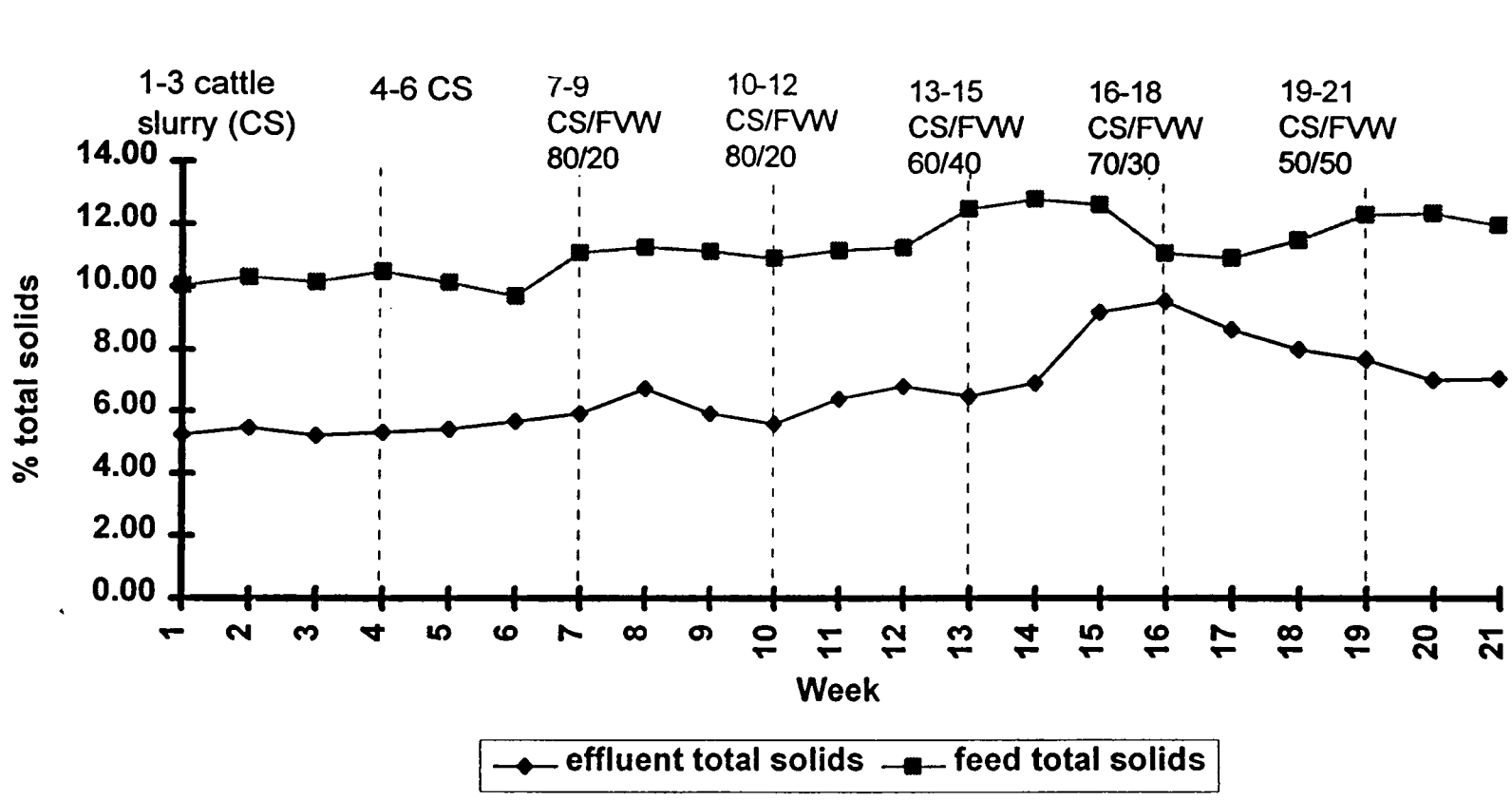


Figure 6.7 Mean daily feed and effluent volatile solids for each week.

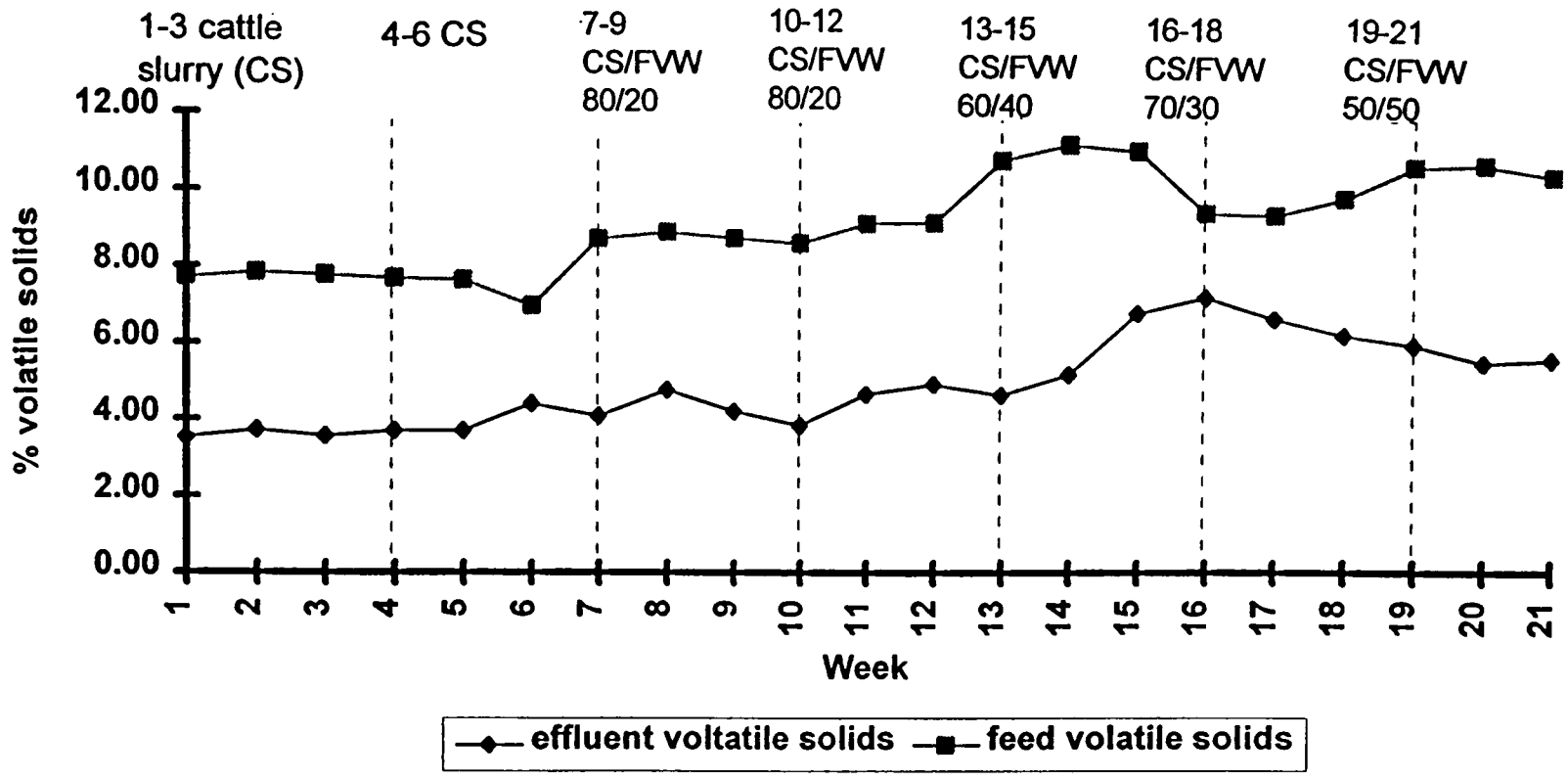


Figure 6.8 Mean daily volatile solids to total solids ratios of digester feedstock and effluent for each week.

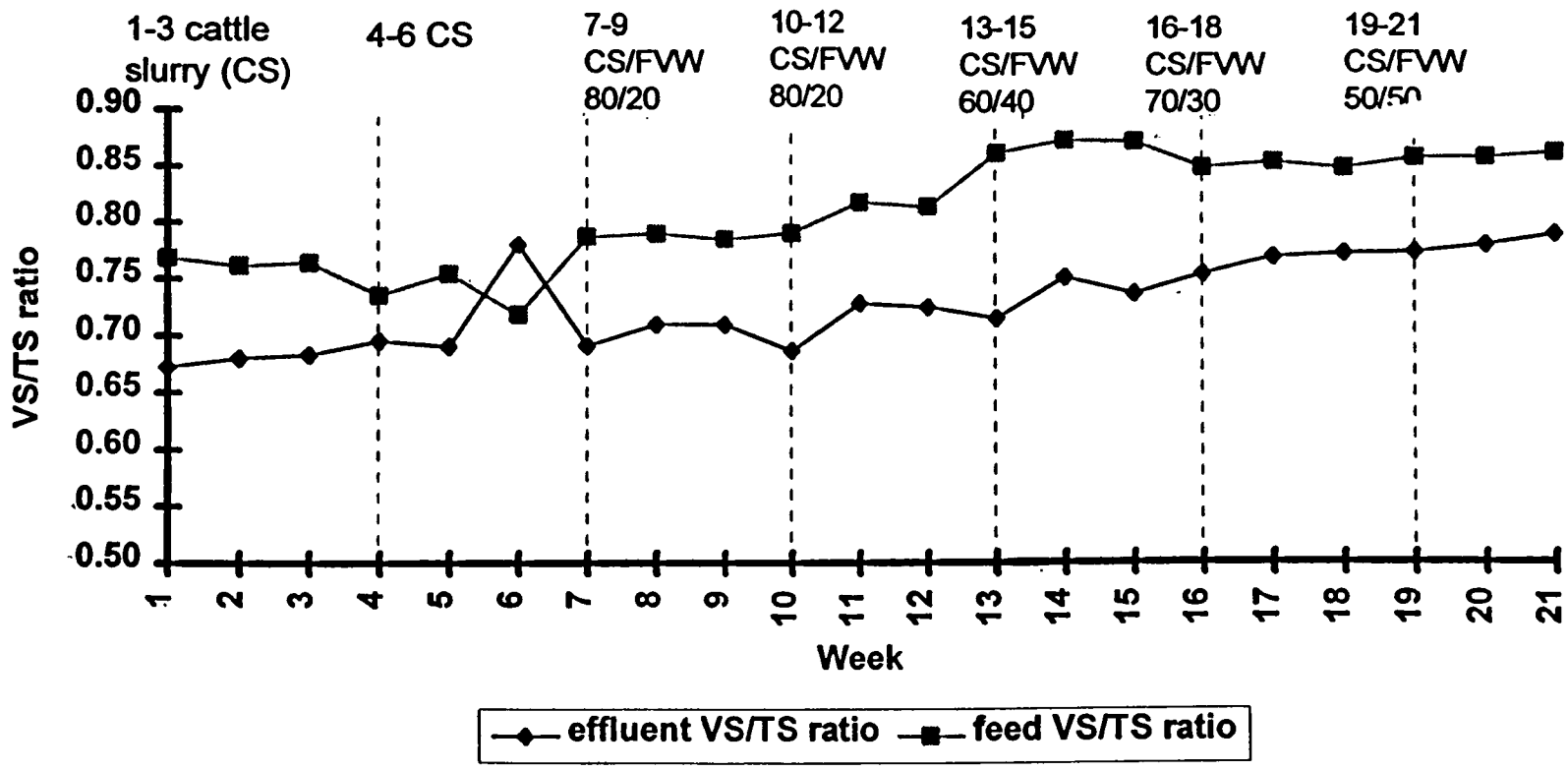


Figure 6.9 Mean daily biogas methane concentration for each week.

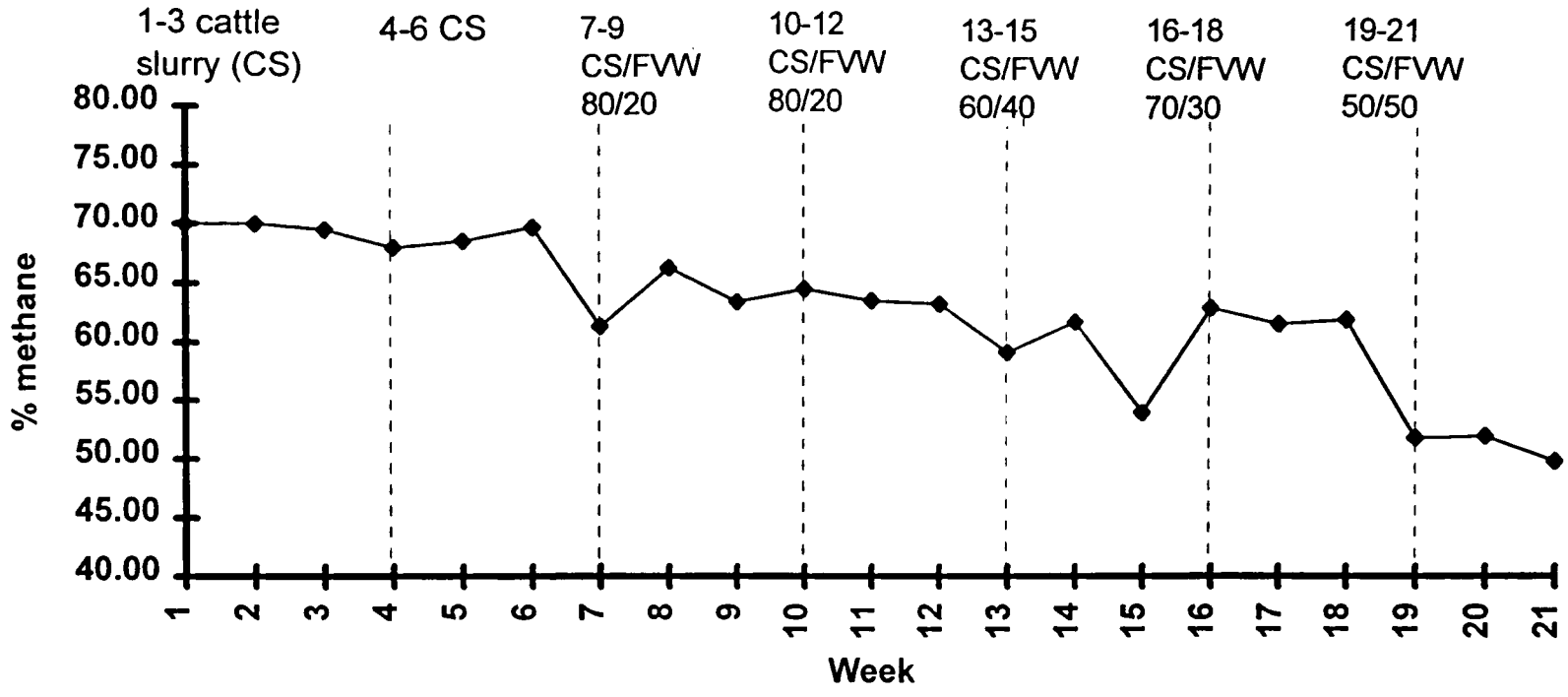


Figure 6.10 Mean daily methane production for each week.

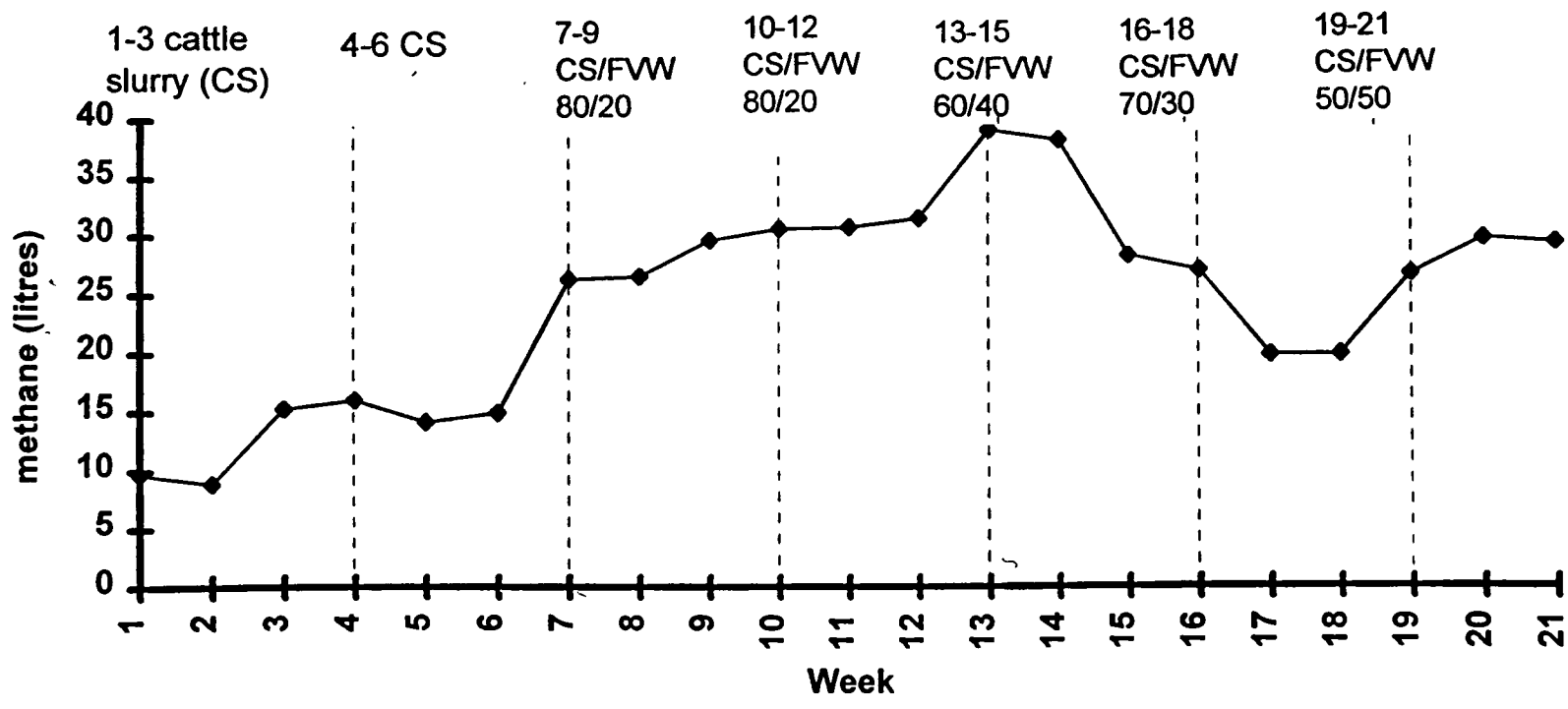


Figure 6.11 Mean daily digester effluent alkalinity values for each week.

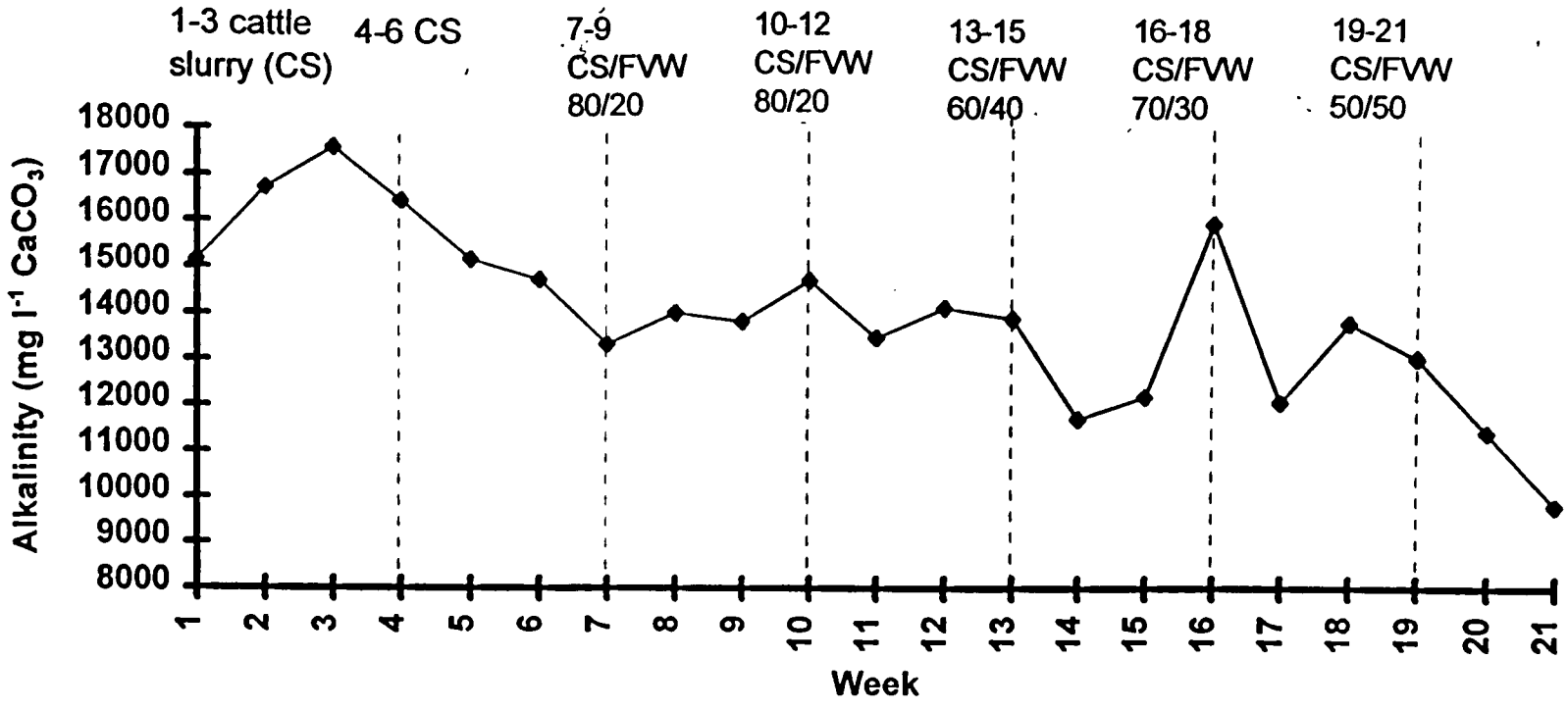


Figure 6.12 Mean daily effluent VFA concentrations for each week.

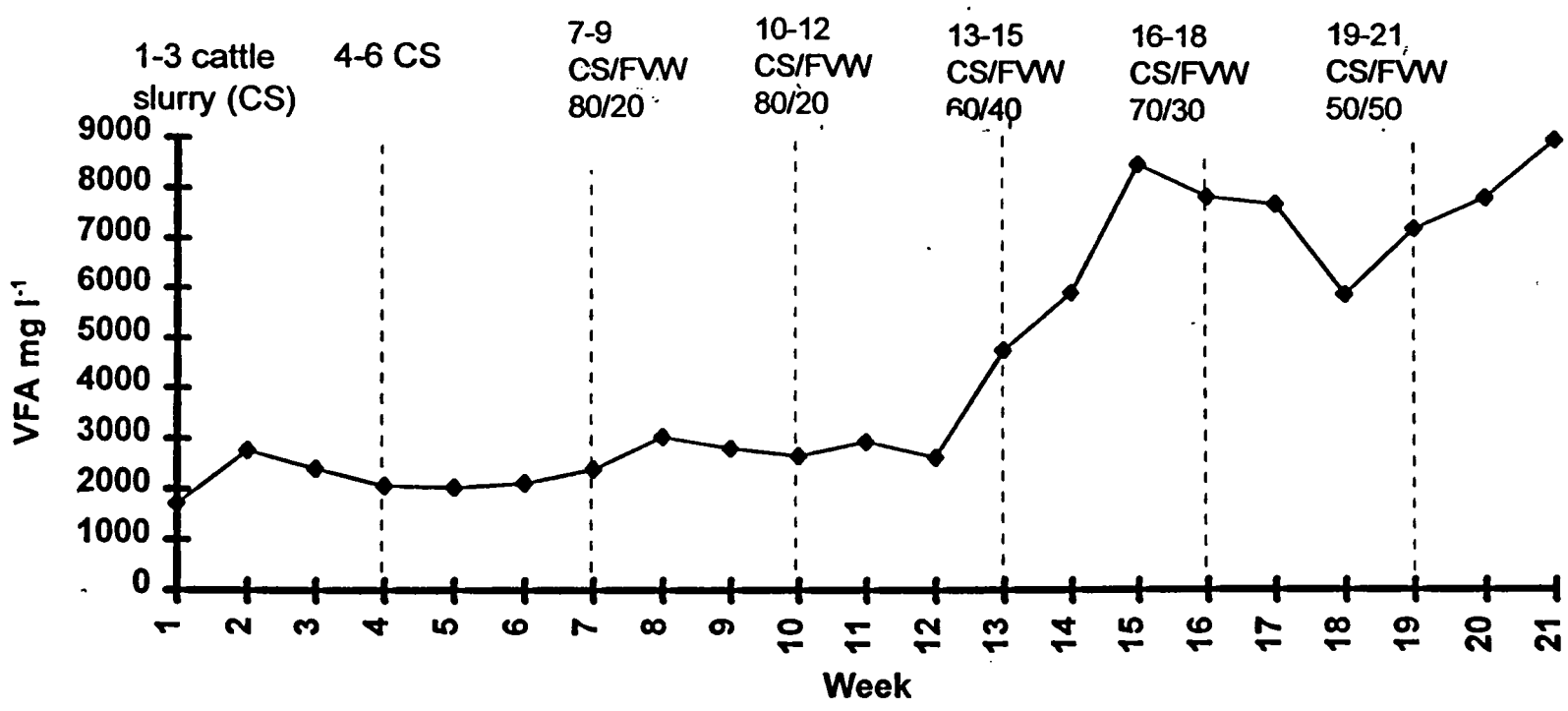


Figure 6.13 Mean daily digester effluent pH for each week.

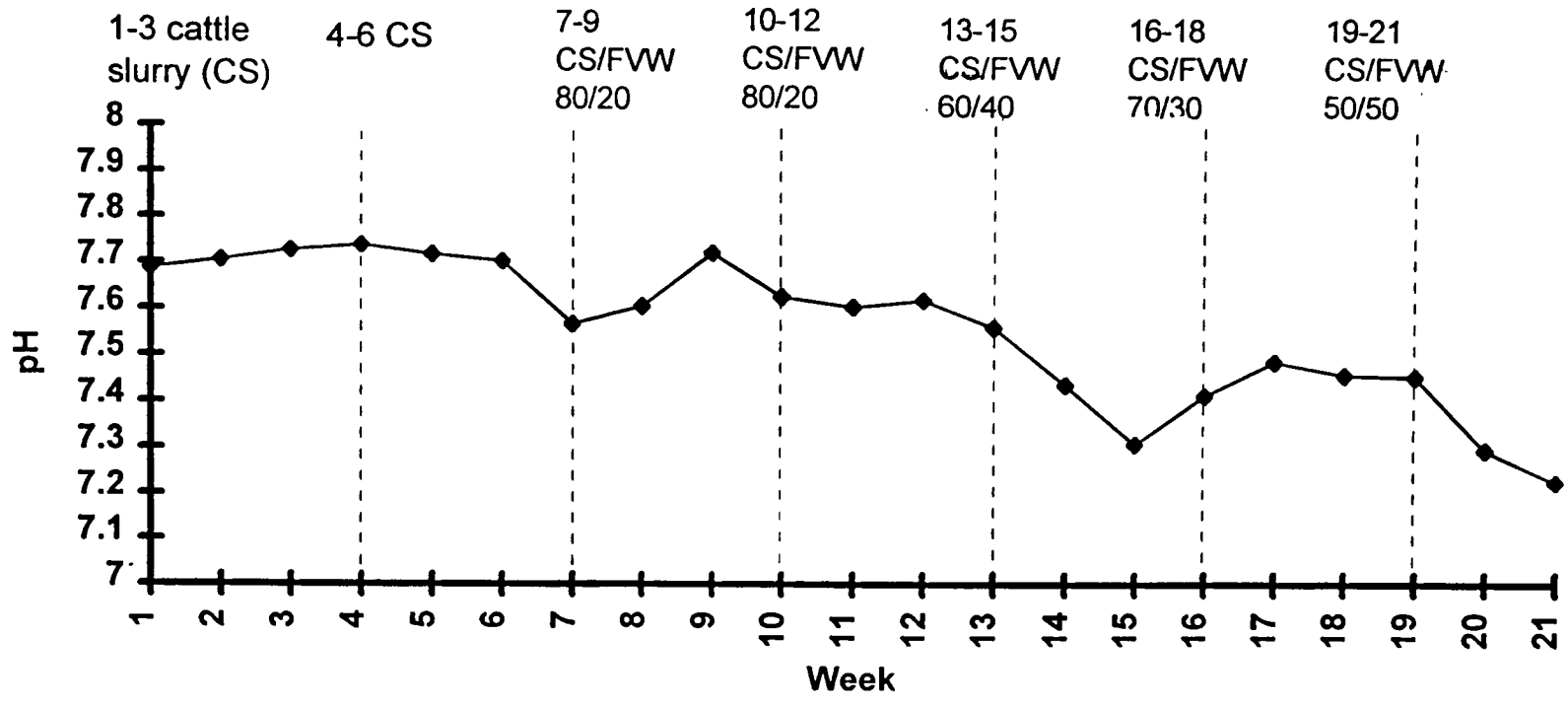


Figure 6.14 Mean digester effluent daily VFA:Total alkalinity ratio for each week.

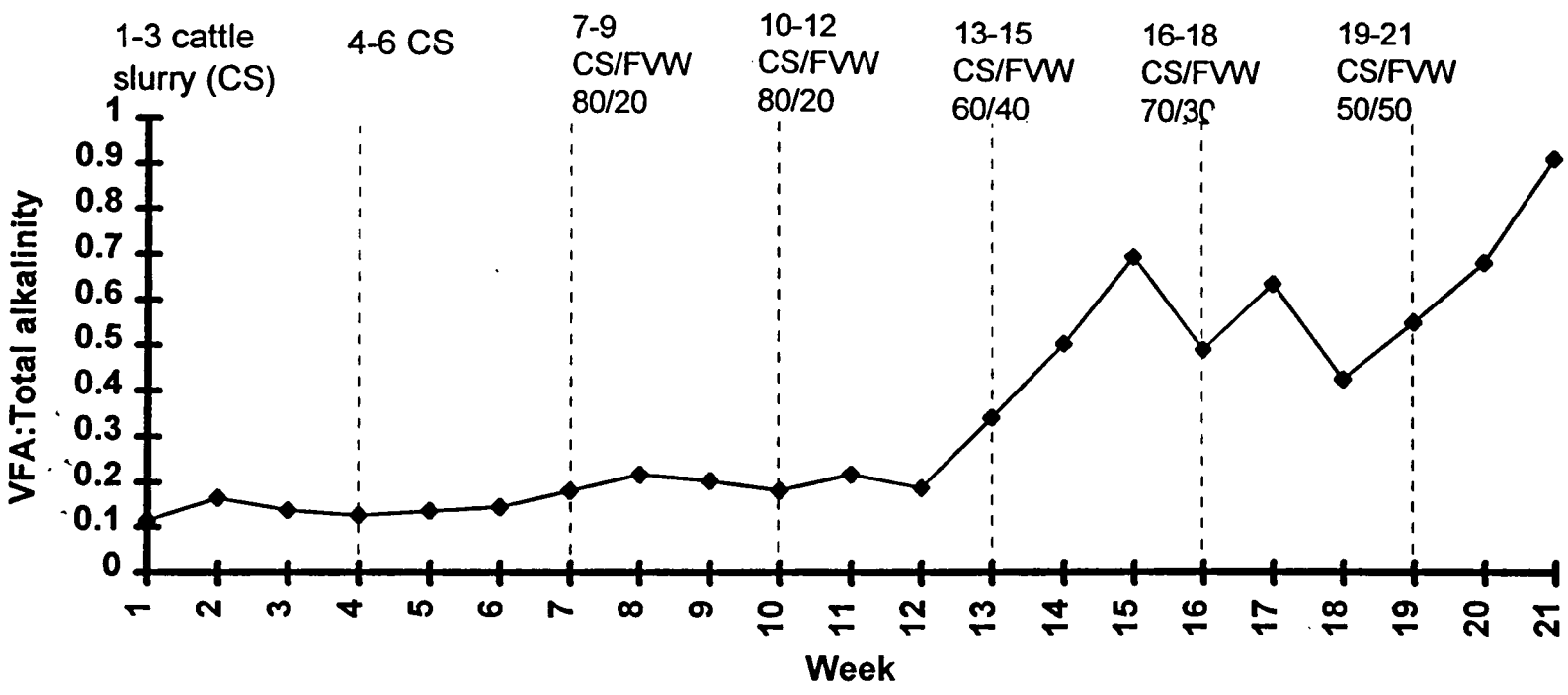


Figure 6.15 Mean daily effluent NH_4^+ and NH_3 concentrations for each week.

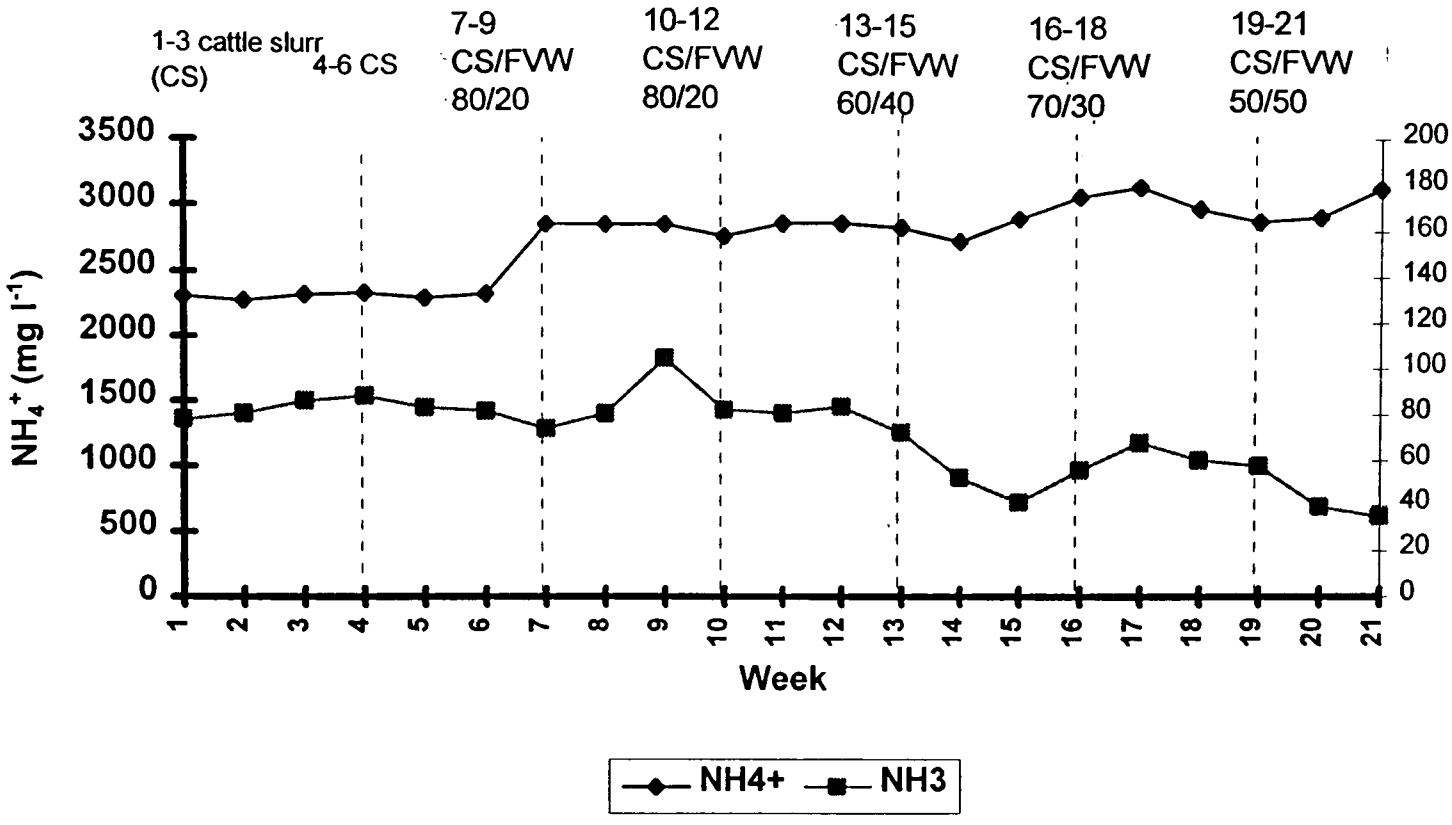
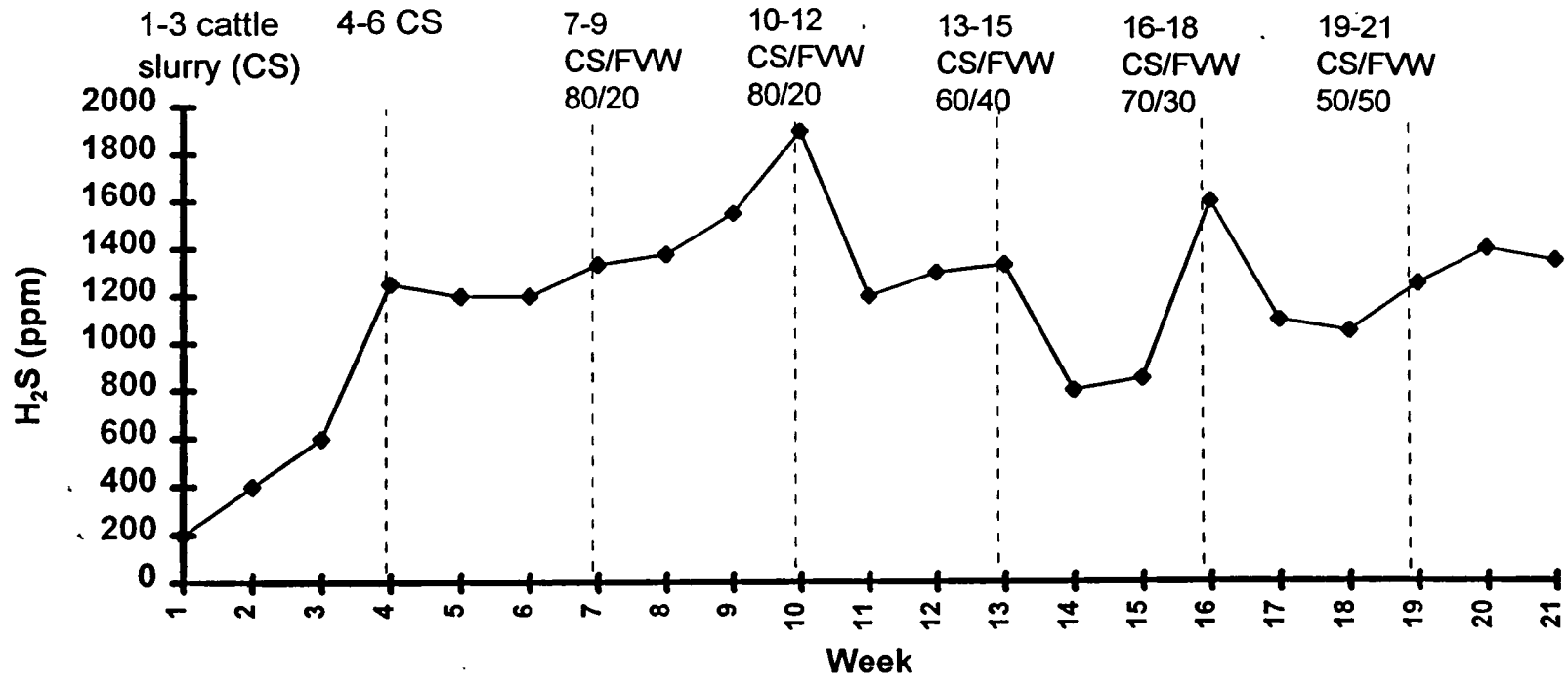


Figure 6.16 Mean daily biogas H_2S levels for each week.



Chapter 7

Anaerobic digestion pilot plant trial 3: co-digestion of cattle slurry and fish offal (FO)

7.1 Pilot plant operating history

The digester start-up procedure was the same as that described in Section 6.1 Feeding of cattle slurry took place from weeks 1- 6. After 2 retention times (the beginning of week 7) feeding of various mixtures of cattle slurry and fish offal (FO) commenced. The digesters were operated for a further 5 retention times, and shut down at the end of this period. No mechanical or electrical failures occurred during the operating period.

7.2 Digester operating regime

The digester was initially operated on cattle slurry as described in Section 6.2. Due to the rapid rate of digestion noted during the batch digestion of cattle slurry and FO which was described in Chapter 5, it was decided that the 21 day retention time would be sufficient to accomplish significant degradation of the FO.

The fish offal (FO) used as the co-digestate was obtained from Donnington Fish Farms Ltd., a commercial company producing rainbow trout for the restaurant trade. The offal consisted of viscera, heads, tails and bones, produced by the fish gutting operation. The offal was macerated

in a Magimix food blender (Magimix SA, France) and stored at -10°C. During the operation of the pilot plant digester, a quantity of FO, sufficient for one weeks operation, was thawed out at the beginning of each week. Although the FO was around 50% total solids, it was a liquid which flowed and could be easily poured. Maceration did not completely reduce all the raw FO to liquid, some segments of fish gut remained in the liquid, and did not seem to be reduced in size to any great degree, even after maceration for 5 minutes.

Initially, the digester was operated for 2 retention times (RT 1 and 2) on cattle slurry, at a loading rate of 5.2 kg VS m^3 d^{-1}, see Figure 7.1 (note: see pages 208-216 for Figures). At the end of this period co-digestion commenced. The initial co-digestion ratio was 96 % wet weight cattle slurry and 4% wet weight FO. This increased the volatile solids loading rate by about 17%, from 5.2 to about 6.1 kg VS m^3 d^{-1}. The digester was operated for 2 retention times (RT 3 and 4) at this ratio, although a slight change in the consistency of the FO occurred in a new batch obtained in week 10, which meant that the volatile solid loading rate dropped slightly to an average of 5.8 kg VS m^3 d^{-1} during weeks 10, 11 and 12, see Figure 7.2.

At the end of this period the FO fraction was increased to 6% wet weight, which increased the volatile solids loading rate by 9% to about 6.3 kg VS m^3 d^{-1} (RT 5) This increased loading rate caused foaming problems and system instability. It was decided to return to feeding cattle slurry only at a loading rate of 5 kg VS m^3 d^{-1} to allow the system to recover over the next retention time(RT 6) and the working volume of the digester was reduced from 18 litres to 12.89 litres, to create more headspace volume in which the foam could build up without blocking the gas outlet ports. The volumes of liquid added to and removed from the digester were adjusted accordingly to ensure the retention time remained constant. At the beginning of retention time 7 (RT 7) the

feed consistency was returned to 96 % cattle slurry / 4% FO which increased the volatile solids loading rate to around 5.4 kg VS m^3 d^{-1}, again slightly lower than expected , due to a further drop in the VS level of the FO. The digester was shut down at the end of retention time 7.

7.3 Variations in feedstock quality during the experiment

Figures 7.2 and 7.3 show the variation in total and volatile solids and VS/TS ratio of FO and cattle slurry over the course of the experiment. The quality of the cattle slurry remained reasonably constant over this time although a slight drop in slurry volatile solids did occur towards the end of the experiment. A number of samples of FO were collected over the course of the experiment, see Figure 7.2. The samples collected in week 7 and week 8 were of reasonably similar quality, but those collected in weeks 10 and 19 differed significantly in terms of VS and VS/TS ratio from the earlier samples. The first 2 samples were around 51.4% and 51.8% TS and had VS/TS ratios of 0.99. The second two had TS levels of 46.6% and 45.5% and VS/TS ratios of 0.98 and 0.96 respectively. It was not clear why this variation occurred.

Figure 7.1 shows the estimated and actual volatile solids loading rates over the course of the experiment. The method for estimating loading rates is described in Section 6.3. The estimated and actual values were quite close throughout the course of the experiment, indicating that the waste samples were reasonably homogenous.

7.4 Digester monitoring and performance

Digester monitoring was as described in Section 6.4.

7.5 Weeks 1-6; operation on cattle slurry

The digester was operated using cattle slurry as a feedstock for the first 2 retention times (weeks 1-6) at a volatile solids loading rate of 5.2 kg VS m^3 d^{-1}. It was operated under the same conditions as the reactor used in the work described in Chapter 6, see Section 6.5 for a full discussion of reactor performance over weeks 1 - 6.

Mean methane productivity values, measured in m^3 CH_4 kg VS^{-1} added, were similar to those values recorded in the work described in Chapter 6 for a cattle slurry digester of the same design, working at the same loading rate, see Figures 6.4 and 7.4, for comparison. The digester used in for the work described in Chapter 6 had a methane productivity of between 0.22 and 0.24 m^3 CH_4 kg VS^{-1} during weeks 3 - 6, whereas the digester in the current work had a methane productivity of 0.23 - 0.26 m^3 CH_4 kg VS^{-1}. Mean volatile solids removal over weeks 1-6 remained between 50 and 52%, which was the same range of values measured in the earlier work, see Figures 6.5 and 7.5. Mean effluent volatile solids and total solids also remained reasonably constant during this period, as did effluent VS/TS ratios, see Figures 7.6., 7.7 and 7.8, indicating that the system was sufficiently mixed.

Mean biogas methane concentrations dropped slightly after digester start up, but remained between 68 and 70 % between weeks 3 and 6, see Figure 7.9. Again these values were within the same range of values observed in the earlier work. Daily methane production stabilised after the first 2 weeks at around 15 litres per day, see Figure 7.10.

Mean digester effluent alkalinity, see Figure 7.11, followed a similar pattern to that observed in the earlier work. The alkalinity was initially around 15,000 mg l^{-1} Ca CO_3, it rose to around

17,000 mg l^{-1} , in week 3 before returning to between 15,000 and 16,000 mg l^{-1} ,during weeks 4, 5 and 6

Mean total VFA (volatile fatty acid) concentrations increased from 1800 mg l^{-1} to 2400 mg l^{-1} in week 2, most likely due to increased acidogenic activity caused by adding fresh slurry, see Figure 7.12. Effluent VFA levels stabilised at around 2000 mg l^{-1} during weeks 4-6, similar to values recorded in the earlier work, see Figure 6.12. Digester pH was stable at around 7.7 during weeks 1-6, see Figure 7.13, again similar to the work described in Chapter 6, see Figure 6.13

The mean VFA to Total alkalinity ratio (VFA:TAlk) was stable at around 0.13 during weeks 3-6, see Figure 7.14, which was the same value recorded for a cattle slurry digester in the work described in Chapter 6 and similar to the values estimated from Hall *et al.* (1985) , of 0.12.

From the above parameters, it can also be concluded that the digester was operating under steady-state, stable conditions during weeks 2-6.

7.6 Weeks 7-12 - digester operation on cattle slurry / FO (96 / 4).

At the beginning of week 7 the digester feedstock composition was altered to 96% wet weight cattle slurry and 4% wet weight FO. This had the effect of increasing the mean volatile solids loading rate by 11 - 17%, and also changing the nature of a portion of the digester feedstock. Using Paul and Southgate (1978) it was possible to approximately determine the percentages of carbohydrate, protein, and fat in the FO. No data for rainbow trout was available from this data source, so the data given for pink salmon was used, as the 2 species are from the same family (Salmonidae) and have the same genus *Oncorhynchus* (pink salmon is *Oncorhynchus gorbuscha*

and rainbow trout is *Oncorhynchus mykiss*) and could be expected to have very similar compositions (USFDA, 1997).

Table 7.1 Estimated amounts of carbohydrate, protein and fat present in the FO sample, expressed as a percentage of total solids and also shows the relative amounts of each in a cattle slurry sample for comparison purposes (cattle slurry data from Peck *et al*,, 1985)

	carb.	protein	fat	Total solids
for 100g FO	0	20.3g	8.2g	29.6g
as a % of TS	0	68.6	27.7	
for 100g of CS	5.35	0.54	0.58	8g
as a % of TS	66.9	6.75	7.25	

The solids values measured for the samples used in the current work were significantly higher than the values estimated using data from Paul and Southgate (44 - 52% TS compared to the estimated value of 29.6%) The increase in solids was possibly due to the inclusion of bone in the fish offal, whereas the Paul and Southgate data was for flesh only.

The addition of the feedstock containing FO to the digester had no immediate effect on mean daily methane production, see Figure 7.10. Mean biogas CO_2 did increase sharply in week 7, causing a corresponding drop in mean biogas CH_4 concentrations, from 68% CH_4 to 62% CH_4, see Figure 7.9 This effect of an organic shock loading on an anaerobic system has been noted by Marsili-Libelli and Beni (1996). Mean biogas CH_4 levels increased to 66% in week 8 and stayed between 64.5 and 66.5% between weeks 9 - 12.

Mean effluent VFA concentrations increased to 3,000 mg l^{-1} in week 7, to around 4,000 mg l^{-1}, then increased to 5,800 mg l^{-1} during weeks 9 and 10, before dropping slightly to 5,000 by week

12, see Figure 7.12. These values suggest that some inhibition of methanogenic activity was caused by the addition of FO to the digester. The mechanism of inhibition will be discussed in detail in Section 7.14. The mean VFA:TAlk ratio also supported the assumption that inhibition was occurring, see Figure 6.14. The ratio increased from 0.12 to 0.23 in week 7 and to 0.40 by week 9, and remained at 0.40 during week 10 before dropping to 0.36 in week 11 and 0.32 in week 12., below the trigger value of 0.35. This pattern suggested that while inhibition of the methanogens, which in turn caused VFA build up did occur, some recovery in the system did occur during weeks 10 - 12, perhaps associated with the slightly lower loading rate during these weeks, see Figure 7.4.

The mean % volatile solids removed fell steadily over weeks 7 - 11, see Figure 7.5, from 55% VS removal in week 7 to 33% by week 11, indicating a build-up of volatile material in the digester which the bacterial population were unable-able to breakdown. The VS removal rose slightly in week 12 to 36%, but essentially the trend was for % VS removal to decrease with time over weeks 7 - 12.

Mean methane productivity, expressed as m^3 CH_4 produced per kg VS added the digester, fell from 0.23 m^3 CH_4 kg VS^{-1} in week 6 to 0.20 m^3 CH_4 kg VS^{-1} in week 7, and then recovered to 0.27 and 0.28 m^3 CH_4 kg VS^{-1} in weeks 8 and 9. It then dropped in week 10 to 0.22 m^3 CH_4 kg VS^{-1}, and then increased again to 0.31 m^3 CH_4 kg VS^{-1} by week 12. It is interesting to note that an increase in the volatile solids loading rate of a similar magnitude to the increase added to the digester in the work described in Chapter 6 (which received an increase in VS loading of 11 - 17% as FVW), did not increase methane productivity by a similar amount (methane productivity in that work rose to 0.35 - 0.41 m^3 CH_4 kg VS^{-1} over weeks 7 - 12, see Figure 6.4). On a

qualitative level it was apparent that the bacterial population in the digester receiving samples FVW were better able to degrade this material than the bacteria receiving the FO. This is not surprising as the bacterial population in a cattle slurry digester comes largely from a herbivorous animal, and would not have to deal with significant amounts of fats in the rumen of a herbivore. The bacterial population in a sewage sludge digester, which are mostly from the human gut, would perhaps be more adapted to the degradation of wastes containing significant amounts of fats, due to the presence of fats in the human diet, although there is nothing in the literature to support this.

7.7 Weeks 13 - 15; digester operation on cattle slurry / FO (94 / 6)

At the beginning of week 13, as the digester seemed to be to have adapted somewhat to change in feedstock composition (mean methane productivity was increased from 0.2 m^3 CH_4 kg VS^{-1} in week 7 to 0.31 m^3 CH_4 kg VS^{-1} in week 12) it was decided to further increase the % of FO in the feedstock, with a consequent increase in the VS loading rate to around 6.3 kg VS m^3 d^{-1}. This change in feedstock composition had an immediate negative effect on biogas composition, which dropped from 65% CH_4 in week 12 to 58% CH_4 in week 13 and to 49% CH_4 in week 14 and 15, biogas CO_2 increased accordingly to around 51% CO_2. Mean effluent VFA increased to 5,500 mg l^{-1} in week 13, and then to 11,700 mg l^{-1} in week 14 and 12,900 in week 15, parameters Figure 7.12. The mean VFA:TAlk ratio also increased from 0.18 in week 12 to 0.34 in week 13, and then to 0.69 by week 15. Mean methane productivity fell sharply from 0.31 m^3 CH_4 kg VS^{-1} in week 12 to 0.09 m^3 CH_4 kg VS^{-1} in by week 15. pH also fell sharply over weeks 13 - 15, from 7.5 in week 12 to 7.1 by week 15. The changes in all these parameters indicated that significant inhibition of VFA removal was occurring in the system, and that the digester could not cope with the increase in feedstock FO levels. Some foaming also occurred during this period, which

caused carry over of solids, indicated in the increase in effluent total and volatile solids in Figures 7.5 and 7.8.

7.8 Weeks 16 - 18; digester operation on cattle slurry

Due to the system instability described Section 7.7, and the severe reduction in methane productivity, it was decide to change the feedstock to cattle slurry only, in attempt to re-establish system stability. The system working volume was also reduced to 12.89 litres to increase the available digester headspace and prevent foam from blocking the gas outlet ports. Feed volume was adjusted accordingly to keep the solids retention time at 21 days. The system was fed a mixture of 10% TS cattle slurry, as in weeks 1-6, but at a slightly lower loading rate of 5.0 kg VS m^3 d^{-1}, due to the slightly lower VS content of the cattle slurry, see Figure 7.3.

The mean %VS removed actually dropped to 0 in week 16, before rising slowly to 3% in week 17 and 6.6% in week 18, and the mean % VS in the effluent remained only a 2-3% below that in the feed, see Figures 7.5 and 7.7, indicating that a significant build up of volatile material had occurred over the previous weeks of operation. System mean pH recovered to 7.65 by week 18, mean effluent VFA dropped to around 4,000 mg l^{-1} by week 18, see Figures 7.12 and 7.13 and mean effluent VFA:TAlk values fell to 0.42 by week 18, see Figure 7.14, all indicating that the change in feedstock, to cattle slurry only, had the effect of restoring a measure of stability to the system, although VFA:TAlk ratios were still higher than the trigger value of 0.35. Mean biogas methane showed a rapid increase in from 49% in week 15, to just over 69% for week 16 and to 73% in weeks 17 and 18. Methane productivity increased to 0.14 m^3 CH_4 kg VS^{-1} in week 16, and then to 0.25 m^3 CH_4 kg VS^{-1} in week 17, before falling to 0.18 m^3 CH_4 kg VS^{-1} in week 18. This pattern co-coincided with a large fall in mean effluent VFA concentrations between weeks

16 and 17, see Figure 7.12, it is reasonable to assume that the increased methane productivity noted during week 17 was due to the conversion of the VFA pool, which had built up during the previous weeks, to methane. The mean methane productivity value of 0.18 m^3 CH_4 kg VS^{-1} in week 18 was lower than the values noted for digster operation on cattle slurry during weeks 2 - 6 (when methane productivity was between 0.22 and 0.25 m^3 CH_4 kg VS^{-1}).

7.9 Weeks 19 - 21; digester operation on cattle slurry / FO(96/4)

As the system had been returned to a reasonably stable state, it was decided to add FO to the feedstock once again, at a ratio of 96% wet weight cattle slurry to 4% wet weight FO. The VS level of the FO samples used had dropped slightly to, so that the sample had a VS/TS ratio of 0.96, compared to previous samples, which had values of 0.98 - 0.99. Therefore the loading rate was slightly lower than it was during weeks 7 - 12, when a 96/4 ratio was also used (5.7 - 6.0 kg VS m^3 d^{-1} during weeks 7 - 12 compared to 5.4 kg VS during weeks 19 - 21).

Biogas mean methane concentrations dropped sharply, during week 19, after commencement of feeding the 96/4 mixture (from 74% to 55% CH_4) as did mean methane productivity (from 0.18 to 0.15 m^3 CH_4 kg VS^{-1}), see Figures 7.4 and 7.9. Mean effluent VFA, VFA and VFA:TAlk ratio increased gradually over weeks 19 - 21, see Figures 7.12 and 7.14, indicating the rate of VFA production was faster than the rate at which the methanogens could remove VFA from the system. Nevertheless mean methane productivity recovered to 0.28 m^3 CH_4 kg VS^{-1} in week 20 and 0.27 m^3 CH_4 kg VS^{-1} in week 21, indicating that the system, although it still had high effluent VFA levels and VFA:TAlk values of greater than 0.35, had achieved a measure of stability. These values were only slightly below the maximum value recorded during weeks 7 - 12 (0.31 m^3

CH_4 kg VS^{-1}), for operation on a 96/4 mixture, at a slightly higher loading rate of 5.7 - 6.0 kg VS m^3 d^{-1}.

By week 21 the VFA:TAlk values had increased to 0.44, again above the trigger value of 0.35, but as had been noted during weeks 7 - 12, the system still had a higher methane productivity value than the values measured when it was operating on cattle slurry alone. This suggests that, although some inhibition of methanogenesis took place, the anaerobic system was able to accept a feedstock containing 4% wet weight FO without being adversely affected. However it should be noted that effluent VS levels remained high during weeks 19 - 21, see Figure 7.8, , and the evidence from weeks 7 - 12 suggests that the digested solids produced by a system operating on a 96/4 mixture would have VS levels 20 - 40% higher than digested cattle slurry. Therefore, while adding small quantities of FO to a cattle slurry digster may enhance methane productivity to some degree, the digested slurry produced could not be considered to have been stabilised by the process.

7.10 Ammonium (NH_4^+) and ammonia (NH_3) levels over weeks 1 - 21

As the FO had a C:N ratio of approximately 17:1 (calculated from Paul and Southgate, 1978), some NH_4^+ production was expected during digestion, due to protein breakdown, although at this C:N ratio FO would not be expected to produce the large quantities of NH_4^+ associated with the anaerobic digestion of wastes such as chicken manure, (C:N ratio 6.8 - 8.8:1) (*calculated from* Webb and Hawkes, 1985). Therefore NH_4^+ levels in the effluent were monitored over the course of the experiment.

NH_3 values were calculated from NH_4^+ and pH values using an equation developed by Abeling, (1994). Figure 7.15 shows mean NH_3 and NH_4^+ levels over the course of the experiment. Mean NH_4^+ levels varied between 2,200 and 2,300 mg l^{-1} during weeks 1- 6, with NH_3 levels remaining at around 80 mg l^{-1}, which was similar to the levels observed during the digestion of cattle slurry during the work described in Chapter 6. The addition of FO in week 7 produced a significant increase in mean effluent NH_4^+ levels to around 2467 mg l^{-1} in week 7 and then to around 3,200 mg l^{-1} in weeks 8 - 12. This increase was most likely due to the degradation of the FO protein fraction. A further increase to around 3,400 mg l^{-1} was noted when the FO fraction was increased to 6% of total feed weight over weeks 13 - 15. The change in feedstock to cattle slurry only, had the effect of reducing NH_4^+ slightly to around 3,200 mg l^{-1}, and levels stabilised around this value over weeks 19 - 21.

Mean effluent NH_3 levels were reasonably low throughout the course of the experiment, through a combination of low NH_4^+ concentrations and low pH values (see Section 1.3.3.4 for a full discussion of the relationship between pH, NH_4^+ and NH_3 levels). The highest value reached during the current work was 95 mg l^{-1} NH_3 during week 18 (due to the increase in pH caused by the addition of a feedstock containing cattle slurry only) and for most of the experiment the mean NH_3 level remained between 40 and 80 mg l^{-1}. Therefore it can be assumed that no inhibition of the system by NH_4^+ and NH_3 occurred over the course of the experiment, see Section 1.3.3.4 for a justification of this assumption). The general trend in effluent NH_3 levels was downwards due to the declining pH noted over weeks 7 - 15, see Figure 7.13.

7.11 Hydrogen Sulphide levels (H_2S) levels in the biogas over weeks 1 - 21.

Figure 7.16 shows mean H_2S levels in the biogas over weeks 1 - 21. As noted in Section 6.11, there is some anecdotal evidence to suggest that biogas H_2S levels are indicators of shock loadings in anaerobic digesters. The H_2S concentrations in the biogas rose sharply on commencement of feeding cattle slurry to the digester, and levelled off at around 1,400 ppm during weeks 4 - 6, a similar pattern to that noted in Figure 6.16. Commencement of addition of FO caused a further gradual increase in biogas H_2S to a maximum of between 1,800 ppm and 2,000 ppm in weeks 10 -12. Levels remained around this range during weeks 12 - 14, before rising to 2,100 ppm in week 15 and 2,500 ppm in week 16, and then fell slightly during week 17 to 2,300 ppm. Levels stabilised at around 1500 ppm over weeks 19 - 21

While the increases in biogas H_2S noted during weeks 1-4 and weeks 6 - 8 can be attributed to the commencement of feeding cattle slurry and the addition of FO to the feedstock, the negative effect of increasing the fraction of FO in the feedstock, during weeks 13 - 15, which was detected by other parameters such as the VFA:TAlk ratio during weeks 14 and 15, had no significant effect on biogas H_2S levels. The addition of a feedstock containing cattle slurry only during weeks 16 - 18 caused a rapid increase in biogas H_2S to 2,500 ppm in week 16, even though again, other parameters, such as VFA:TAlk, effluent VFA and pH were indicating that the cattle slurry had a positive effect on the system. There was no indication that biogas H_2S levels were changing in response to system instability and it can be concluded, in concurrence with observations made in Section 6.11 and Section 4. that H_2S levels in the biogas are of little practical use in controlling an anaerobic digestion process.

7.12 Methane production potential of FO and actual methane production

Due to the large difference between the predicted values for FO VS and the measured values (29.6% VS predicted, see Table 7.1, compared to 45 - 51% VS measured) , it was not possible to directly predict the methane production values which would have been expected if the FO was completely degraded under anaerobic conditions. Table 7.2 shows the theoretical methane production which would be expected if the FO added to the digester was of the consistency predicted by the literature (29.6% VS) and that all of this FO was completely converted to methane. It also shows the predicted amount of CH_4 which would be produced if 1 kg of FO was completely degraded under anaerobic conditions. Although the methane productivity of the FO used could not be directly calculated, the estimated methane productivity of the lower %VS FO could be used as a useful measure of the degree to which the FO which was added to the digester was digested. For example, if the volume of methane produced by adding the FO to the digester was less than the predicted value for a sample that had a much lower VS level, it could be reasonably assumed that the anaerobic degradation of the FO was being inhibited in some way. Also it was noted in Section 6.12 that the values used for predicting methane production were determined for cattle slurry, and that these values underestimated the methane production potential of FVW, so again the values estimated in Table 7.2 could be expected to be underestimates.

Table 7.2 Amounts of FO added to the digestion system during weeks 7 - 21 and theoretical methane yield, based on estimated composition of FO (calculated using values of 0.68 m^3 CH_4 kg^{-1} protein destroyed and 0.98 m^3 CH_4 kg^{-1} of fat destroyed from Peck *et al.*, 1985, at 273 K and 760 mm Hg. The methane values in the current work have been calculated at 298 K and 760 mm Hg, therefore the values from Hawkes and Hawkes were adjusted to 298 K).

period	kg FO	kg protein	kg fat	CH_4 kg protein	CH_4 kg fat	total m3 CH_4/ mass FO destroyed
wk.-6	0	0	0	0	0	0
wk 7-12	0.048	0.09744	0.00385	0.0072332	0.004118	0.011351
wk 13-15	0.072	0.014616	0.00574	0.010848	0.006210	0.017058
wk 16-18	0	0	00	0	0	0
wk 19-21	0.048	0.009744	0.00385	0.0072332	0.004118	0.011351
1 kg FO	1	0.203	0.0802	0.1506706	0.085787	0.242847

The methane production potential of cattle slurry was previously estimated at 0.508 m^3 CH_4 VS degraded, see Section 6.12.

Similarly to the digester used in the work described in Chapter 6, prior to the commencement of co-digestion mean daily methane production was running at around 15 l CH_4 d^{-1}, see Figure 7.10 Mean volatile solids reduction was around 51% over weeks 2- 6, see Figure 7.5. Based on this % reduction in volatile solids, the theoretical methane production would be 0.26 m^3 CH_4 kg VS. It was actually measured at 0.23 - 0.26 m^3 CH_4 kg VS^{-1} over this period. The slight discrepancy can be attributed to conversion of a portion of VS to cell mass and errors associated with the VS analysis technique. Also the addition of 91.8 g VS d^{-1}, 5 days per week to the digester, and a 51% reduction in VS, gives a theoretical daily methane production of 23.8 l for each of the 5 days that the cattle slurry was added to the digester which is 17 l CH_4 d^{-1}, when averaged over 7 day week. This compared reasonably closely with the measured range values of 14.9 - 16.9 l CH_4 d^{-1} over weeks 3- 6, with the mean value being 16.2 l CH_4 d^{-1}.

The amount of cattle slurry being added to the digester was reduced by 4%, to 1.16 kg d^{-1}, and consequently the amount of volatile solids being added was reduced from 91.8g VS d^{-1} to 88.1g VS d^{-1}. This meant that the contribution of cattle slurry to daily methane production would have dropped by 4% from around 16.2 litres CH_4 d^{-1} (its mean value over weeks 2- 6) to 15.5 l CH_4 d^{-1}, assuming the %VS removed remained constant).

If it is assumed that the potential contribution of the amount of cattle slurry added to the digester each day to daily methane was around 15.5 l CH_4 d^{-1} during weeks 7 - 12, then it could also be reasonably be assumed that any value noted above this value was due to the FO and any value noted below this value was due to inhibition of the methane production process by the FO. Similarly, when the amount of cattle slurry added to the digester each day was reduced to 1.15 kg during weeks 13 - 15, the contribution of the cattle slurry to mean daily methane production would be reduced to 15.2 l CH_4 d^{-1}. These assumptions can be used to generate a figure which compares the expected daily methane production with the actual value recorded, to give an idea of by how much the methane production process was enhanced or inhibited by the addition of the FO, see Figure 7.17. The addition of FO to the feedstock made no contribution to mean daily methane production during week 7, although mean daily methane production did rise above the "base rate" mean daily methane production expected from the cattle slurry by 5.5 l CH_4 d^{-1} in week 8 and 6.5 l CH_4 d^{-1} in week 9, before dropping to only 0.5 l CH_4 d^{-1} above "base-rate" in week 10, for reasons which are not clear. Mean daily methane production then recovered somewhat during weeks 11 and 12, to 3.1 and 7.4 l CH_4 d^{-1} respectively. The increase in FO level in the feedstock brought about a rapid fall in mean daily methane production to only 0.6 l CH_4 d^{-1} in week 13, a similar value to that observed when FO was first introduced to the feedstock in

week 7. However, on this occasion, mean daily methane production fell rapidly and remained between 28 and 50% less than the "base-line" value during weeks 14 - 18", even restoration of cattle slurry only feed did not have any long term effect. Addition of FO to the feedstock in week 19 again caused a drop in mean daily methane production, to 7.5 l CH_4 d^{-1}, only 50% of the base line value. Mean daily methane production did recover somewhat during weeks 20 and 21, but was still about 15% below the "base line". It would seem that 4% FO in the feesdstock was the maximum percentage the bacterial population could endure.

Overall it can be concluded that the addition of FO to the feedstock made only a slight contribution to daily methane production, initially enhancing it by up to 33% but then suppressing methane production by up to 50% of the value estimated for cattle slurry alone. The figure in Table 7.2, suggest that methane productivity should have been enhanced, as even a feedstock of the consistency of that in Table 7.2, which had a lower VS than the samples of FO actually used in the work, would have enhanced mean daily methane production by around 6.5 l CH_4 d^{-1} at a VS reduction level of 50% and at 6% FO, would have enhanced ean daily methane production by around 8.5 l CH_4 d^{-1} .

Clearly methane production was inhibited by the addition of FO to the digester feedstock.

7.13 Proposed mechanism of inhibition of methanogenesis

The addition of FO initially caused a slight increase in mean daily methane production, although of lesser magnitude than was expected, and then caused inhibition of methanogenesis during week 10, before the system recovered slightly. However a 50% increase in the amount of FO added caused severe inhibition of the digestion process, an effect which lasted for a number of weeks

after the additions of FO ceased, see Figure 7.17 Clearly some component or fraction of the FO was inhibiting methane production.

Fish contain large amounts of long chain fatty acids (LCFA) such as oleic acid which have been shown to cause inhibition of methanogenesis, (Hobson and Wheatley, 1993). Much work has been done on the characterisation of the fatty acid profile of the pink salmon but little information is available on rainbow trout. As both fish are from the same family (Salmonidae) and have the same genus *Oncorhynchus* (pink salmon is *Oncorhynchus gorbuscha* and rainbow trout is *Oncorhynchus mykiss*) it would be reasonable to assume that they would have broadly the same fatty acid composition (USFDA, 1997)

Paul and Southgate (1978) found that pink salmon had a LCFA acid (C12 - C24) concentration of 7.65%. Oleic acid accounted for 5.5 % of all LCFA acids present. Therefore 48g of FO added to the digester for 5 days per week during weeks 7 - 12 would have consisted of 3.7g of LCFA and 203 mg of this would have been oleic acid. The initial dilution would have been 3.7 g and 203 mg in 18 litres, giving digester LCFA and oleic acid concentrations of 205 mg l^{-1} and 11.3 mg $^{-1}$ respectively, after one addition of FO.

Hanaki *et al.* (1981) found that adding increasing amounts of oleic acid to batch digesters (from 250 - 2000 mg l^{-1}) increased the delay before the onset of methane production from the digester. They postulated that this was because the LCFA was inhibiting the - oxidation cycle, by which LCFA are converted to acetic acid. Further experiments showed LCFA levels above 250 mg l inhibited methane production from both hydrogen and acetic acid, that is both the acetate utilising methanogens and the hydrogen utilising methanogens were inhibited. Petruy and Lettinga (1997)

found that LCFA from milk fat, at a concentration of 874 mg l^{-1}, severely inhibited liquefaction of fats and their subsequent conversion to methane. Petruy and Lettinga also found that LCFA from milk fat (C10 - C18) were quickly adsorbed onto the sludge particles within a digester, increasing their concentration in the micro-environment around bacteria still further.

If it is assumed that no LCFA or oleic acid was degraded in the digester during the first week of FO addition then LCFA and oleic acid concentrations would have been approximately 1,000 mg l^{-1} and 56.5 mg l^{-1} by the end of the week, ignoring any losses due to removal of some effluent each day. Hanaki *et al.* did not observe the effect of other LCFA on the anaerobic digestion process, but suggested their effect is likely to be similar to that observed for oleic acid. Therefore inhibitory concentrations of LCFA could have already built up in the digester by the end of the first week of feeding FO. The mean daily % VS removed values noted over weeks 7 - 12, see Figure 7.5, suggested that there was accumulative inhibition of the breakdown of organic material, as mean % VS removed decreased almost linearly from 57% in week 7 to 33% in week 12. This build up of organic material in the digester effluent could have been caused by a combination of the inhibition of the - oxidation cycle mentioned above by the LCFA, meaning that LCFA were passing through the digester un-degraded, and inhibition of methane production from acetic acid by LCFA, which would have caused the gradual VFA increase noted over weeks 7 - 10.

LCFA concentrations in the batch digesters containing cattle slurry / FO mixtures, described in Chapter 5, were calculated to be 1350 mg l^{-1}, using the assumption that FO consists of 7.65% LCFA. The lag time of 2 weeks before the FO contributed to methane production, could be attributed to inhibition of methanogenesis by this LCFA level. Rapid digestion of FO began once

the level of LCFA had been reduced below inhibitory concentrations. An alternative explanation is provided in Section 7.15. In the continuous system, further additions of FO meant that LCFA levels remained well above inhibitory concentrations.

7.14 Reasons for the difference between batch and continuous experiments with FO

The batch trials and continuous trials for FO produced conflicting data. The FO used was from the same source and the same fish. The only difference was that the material used for the batch trials had been stored in an out-house at the fish farm for 2 weeks during the summer and the FO used for the continuous trials was fresh. The FO used for the batch trials, unsurprisingly, had a very strong odour, and was undergoing de-composition. It is likely that some, and perhaps a significant proportion, of the LCFA present was degraded by a combination of oxidation, lipase enzymes from fish stomach contents and bacterial action, during the storage period. Hence the initial concentration of LCFA would have been a lot lower than for a fresh FO sample. If this suggestion proves to be correct, co-digestion of FO and cattle slurry may be possible at higher FO / cattle slurry ratios, provided the FO is allowed to aerobically degrade for a period of time.

7.15 Preliminary conclusions

The addition of FO fish (offal) to an anaerobic digester operating on cattle slurry slightly enhanced mean daily methane productivity at a ratio of 96% cattle slurry : 4% FO, but there were indications of a build up of inhibitory materials over time. Increasing the FO fraction to 6% caused rapid digester failure. The digester did not fully recover for a considerable period after

cessation of feeding of FO, suggesting that inhibitory compounds remained in the digester for a number of weeks.

Figure 7.1 Estimated and measured mean volatile solids loading rates for each week.

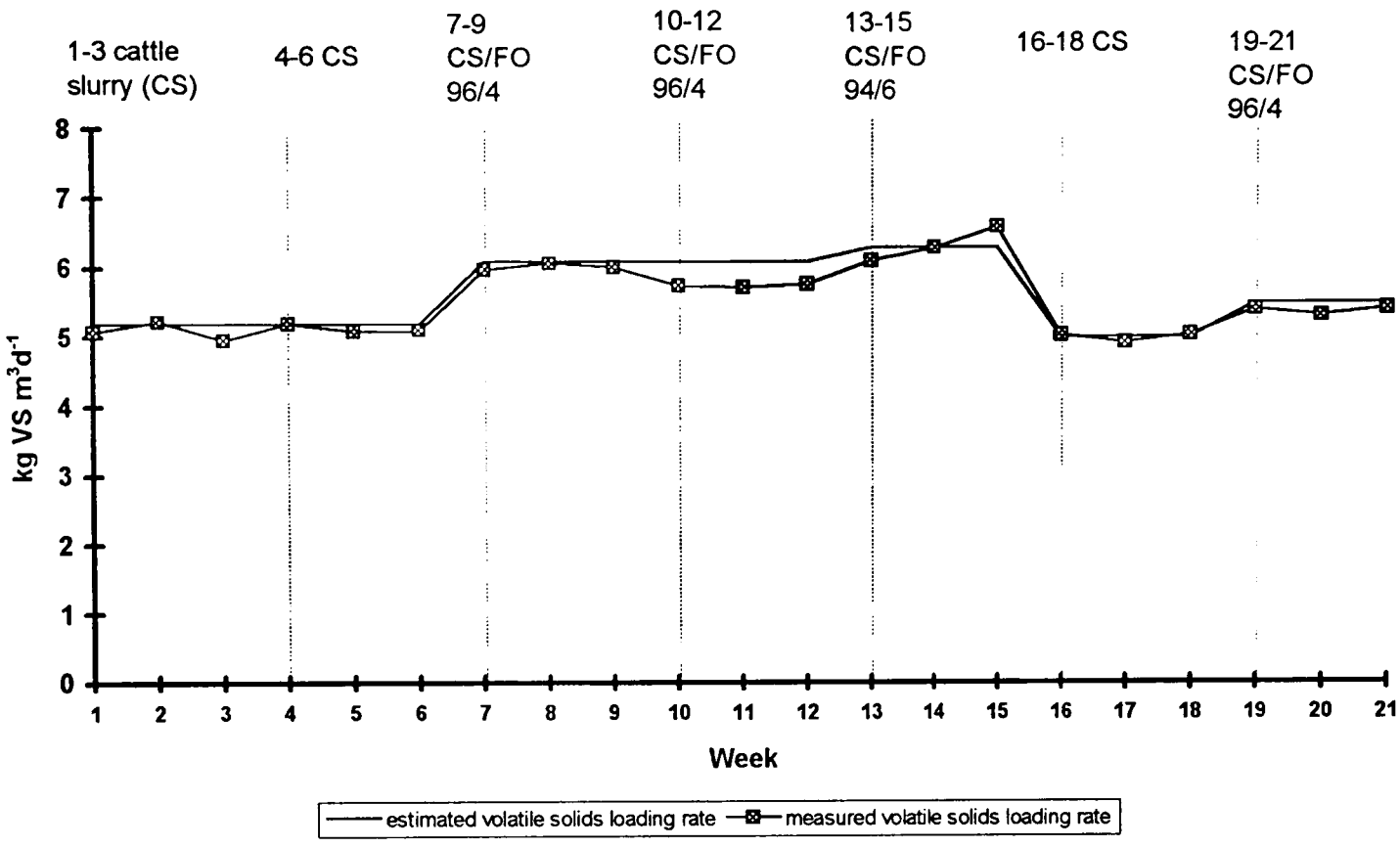


Figure 7.2 Variation in fish offal TS, VS and VS/TS ratio over the course of the experiment.

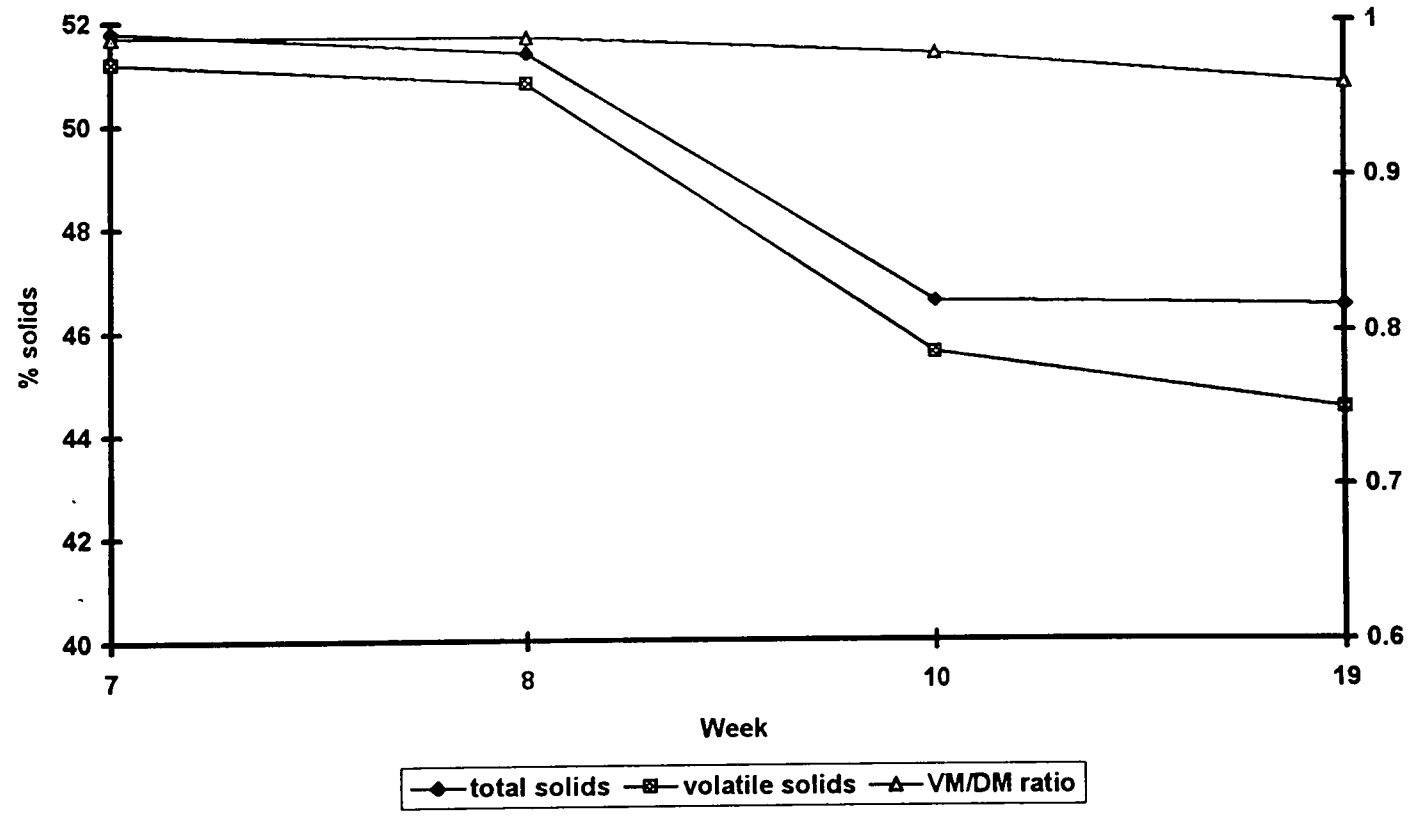


Figure 7.3 Variation in cattle slurry total and volatile solids and VS/TS ratio over the course of the experiment.

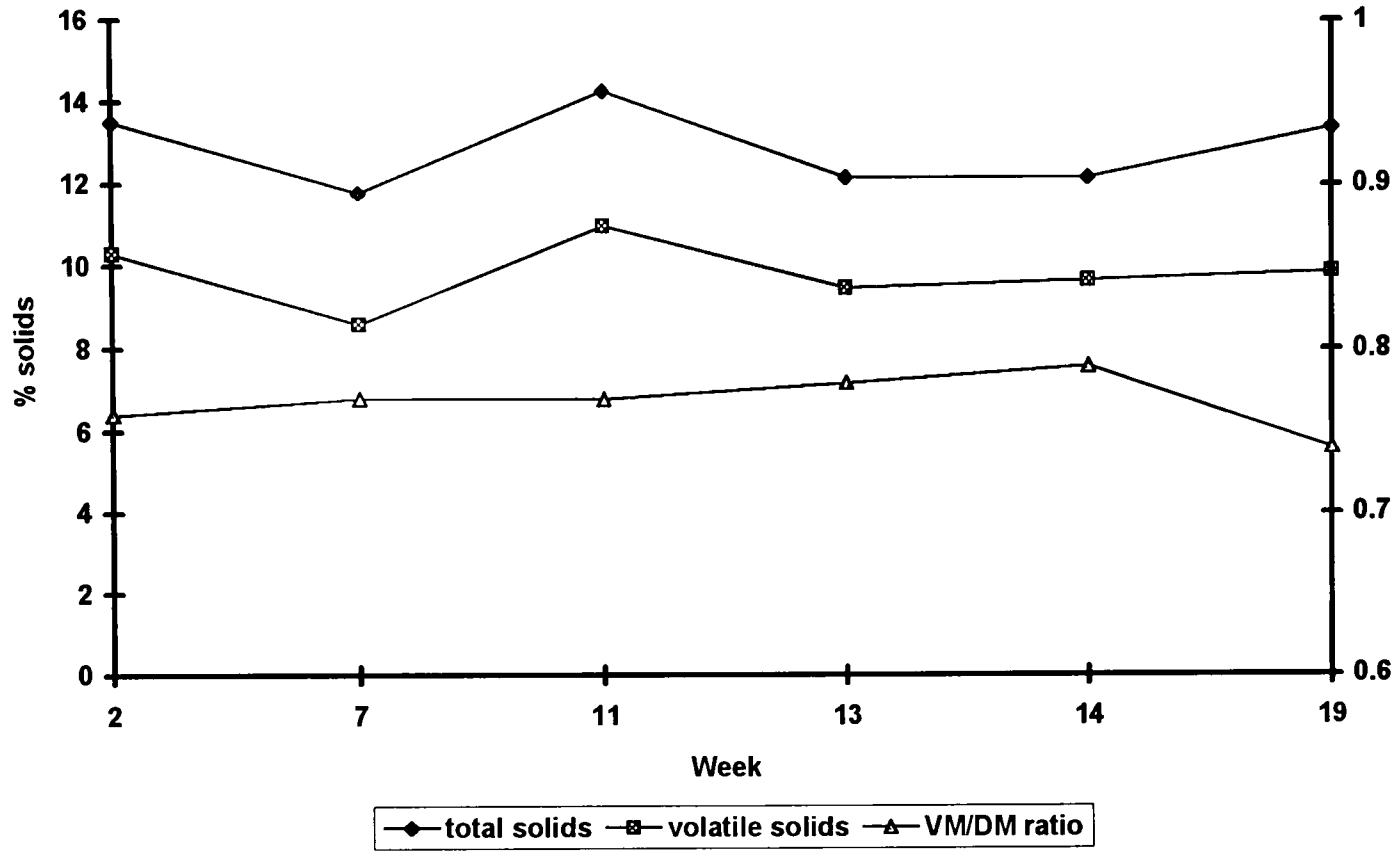


Figure 7.4 Mean daily methane production per kg VS added and volatile solids loading rate, for each week.

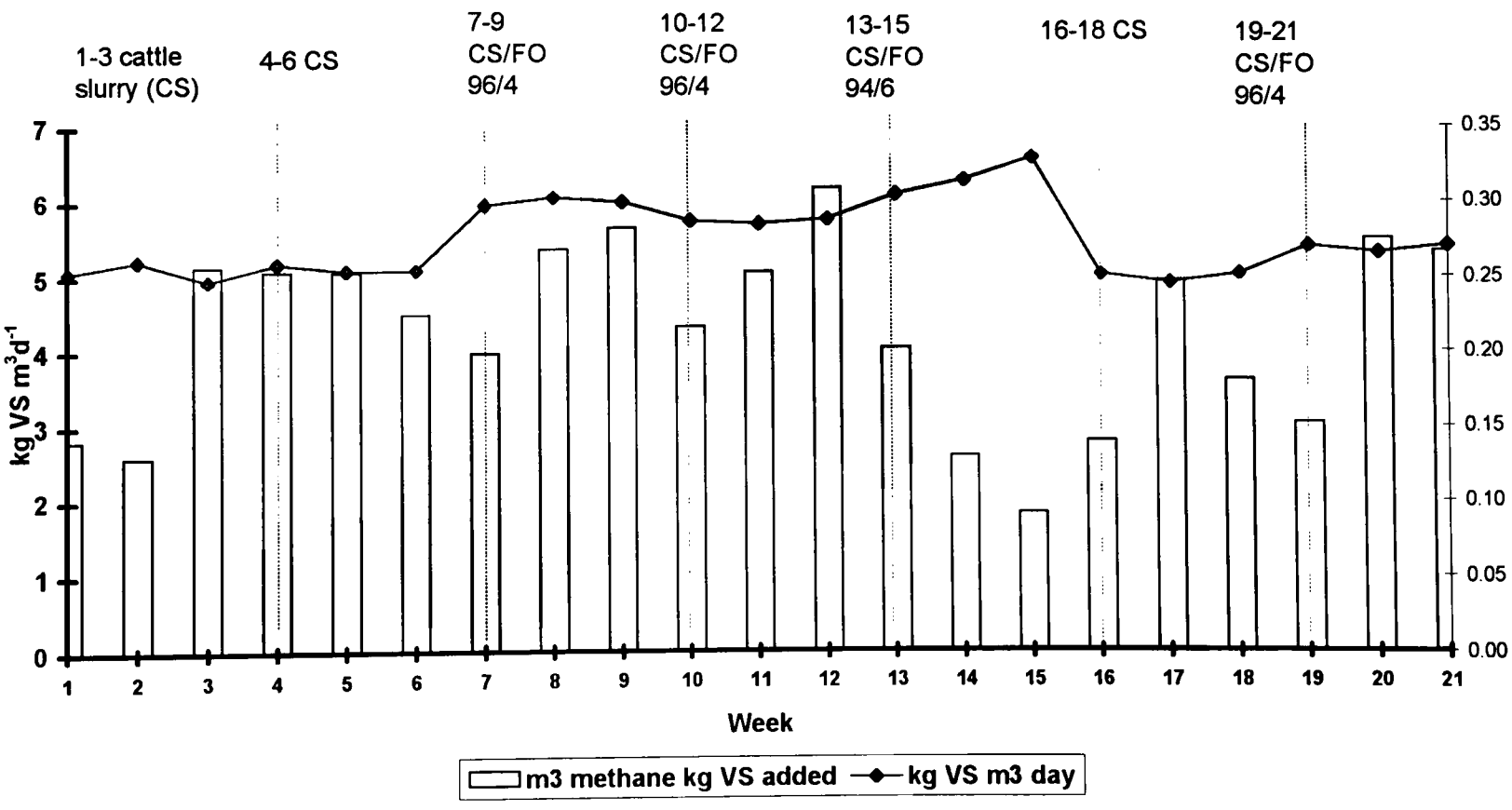


Figure 7.5 Mean daily % volatile solids removal for each week.

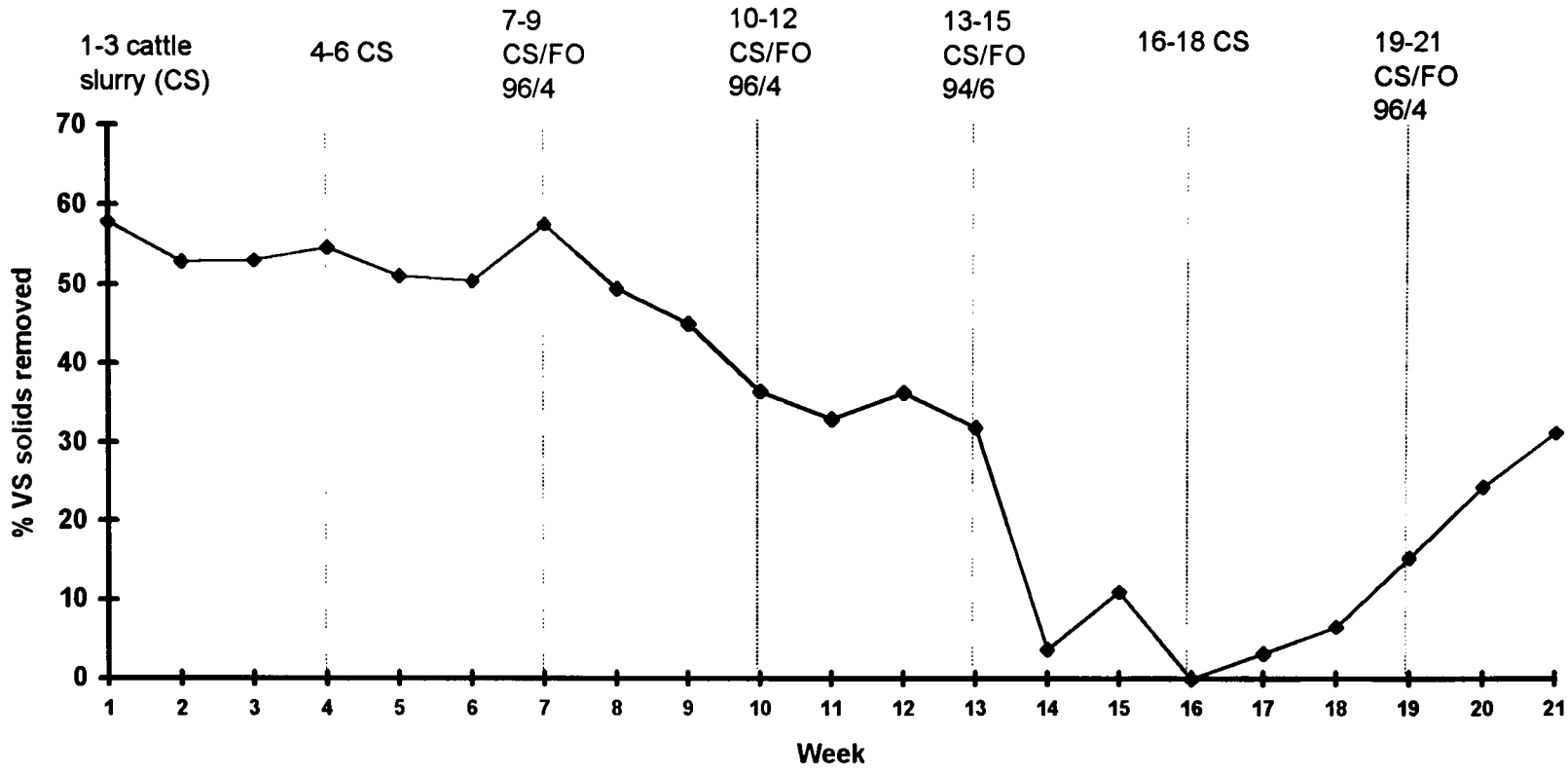


Figure 7.6 Mean weekly digester feedstock and effluent volatile solids/total solids ratio.

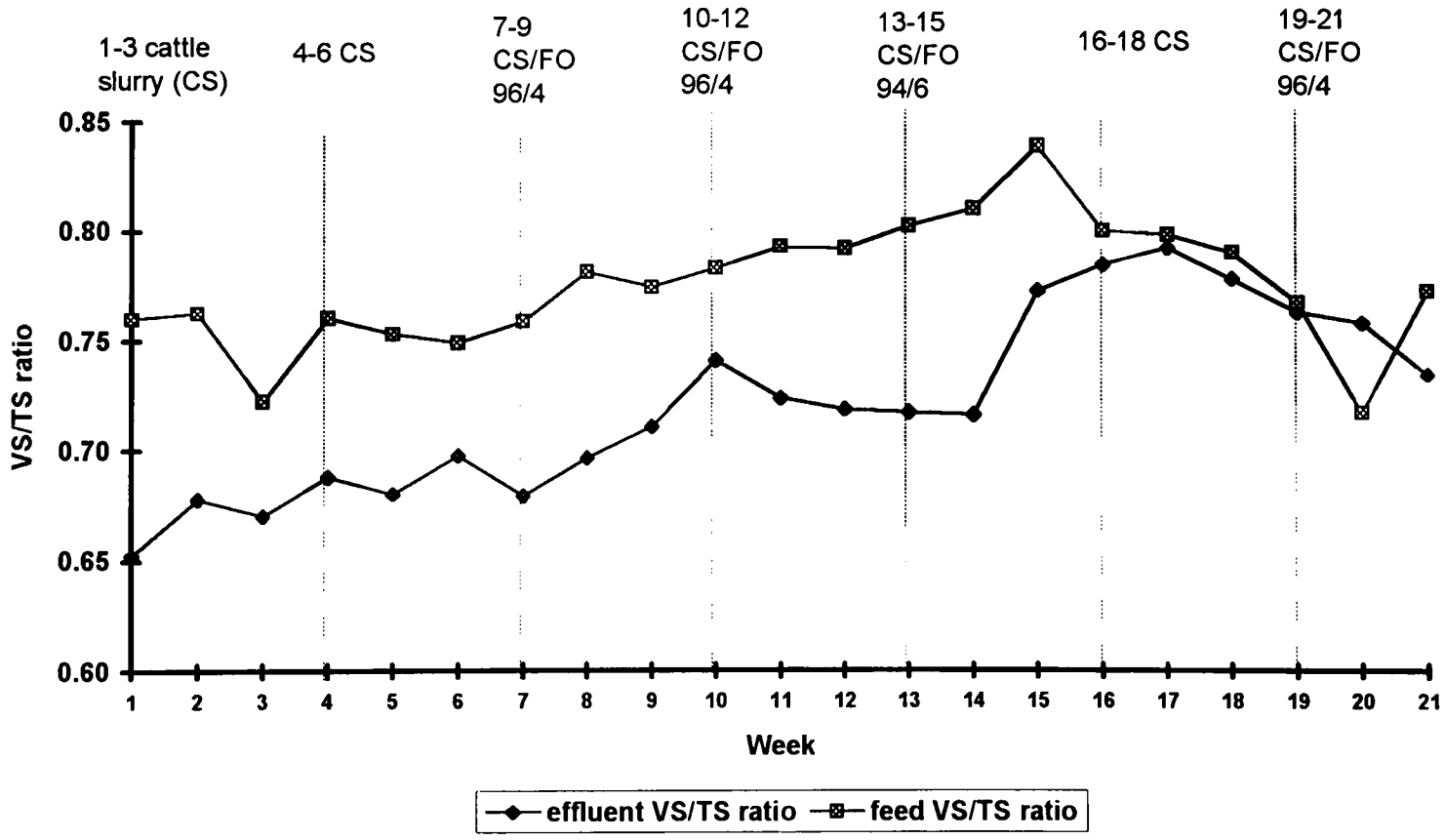


Figure 7.7 Daily mean feed and effluent volatile solids for each week.

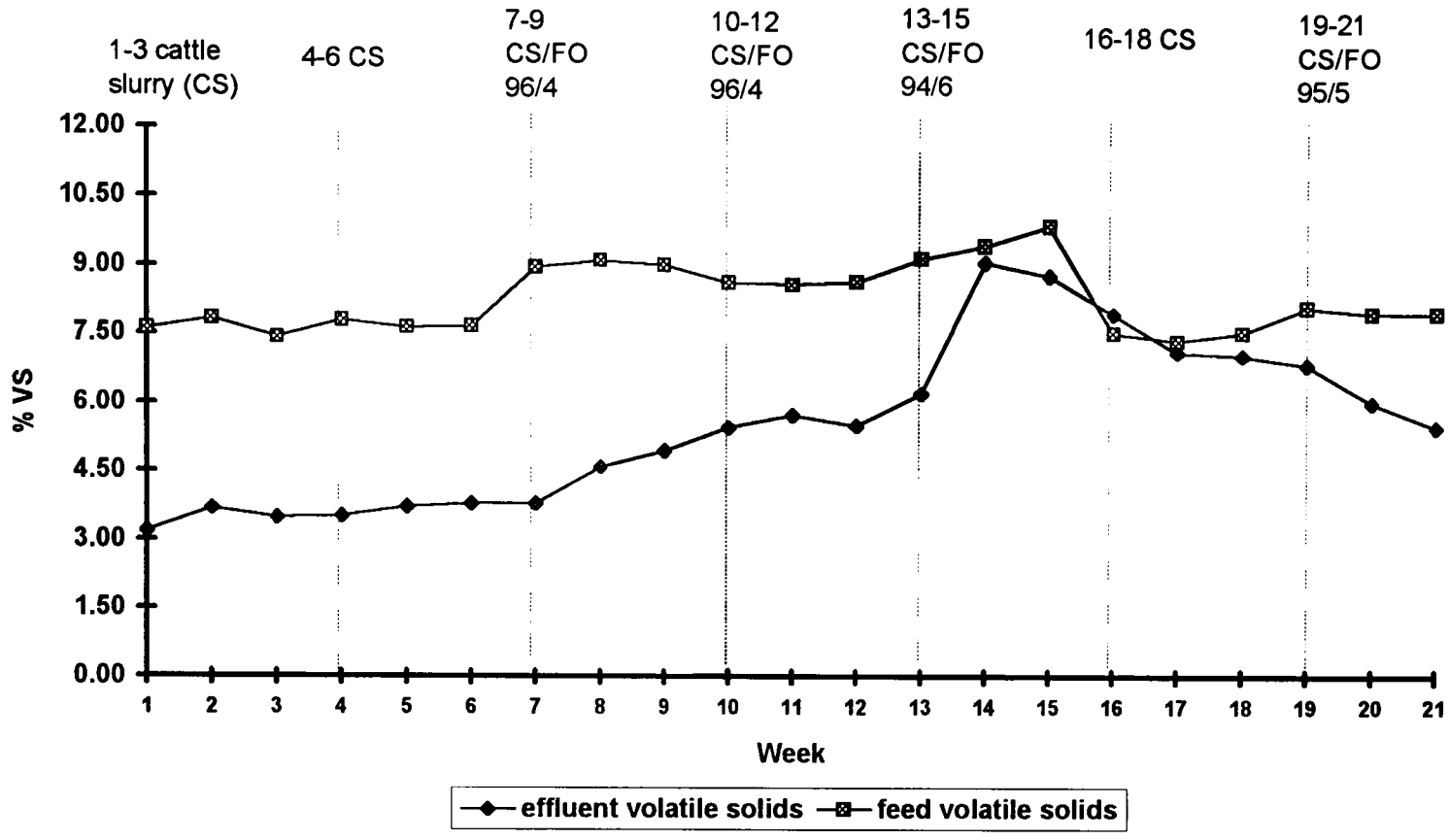


Figure 7.8 Daily mean feed and effluent total solids for each week.

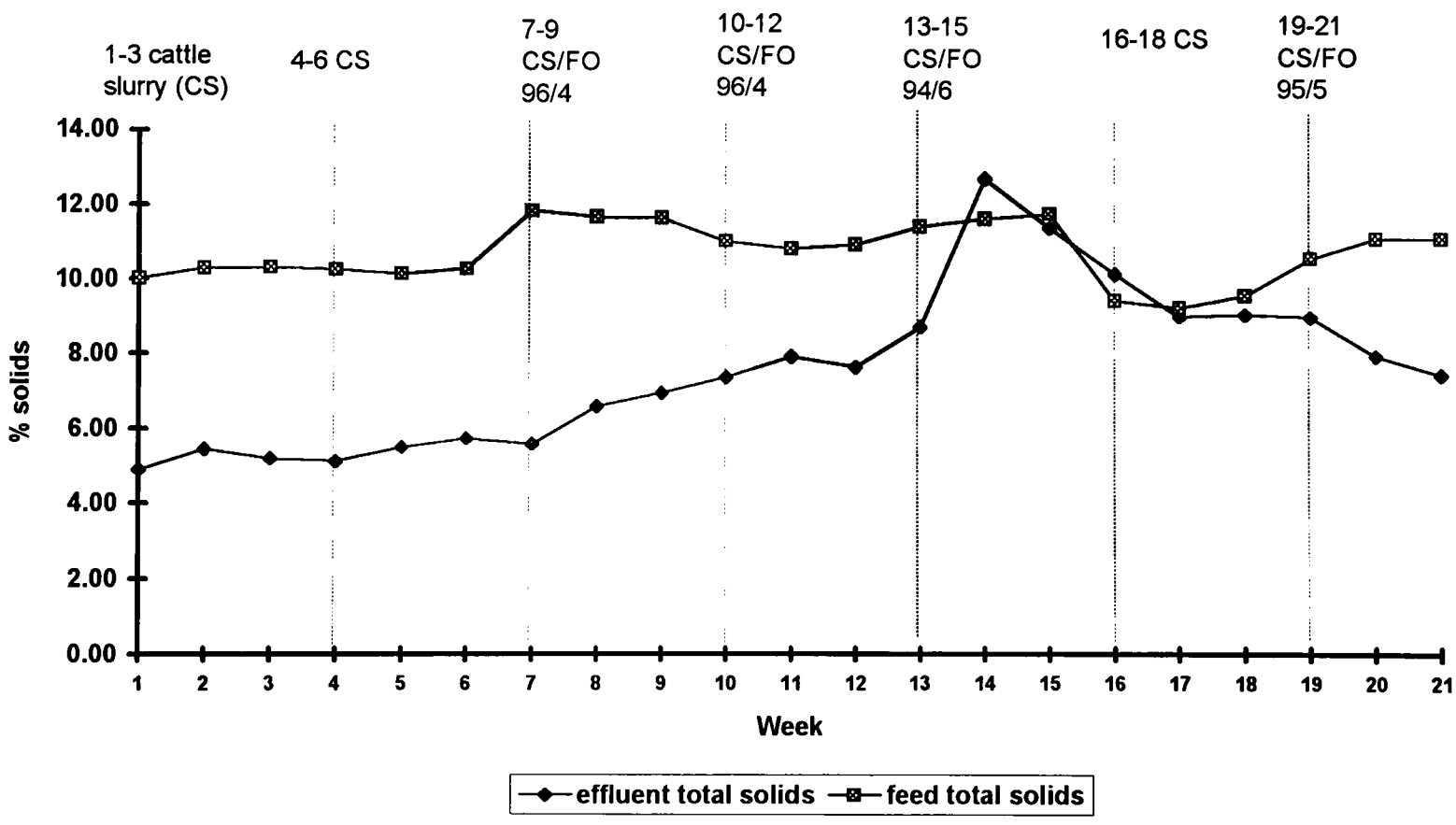


Figure 7.10 Mean daily methane production for each week.

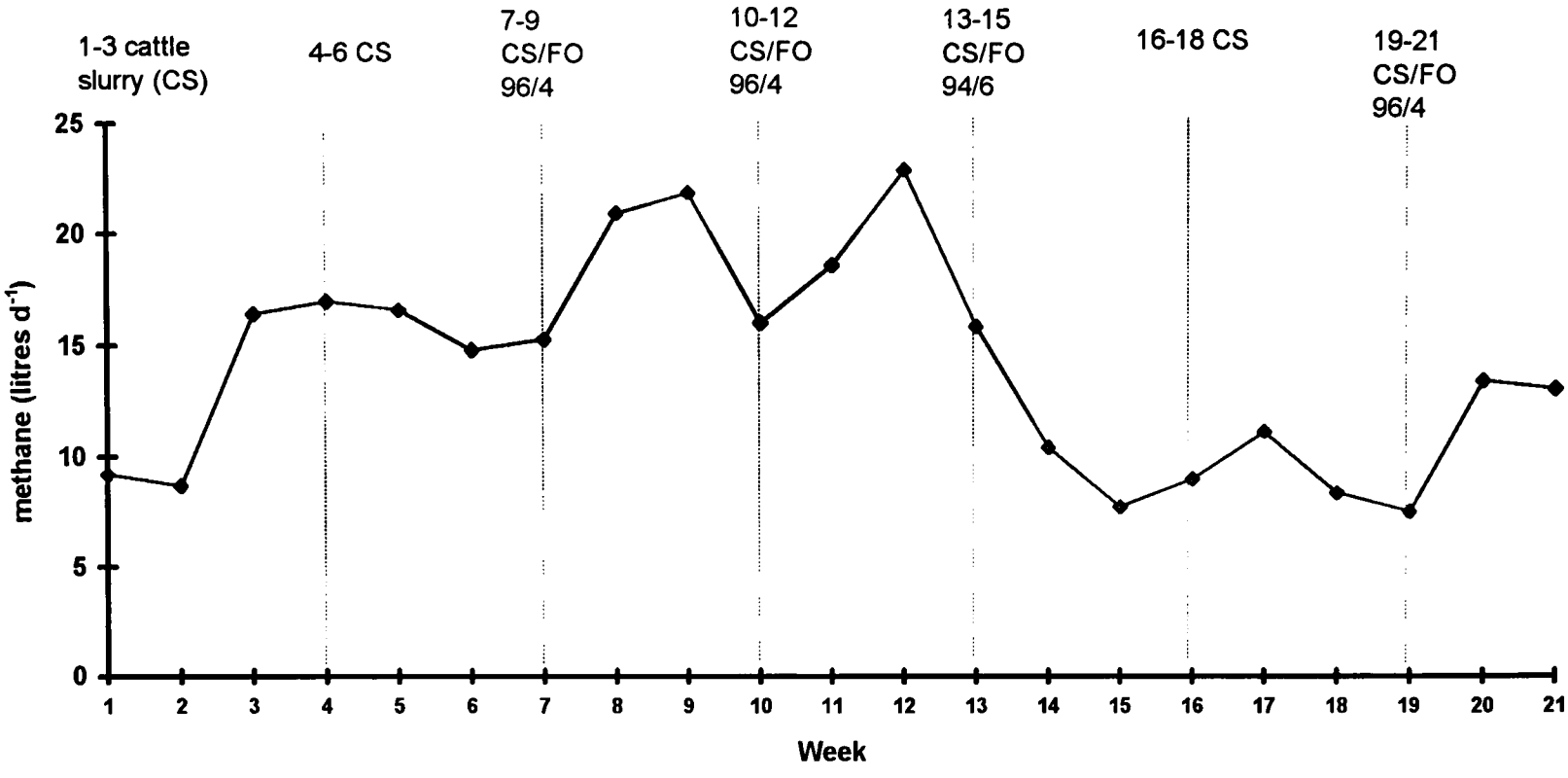


Figure 7.9 Mean daily biogas methane concentration for each week.

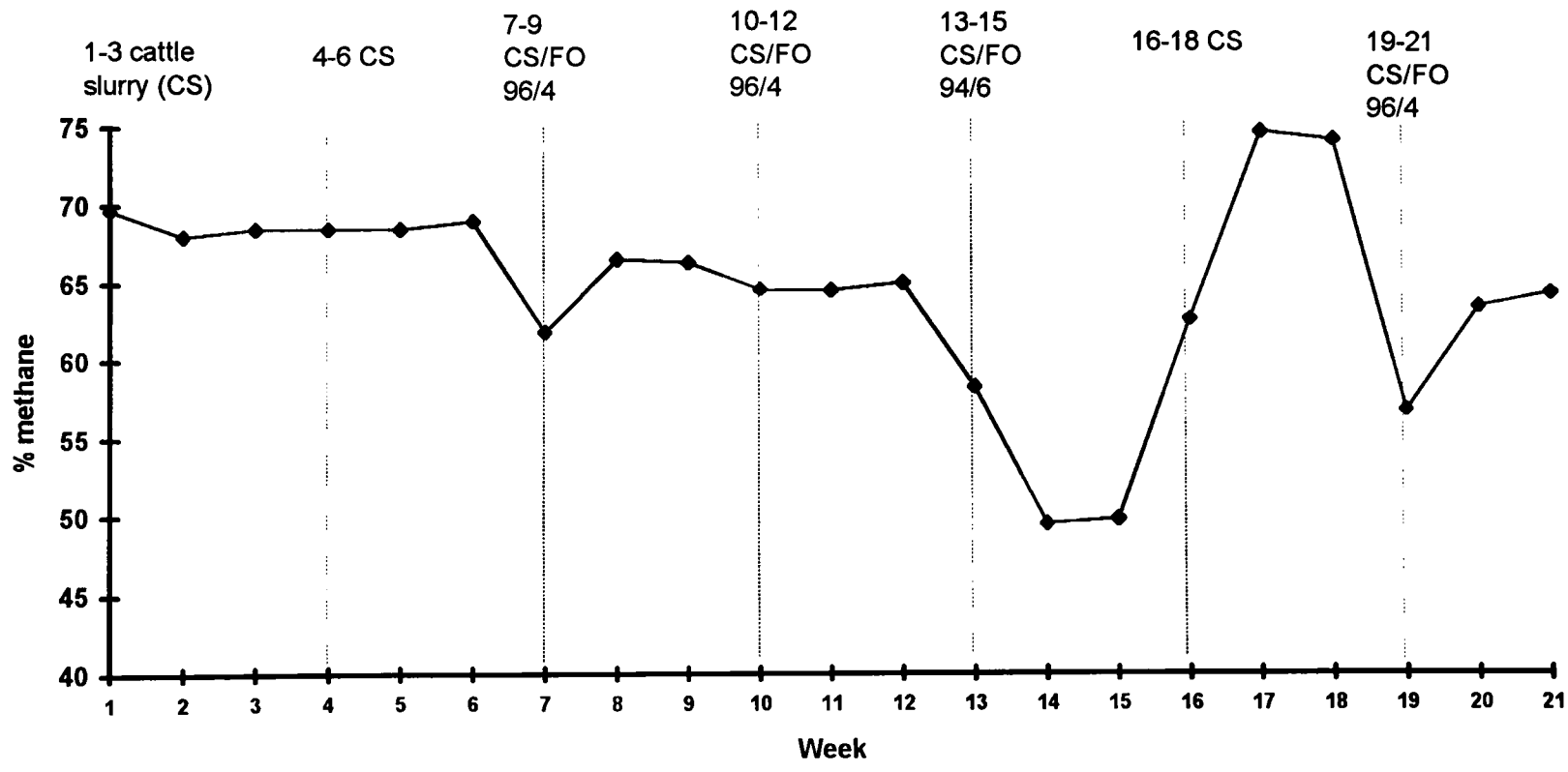


Figure 7.11 Mean daily effluent alkalinity for each week.

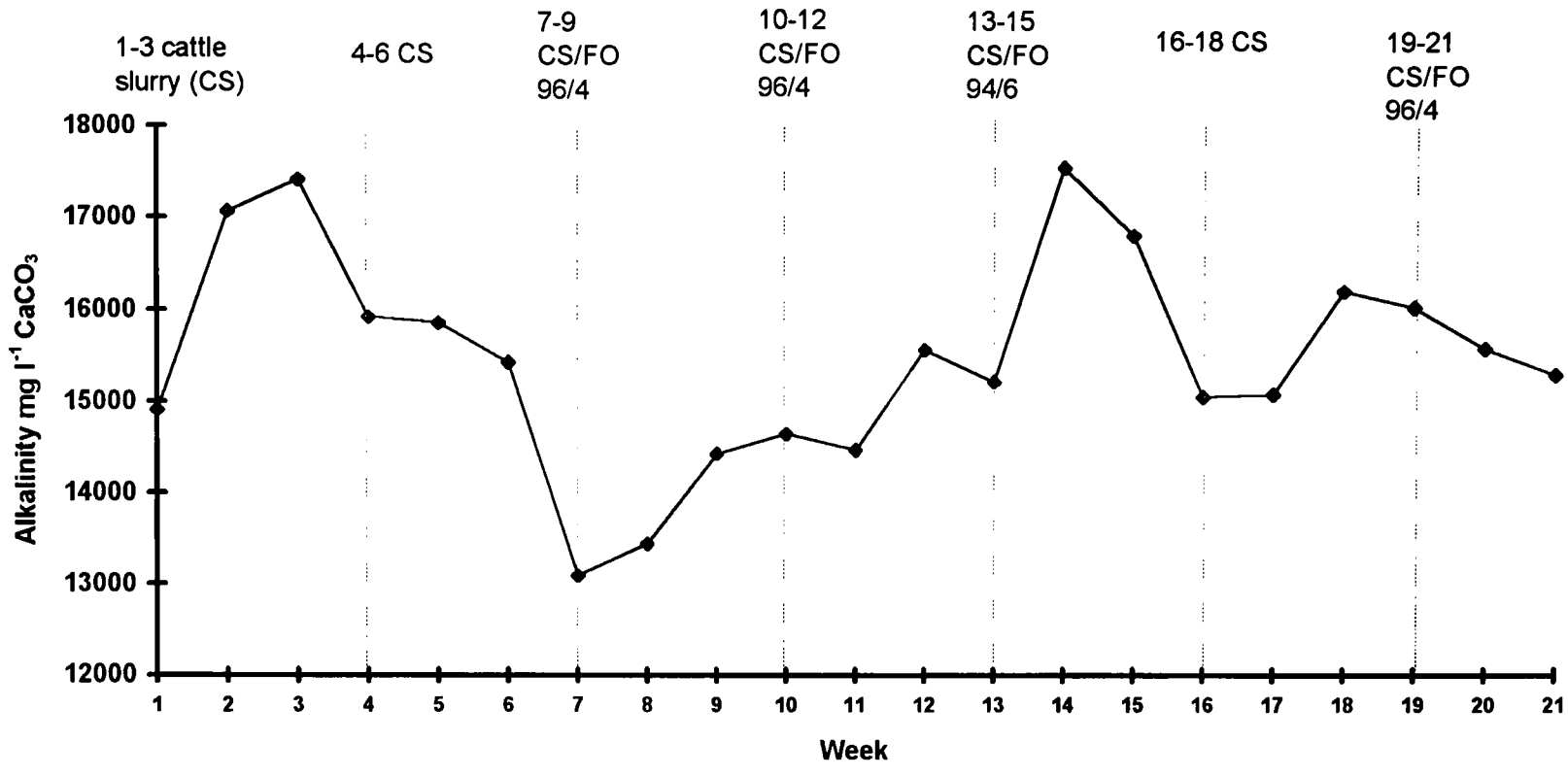


Figure 7.12 Mean daily effluent VFA for each week.

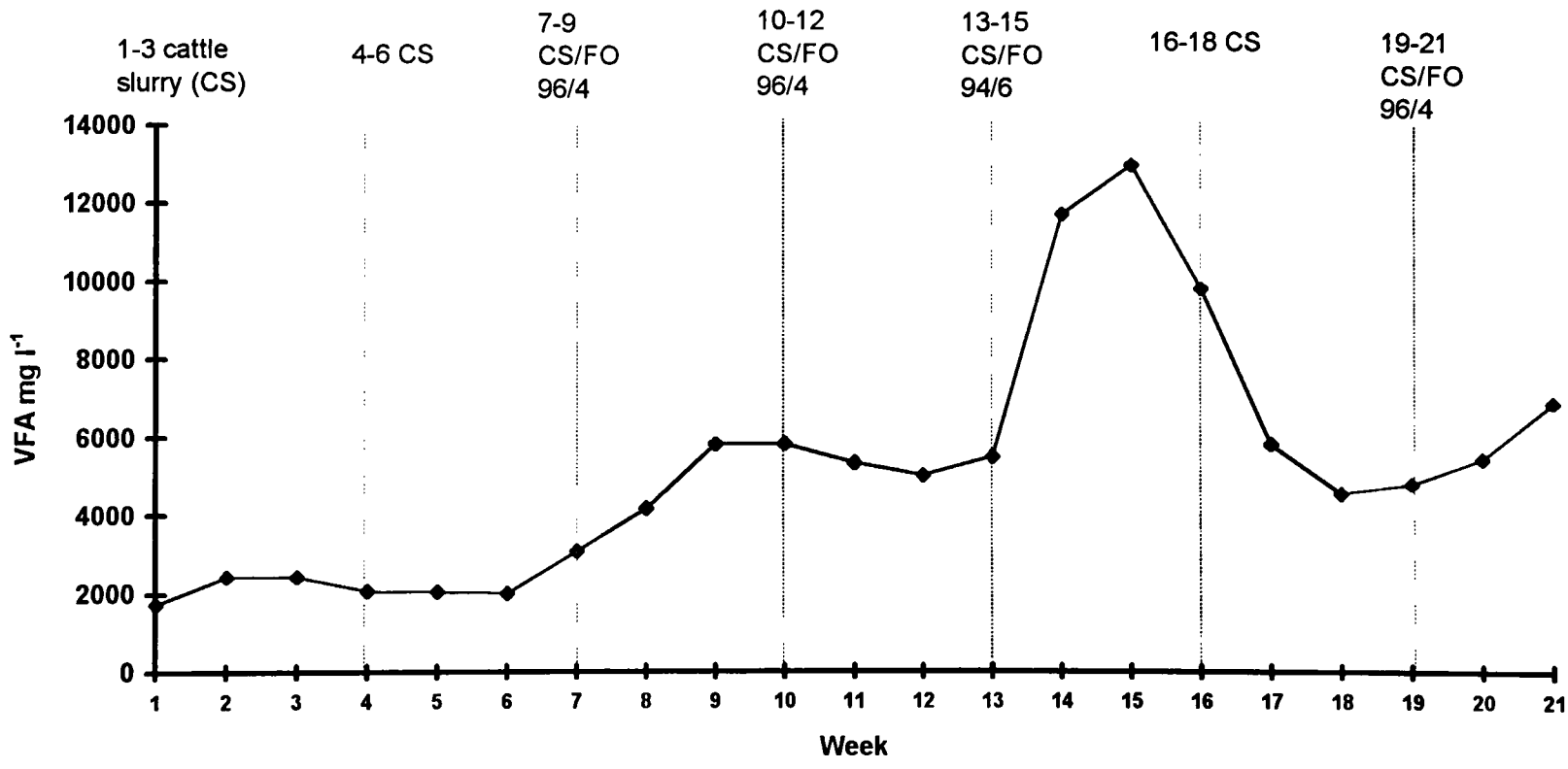


Figure 7.13 Mean daily effluent pH for each week.

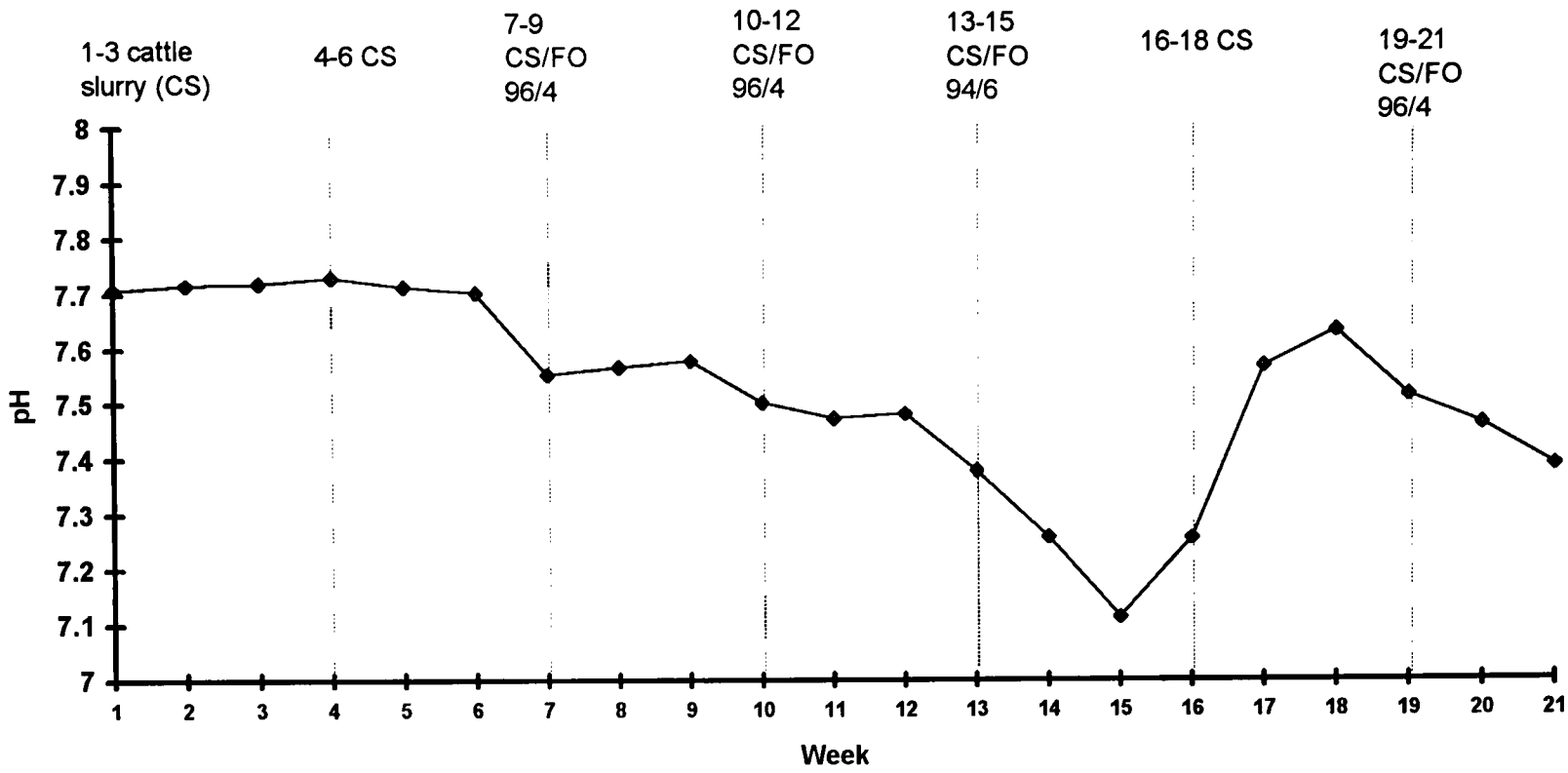


Figure 7.14 Mean VFA:TAlk ratio for each week.

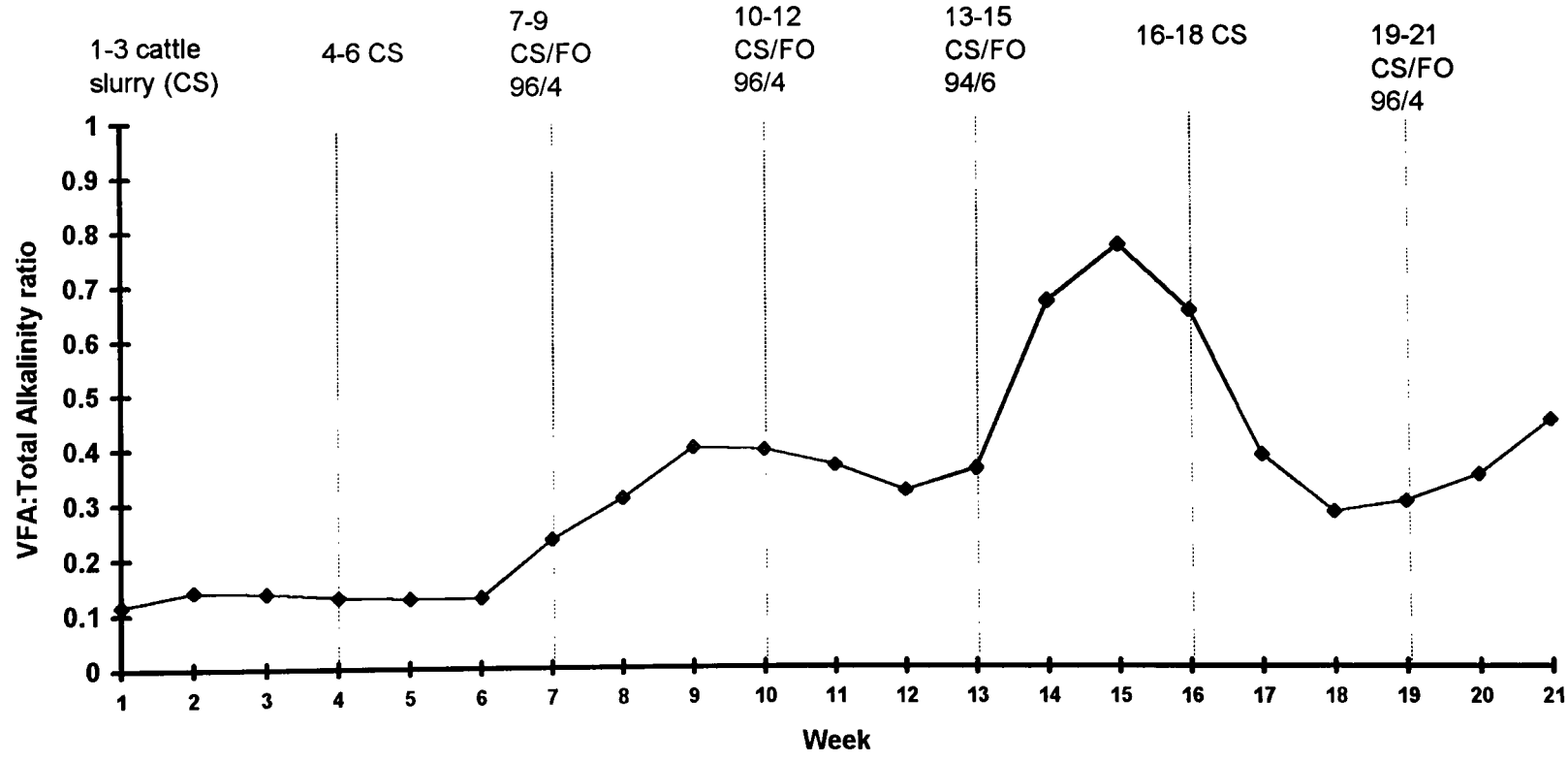


Figure 7.15 Mean daily effluent NH_4^+ and NH_3 for each week.

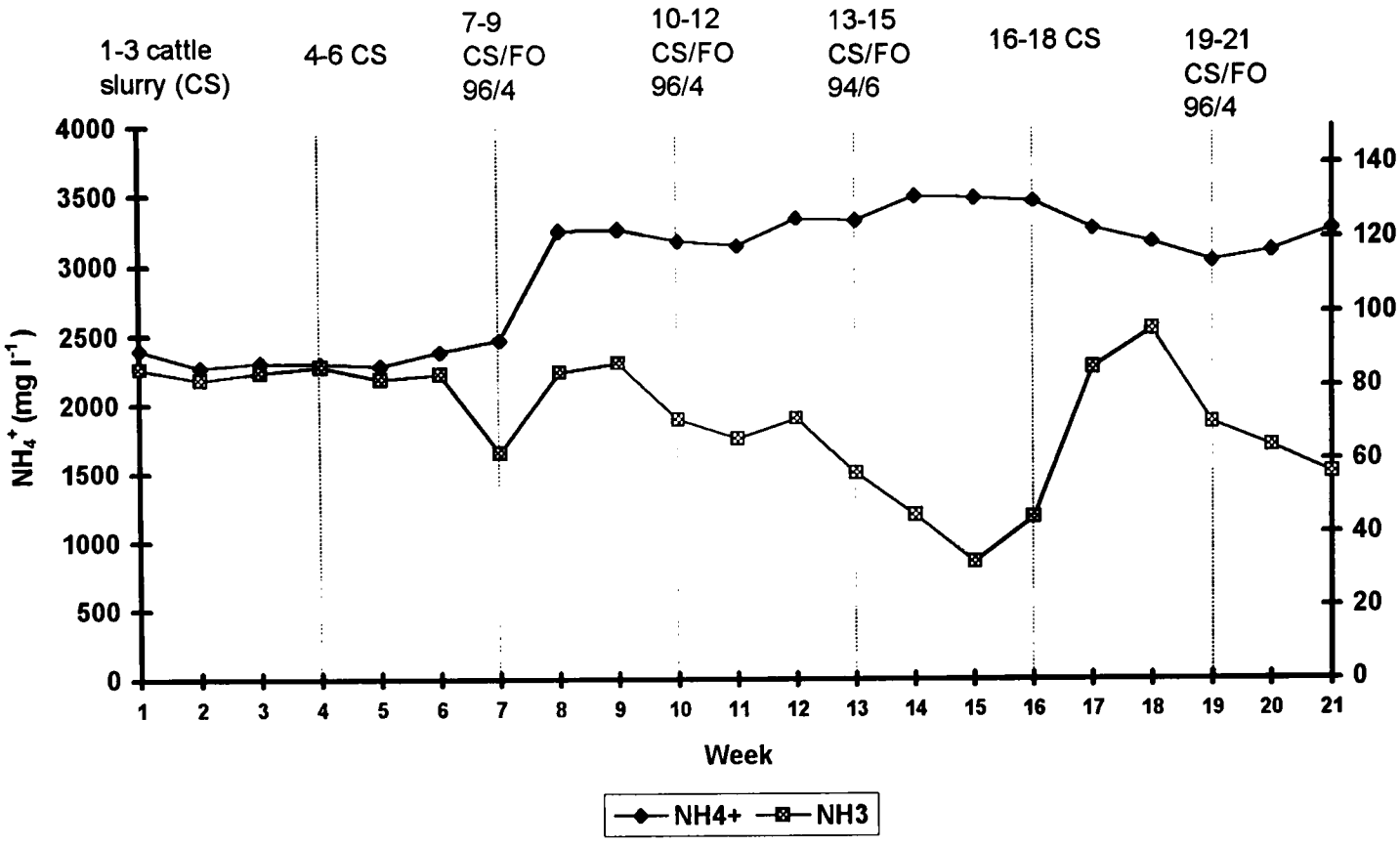


Figure 7.16 Mean daily biogas H_2S levels for each week.

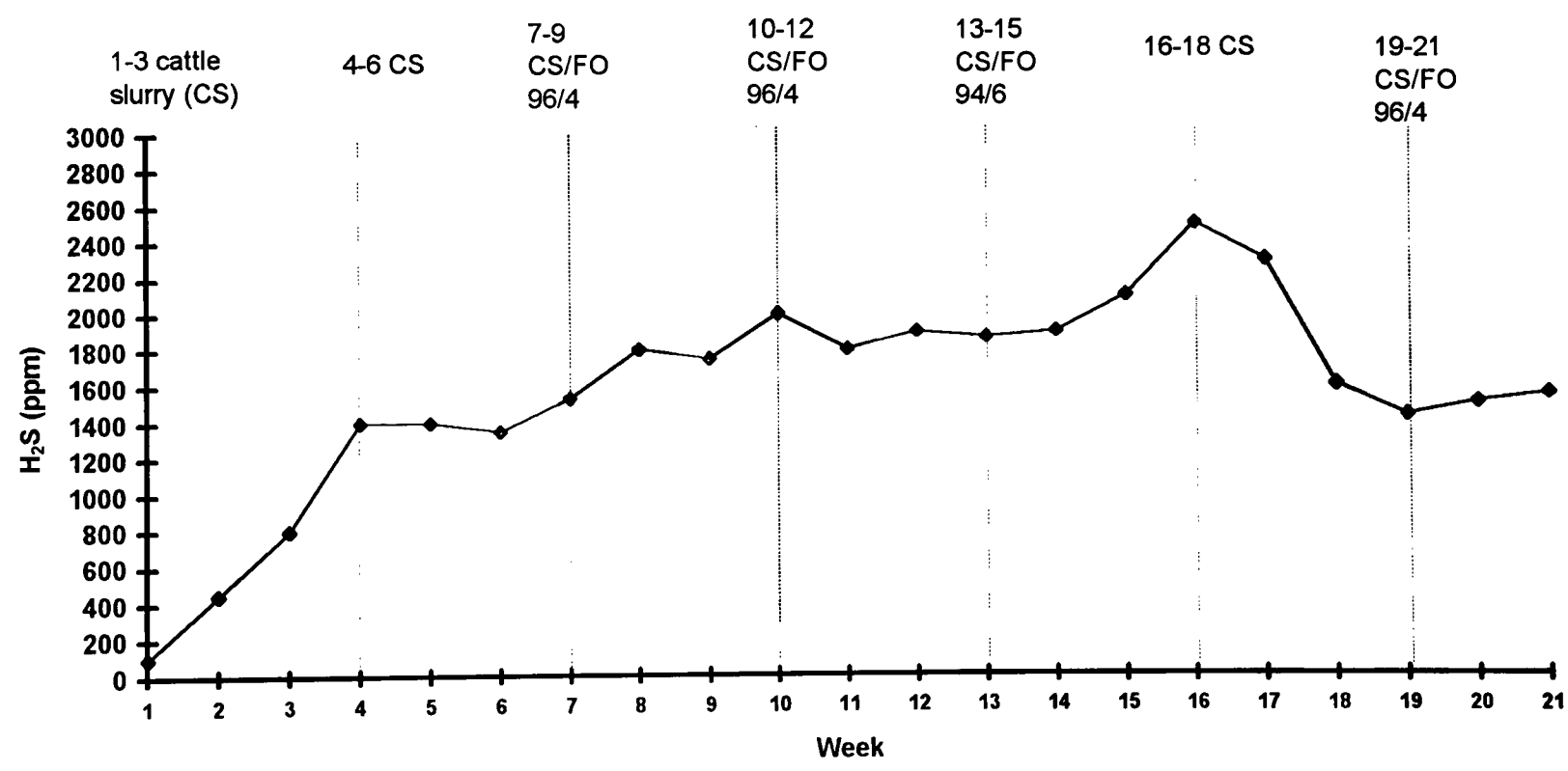
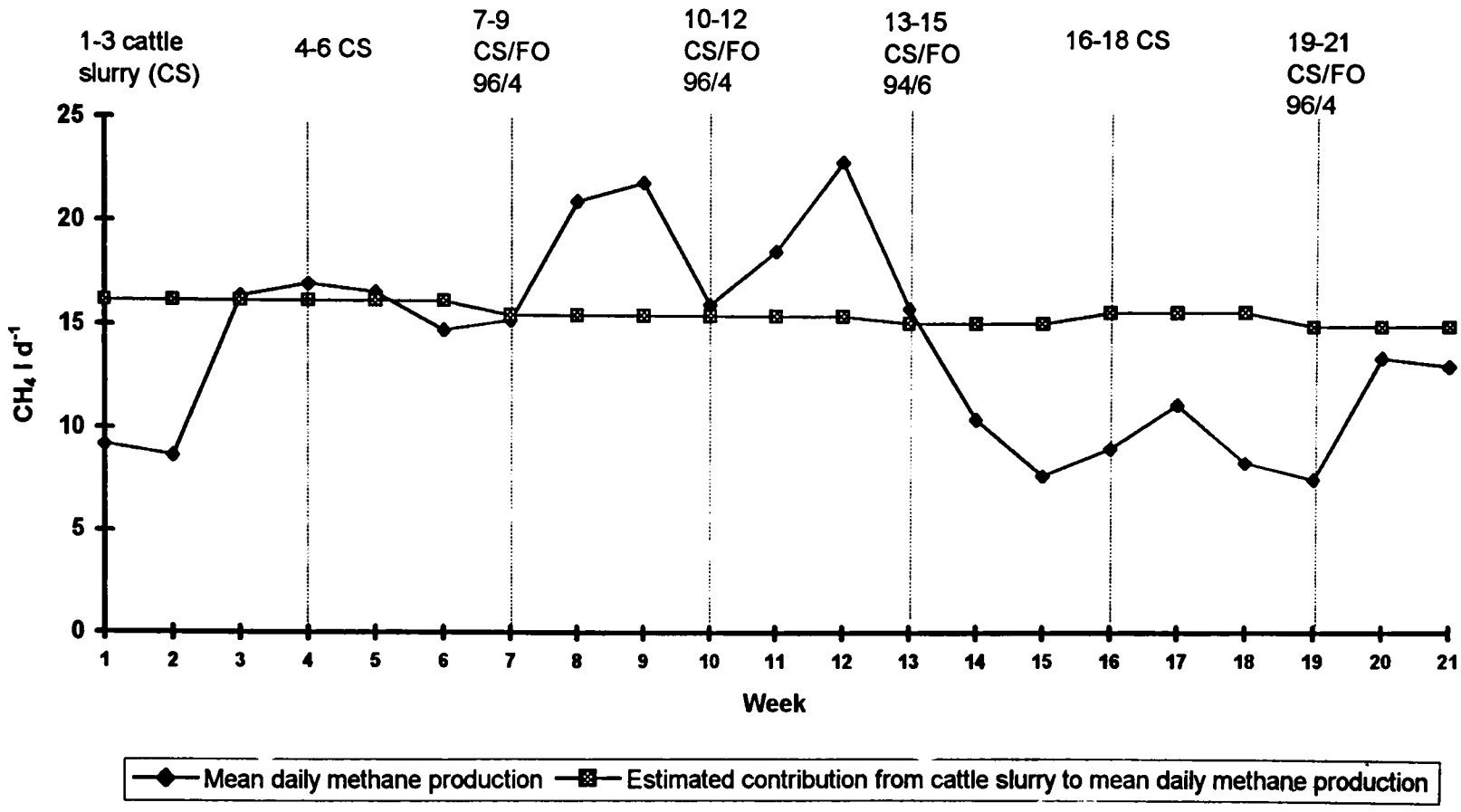


Figure 7.17 Estimated contribution of cattle slurry in feed to mean daily methane prodcution.



Chapter 8

Co-digestion of waste milk and cattle slurry

8.1 Introduction

For many farmers, the disposal of waste milk has become a problem in recent years due to the introduction of the European Community Milk Quota System for regulating milk production from dairy cattle under the Common Agricultural Policy (The Environment Agency, 1995). Each farm is given a quota, in litres of milk, which they must not exceed. If they do exceed the permitted milk volume, farmers have to pay a fine for each extra litre of milk produced, this fine is known as the "super levy". If dairies collect the waste milk, it is usually disposed of through the dairy effluent treatment plant or to sewer . If dairies refuse the milk or if farmers wish to avoid paying the fine, they have to dispose of it by spreading it on land or in soakaway pits. Often this can lead to contamination of surface and ground waters. Milk is a highly polluting effluent, with a COD of around 190,000 mg l^{-1}; hence even small quantities which enter water courses can be highly polluting.

8.2 Waste milk as a co-digestate

Whole cows' milk typically consists of 3.2% protein, 3.9% fat, 4.8% carbohydrate (most of which is lactose) and 0.7% ash (McCance and Widdowson's, 1978). As milk is obviously very biodegradable and is produced on farm sites, it was decided to investigate if a cattle slurry

digester could provide a disposal route for this highly polluting waste. The investigation took the form of two experiments, the first to ascertain the effect of waste milk additions on batch anaerobic digesters, and the second to determine the maximum amount of milk which could be applied to a working batch digester without inhibiting the methanogenic process. It was decided to measure the milk loading on the batch digesters as COD instead of volatile solids (VS), as milk is a uniform mixture containing no particulate matter which can cause errors in COD measurement. Consequently, the slurry had to be extensively sieved to remove any large particles, in order to ensure that any error in measurement of slurry COD was minimised.

8.3 Batch study 1 - the effect of milk additions on batch anaerobic digesters

8 x 1 litre digesters were constructed using 1 litre glass flasks. 600 ml of a mixture of 50% fresh cattle slurry and 50% digested cattle slurry from a 20 litre laboratory anaerobic digester was placed in each flask. Previously, the slurry had been extensively macerated and then sieved to remove particles larger than 5 mm to ensure a more uniform mixture, the COD of which could be more accurately determined than that of whole slurry due to the absence of most of the large particles. Table 8.1 shows the COD concentrations of each digester at the beginning of the experiment. The digesters were sealed with neoprene bungs, which contained an injection port to allow injection of slurry or waste milk, and with silicone sealant. They were then placed in a water bath which was maintained at 35 °C. The flasks were connected to clear, acid-resistant, graduated PVC tubes filled with water acidified to pH 4 with H_2SO_4. Biogas was collected by displacement of water. Methane and carbon dioxide concentrations in the biogas were measured daily. Samples of the mixture in the flasks were analysed for chemical oxygen demand (COD), ammonium (NH_4^+) and pH at the beginning and end of the experiment, see Sections 2.1 - 2.10 for a full description of analytical techniques and apparatus used.

Table 8.1 Contents of each digester at beginning of experiment

Digester	Digester contents	Average COD of mixture (mg l^{-1})
1	50% slurry/50% inoculum	75,600
2	50% slurry/50% inoculum	68,000
3	50% slurry/50% inoculum	80,600
4	50% slurry/50% inoculum	85,000
5	50% slurry/50% inoculum	88,950
6	50% slurry/50% inoculum	82.800
7	50% slurry/50% inoculum	84,900
8	50% slurry/50% inoculum	77,600

Table 8.2 Volumes of slurry and milk added to digesters after 14 days

Digester	Volume of waste added (ml)	COD of waste (mg l^{-1})	Weight of COD added(g)	COD loading (kg m^{-3})
1	30 (Milk)	196,000	5.8	9.6
2	30 (Milk)	196,000	5.8	9.6
3	60 (Milk)	196,000	11.8	19.7
4	60 (Milk)	196,000	11.8	19.7
5	90 (Milk)	196,000	17.6	29.3
6	90 (Milk)	196,000	17.6	29.3
7	60 (Slurry)	88,300	5.3	8.8
8	60 (Slurry)	88,300	5.3	8.8

8.3.1 Digester monitoring and operation

In order to present the data clearly, the mean biogas or methane production was calculated for each pair of digesters. Each pair of digesters performed very similarly, due largely to the extensive pre-treatment of the slurry to remove all significant particulate matter, and also the homogenous nature of milk. There was rarely more than a 5% difference in values recorded for each pair of digesters.

Daily methane production was monitored on each digester, and was found to peak at 7 - 11 days after commencement of the experiment see Figure 8.1 (**note:** see pages 234 - 242) for Figures). On day 14, waste milk was added to six of the digesters and cattle slurry to a further two in the amounts listed in Table 8.2. Digester performance was then monitored over the next four weeks. At the end of this period, methane production in all digesters had dropped to below 10% of the maximum value observed and the experiment was stopped.

8.3.2 Biogas and methane production over the course of the experiment

An examination of Figures 8.1 and 8.2, which show the daily methane and biogas production shows that they both follow the expected pattern for batch digestion of slurry as described by Hobson (1985) up to day 14 of the experiment, essentially a small peak in methane production a few days after the commencement of digestion, followed by a lag period and then a much larger peak.. After injection of the waste (milk or slurry), on day 14, biogas production increased rapidly in all digesters, to a maximum of 1.4 l d^{-1} in the digesters receiving the highest loading of COD, (digesters 5 and 6). Methane production also followed a similar pattern, up to a maximum of 0.75 l d^{-1}, and stayed at elevated levels for a longer period in the digesters which received the highest milk load.

Figure 8.4 shows mean cumulative methane production for each pair of digesters and Figure 8.5 shows total methane produced compared to COD loadings for each pair of digesters. It can be seen that digesters 1 and 2 received similar COD loadings (as milk) to the COD loading (as slurry) received by digesters 7 and 8, but produced significantly more methane over the course of the experiment, an average of 6.31 litres, compared to an average of 5.16 litres for digesters 7 and 8. Although it will be noted that digesters 7 and 8 did produce slightly less methane than the

other digesters over days 1 - 12, production over days 12, 13 and 14 was approaching that of the other digesters. The difference in total methane produced by digesters 1 and 2 and 7 and 8 can be attributed to the greater biodegradability of the milk.

Figure 8.6 shows % COD reduction at each COD loading. The large difference in % COD removal between the digesters 1 and 2 (receiving milk) and digesters 7 and 8 (receiving slurry) indicates how much more readily degradable the milk was compared to a similar loading of cattle slurry. Taking into account the standard error, there was a slight, but significant increase in % COD removal as the COD loading increased from 9.6 to 29.3 kg COD m^{-3}. Certainly no decrease in COD removal efficiency was noted, indicating that methanogenesis was not inhibited at milk loadings of 29.3 kg COD m^{-3}.

The methane concentration in the biogas provided an accurate picture of the effect the shock load had on the anaerobic systems. As can be seen in Figure 8.3, the control digesters, which received a loading of cattle slurry, experienced only a slight decrease in methane concentration in the days after the shock loading. The digesters receiving loadings of waste milk experienced a sharp drop in the methane concentration, with the effect becoming more pronounced as the loading rate increased. It is also interesting to note how quickly the systems recovered from the shock load. If recovery time is defined as the time taken for biogas methane concentration to return to the level it was before the addition of waste milk, the digesters receiving the highest shock load recovered quickest, followed by the systems receiving the medium shock load and finally the system receiving the lowest shock load.

The decline in methane concentration followed by recovery to a concentration slightly higher than it was before the shock load was similar to the trends noted by Peck *et al* (14) in their investigations of the effect of temperature shocks on anaerobic digestion systems. It is interesting to note that they recorded this phenomenon in a digester which was not fed after the shock event. The digesters they did continue to feed experienced a gradual decline in biogas methane concentration to levels well below the initial values. They proposed that this was due to potentially toxic fatty acids, principally *i* - butyrate, *i* - valerate, *i* - caproate, and propionate, which were produced in large quantities during and immediately after the shock event. Not feeding the digesters allowed the system to remove these fatty acids and, hence, restore a balance to the system, whereas continued feeding led to further fatty acid production and, therefore prolonged the inhibitory effect. It is possible that the continued application of shock loadings of waste milk to a fed batch digester might also produce this gradual decline in methane concentration.

8.3.3 Reasons for observed changes in biogas composition

Raw milk, as well as having high concentrations of proteins, sugars and minerals has a high fat concentration (3.9 % w/w) (McCance and Widdowson, 1978). Some of these fats are present as volatile fatty acids, particularly butyric acid (Fessenden and Fessenden, 1986), which is a product generated by acidogenic bacteria during the anaerobic digestion process (Parkin and Owen, 1986). During the anaerobic fermentation of cattle slurry, butyric acid is formed from the digestion of polysaccharide residues. It is converted to acetic acid by a number of pathways (Schoberth, 1981). About 70% of the methane produced by an anaerobic fermentation comes from bacteria which use acetic acid as a food source. Lactose which is present in raw milk at a concentration of about 4.6% w/w (McCance and Widdowson, 1978), is readily converted to

glucose and then by glycolysis to pyruvate which can be converted to propionic, butyric and acetic acids or lactic acid (Conn *et al.*, 1987), (Nicholson, 1996). Uribelarrea and Pareilleux (1981), have suggested that lactic acid is also converted to propionic and butyric acids in anaerobic systems.

The introduction of significant quantities of these readily degradable materials into the digesting systems explains the increasing volumes of methane produced by the digesters as the loading of waste milk increased. The rapid rise in CO_2 levels seen immediately after waste addition can be explained by referring to the work of Marsili - Libelli and Beni (1996) who developed a model to describe the behaviour of anaerobic systems under shock loading conditions. Experimental evidence supported the model's prediction that an organic shock loading would produce a short term increase in the CO_2 concentration over time. This was assumed to be due to the conversion of the excess substrates described above to acetic acid. Figure 8.3 shows the dramatic fall in the methane content of the biogas immediately after the shock loading.

The application of a shock load to an anaerobic system can cause failure of the digester, which is usually defined as a significant and prolonged decrease in the methane concentration of the biogas. This can happen in a number of ways. The production of large quantities of volatile fatty acids, as described above, can reduce the pH of the system to a point where the methanogenic bacteria are inhibited. This is generally accepted to be below pH 6.2 (Metcalf and Eddy, 1996). As can be seen from Table 8.3, no such decrease was apparent at the end of the batch digestion. However a decrease may have occurred directly after the application of the shock load to the system and the pH of the system may have been gradually restored as the pool of acids generated

was converted to methane. Careful monitoring of pH during the operation of a fed batch system working on waste milk and cattle slurry would therefore be necessary to avoid digester failure.

Table 8.3 Ammonium (NH_4^+), pH and un-ionised ammonia (NH_3) concentrations at the beginning and end of the experiment

Digester	NH_4^+ at start of experiment (mg l^{-1})	pH at start	NH_3 (mg l^{-1}) at start	NH_4^+ at end of experiment (mg l^{-1})	pH at end	NH_3 (mg l^{-1}) at end
1	2820	7.69	66.5	3745	7.87	138.3
2	3016	7.71	71.1	4212	7.86	155.6
3	3029	7.73	71.4	4394	7.87	162.3
4	3043	7.71	71.7	4292	7.92	158.5
5	3057	7.72	72.1	4415	7.83	130.4
6	3029	7.76	71.4	4649	7.88	171.7
7	3043	7.77	71.8	3745	7.85	138.3
8	2936	7.79	69.2	3781	7.86	139.7

8.3.4 Ammonium (NH_4^+) and ammonia (NH_3) levels at the beginning and end of the experiment

The ammonium (NH_4^+) and free ammonia (NH_3) levels in each digester, at the beginning and end of the experiment are shown in Table 8.3. The initial high values suggest that the slurry used may have been stored for some time at the farm. As would be expected, NH_4^+ and NH_3 concentrations rose during the digestion process in all digesters, with increasing levels being produced in those digesters which received additions of waste milk. This was most likely due to hydrolysis of milk protein during digestion, with consequent liberation of ammonia (Hawkes, 1981). Un-ionised ammonia levels between 138 and 220 mg l^{-1} NH_3 have been shown to inhibit methane production significantly (Webb and Hawkes, 1985). Un-ionised ammonia levels present at the end of the experiment in those digesters receiving waste milk suggest that ammonia inhibition of the anaerobic digestion process must also be considered in the design of larger systems for co-

ammonia inhibition of the anaerobic digestion process must also be considered in the design of larger systems for co-digesting milk and slurry, although there seems to have been no inhibition of COD conversion to methane in this instance.

8.3.5 Case study

A case study of a local farm situation was undertaken to determine if the volume of milk produced by a herd of cows could be feasibly disposed of in an anaerobic digester operating on cattle slurry, based on the data obtained above. As batch data cannot reliably be adapted to continuously operating systems, it was assumed that the waste milk would be disposed of as a once-off event and would not be added to the digester on a continuous basis.

The farm in question operated a $100m^3$ digester, and had a herd of 100 cows. The digester operated at a loading rate of $4m^3$ of slurry per day, which, assuming the slurry had an average COD of 88,000 mg l^{-1} , was a loading rate of 352 kg COD d^{-1} and a specific COD loading rate of 3.5 kg COD m^3 d^{-1}. Each cow produced about 40 litres of milk per day, which was a total of $4m^3$ of milk per day, with an average COD of 190,000 mg l^{-1}. This was equivalent to 784 kg COD d^{-1}. Adding this to the slurry loading on the digester made a total COD loading rate of 11.4 kg COD m^3 d^{-1} which was a 220% increase in COD loading rate. This corresponded to the lowest loading applied to the batch digesters in this experiment, which suggested that a farm of this size, with a similar herd, would be able to dispose of its waste milk by co-digestion, without adversely affecting digester performance.

However, on a full scale digestion plant, biogas with a methane content of 35%, which was produced by the digesters receiving the highest milk load for a short period, see Figure 8.3, would cause difficulties for any equipment burning the biogas (Cheshire, 1997). Hence, even

though total methane production per day would be elevated, the biogas could not be used for energy production. Therefore, methane content of the biogas will also play a part in determining the maximum loading rate of milk for the system.

8.3.6 Preliminary conclusions

The addition of waste milk to a batch anaerobic digestion of cattle slurry produced elevated methane production levels in all digesters receiving additions of waste milk, with the highest methane production being observed in those digesters receiving the highest loading of milk. However, excess carbon dioxide production meant that the overall methane concentration in the biogas was quite low for a number of days after the addition of waste milk to the digester.

8.4 The effect of high loadings of milk on batch digesters

The study described in Section 8.3 was repeated using higher COD loadings, see Table 8.4.

8.4.1 Digester monitoring and operation

The rate of methane production was monitored for each pair of digesters and was found to peak at 5-7 days after the commencement of the experiment with a second smaller peak 11 days after commencement, see Figure 8.8. After day 11 the daily methane production rate was constant at about 0.1 l d^{-1}. On day 20 of the experiment, waste milk was added to 6 digesters and cattle slurry to both the control digesters in the amounts described in Table 8.4. Digester performance was monitored over the next four weeks At the end of this period the methane production rate was again steady at around 0.1 l d^{-1} and the experiment was terminated.

Table 8.4 Volumes of slurry and milk added to digesters after 20 days

Digester	Volume of waste added (ml)	COD of waste (mg l^{-1})	Weight of COD added(g)	COD loading (kg m^{-3})
1	60 (Slurry)	89,625	5.4	8.9
2	60 (Slurry)	89,625	5.4	8.9
3	108 (Milk)	161,500	17.4	29.1
4	108(Milk)	161,500	17.4	29.1
5	132(Milk)	161,500	21.3	35.5
6	132(Milk)	161,500	21.3	35.5
7	150(Milk)	161,500	24.2	40.4
8	150(Milk)	161,500	24.2	40.4

8.4.2 Changes in biogas methane and car bon dioxide concentrations

Figures 8.7 and 8.8, which show the average daily methane and biogas production rates for each pair of digesters, both followed a pattern similar to that noted in Section 8.3, up to day 20 of the experiment, when additional waste was added to each digester. After injection of waste, biogas production increased rapidly in all digesters with the highest mean rate of biogas production, 1.8 l d^{-1}, occurring in the digesters receiving the highest loading of waste milk (digesters 7 & 8). The mean methane production rate followed a similar pattern, except that the highest rate, 1.14 l d^{-1} was seen in those digesters receiving the second highest loading of waste milk (digesters 5 & 6), suggesting that perhaps some slight inhibition of methanogenesis was occurring in the system receiving the highest loading. Figure 8.12 shows that, taking the standard error into account, there was little significant difference in the total quantities of methane produced by digesters 5 & 6 and digesters 7 & 8 over the duration of the experiment. The respective average values were 13.8 l (±0.58) per digester compared with 13.4 l (±0.12) per digester.

Figure 8.10, the methane concentration in the biogas from each pair of digesters, demonstrates how the shock loadings affected the systems. The methane concentration in the biogas from those

digesters receiving waste milk dropped to around 30% in the 24 hours immediately following the application of the shock load to the system, whereas biogas methane concentration only declined to around 55% in the control digesters. The methane concentration in the digesters receiving waste milk eventually recovered to a value slightly higher than that noted before the shock loading, (80% compared with 76% methane). In each case the methane concentration had recovered to the level it was at before the shock load within 4 days. There was no discernible difference between each pair of digesters in the rate of recovery from the shock load. The pattern of a sudden decrease in biogas methane concentration, followed by a return to previous biogas methane levels after a number of days, was similar to the pattern noted in Experiment 1, see Section 8.3.2. Section 8.3.3 discusses the reasons for the observed fall in methane biogas concentrations immediately after the shock loading event.

Table 8.5 Ammonia (NH_4^+), pH and un-ionised ammonia (NH_3) concentrations at the beginning and end of the experiment.

Digester	Initial NH_4^+ (mg l^{-1})	Initial pH	Initial NH_3 (mg l^{-1})	Final NH_4^+ (mg l^{-1})	Final pH	Final NH_3 (mg l^{-1})
1	2469	7.79	77.2	2913	7.87	118.3
2	2572	7.76	80.1	3276	7.86	133.6
3	2637	7.76	82.5	3418	7.92	139.4
4	2778	7.75	86.6	3339	7.92	136.1
5	2583	7.8	80.1	3434	7.88	140.8
6	2643	7.76	82.6	3616	7.88	147.5
7	2430	7.77	75.9	2913	7.86	118.3
8	2474	7.79	77.4	2941	7.86	119.9

8.4.3 Ammonium (NH_4^+) and ammonia (NH_3) levels at the beginning and end of the experiment

Digester failure can also be caused by the build up of un-ionised ammonia (NH_3), which is highly toxic to bacteria, see Section 8.3.4. Table 8.5 shows that the initial un-ionised ammonia concentration was around the 80 mg l^{-1} level for some digesters, possibly due to the fact that 50% of the initial mixture was taken from a working laboratory digester with a concentration of about 1800 mg l NH_4^+. The un-ionised ammonia levels observed after digestion indicate that the suggested threshold value of 138 mg l^{-1} was exceeded for some digesters. This supports the evidence from Experiment 1 that ammonia inhibition may be an important consideration in the design and operation of a fed batch system operating on this waste mixture.

8.4.4 Evidence for inhibition of methane production by shock loadings, and maximum milk loading

The COD removal for each pair of digesters, expressed as % COD removed, is shown in Figure 8.11. It is clear that some slight inhibition of COD removal occurred at a COD loading of 35.5 kg m^{-3} and significant inhibition was apparent at 40.4 kg COD m^{-3}. Figure 8.12 shows the increase in total methane production with increasing COD loading. It can be seen that the increase in COD loading from 35.5 kg m^{-3} to 40.4 kg m^{-3} produced no significant increase in total methane production. This, coupled with the significant drop in COD removal for the highest COD loading, suggests that inhibition of the system took place. It is interesting to note that although there was a very slight drop in % COD removal at the 35.5 kg COD m^{-3} loading there was a small but significant rise in total methane produced, it is most likely that the increase in methane production was due to the extra readily degradable material added to the system. In the digesters receiving

the 40.4 kg m^{-3} COD loading, it was likely that the most readily degradable fatty acids and sugars were converted to methane but that some of the bacteria involved in more complex hydrolysis reactions were inhibited, hence the amount of volatile fatty acids directly available to the methanogens was reduced. This theory is supported by the trend in ammonium (NH_4^+) and un-ionised ammonia (NH_3) concentrations, see Figures 8.13 and 8.14. Initially, the trend for both these parameters was to increase with increasing digester loading. This would be expected, as one of the major sources of ammonium nitrogen in this type of anaerobic system would be the hydrolysis of milk protein. Increasing amounts of protein added to the system should lead to increasing levels of both NH_4^+ and NH_3. However, for the highest loading, both these parameters were actually lower than the control value suggesting that protein hydrolysis has not taken place to any great degree. Hence the bacteria which normally carry out this function must have been inhibited in some way.

Using figures provided by Petruy and Lettinga (1997) who determined that raw milk fat consists of 99.8% triglycerides, 73.8% of which are LCFA (Long Chain Fatty Acids), and knowing that raw milk consists of 3.9% fat, the amount of LCFA added to the digesters and the concentration of LCFA can be estimated for each pair of digesters, see Table 8.6.

Table 8.6 Estimated LCFA concentrations in each pair of digesters

Digester	LCFA mg l^{-1}
1&2	-
3&4	5,496
5&6	6,718
7&8	7,634

It will be noted that Petruy and Lettinga (1997) found significant inibition of fat liquefaction at LCFA concentrations of 834 mg l^{-1} and that Hanaki et al. (1981) found significant inhibition of methanogenesis at LCFA levels of 250 mg l^{-1} It is therefore suprising that methanogenesis was not severely affected by the LCFA levels present. The studies on co-digestion of cattle slurry and fish offal described in Chapter 7 tend to support the work of the above authors. Batch digesters receiving additions of fish offal (FO), which gave a LCFA concentration of 1,350 mg l^{-1} in the batch digester, showed a lag time of 2 weeks before the FO began to contribute to methane production, whereas the methane production rates from the digesters receiving additions of milk increased almost immediately after receiving the milk additions. Interestingly methane production from cattle slurry did not appear to be significantly affected by the LCFA concentration, as methane production from the batch digesters receiving FO additions was similar to the baseline methane production from the cattle slurry control digesters.

If it is assumed that the LCFA concentration in both milk and FO systems was high enough to inhibit liquefaction of fats, the extra methane production observed would be from either protein or lactose in milk, or protein in FO. As methane production increased significantly within 24 hours of the addition of milk and did not increase until 2 weeks after the addition of FO, it can be concluded that the lactose in milk was the reason for the difference between the 2 systems.

8.4.5 Comparison of cumulative methane production for the two experiments

The control digesters in the first experiment produced a mean total methane volume over the course of the experiment of 5.16 l ($\pm$ 0.25) after 33 days of operation, compared to a value of 5.08 l ($\pm$ 0.26) after 33 days of operation for the control digesters in the second experiment, see

Figures 8.4 and 8.9. These values are quite close, due in part to the fact that the same apparatus and procedures were used for both experiments.

A COD loading of 29.3 kg COD m^{-3} d^{-1} as milk in the first experiment produced a total methane volume of 9.34 ($\pm$0.46)litres after 33 days of operation, and a COD loading of 29.1 kg COD m^{-3} d^{-1} as milk in the second experiment produced a total methane volume after 33 days of 10.4 ($\pm$0.5) after 33 days. While these figures are reasonably similar, they are not as close as one would expect from comparing the cattle slurry controls in both experiments. The difference in performance may have been due to differences in the composition of the milk, as the first experiment was conducted during the winter and the second during the summer, when the dairy herd are fed a richer diet, which increases milk production. It is interesting to note that this change in diet seemed to affect the milk, but not the cattle slurry.

8.4.6 Problems with slurry stabilisation at higher COD loadings

One of the main aims of anaerobic digestion is slurry stabilisation, so that after separation of the digester effluent into solids and a liquid, the solids can be stored for some time without significant further degradation. It is likely that these separated solids from the digesters receiving the highest COD loading would not be very biologically stable as a portion of the COD of the waste would still be readily available to micro-organisms. This could lead to odour and insect problems in slurry solids storage areas.

8.4.7 Problems with biogas quality

It is also worth noting that methane concentration in the biogas dropped to levels approaching 30%, immediately after the shock loading event. On a full scale anaerobic digestion system

biogas of this quality would be unsuitable for use in generating engines or water boilers. Careful attention would need therefore to be paid to biogas methane levels on systems operating on cattle slurry /waste milk mixtures.

8.4.8 Preliminary conclusions - Experiment 2

This work suggests that a one off shock loading of milk of between 29.1 kg COD m^{-3} and 35.5 COD kg m^{-3} could be tolerated by a stable anaerobic digester with little significant negative effects on the stability of the digestion system and that COD loadings of 40.4 kg COD m^{-1} produced inhibition of methane production.

Figure 8.1 Experiment 1 - daily biogas production rate for each pair of digesters

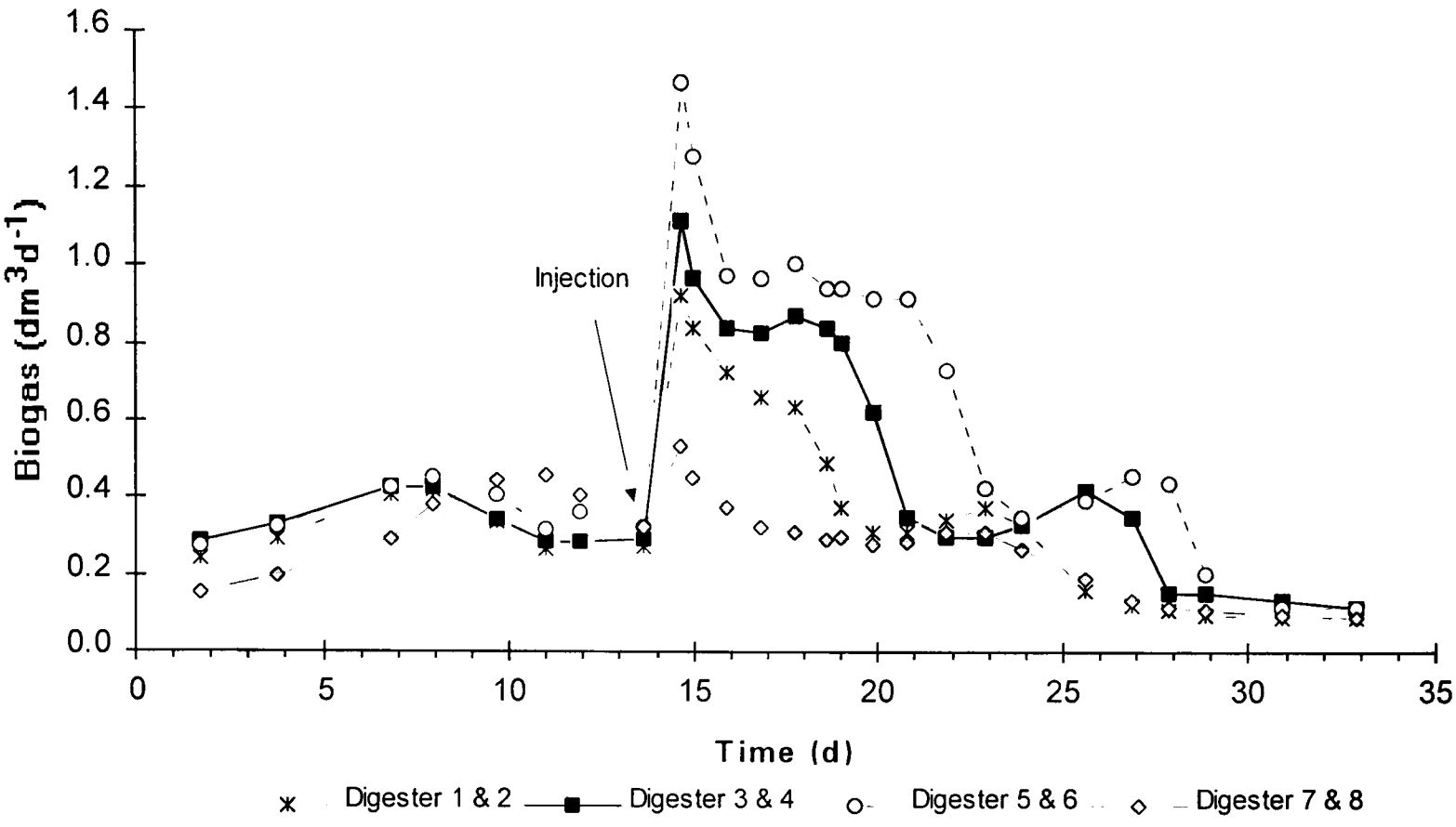


Figure 8.2 Experiment 1 - methane production rate for each pair of digesters

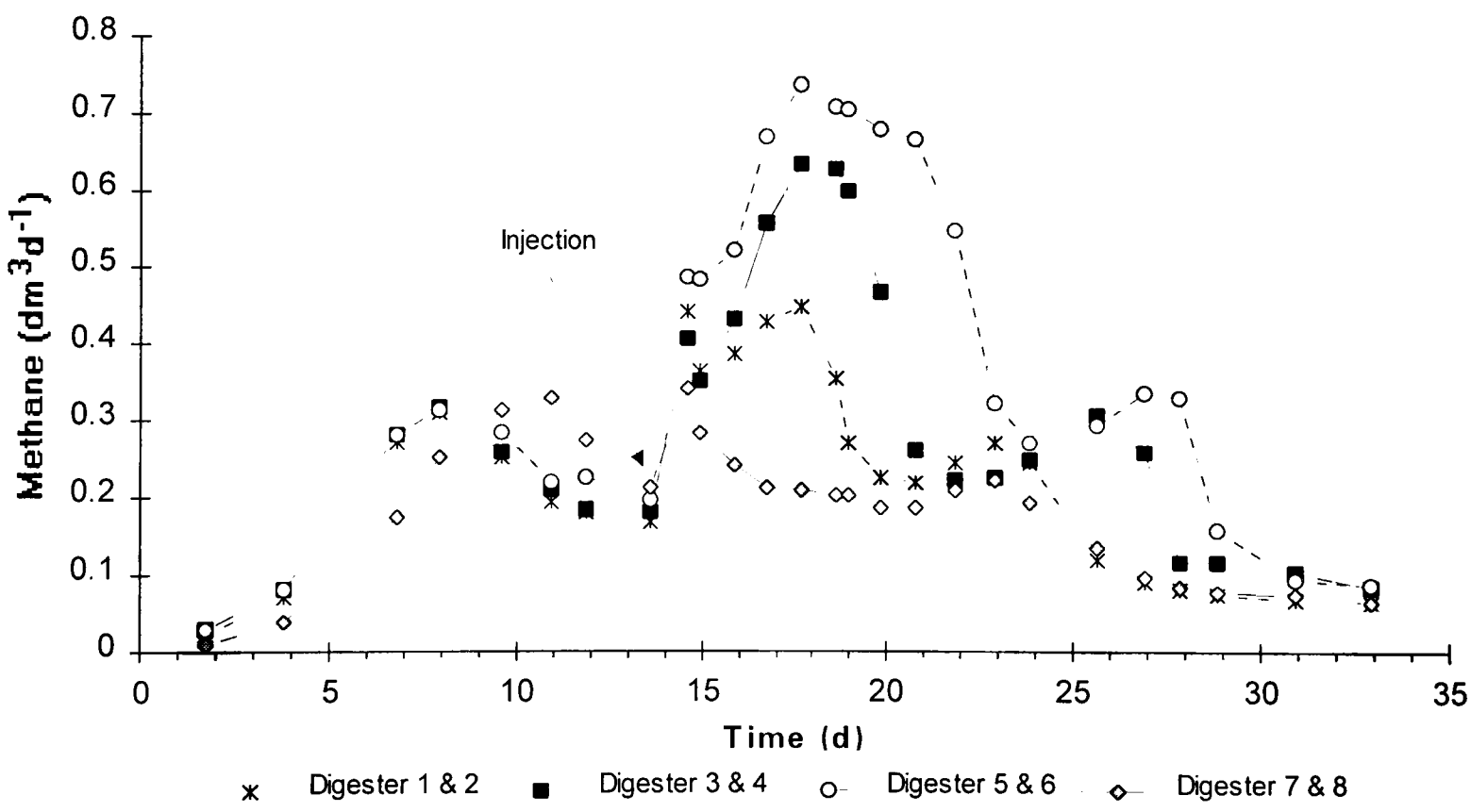


Figure 8.3 Experiment 1 - methane concentration in the biogas produced by each pair of digesters

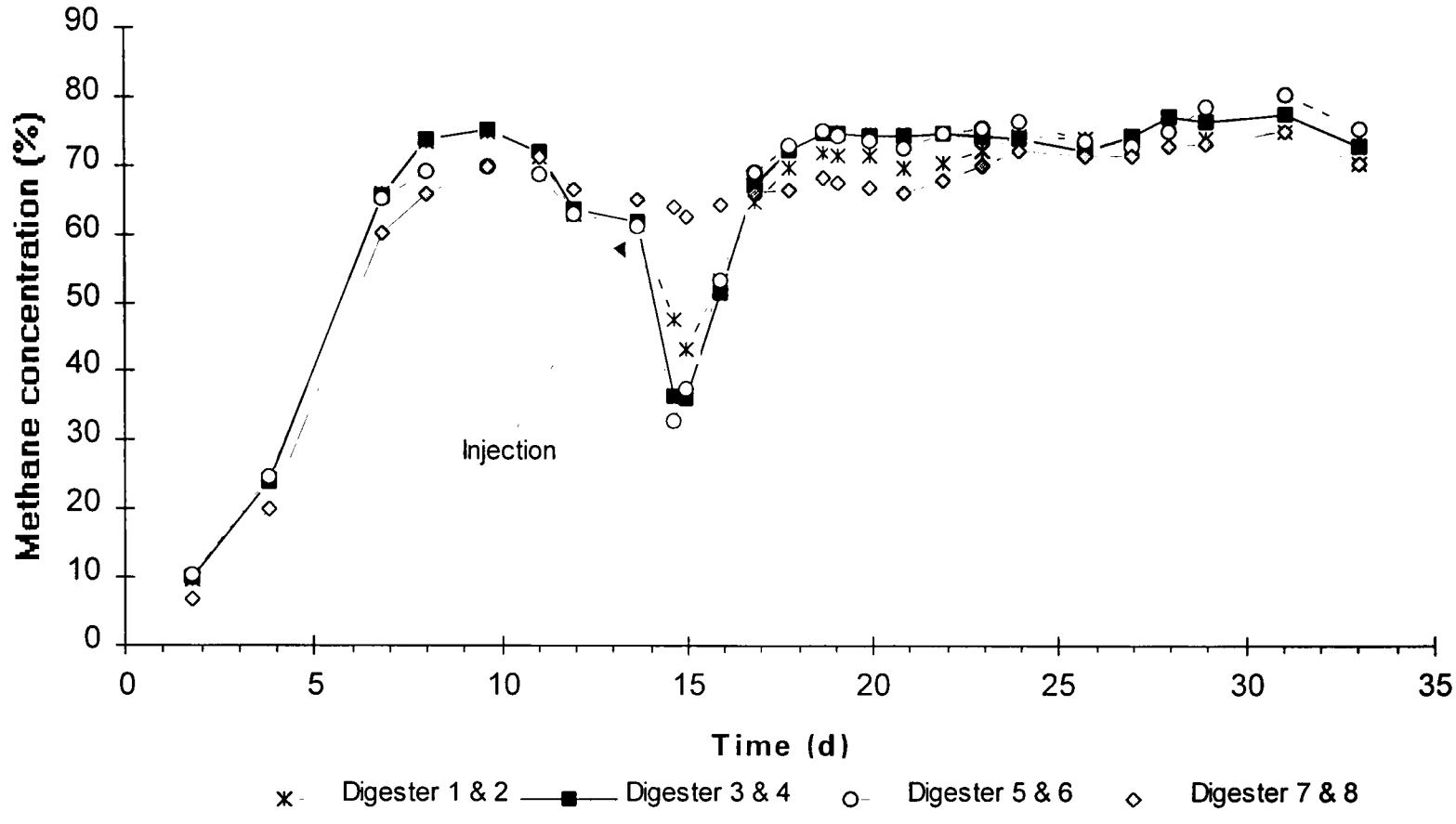


Figure 8.4 Experiment 1 - cumulative methane production for each pair of digesters

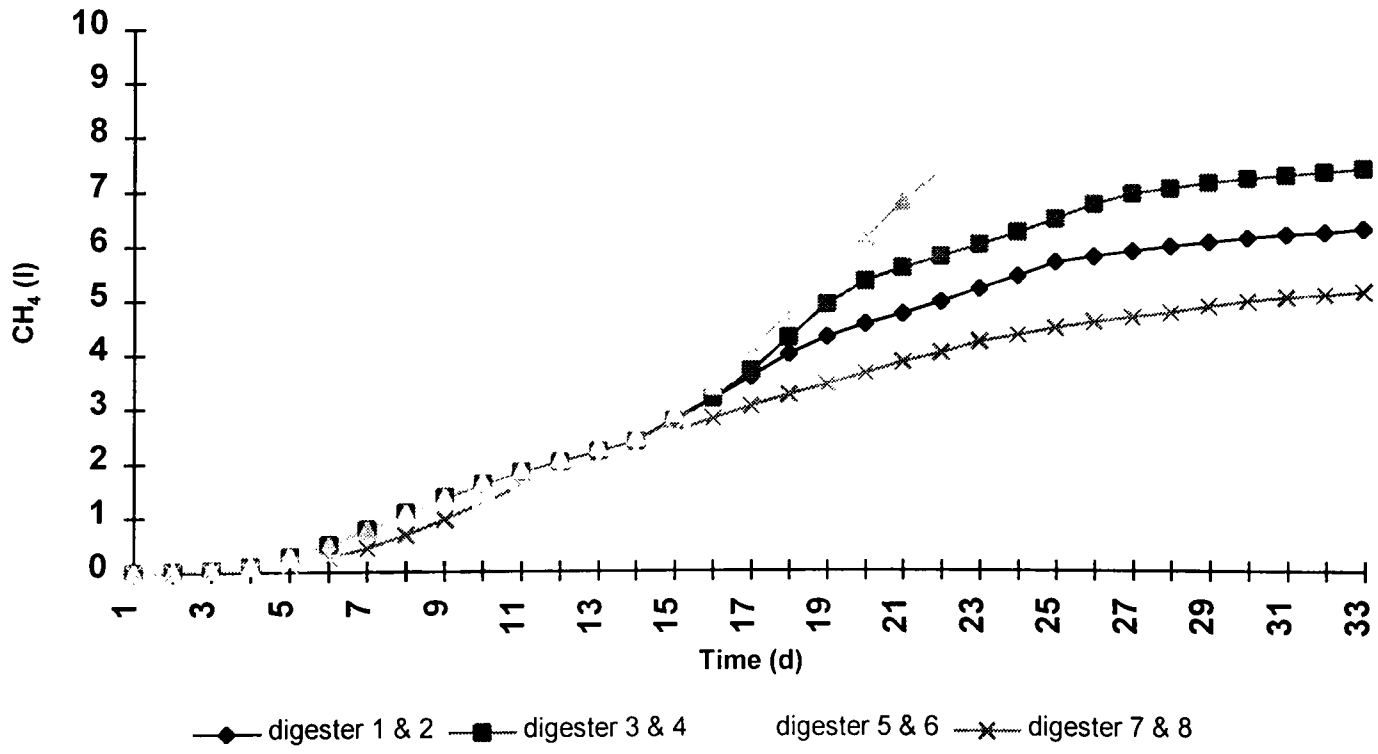


Figure 8.5 Experiment 1 - mean total methane production at each COD loading

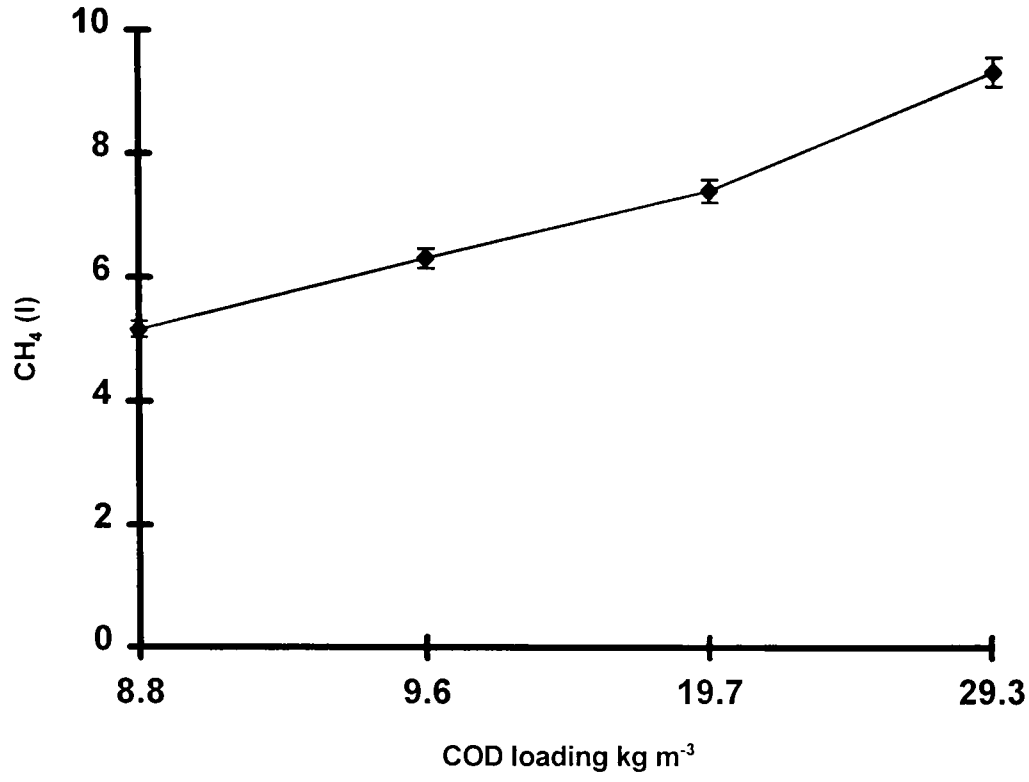


Figure 8.6 Experiment 1 - mean %COD removal at each COD loading

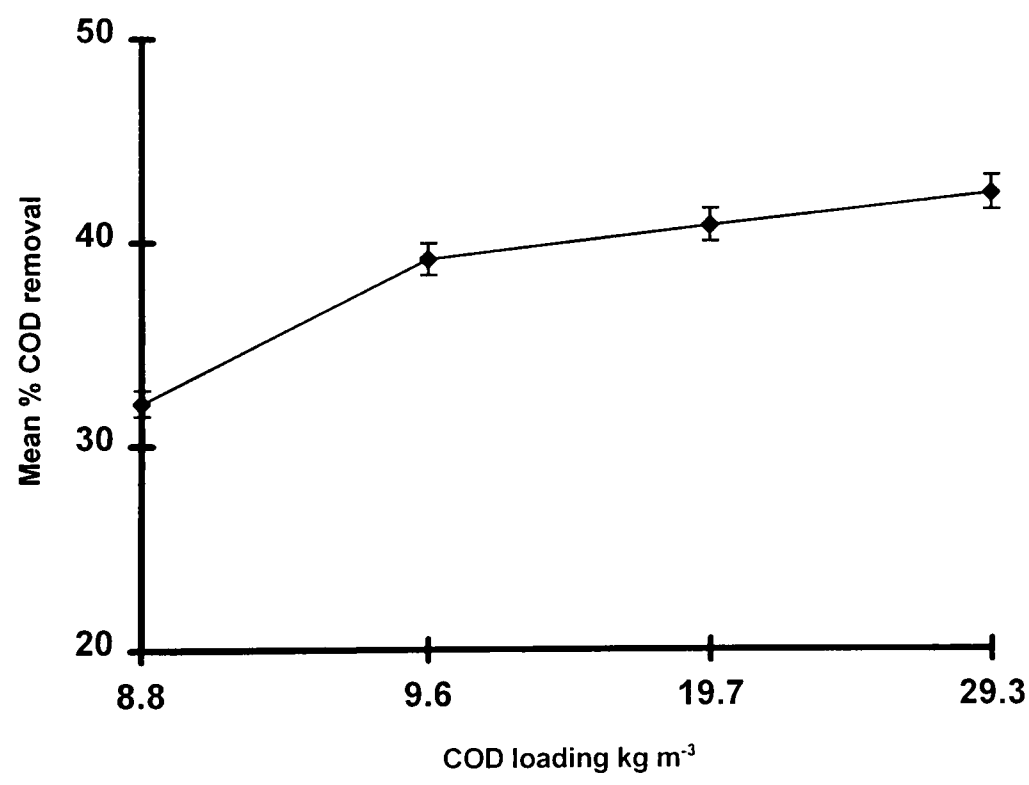


Figure 8.7 Experiment 2 - mean daily biogas production rate for each pair of digesters

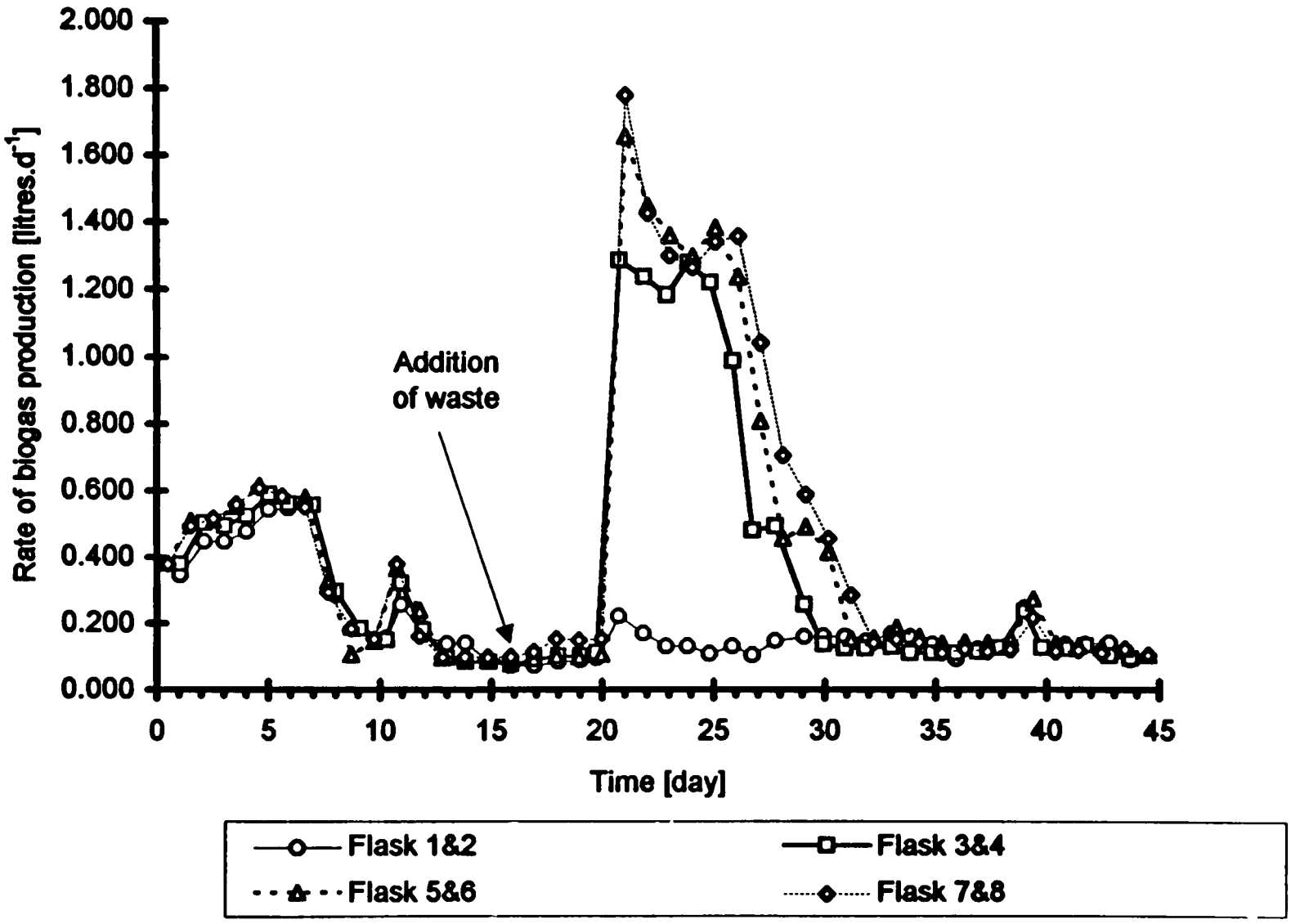


Figure 8.8 Experiment 2 - mean daily methane production rate for each pair of digesters

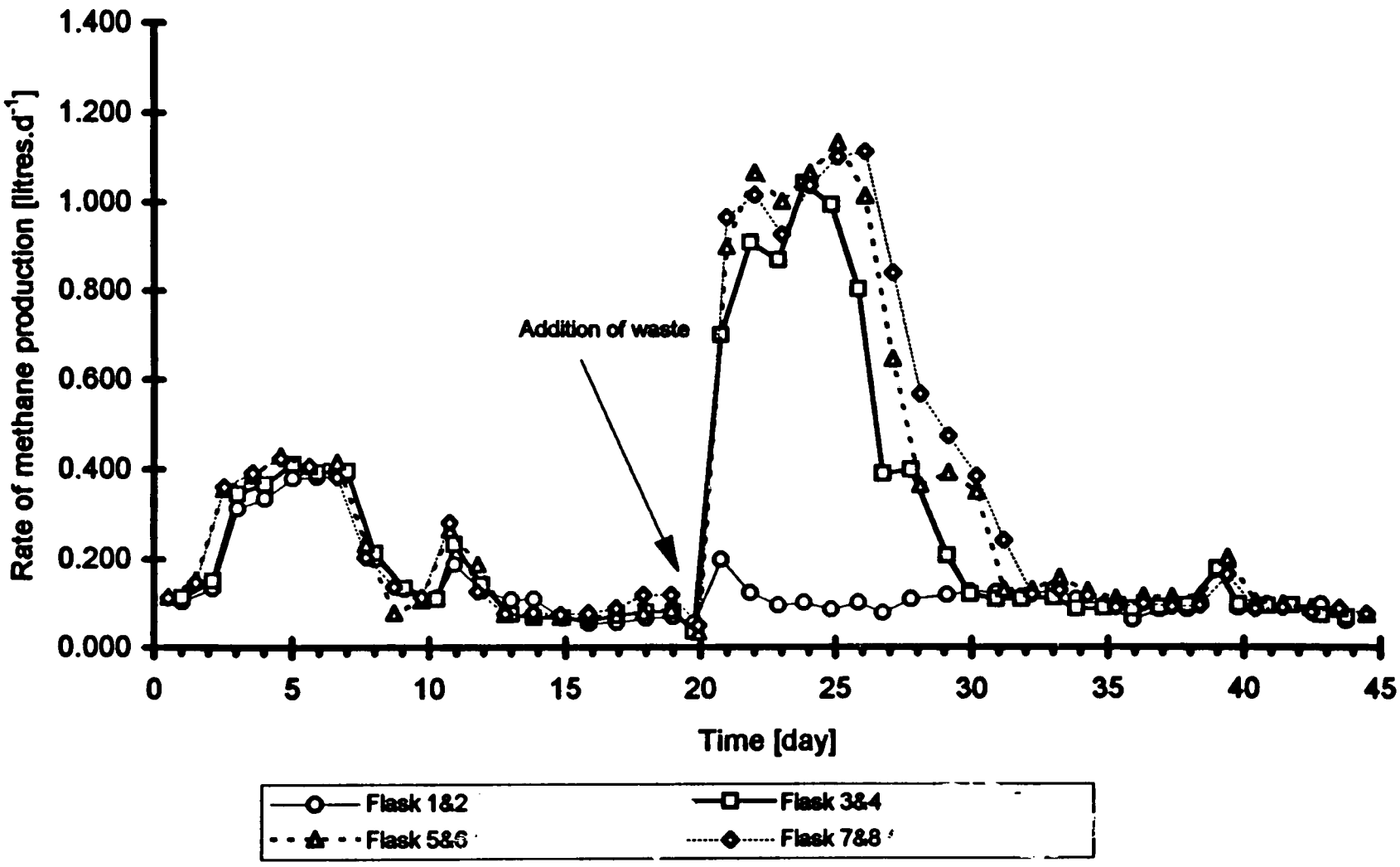


Figure 8.9 Experiment 2 - mean cumulative methane production for each pair of digesters over duration of experiment

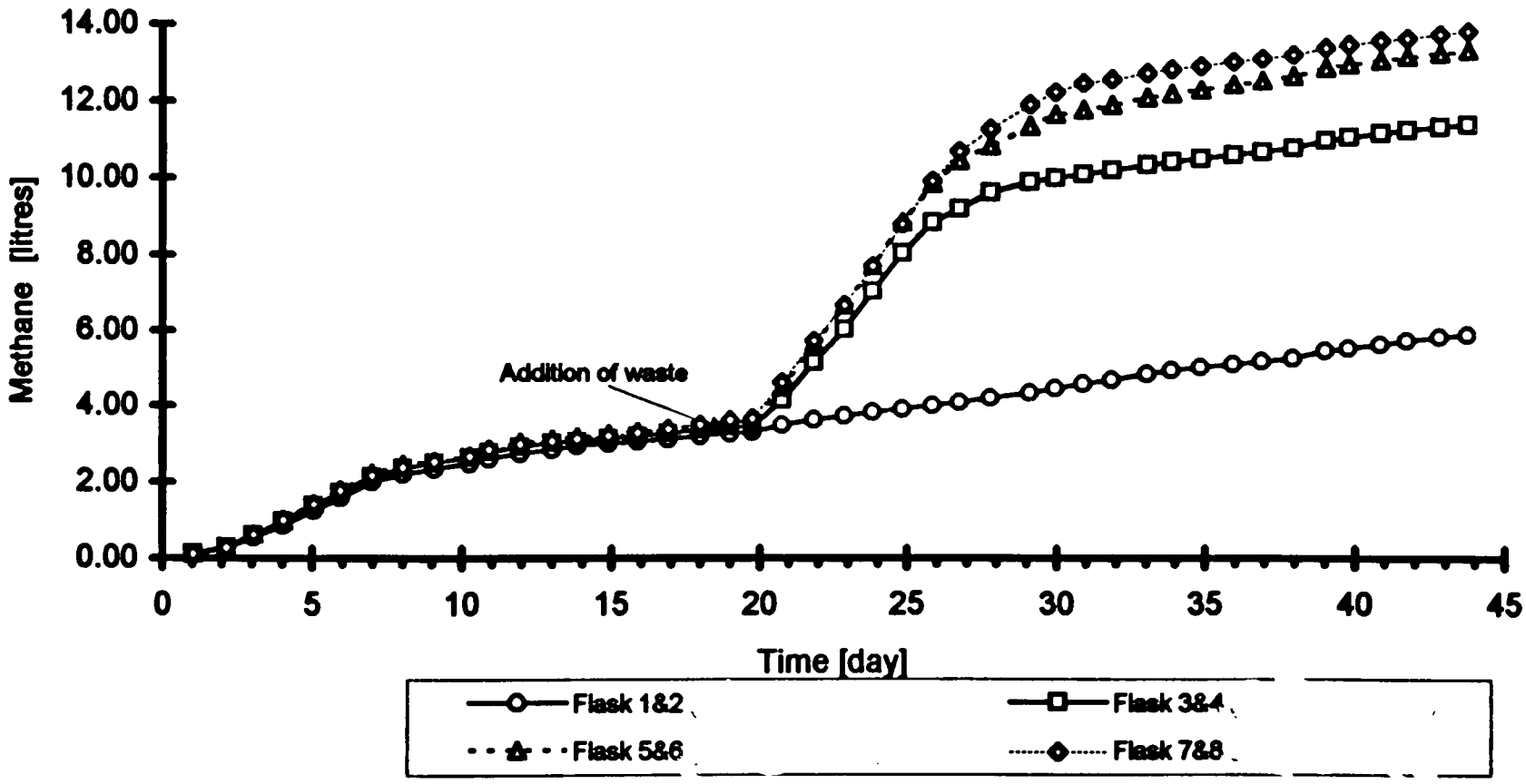


Figure 8.10 Experiment 2 - mean biogas methane concentration for each pair of digesters

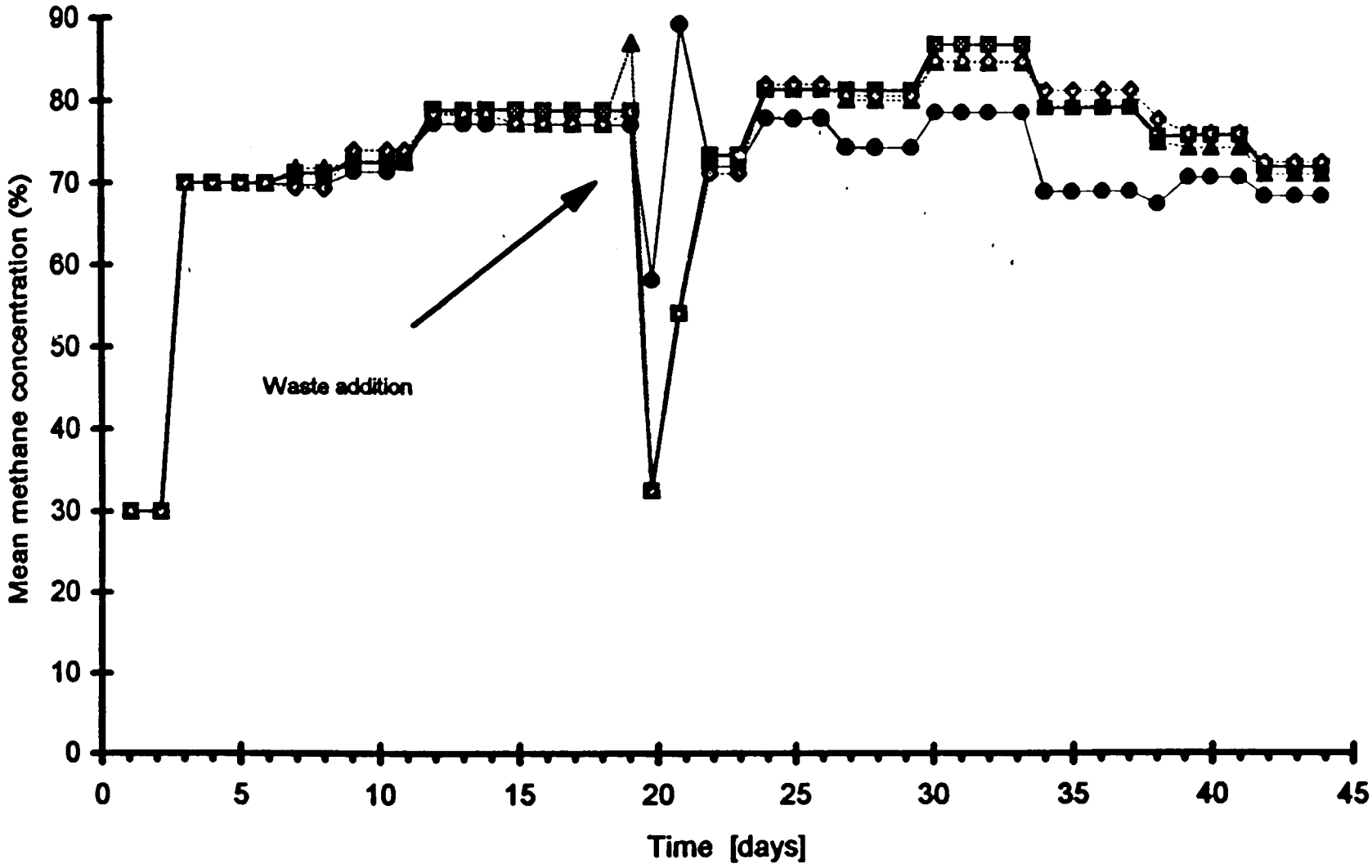


Figure 8.11 Experiment 2 - mean percentage COD removal at each COD loading

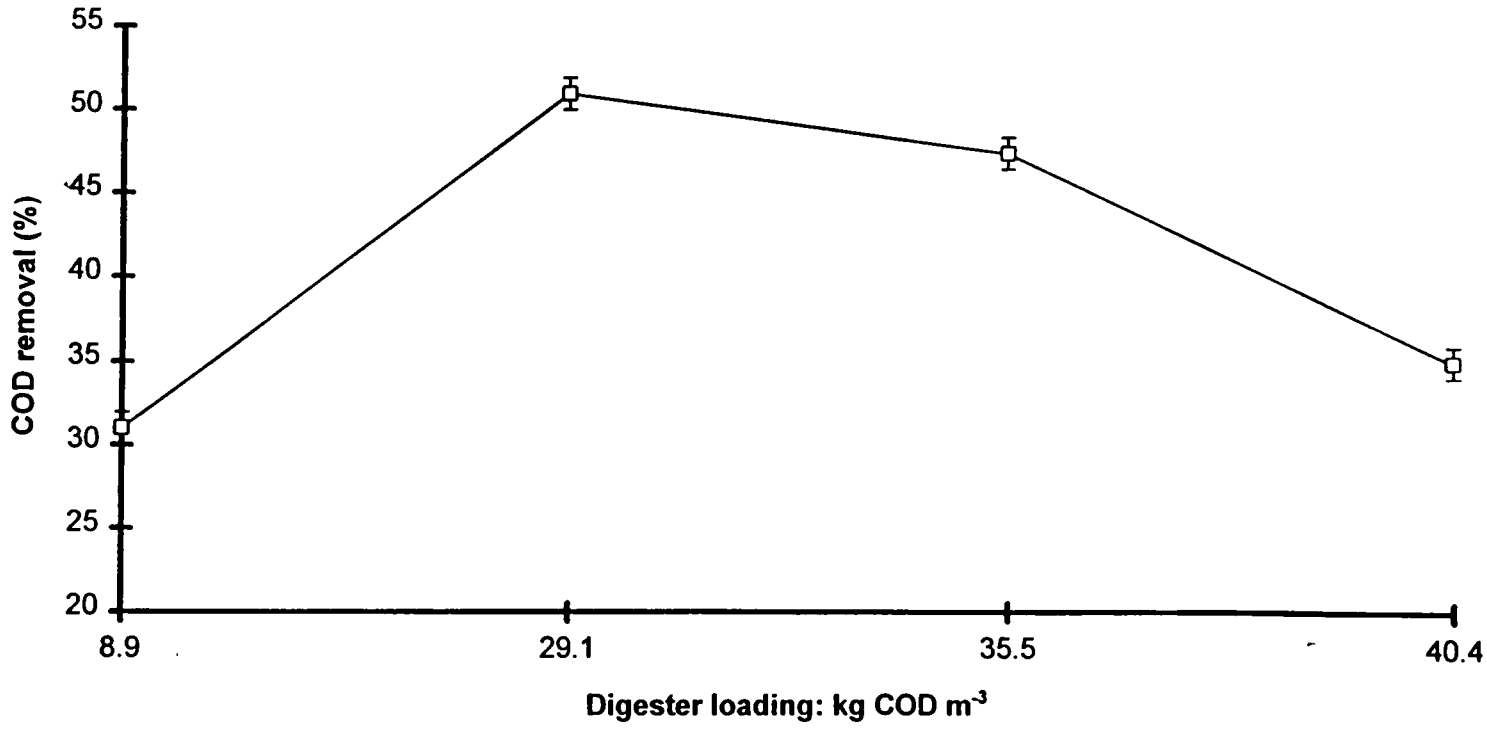


Figure 8.12 Experiment 2 - mean methane productuion at each COD loading

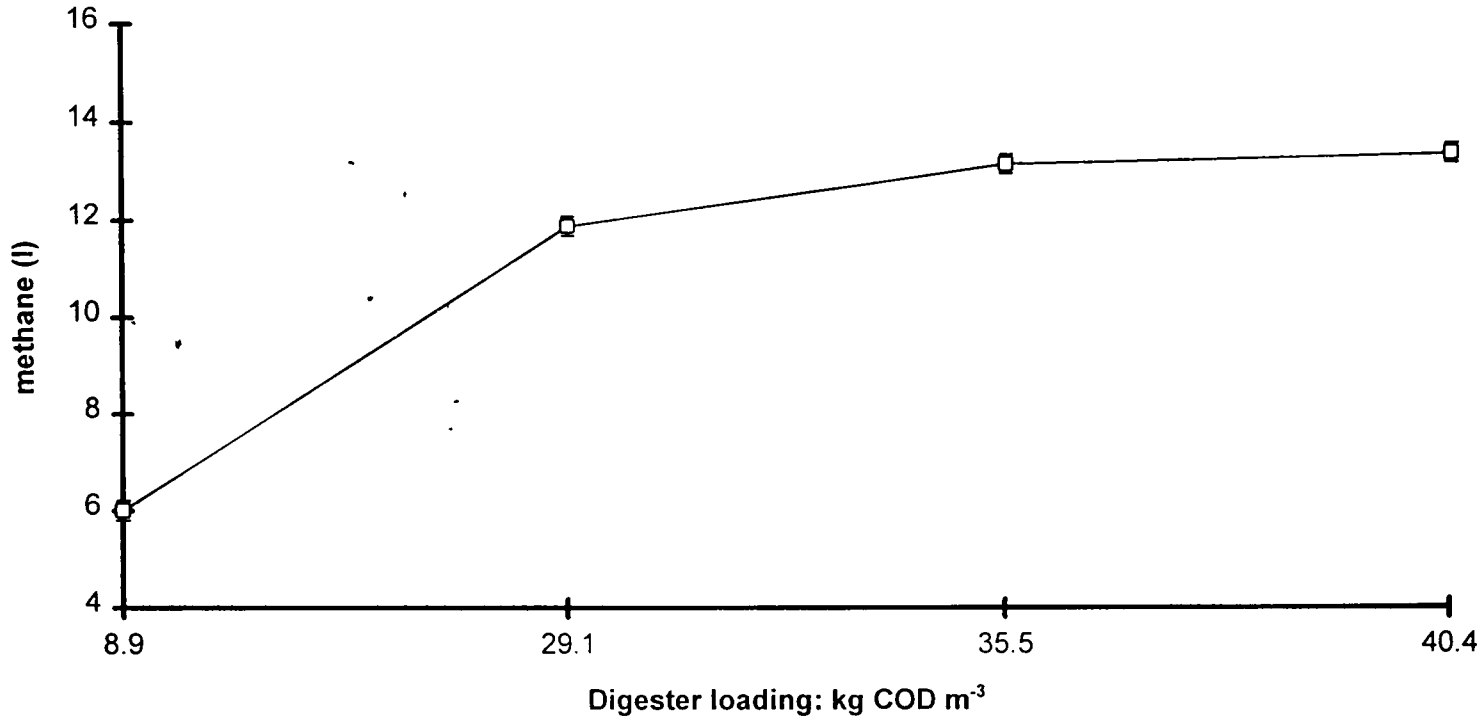


Figure 8.13 Experiment 2 - mean final ammonium conentration at each COD loading

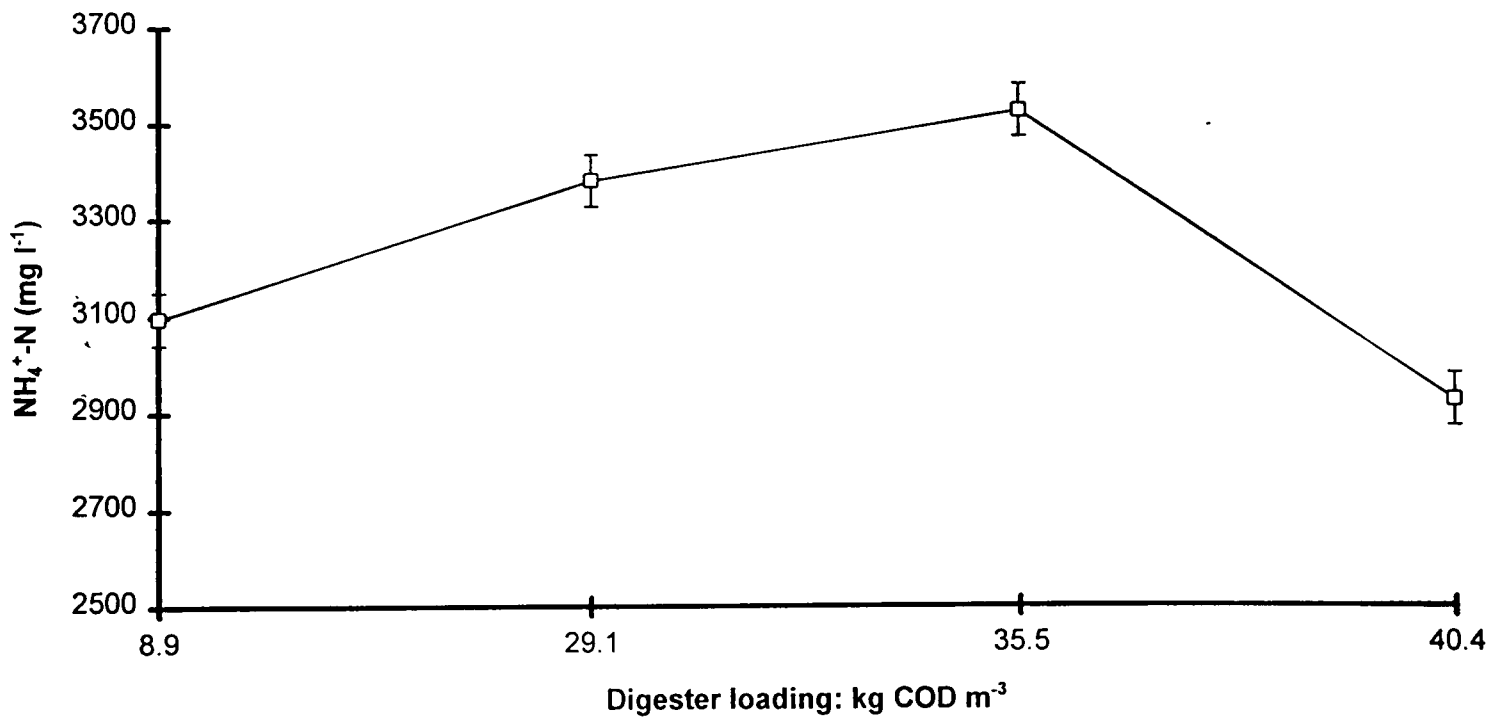
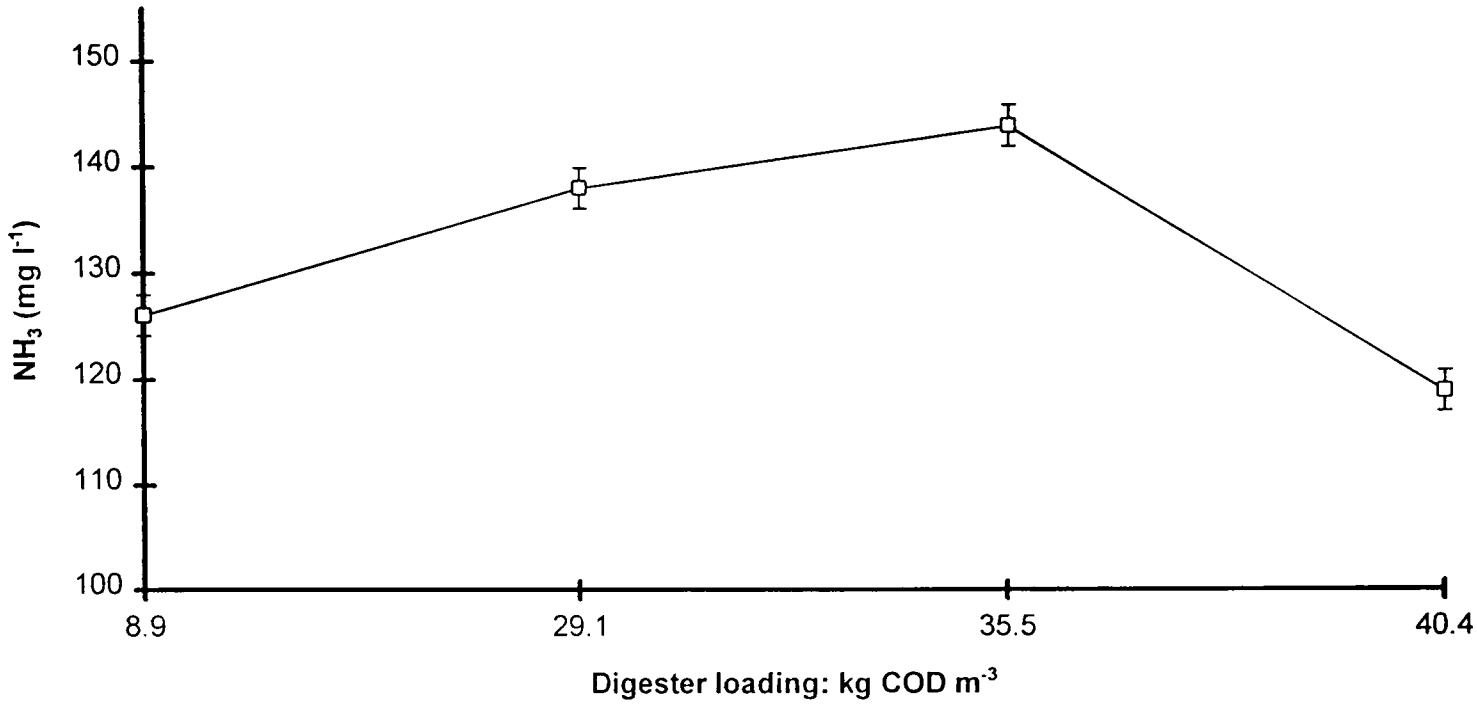


Figure 8.14 Experiment 2 - final mean ammonia concentration at each COD loading



Chapter 9

Discussion

9.1 Project aims

At the beginning of this project the stated aims were:

1. To determine what types and quantities of wastes which co-digest best together.

2. To determine the ratio of waste to animal slurry which produced optimum methane production.

3. To investigate the impact of adding wastes to a digester on the economic viability of a co-digestion facility.

9.2 Key points illustrated by project results

Sub-sections 9.2.1 - 9.2.8 will summarise the key points highlighted during each part of the project. These issues will then be used in Section 9.3 to examine the effect of co-digestion on the economic viability of a co-digestion facility.

9.2.1 Chapter 3 - Batch co-digestion of cattle slurry and industrial wastes - trial 1

Cattle slurry was chosen as the most suitable animal slurry for co-digestion, due to its high buffering capacity (alkalinity values of around 11, 000 mg l^{-1} $CaCO_3$), digestibility and the relative ease with which it can be pumped and mixed. The first batch digestion trial indicated that the co-digestion of chicken manure significantly enhanced the rate of methane production in a batch anaerobic digester, compared to a cattle slurry batch digester. The maximum methane production rate in a batch cattle slurry digester was found to be 0.65 l CH_4 wk^{-1} compared to 1.6 l CH_4 wk^{-1} for a chicken manure (15% TS)/cattle slurry mixture. Total methane produced over the course of the experiment by the chicken manure/cattle slurry batch digester was also significantly greater than that produced by the cattle slurry digester (4.5 l CH_4 compared to 6.9 l CH_4). While other mixtures such as cattle slurry/sugar beet effluent and cattle slurry/potato processing effluent were found to have similar or higher maximum methane production rates and produced more methane over the course of the experiment, it was decided that the lack of an alternative chicken manure disposal route to the increasingly restricted practice of land spreading meant the investigation of co-digestion as a disposal route for chicken manure should be investigated. Also as the cost of mains water is increasing steadily, it was decided to dilute the chicken manure by the minimum amount, to the maximum solids level which would still allow the manure to be pumped or moved by gravity flow. This was determined to be around 15% TS. It was noted that the final ammonium and ammonia levels were quite high in the chicken manure batch digester (8,800 and 1,087 mg l^{-1} respectively), which may cause problems on a continuous pilot plant.

9.2.2 Chapter 4 - anaerobic digestion pilot plant trial 1 - co-digestion of cattle slurry and chicken manure

20 litre anaerobic digestion pilot plants were initially operated on cattle slurry at a 28 day retention time and a loading rate of 2.92 kg VS m^3 d^{-1}, and then the feed was changed to a

mixture of 70% wet weight cattle slurry and 30% wet weight chicken manure at 15% TS. Initial mean methane productivity on cattle slurry was around 0.1 m^3 CH_4 kg VS^{-1} added and rose to 0.12 - 0.125 m^3 CH_4 kg VS^{-1} during the first retention time in which chicken manure was added to the feedstock. However a slight levelling off of mean methane productivity occurred during the second retention time, to 0.1 to 0.11 m^3 CH_4 kg VS^{-1} added, due to ammonia inhibition of the methanogenic bacteria present. Typical methane productivities from cattle slurry digesters can vary between 0.08 and 0.25 m^3 CH_4 kg VS^{-1} added and are dependent on a number of factors, the most important of which is volatile solids loading rate, see Section 1.4. The initial cattle slurry volatile solids loading rate in the work described in Chapter 4 was quite low, at around 2.9 kg VS m^3 d^{-1}, and hence low methane productivity's would be expected at this loading rate. Linke (1997) reported that cattle slurry digesters operating at 4.5 kg VS m^3 d^{-1} had methane productivity's of 0.2 m^3 CH_4 kg VS^{-1} added. Operating the digesters in the current work on 70/30 cattle slurry/chicken manure at VS loadings of 3.5 - 4 kg VS m^3 d^{-1} produced only 0.12 - 0.125 m^3 CH_4 kg VS^{-1} added, indicating the chicken manure was less degradable than cattle slurry, and certainly had less methane producing potential.

Higher ratios of chicken manure to cattle slurry were found to decrease the methane productivity of the digesters, and therefore a ratio of 70 cattle slurry / 30 chicken manure was deemed to be the optimum ratio.

9.2.3 Chapter 5 - batch co digestion of agricultural and industrial wastes - trial 2

Batch digestion of a number of wastes indicated that fish offal (FO)and fruit and vegetable waste (FVW) significantly enhanced total methane production and the methane production rate of batch cattle slurry digesters. The maximum rate of methane production of the batch digesters operating

on cattle slurry only was between 0.78 and 0.87 l CH_4 wk^{-1}. The addition of FO to batch cattle slurry digesters was found to increase the maximum methane production rate to between 4.25 and 4.6 l CH_4 wk^{-1}. The addition of FVW to a batch cattle slurry digesters was found to increase the maximum methane production rate to between 1.4 and 1.55 l CH_4 wk^{-1}. Also total methane produced over the course of the experiment was much higher than the control digester values of 4.7 -5 l CH_4 in the digesters receiving FO (12.2 - 12.4 l CH_4) and FVW (7.4 - 7.8 l CH_4).

Some of the other wastes used in this trial, brewery sludge, silage effluent and the sludge from a DAF (dissolved air floatation) effluent plant treating yoghurt manufacturing wastewater also produced encouraging methane production results. It was decided to examine the co-digestion of FO on the anaerobic digestion pilot plant due its high methane production potential and the fact the only alternative disposal routes available, landfilling and spreading on land, are becoming restricted. It was also decided to examine the co-digestion of FVW on the anaerobic digestion pilot plant, due to its methane production potential and legislative pressures which are driving local authorities to look for alternative disposal routes for up to 25% of the MSW (Municipal Solid Waste)they collect (The ENDS Report, 1997), significant proportion of which is FVW.

9.2.3.1 The effect of waste composition on digester performance

At this point, it is worth noting how the the batch trials described in Chapters 3 and 5 have demonstrated the effect of waste biodegradability on the conversion organic solids to methane.

In Section 3.6.2, it was noted that the addition of chocolate manufacturing wastewater to a batch cattle slurry digester, at a COD loading of 48 kg COD m^{-3} produced digester failure. This was characterised by the digester pH dropping to 4.5 and no significant methane production being

observed. Milk loadings as high as 40.4 kg COD m^{-3} were applied to the digesters in the work described in Chapter 8 without digester failure occurring. It is possible that the application of 48 kg COD m^{-3} as milk may have caused the digester to fail but this was considered unlikely, as a loading rate which was only 20% lower than that used in the chocolate manufacturing wastewater work, would have been expected to depress the system pH to at least some degree, whereas the final pH in the 2 digesters receiving additions of waste milk at loadings of 40.4 kg COD m^{-3} was 7.86.

The clear difference in ability to cope with the increased COD loading as chocolate manufacturing effluent and as milk may have been due to the different methods of co-digestion used. Chocolate manufacturing wastewater was mixed with the cattle slurry and digester inoculum and then placed in the digesters, whereas waste milk in the current work was added to a working batch digestion system. In the former case, it is possible that the methanogenic bacteria would have had no chance to grow as the system would have quickly turned acidic, and with no methanogens to remove the acids, further acid build up would occur leading to failure. In the case of the waste milk additions, the established methanogenic population was able to degrade the excess fatty acids and hence prevent the detrimental pH drop from occurring. This highlights the importance of establishing a stable anaerobic digestion system before attempting to introduce other wastes into a digester.

However the different outcomes may also have been due to the chemical nature of the wastes involved. The chocolate manufacturing effluent was essentially an 18% w/w glucose solution. Milk, as has been mentioned earlier, is a complex mixture, containing about 3.4% carbohydrate as lactose. On hydrolysis, one molecule of lactose yields one molecule of galactose and one

molecule of glucose (Conn *et al.*, 1987). Even assuming 100% lactose hydrolysis the available glucose would still be an order of magnitude lower than that available from the chocolate manufacturing effluent. Also the rate at which glucose became available would be determined by the rate of lactose hydrolysis.

In an anaerobic system, glucose is converted to pyruvate via the Embden-Meyerhof-Parnas pathway and then to acetic acid (McInerney and Bryant, 1981). It follows that the more glucose is present in an anaerobic system, the higher the rate of acetic acid production will be, until the maximum rate of production is reached. If the acid is produced faster than the methanogens can utilise it the pH drops as described above. Therefore in addition to using the COD loading in kg m^{-3} to determine the maximum loading on a digestion system, it is also necessary to consider the potential rate at which that COD could be converted to fatty acid. Perhaps this could be referred to as the Potential Rate of Acetate Production (PRAP) of a waste.

The cattle slurry / FO and cattle slurry / FVW mixtures described in Chapter 5 demonstrate how the same amount of volatile solids added to a system can give significantly different methane production values. 17.1 kg VS m^{-3} digester volume added as FO produced significantly more methane over the course of the experiment, than the same VS loading as FVW produced, indicating that, under batch digestion conditions, FO was much more readily converted to methane than FVW. They both in turn were much more readily converted to methane than cattle slurry, as the cattle slurry digesters, although operated at a slightly lower VS loading, 14 kg VS m^{-3} digester volume, as cattle slurry, produced much lower methane production rate and total methane production figures.

These points indicate how it is important to consider not only the increase in volatile solids or COD loading that the addition of another waste to a cattle slurry system will cause, but also the rate at which that material wil be converted to fatty acids.

9.2.4 Chapter 6 - Anaerobic digestion pilot plant trial 2 - co-digestion of cattle slurry and FVW

The pilot plant was initially operated at quite a high volatile solids loading rte of 5.2 kg VS m^{-3} d^{-1} for the first 2 retention times. Mean methane productivity was in the region of 0.22 to 0.24 m^3 CH_4 kg VS^{-1} added, consistent with cattle slurry digesters operated at such loading rates. Addition of FVW to the feedstock, at a ratio of 80% wet weight cattle slurry / 20% wet weight FVW, produced an increase in the volatile solids loading rate to about 6 kg VS m^3 d^{-1} and caused a rapid increase in mean methane productivity which stabilised between 0.35 and 0.4 m^3 CH_4 kg VS^{-1} for the next 2 retention times. A further increase to a ratio of 60/40 cattle slurry/FVW, increased the VS loading rate to 7.2 kg VS m^3 d^{-1} and caused a build-up of VFA and digester foaming. The cattle slurry/FVW ratio was reduced for one retention time to 70/30, to allow the system to stabilise, and then increased to 50/50, and a VS loading rate of 7.1 kg VS m^3 d^{-1} (lower than expected at this ratio due to a decrease in cattle and FVW VS levels). This loading rate and ratio produced a further increase in mean methane productivity to 0.41 - 0.46 m^3 CH_4 kg VS^{-1}, despite the fact that digester pH was low and VFA and the VFA:TAlk ratio were both significantly increased. The digester could only be operated at this loading rate and ratio for one retention time due to time constraints, therefore it is difficult to predict if this loading rate and ratio would be sustainable. However it was noted that the mean methane productivity was between 0.35 and 0.40 m^3 CH_4 kg VS^{-1} at a ratio of 80/20 cattle slurry/FVW and increased to only 0.41 - 0.46 m^3 CH_4 kg VS^{-1} on changing the ratio to 50/50. This is a only 15 - 17% increase

in m^3 CH_4 kg VS^{-1} for a 250% increase in the amount of FVW in the feedstock. Also it was clear from the digester operational parameters during the 2 retention times that the digesters were operated on the 80/20 mixture, that the digester was quite stable while operating over an extended period of time on this mixture.

Therefore the optimum ratio cattle slurry to FVW taking into account the greatly increased methane productivity and digester stability associated with this ratio was determined to be 80/20 on a wet weight basis. This ratio produced mean methane productivity figures of 0.35 - 0.40 m^3 CH_4 kg VS^{-1} added.

9.2.5 Chapter 7 - Anaerobic digestion pilot plant trial 3 - co-digestion of cattle slurry and FO

The pilot plant was again operated at a loading rate of 5.2 kg VS m^3 d^{-1} and had a mean methane productivity of 0.23 - 0.26 m^3 CH_4 kg VS^{-1} added over the first 2 retention times. Addition of FO to the feedstock, at a ratio of 96% cattle slurry : 4% FO, increased the VS loading rate to around 6.1 kg VS m^3 d^{-1}. This caused an initial drop in mean methane productivity, to 0.20 m^3 CH_4 kg VS^{-1} added. Weekly mean methane productivity increased over the next 2 weeks to 0.28 m^3 CH_4 kg VS^{-1} added, but then fell sharply again in the next week before rising to 0.31 m^3 CH_4 kg VS^{-1} added for the 6th week of feeding cattle slurry/FO (week 12 of operation). Further increases in FO concentrations in the feedstock had the effect of drastically reducing mean methane productivity to 0.08 m^3 CH_4 kg VS^{-1} added. The system did partially recover after the feed was returned to cattle slurry, and feeding of the 96/4 mixture after this period of recovery did bring methane productivity back to 0.28 m^3 CH_4 kg VS^{-1} added. Addition of FO to the feedstock caused an initial build up of VFA in the digester, but this had began to drop during

weeks 10 - 12. % VS removal which had been falling since just after FO was introduced to the feedstock, had been reasonably constant over weeks 11 and 12. The VFA:TAlkalinity ratio had also began to fall over weeks 10 - 12. These figures, coupled with the higher methane productivity's recorded in weeks 11 and 12, indicated that the system was beginning to acclimatise to the FO fraction to some degree, but that, in contrast to the batch digestion of FO and cattle slurry, repeated additions of FO to a working cattle slurry digester had the effect of initially inhibiting digester operation for a number of weeks and further increases in the FO fraction of the feedstock has the effect of severely inhibiting methane production.

It can be concluded that a feedstock with a ratio of 96% cattle slurry: 4% FO, after an initial period of inhibition, marginally increased the mean methane productivity of a cattle slurry digester, to between 0.28 and 0.31 m^3 CH_4 kg VS^{-1} added.

9.2.6 Chapter 8 - batch digestion of waste milk and cattle slurry

Initial experimental work focused on the effect of adding waste milk to batch cattle slurry digesters and found that additions of waste milk, at loading of up to 29.3 kg COD m^{-3}, no negative effects on the methane productivity of a batch cattle slurry digester. Further studies indicated that milk loading above 35.5 kg COD m^{-3} did produce inhibition of methane production. A case study determined that all the waste milk form a 100 cow farm could be safely disposed of to a cattle slurry digester on that farm, without having any inhibitory effect on methane production.

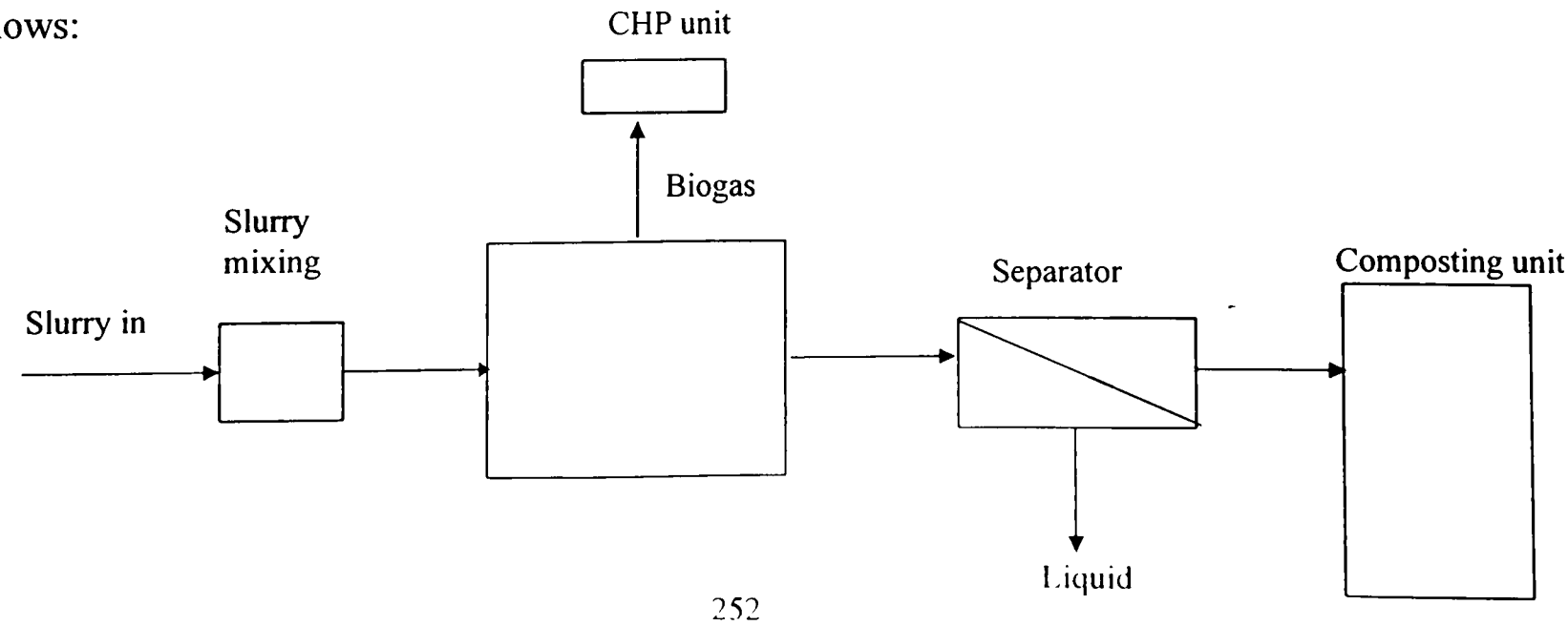
9.3 The potential of co-digestion to improve the economic viability of an anaerobic digestion facility

The work described above has shown that co-digestion can enhance the methane productivity of a cattle slurry digester by varying amounts, depending on the material used and the rate at which it is added to the digester. In Section 1.7, the existing income streams from a cattle slurry digester were identified as methane use for heat and power, sales of compost material, reduced slurry handling charges and reduced expenditure on fertiliser. It was proposed that the operation of an anaerobic digester as a co-digestion facility could provide 3 additional sources of income to the digester operator. These were (i) charges for accepting waste for disposal in the digester, (ii) additional income from extra methane produced and (iii) possible enhanced fertiliser value of the digester effluent.

An economic model of an anaerobic digestion facility has been prepared, using economic data from an existing cattle slurry digestion facility(Dahn and Robbins, 1996). The results of the co-digestion trials described above will be used in the following sections to assess the economic benefits of co-digestion of cattle slurry and chicken manure FVW and FO on this facility.

9.3.1 Baseline study - digester operating on cattle slurry

The digester in question has a working volume of $300m^3$ and for the purposes of the model will be operated on cattle slurry only. The digester is linked to a CHP (combined heat and power unit) and also has a composting facility attached to the main plant. The plant flow diagram is as follows:



The Dahn and Robbins case study, referred to in the following paragraphs, was on a digester operating on cattle and pig slurry, therefore all digester performance data for the unit operating on cattle slurry only were calculated from known data. Construction costs for this facility were as follows (Dahn and Robbins, 1996):Digester, £89,349. CHP unit (including electrical links to National Grid), £34,700 and Composting unit and slurry mixing tank, £9,600, making a total of £133, 649. Operating costs were about £2,100 per year.

An economic model, described below, was designed on an Excel spreadsheet and used to estimate the effect of adding different feedstocks on the economic viability of an anaerobic digester. For the purposes of the model, the digester is operated at a VS loading rate of 5.2 kg VS m^3 d^{-1} and retention time of 21 days To give this loading rate and retention time, 353 dairy cows, each producing 40kg of slurry d^{-1} are required. 19,747 kg cattle slurry, at 10% TS and 7.9% VS is fed to the digester once per day. 5 days per week, making a total feed of 98,735 kg wk^{-1}. This equates to 7,800 kg VS added each week. Methane productivity is assumed to be 0.22 m^3 CH_4 kg VS^{-1} added (see Section 6.12 for the basis of this assumption). This is gives 1716 m^3 CH_4 wk^{-1}, or 10.2 m^3 CH_4 hr^{-1}.

For the purposes of the model it is also assumed that there is a 40% reduction in the mass of solid leaving the digester, therefore 98,735 kg wk^{-1} of slurry (of which 10% is solid material) enters the digester and 94,786 kg wk^{-1} of slurry leaves the digester (of which 6% is solid material). The liquid /solid separator is assumed to split this stream into 80% liquid / 20% solid, based on observations made by Dahn and Robbins, (1996). This equates to 75,829 kg of liquid per wk and 18,957 kg solids wk^{-1}.

Of the 10.2 m^3 hr^{-1} of CH_4 generated, experience has shown that about 25% of this is required to maintain the digester working temperature at 35 ^oC (Dahn and Robbins, 1996). This leaves 7.8 m^3 hr^{-1} available to the CHP plant. Due to design constraints of the installation studied by Dahn and Robbins, the heat produced by the CHP unit could not be made available for heating the digester.

Methane at STP has a heating value of 35,800 kj m^{-3} (Metcalf and Eddy, 1991). This equates to 279,240 kj hr^{-1} for this system. An energy recovery efficiency of about 30% is typical for the spark ignition generator (Sincero and Sincero, 1996). hence 83,772 kj can be converted to electricity. Dividing by 3,600 (Sincero and Sincero, 1996) converts this figure to 23.27 kW hr^{-1}. This equates to 569.3 kW d^{-1}, and 207,794 kW yr^{-1}. If electricity sold to the National Grid were to be eligible for a Non Fossil Fuel Obligation (NFFO) contract price of £0.08 kW hr^{-1}, this would be **an income of £16,308 from electricity sales.**

75,829 kg wk^{-1} of liquid are produced. If the liquid is assumed to have a total nitrogen concentration of 2.32 g N kg^{-1} (Dahn and Robbins, 1996), this equates to 175.9 kg N wk^{-1}. Artificial fertilisers cost about £0.32 kg N^{-1} (Troop, 1997), if it is assumed that all the nitrogen produced in the liquid can be used on the farm or sold to other farmers, **this represents a yearly income of £2,927 from the fertiliser value of the separated liquid.**

18,957 kg of solid material are produced from the separator each week. If this is composted with straw, at a ratio of 3 parts solids to one part straw and it is assumed that there is a 40% reduction in the weight of the material over the composting period (Gray, 1997), this equates to 15,168 kg

of compost produced each week. Dahn and Robbins (1996) suggest a value for this type of compost of £10 tonne^{-1}, **this gives a yearly income from compost sales of £7,886.**

Most farmers rely on contractors with specialist machinery to spread their slurry (Windridge, 1997). Average spreading costs are around £0.38 tonne slurry (Dahn and Robbins, 1996). Digestion means that the slurry can be irrigated as a liquid onto fields, dispensing with the need for specialist spreading equipment. 98.735 tonnes of slurry per week, 52 weeks per year would cost £1,951 in spreading charges. Elimination of this charge gives **a saving of £1,951 on slurry spreading costs each year.**

This gives a total gross income per year from the digester of £29,071.

Subtracting £2,100 running costs gives **a net yearly income of £26,971.**

Ignoring interest charges and inflation, this gives a **return on investment (ROI) of 5 years.**

9.3.2 Addition of other wastes to the digester feedstock

Using the model described above, it was possible to estimate the economic benefits of adding the other wastes used during this project to the digester.

A mix of 80% cattle slurry / 20% FVW was found to be the optimum mixture in terms of methane production and digester stability during the trials with FVW, see Section 9.2.6. This feedstock had a mean %VS level of 8.7%, see Figure 6.7, and mean methane productivity was assumed to be 0.37 m^3 CH_4 kg VS^{-1} added, see Figure 6.4. Mean effluent NH_4^+ levels rose

slightly in the pilot plant digester during the digester of this waste, see Figure 6.12, to an average of 2,800 mg l^{-1}, therefore the mean digested slurry nitrogen value in the model was adjusted to 2.8 kg N $tonne^{-1}$ Inputting these figures into the model gave the following outputs listed in Table 9.1

An additional income source from disposal of FVW would be a gate fee for disposing of the waste. Landfill charges are currently around £30 $tonne^{-1}$ for household waste (Dudley-Toole, 1996). 20% of digester feedstock as FVW equates to 19.7 tonnes wk^{-1}, 52 weeks a year is 1024 tonnes, at £30 $tonne^{-1}$ is a yearly income of £30,732.

The optimum FO ratio was found to be 96/4 cattle slurry/FO, see Figure 7.4, this increased feed volatile solids to around 5.8 kg VS m^3 d^{-1}, and marginally increased methane productivity to around 0.27 m^3 kg VS^{-1} added. The NH_4^+ level in the digester effluent also increased to around 2,900 mg l^{-1} during the pilot plant trials, the nitrogen value for the digested slurry was adjusted accordingly in the model. Disposal charges for FO were indicated to be in the region of £80 tonne (Hatton, 1997). At 4% of total feed, this equates to 3.9 tonnes wk^{-1} FO, for 52 weeks yr^{-1} and £80 $tonne^{-1}$ this is an yearly income income of £16,224. See Table 9.1 for the model outputs for FO.

The optimum ratio of chicken manure to cattle slurry was found to be 70% cattle slurry / 30% chicken manure, this increased the volatile solid loading rate by about 25% and methane productivity by 10%. The pilot plant digesters used in the work on chicken manure, described in Chapter 4 were operated at a loading rate of only 2.92 kg VS m^{-3} d^{-1} as cattle slurry, considerably lower than the loading rate at which the model was operating, however if it is assumed that the

percentage increase in methane productivity and VS in the feed would be the same, if the feedstock for the model was changed to 70% cattle slurry/30% chicken manure, an assessment of adding chicken manure to the digester described in the model can be made. It is generally agreed (Attwell, 1997) that farmers would not pay for disposal of chicken manure, hence no gate fee income would be available for chicken manure. The nitrogen value of the slurry could be expected to increase significantly, to around 6,500 mg l^{-1} NH_4^+, see Figure 4.29. The model outputs for the co-digestion of chicken manure and cattle slurry are shown in Table 9.1

Table 9.1 Projected income streams from disposal of different wastes by co-digestion. ROI calculated by assuming capital and running costs as for cattle slurry digester described in Section 9.3.1.

Income stream	Cattle slurry (£)	FVW (£)	FO (£)	Chicken manure (£)
Electricity sales	16,308	29,664	21,895	16,308
Fertiliser value	2,927	3,533	3,659	8,202
Compost sales	7,886	7,886	7,886	7,886
Slurry handling	1,950	1,600	1,880	1,370
Gate fees	0	30,732	16,224	0
Estimated ROI	5 years	1.8	2.5	3.9

9.4 Conclusions

From Table 9.1 it is clear that the addition of FVW to the digester feedstock is the most economically viable option and that co-digestion of organic and industrial wastes under controlled conditions can improve the viability of an anaerobic digestion system. It should be noted that the site from which the capital costs were obtained already had a slurry mixing tank, which contained a chopper pump. It was assumed that this could be used to mix slurry and organic waste prior to addition to the digester. This facility may not exist on other sites and would add to the capital cost of the system.

As an alternative to making an existing system more viable, the model, by demonstrating the viability of a co-digestion system, suggests that a purpose built co-digestion facility, could also be a viable economic proposition.

It is hoped that this work will contribute, in some way, to the construction of such a facility.

Chapter 10

Conclusions and recommendations for future work

10.1 Conclusions

1. Cattle slurry was found to be the agricultural waste most suitable for use in co-digestion systems.

2. Batch co-digestion of agricultural and industrial wastes, was shown to be a simple and relatively fast technique for determining the effect of additions of an organic waste to a cattle slurry digester.

3. Co-digestion with cattle slurry was found to be a possible disposal route for chicken manure, however ammonia toxicity limits its effectiveness and pre-treatment of the chicken manure to reduce ammonium levels, or digestion with an additional waste to reduce the pH of the system, would be necessary to reduce the effects of ammonia toxicity.

4. When undertaking co-digestion work, it is important to determine not only the volatile solids or COD loading of a waste being added to the digestion system,

but also the chemical nature of the material, as this will determine the rate at which the material is converted to acetic acid. Over production of acetic acid leads to a kinetic de-coupling of acidogenesis and methanogenesis and eventually to digester failure.

5. The addition of Fruit and Vegetable Waste (FVW) to a cattle slurry digester, at the ratio of 80% cattle slurry to 20% FVW (w/w) was found to significantly methane production per kg volatile solids added, with no indication of digester instability over 2 retention times. Digester instability and foaming was noted initially noted as greater amounts of FVW were added, although there were indications that this problem may have been overcome by increasing the headspace volume of the digester..

6. Batch co-digestion of fish offal (FO) and cattle slurry indicated this material could significantly increase methane productivity in batch cattle slurry systems. However the addition of 4% FO to the feed to a cattle slurry digester had little positive impact on methane production per kg volatile solids added. A further increase to 6% FO caused digester instability and a drastic reduction in methane productivity. The difference in performance between batch and continuous systems was attributed to the removal of long chain fatty acids, which inhibit methanogenesis and liquefaction of fats, from the sample used in the batch work, by aerobic decomposition prior to commencement of the batch experiment.

7. Batch co-digestion with cattle slurry was found to be a suitable method for disposal of waste milk. It was shown that the waste milk produced by a herd of 100 dairy cows could be successfully disposed of by addition to an on-farm digester which was already treating slurry produced by the cows. It was also shown that the maximum COD loading, as milk, which could be added to a batch cattle slurry digester digester without affecting COD removal, was between 29.1 and 35.3 kg COD m^{-3}.

8. An economic model of an existing digester facility was developed, to assess the effects of operating the system as a co-digestion unit, on the economic viability of the system. Co-digestion of FVW and cattle slurry was found to enhance the economic viability of the system, by the greatest degree, due to the beneficial effects of FVW additions on methane productivity and the gate fees charged for FVW. The model also showed that the fertiliser value of the effluent produced by the digester can also provide a significant income stream.

10.2 Recommendations for future work

1. The co-digestion of "complimentary" wastes should be investigated. For example, co-digestion a waste high in soluble sugars, with chicken manure and cattle slurry could be a method of reducing the high pH of the chicken manure cattle slurry system (through rapid VFA production) and hence reducing the

effects of ammonia inhibition of methanogenesis. Alternatively an acidic waste could be used for this purpose.

2. Washing of chicken manure, prior to co-digestion, should be investigated to determine its effect on chicken manure ammonium levels. The effluent from such a process could be used as a liquid fertiliser on grassland.

3. Continuous co-digestion of 7.5% solids chicken manure and cattle slurry should be undertaken to determine if any extra methane productivity produced by this dilution would offset the cost of buying the dilution water.

4. Some evidence was presented in Chapters 3 and 4 concerning predominance of methanogens of the *Methanosarcina* strain at high ammonia concentrations, The specific methanogenic activity of a system containing only *Methanosarcina* and a system containing only *Methanobrevibacter* , which are strongly inhibited at high ammonia concentrations, should be compared, to determine if the reduction in methane productivity noted at high ammonia concentrations is due to the selection of a bacterial strain which is less efficient at converting COD to methane.

5. The effect of co-digestion on the composting of digested solids should be investigated. During the batch digestion of milk and cattle slurry it was noted that, due to initial high COD loadings of milk, the COD of the digested slurry was much higher than digested cattle slurry. This 'extra' COD may contribute

to a higher rate of composting. Also the fertiliser value of a compost may be enhanced by the co-digestion of slurries and wastes high in nitrogen, potassium or phosphate.

6. The effect of anaerobic digestion on the viability of fruit and vegetable seeds, contained in FVW, should be studied. Some authors have reported that anaerobic digestion significantly reduces the viability of weed seeds.

7. Batch co-digestion of milk and cattle slurry was found to be successful. Continuous studies should be carried out to assess the potential of an anaerobic digester to act as a disposal route for waste milk for an extended period of time.

8. Fish offal which had been allowed to degrade for a number of weeks digested much better than fresh fish offal. An analysis of long chain fatty acids in both samples would be useful to determine if oxidation and the action of lipase enzymes from fish stomach contents accomplished significant acid degradation.

9. Attempts should be made to determine whether ratios of 50% FVW/ 50% cattle slurry (and higher) could be used for co-digestion without overloading the system, or reducing the biogas methane content to levels un-suitable for methane combustion equipment. The foaming problems, noted at ratios of 60% cattle slurry / 40% FVW, were not found to be present during digestion

of ratios of 50% cattle slurry / 50% FVW, for reasons which were not clear. Operation of a digester on the latter mixture over a number of retention times would indicate whether it is possible to continuously add this level of FVW to a cattle slurry digestion system.

10. The effect of including waste meat, paper and garden waste in FVW, on methane productivity of MSW/cattle slurry systems should be addressed.

11. It was proposed in Chapter 9 that the potential rate of acetate production (PRAP) of a waste, the rate at which it is converted to acetate in an anaerobic system, should be addressed when assessing the impact of a waste on a digesting slurry system. Attempts should be made to determine this figure for a waste before co-digestion, if the waste is known to be high in soluble sugars or other readily degradable material.

12. While time constraints and the need to find alternative disposal routes for other wastes dictated that continuous co-digestion of DAF and brewery sludges, potato processing effluent and sugar beet processing effluent could not be investigated in the current work, the effect of these systems on the methane productivity of digestion systems should be addressed.

13. Some authors have reported that a significant proportion of the running cost of an anaerobic digestion installation is the cost of maintaining the spark ignition engines used to convert methane to mechanical and hence electrical power.

Much of the energy available from the methane is lost in this conversion. Fuel cells which can run on pure methane streams are currently being developed, as are low pressure ceramic filters for gas separation. The potential energy savings of using fuel cells to produce electricity from the methane produced by a digestion or co-digestion system, should be investigated.

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APPENDIX 1

Table 2.1 Values for COD standards as measured using Hach COD assay.

Sample	750 mg COD l^{-1} Standard measured value (mg l^{-1})	1500 mg COD l^{-1} Standard measured value (mg l^{-1})
1	745	1509
2	748	1495
3	754	1507
4	751	1513
5	756	1512
Mean	**751**	**1507**
Standard Deviation	**3.97**	**6.46**

Table 2.2 COD values obtained using COD assay for slurry sample

Slurry sample	Measured COD value mg l^{-1}
1	153,500
2	139,300
3	144,000
4	140,700
5	148,100
Mean	**145,120**
Standard Deviation	**5172**

Table 2.3 Mean and standard deviations of cattle slurry samples for total, fixed and volatile solids

Slurry sample	Total solids (%)	Fixed solids (%)	Volatile solids (%)
1	16.9	6.6	10.3
2	16.5	6.5	10.0
3	16.6	6.5	10.1
4	16.7	6.6	10.1
5	16.9	6.6	10.3
Mean	**16.7**	**6.6**	**10.2**
Stand. Deviation	**0.16**	**0.06**	**0.13**

Table 2.4 Mean and standard deviation of alkalinity samples

Sample	Alkalinity
1	13,744
2	13,566
3	13,030
4	13,387
5	13,411
Mean	**13,427**
Standard Deviation	**235**

Figure 2.1 Standard plot for ammonium assay

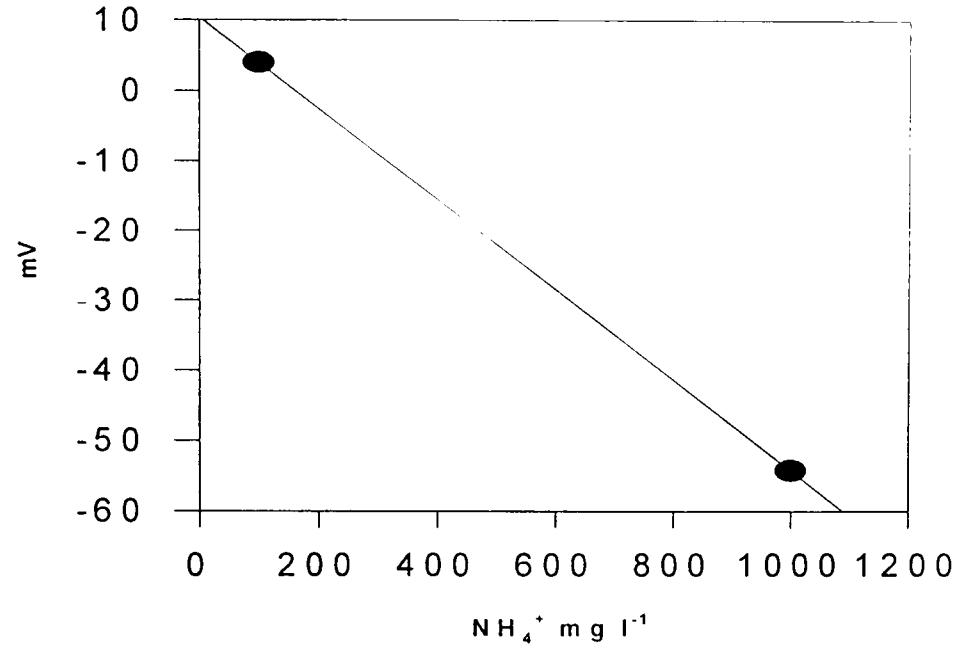


Table 2.5 Values for 1000 mg l^{-1} NH_4 standards as measured by ammonium probe assay.

Sample	Measured NH_4^+ (mg l^{-1})
1	980
2	977
3	966
4	972
5	984
Mean	**976**
Standard Deviation	**6.3**

Table 2.6 Values used to determine the value of the recovery factor f.

Sample	Acetic acid recovered in distillate (mg l^{-1})
2000 mg l^{-1} acetic acid standard	1740
2000 mg l^{-1} acetic acid standard	1740
2000 mg l^{-1} acetic acid standard	1730
2000 mg l^{-1} acetic acid standard	1734
2000 mg l^{-1} acetic acid standard	1735
Mean concentration of acetic acid in distillate	**1736**

Table 2.7 Analysis of 2000 mg l^{-1} acetic acid standard using distillation assay

Sample	Measured value mg l^{-1} acetic acid
1	2000
2	2000
3	1965
4	1995
5	2002
Mean	**1992**
Standard Deviation	**13.5**

Table 2.8 Analysis of 48% methane and 52% carbon dioxide standard using GC.

Sample	% CH_4	% CO_2
1	48.455	53.195
2	47.764	53.422
3	48.661	52.146
4	47.543	53.536
5	48.134	53.463
Mean	**48.111**	**53.152**
Standard Deviation	**0.415**	**0.252**

APPENDIX 2

Figure 2.2 Batch digestion apparatus

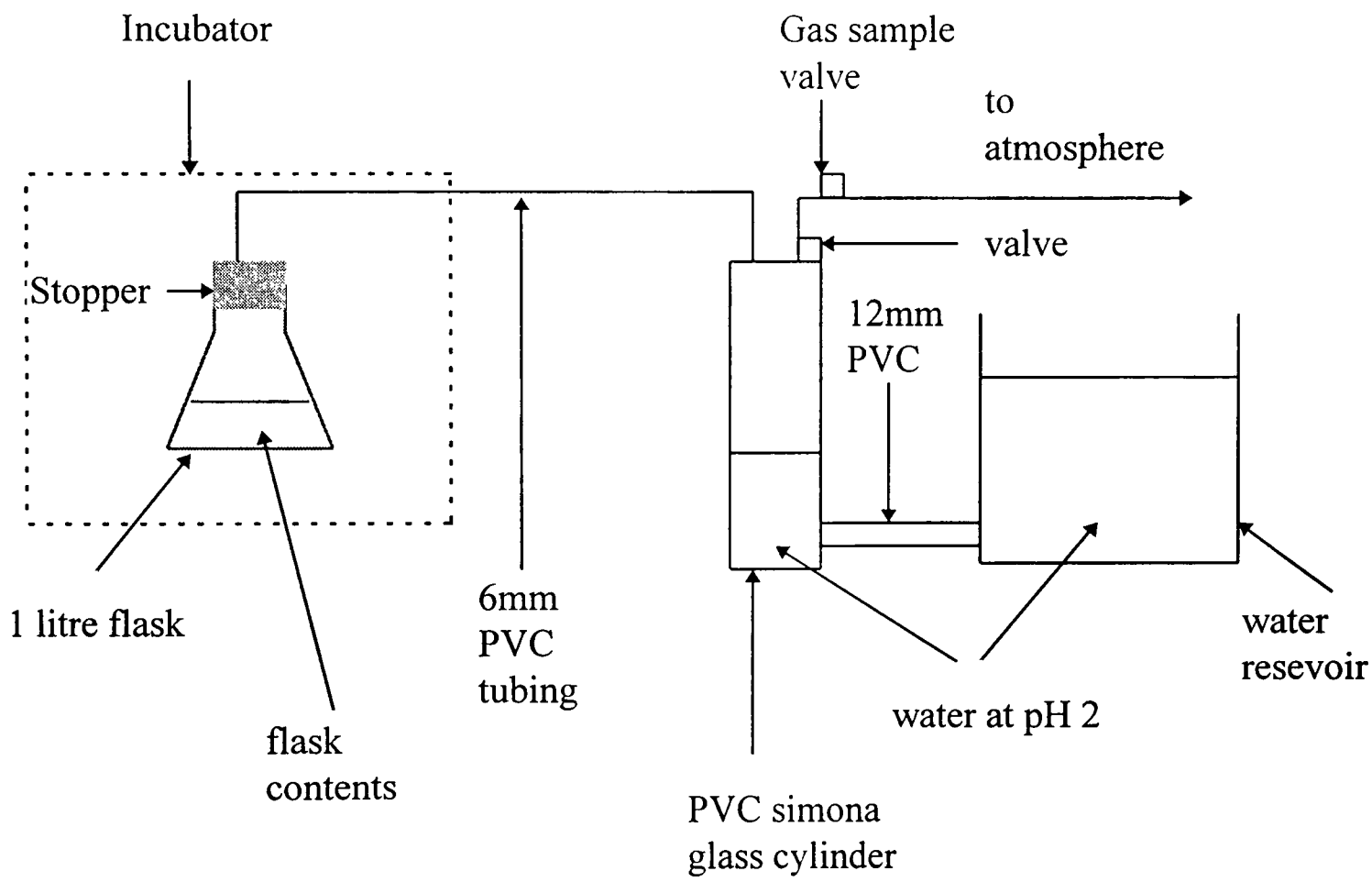
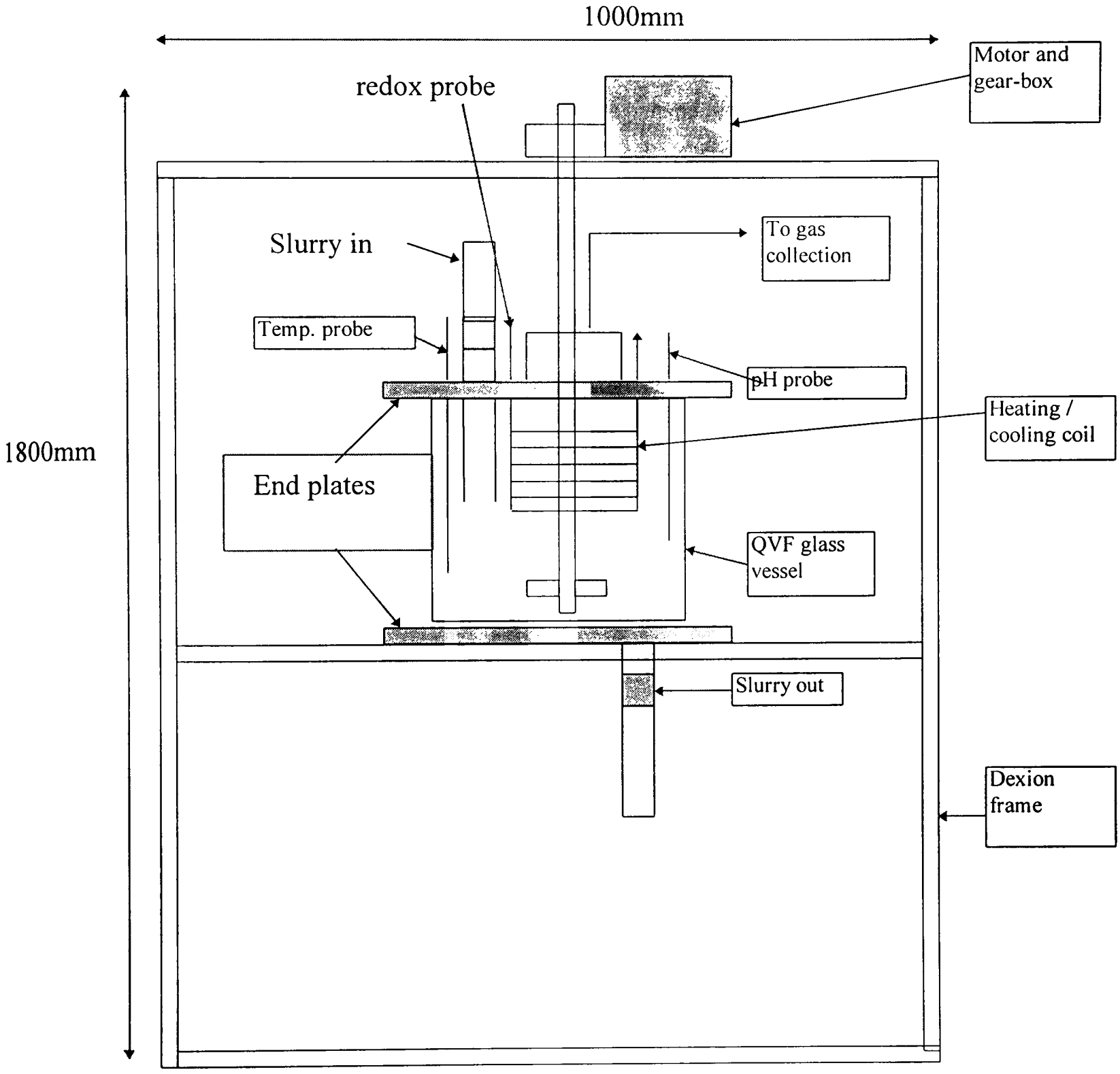


Figure 2.5 Anaerobic digester pilot plant



Engineering drawings for anaerobic digester pilot plant end plates.

NOTES - Top End Plate

Holes marked A were threaded to take 0.5 in. BSP valve and probe assemblies.

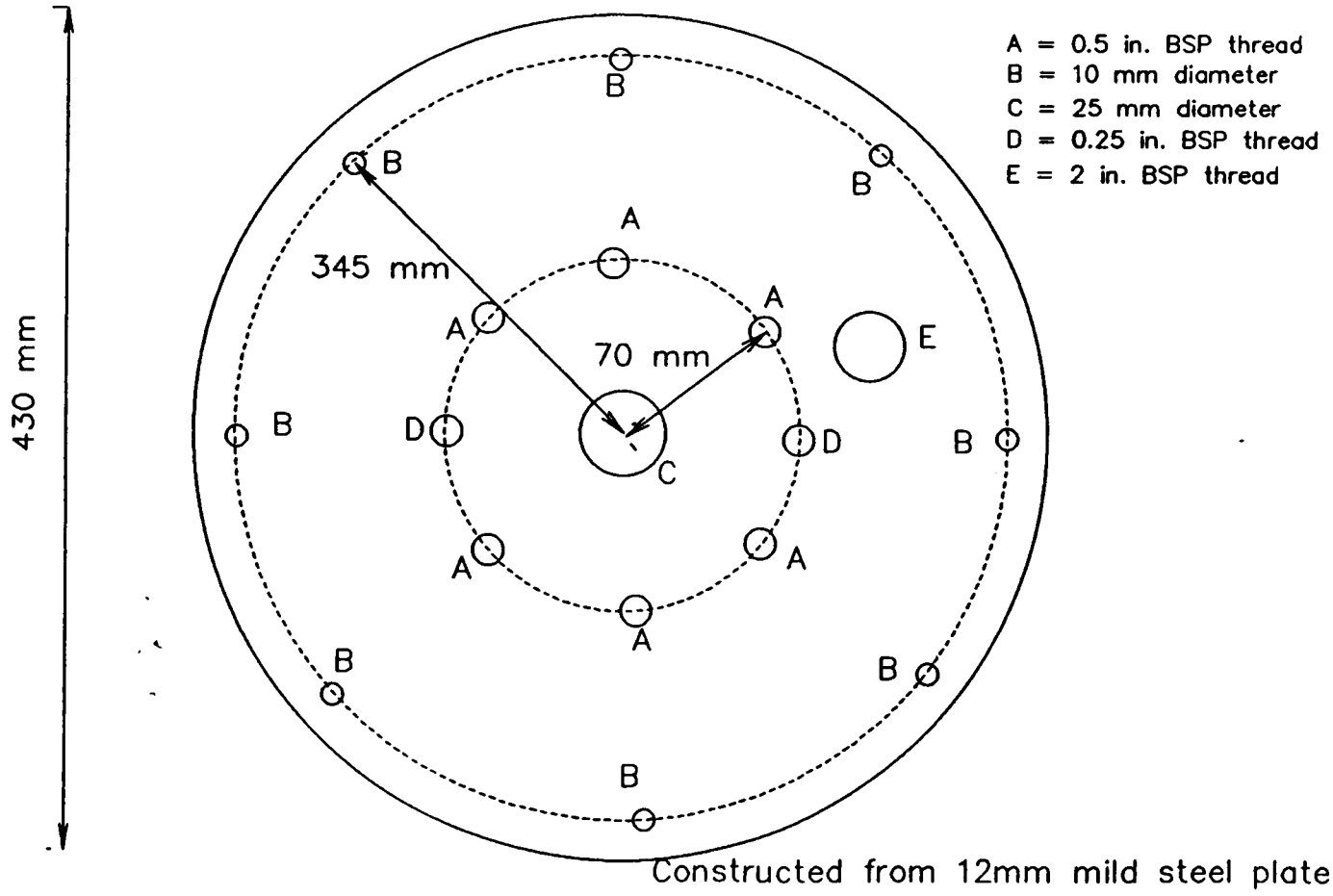
Holes marked B were for the bolts attaching the end plate to a flange on the digester.

Hole marked C was for the bearing housing and shaft sealing system.

Holes marked D were threaded to take the 0.25 in.BSP gas outlet ports and valve assemblies.

Hole marked E was threaded to take to take a 2 in. BSP PVC ball valve for slurry addition to the system

Top End Plate – Anaerobic Digester Pilot Plant



Constructed from 12mm mild steel plate

NOTES - Bottom End Plate

This end plate consisted of a rectangular mild steel plate of 6mm thickness, which was attached to the frame of the pilot plant, and a circular end plate of 12mm thickness, attached to the 6mm plate, which formed the base of the digester.

Hole marked A was threaded to take a 2 in. BSP PVC ball valve for slurry extraction from the system.

Holes marked B were for the bolts joining the end plate to the digester body. These holes were continued into the rectangular steel plate to allow the circular plate to be fixed to it.

Holes marked C were for the bolts joining the rectangular steel plate to the pilot plant frame

Bottom End Plate – Anaerobic Digestion Pilot Plant

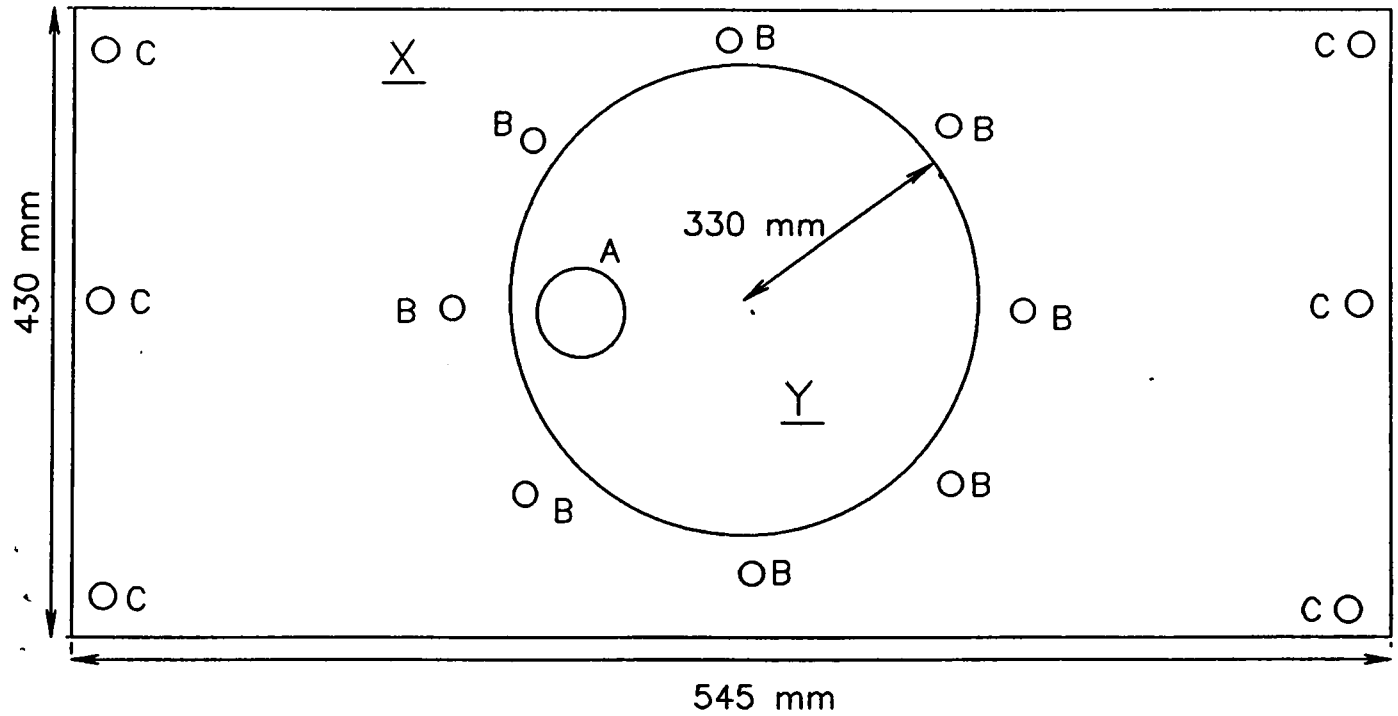


Figure 2.8 Temperature controllers, pH and redox meters for pilot plant. The controller on the left displays 34.9 °C, and is operating the water pump to return the temperature to 35 °C, as indicated by the ON light in the middle of the front panel. Due to the angle of the camera, the second pH meter is not visible.

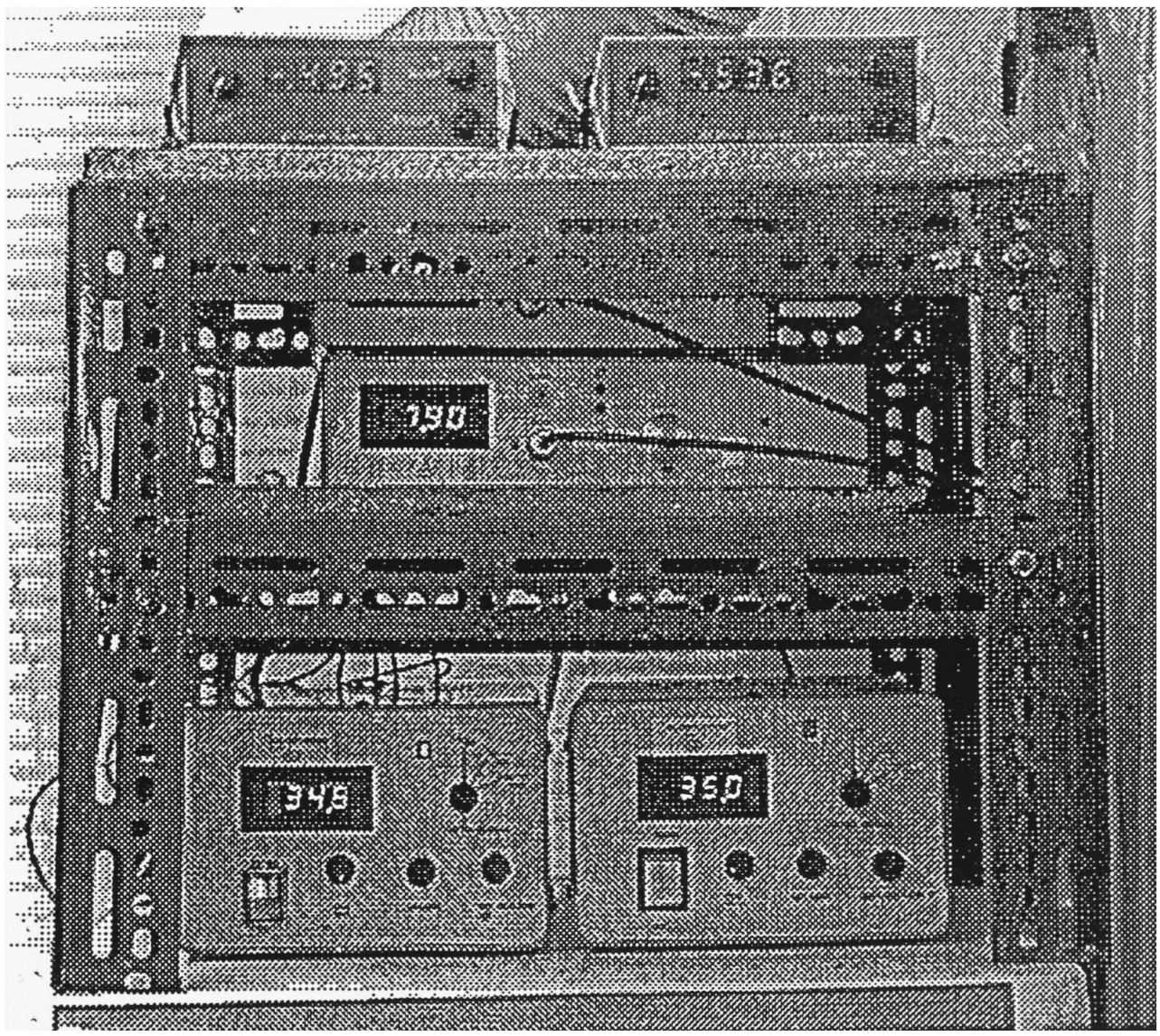


Figure 2.9 Hot water pumps and water bath.

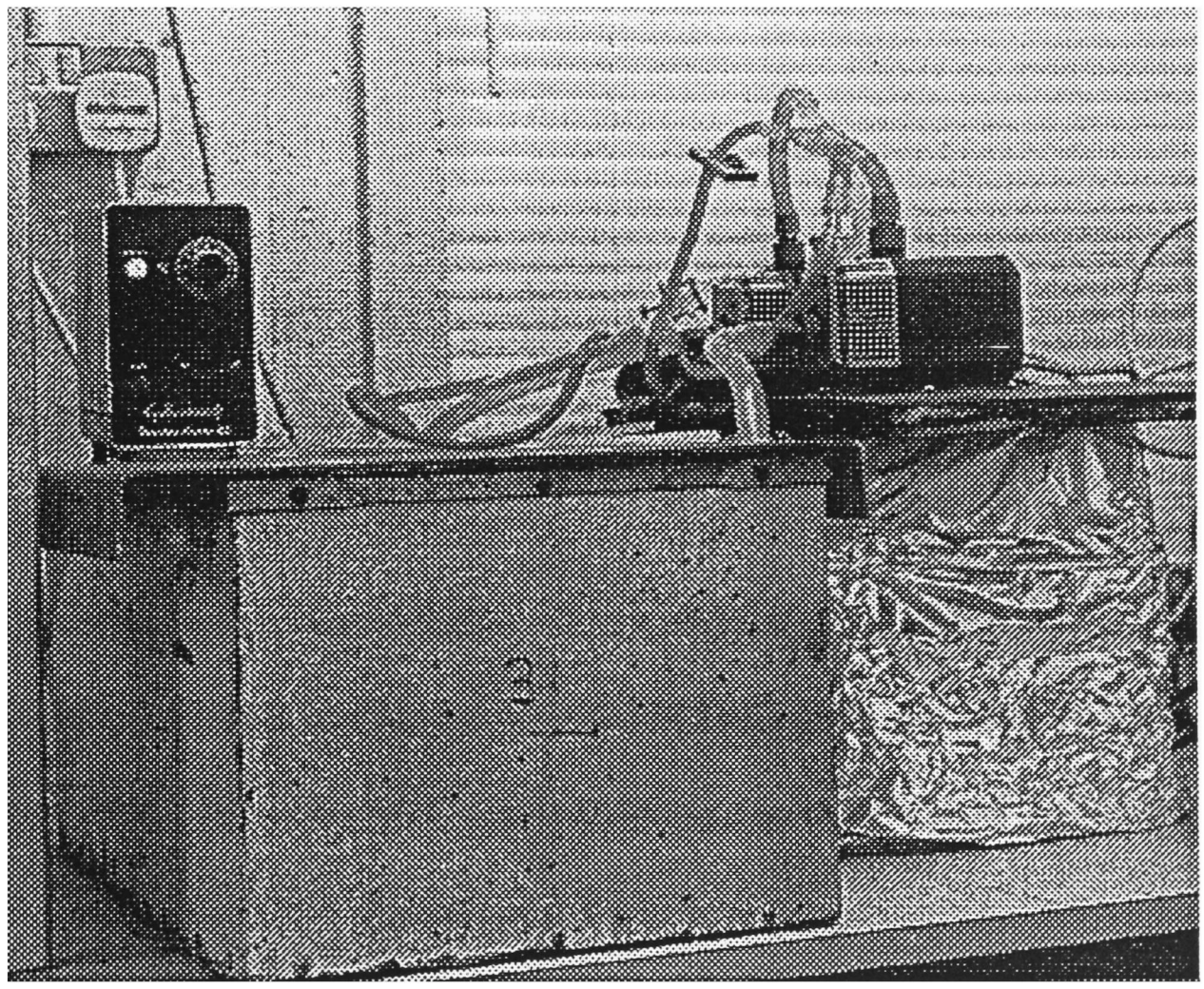
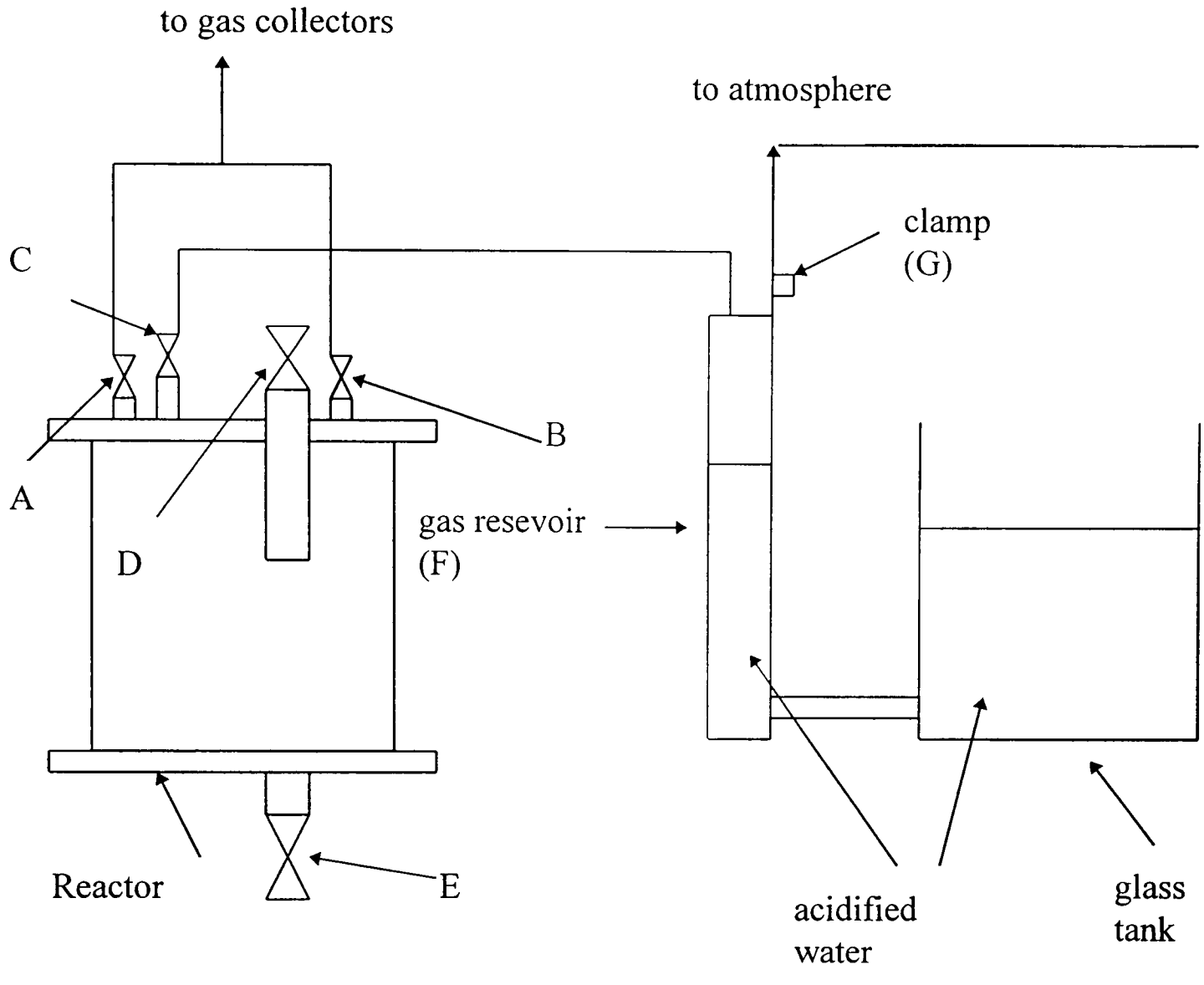


Figure 2.10 Gas reservoir system to prevent ingress of air during slurry withdrawal



Slurry withdrawal from, and addition to, the reactor was accomplished in the following manner. Prior to withdrawing slurry. valve C was opened and biogas from the headspace and collection cylinders, driven by the pressure head from the collection vessel reservoir, was allowed to flow into the gas reservoir (F). After 2 - 3 litres of biogas had flowed into the reservoir, valves A and B were closed and slurry was withdrawn from the bottom of the digester through valve E. The same volume of fresh slurry was then added through valve D at the top of the digester, and the water in the gas reservoir was allowed to stabilise for a short period. Valve C was then closed and valves A and B were re-opened and biogas collection commenced as normal. The

clamp G on the vent line from the biogas reservoir F was then opened and the waste biogas vented to atmosphere.

Figure 2.11 Initial design for shaft sealing system

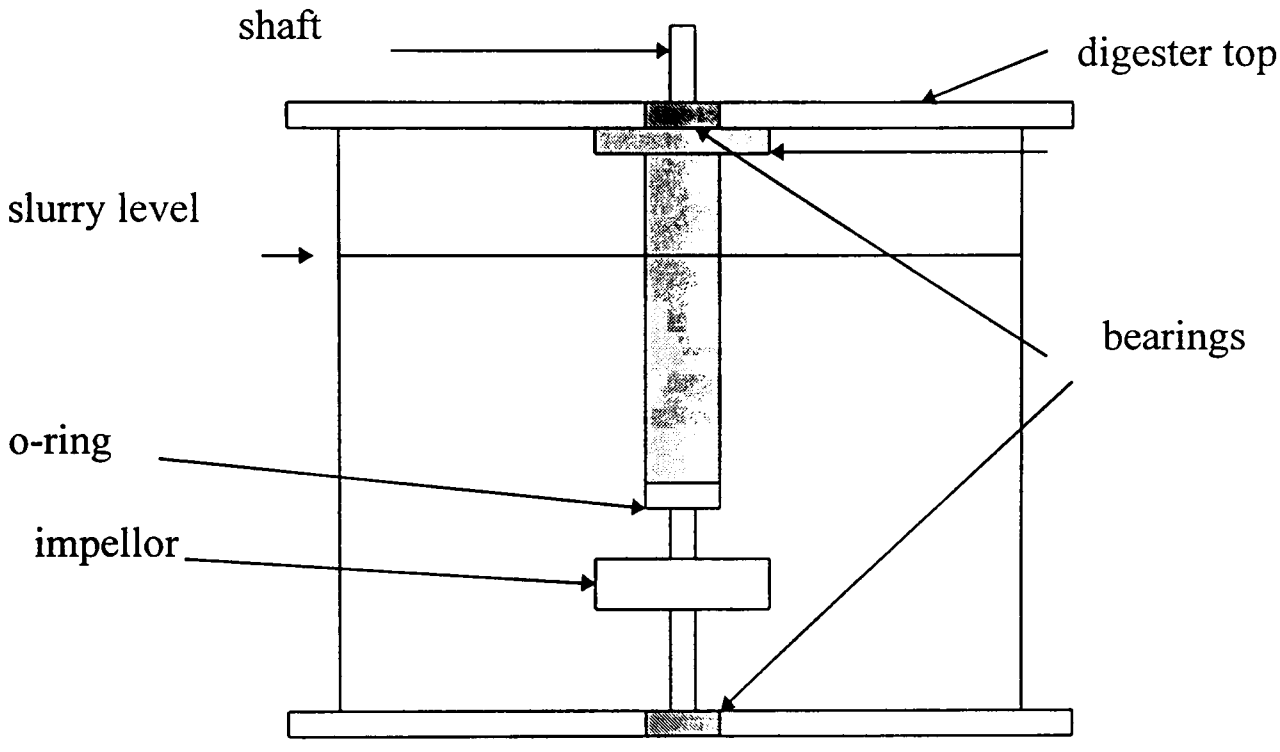
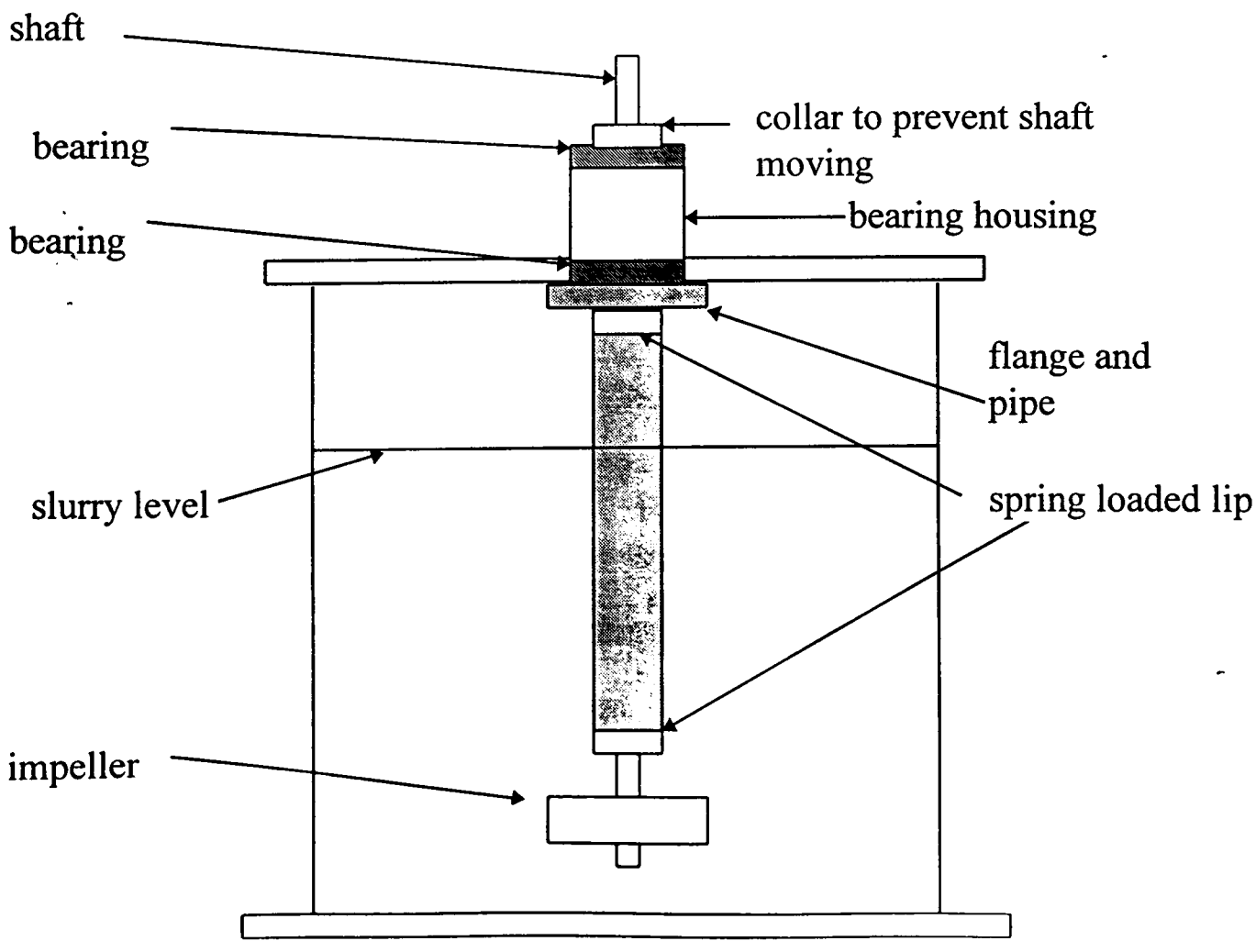


Figure 2.12 Modified shaft sealing system



APPENDIX 3

Calculation of impeller speed for digester mixing

The N_{js}, the impeller speed necessary to just fully suspend the particles:

$$N_{js} = Sv^{0.1} d_p^{0.2} (g \Delta\rho / \rho_L)^{0.45} X^{0.13} D^{-0.85}$$ (Zwietering,1958)

where:

S = suspension parameter (dimensionless), dependent on impeller type and impeller diameter to tank diameter ratio

v = kinematic viscosity ($m^{-2}\ s^{-1}$)

d_p = Particle size (m)

g = gravitational constant (9.81 $m^{-2}s^{-1}$)

$\Delta\rho$ = density of solid - density of liquid ($kg^{-1}m^{-3}$)

ρ_L = density of liquid ($kg^{-1}\ m^{-3}$)

X = concentration of solid (%)

D = tank diameter (m)

The values for used for each variable were:

S = 4.5 (from published data)

v = 1.003 (m^{-2} s^{-1}) (published data)

d_p = 300x10^{-6} m (Hawkes *et al*, 1985)

g = 9.8 m^{-2} s^{-1}(published data)

$\Delta\rho$ = 200 kg^{-1} m^{-3} (estimated)

ρ_L = 1000 kg^{-1} m^{-3} (published data)

X = 10% (analysis)

D = 0.15m (analysis)

Solving the equation for these values gives a value for **N_{js} of 8.13 rev s^{-1}**

This corresponds to an impellor speed of 488 revolutions per minute. An impellor rotating at this rate in anaerobic system would quickly cause foaming in the digester, and also cause motors and gearboxes to wear quite quickly. Also the above equation does not take into account the mixing effect of biogas bubbles rising to the surface of the digester liquid, which would also aid mixing and solids suspension. An impellor speed of 60 rpm was chosen as a compromise between the need to fully suspend all slurry particles and the need to avoid foaming.

In order to calculate the power required to acheive this mixing speed the **power number** must first be calculated from the following equation:

$P_0 = 0.78\ (X/D)^{-0.14}\ x\ (D/T)^{0.17}$ (Bujawlski, Ph.DThesis, Birmingham University, 1986).

where:

P_0 = Power number (dimensionless)

X = Impeller blade thickness (m)

D = Impeller diameter (m)

T = Tank diameter (m)

The values used for each variable were:

X = 0.003m

D = 0.15m

T =0.3m

Solving for these values yields a **P_0 of 1.1987**

Power consumption is calculated from the following equation:

$$P = P_0 \rho N^3 D^5$$

where:

P = Power consumption (W)

P_0 = Power number

ρ = liquid density ($kg^{-1}m^{-3}$)

N = Impeller speed (rev s^{-1})

D = Impeller diameter (m)

The values used for each variable were:

P_0 = 1.1987

N = 1.0 rev s^{-1}

ρ = 1000$kg^{-1}m^{-3}$

D = 0.15m

Solving for these values yields a value for **power consumption 0.09 W s^{-1}**

Starting moment could require a power consumption of 100 times this value (Bujawlski, personal communication), hence at least 9 W s^{-1} would be required from the motor. Mechanical losses through the gearbox and particularly -

bearings could account for up to 90% of power produced hence a 100W motor was required to allow for a large safety factor.

APPENDIX 4

DATA USED FOR FIGURES

Chapter 3

Figures 3.1 - 3.4

Flask1	2	3	4	5	6	7	8	9	10
0.0000	0.0000	0.0000			0.0000	0.0000	0.0000	0.0000	0.0000
0.0000	0.0000	0.0000			0.0000	0.0000	0.0000	0.0000	0.0000
0.0000	0.0000	0.0000			0.0000	0.0000	0.0000	0.0000	0.0000
0.1760	0.7720	0.0000			0.0000	0.0000	4.0e-3	0.0560	0.0000
0.0000	0.2440	0.0000			0.0000	0.0000	0.0530	0.4310	0.0000
0.0000	0.2440	0.0000			0.0000	0.0000	0.0530	0.4310	0.0000
0.2070	0.5360	0.0000			0.0000	0.0000	0.3430	0.4040	0.0000
0.4460	1.4810	0.9810			0.0000	0.0000	0.7880	1.3910	0.0000
0.4250	1.5200	1.8430			0.0000	0.0000	0.3990	1.9130	0.0000
0.7390	1.2950	1.4260			0.8690	0.7690	1.1650	0.8780	1.6090
0.5610	0.8920	0.4820			1.7070	1.2440	1.3100	1.5260	1.5760
0.3630	0.3680	0.2450			1.5610	2.4630	0.3480	2.1620	0.8130
0.6080	0.1160	0.3100			0.5590	2.5830	0.0930	1.3440	0.8150
0.4560	0.4890	0.3230			0.3050	0.3720	0.1600	0.4360	0.6580
0.2030	0.3600	0.2390			0.2320	0.3550	0.1540	0.3430	0.6300
0.1550	0.1510	0.1670			0.1850	0.2470	0.1190	0.2220	0.4750
0.0840	0.2460	0.1680			0.2000	0.1750	0.0300	0.2330	0.3100
0.0700	0.2070	0.1450			0.1850	0.1440	0.0240	0.5610	0.1460
0.0320	0.1080	0.0600			0.1370	0.0700	9.0e-3	0.3010	0.0750
0.0120	1.0e-2	0.0420			0.1880	0.0720	6.0e-3	0.1000	0.0950
0.0120	5.0e-3	0.0420			0.0790	0.0430	0.0170	0.0170	0.1500
0.0120	5.0e-3	0.0300			0.0700	0.0400	0.0160	0.0160	0.0900

Figures 3.5 - 3.7

Flask	%solids reduction		maxch4wk		total ch4
1	52		0.65		4.6
2	50		1.5		8.3
3	55		1.8		6.5
4	37				
5	34				
6	51		1.6		6.2
7	52		2.5		8.5
8	48		1.3		5.1
9	50		2.2		12.5
10	45		1.6		7.4

Chapter 4 - Figures 4.1 - 4.36

Digester 1

1week	%mnTSolF1	1mean TS%/wk	1F%mnFS	1MnFS%	1F%MVS	1Mn%VS	1FVM/DM	1VM/DM
1	7.265081	4.4996865	1.700815	1.341877	5.5642665	3.0127538	0.7665495	0.6916048
2	7.316312	4.6529584	1.7363125	1.4025896	5.58	3.2503688	0.76269	0.6953026
3	7.982613	5.1667972	1.8060348	1.507378	6.1765784	3.6594192	0.7739778	0.7082586
4	8.487683	5.1918868	2.0333318	1.5700678	6.4543515	3.6218188	0.7603773	0.697658
5	11.24844	5.2063398	3.8019203	1.5607394	7.44652	3.6456006	0.661765	0.7000528
6	11.756776	5.6544254	4.003377	2.0184682	7.753398	3.6359574	0.659543	0.641516
7	12.428022	5.9220386	4.3752048	2.0670638	8.0528192	3.854975	0.6478856	0.650391
8	10.724724	5.5566403	3.599459	2.0429778	7.1252633	3.5136625	0.6647788	0.6302268
9	10.673731	6.5115266	3.4967146	2.4196566	7.177019	4.09187	0.672118	0.6322318
10	11.164954	6.0554436	3.6806005	2.0124758	7.4843538	4.042968	0.6707411	0.6669382
11	11.250998	5.7725098	4.000494	1.8537032	7.2505082	3.9188064	0.6442092	0.6779852
12	11.450948	5.608112	3.7170356	2.301793	7.7339148	3.306319	0.6746598	0.5881874
13	14.322908	5.9828452	6.2580474	2.2632232	8.0648612	3.7196224	0.570764	0.6219126
14	13.656433	6.4770693	6.3790568	2.3077503	7.2773775	4.1693193	0.535797	0.6440978
15								
16								
17								
18	11.72383	4.930024	4.1335433	2.2931525	7.5902853	2.6368705	0.6470797	0.5422335
19	11.256316	5.7523814	4.1664472	2.5149402	7.0898726	3.2374414	0.6300516	0.5625582
20	10.690606	5.4161498	4.0201318	2.0708546	6.6704732	3.3452954	0.6256224	0.6162928
21	10.289782	5.2386202	3.7591114	2.0187306	6.5306714	3.21989	0.6352104	0.6145814
22								
23	11.604578	7.9591562	4.6111582	3.486606	6.9934188	4.4725498	0.6021256	0.5649638
24	11.955528	10.204628	4.5090728	3.6977616	7.446457	6.506866	0.6221902	0.6386754
25	13.196752	10.697813	4.71816	4.0053996	8.4785924	6.692415	0.64191	0.6270938
26	13.436194	11.896028	5.6786892	4.648667	7.7575044	7.2473602	0.577325	0.6080158
27	7.8396738	9.6686206	2.2698912	3.8007466	5.569783	5.8678736	0.7103692	0.6054368
28	7.1766226	8.6028692	1.7349512	2.9711602	5.4416716	5.631709	0.758336	0.6539384
29	7.2658978	6.9441282	1.5726856	2.0448084	5.6932122	4.89932	0.7836004	0.7085656
30	7.2217128	6.841733	1.917864	1.9647383	5.3038485	4.8769948	0.735135	0.7136675

	1mnkgvsm3 d	est kgvs1	1meankgvsadd	1meanch4d		m3 ch4 kg vs ad	1%vsremeawk	1%CH4
1	2.85	2.92	0.0513	4.5023616	1	0.0877653	41.99205	65
2	2.84	2.92	0.05112	4.69381	2	0.0918194	38.39386	67
3	3.17	2.92	0.05706	6.1742514	3	0.1082063	40.43476	65
4	3.31	2.92	0.05958	6.1868003	4	0.1038402	54.86715	65
5	3.6	3.64	0.0648	6.2960657	5	0.0971615	49.57873	65
6	3.97	3.64	0.07146	7.628339	6	0.1067498	54.3656	64
7	4.09	3.64	0.07362	8.8720303	7	0.1205111	53.41573	65
8	3.81	3.64	0.06858	8.1015336	8	0.1181326	51.47886	66
9	3.52	3.64	0.06336	6.079722	9	0.0959552	44.51912	66
10	3.9	3.64	0.0702	7.6386536	10	0.1088127	47.43319	66
11	3.74	3.64	0.06732	6.2519346	11	0.0928689	47.40421	66
12	4.1	3.64	0.0738	6.5942634	12	0.0893532	58.39831	65
13	4.2	4.6	0.0756	7.1039874	13	0.0939681	55.87298	68
14	3.61	4.6	0.06498	6.5312297	14	0.1005114	44.29181	67
15				5.6908307	15			68
16				3.2208956	16			73
17				1.4762076	17			72
18	4.2	3.5	0.0756	2.8777841	18	0.0380659	65.24046	62
19	3.7	3.5	0.0666	3.9132853	19	0.058758	55.84115	62
20	3.36	3.5	0.06048	4.8950277	20	0.0809363	52.60622	65
21	3.49	3.5	0.06282	3.7822563	21	0.0602078	52.81988	67
22			0	1.2592824	22	0		61
23	3.68	3.8	0.06624	2.6078676	23	0.03937	39.07569	58
24	3.82	3.8	0.06876	3.1675673	24	0.046067	17.62402	62
25	4.2	3.8	0.0756	3.0155311	25	0.039888	25.40292	64
26	4.19	3.8	0.07542	2.9315314	26	0.0388694	13.20541	65
27	2.97	2.92	0.05346	2.0770113	27	0.0388517	0.864063	68
28	2.9	2.92	0.0522	1.7467307	28	0.0334623	2.450477	70
29	3	2.92	0.054	2.0064631	29	0.0371567	18.70832	71
30	2.87	2.92	0.05166	2.354248	30	0.045572	0	72

1	1NH4+wk	NH3wk	1Talkwk	1Redoxwk	1-redox	H2S1wk	VFA1	pH1	VFA:TALK 1
1	1000	46.9	13100	-482	482	700	2010	7.65	0.1534351
2	900	46.1	13308	-481	481	600	2300	7.69	0.1728284
3	900	45.1	13200	-482	482	700	2100	7.68	0.1590909
4	800	40.95	13209	-486	486	600	2100	7.69	0.1589825
5	1839	99.23092	13673	-481	481	1190	1134	7.704	0.0829372
6	3687	224.56502	15815	-482	482	2020	4421	7.77	0.2795447
7	3963	280.0888	17529	-482	482	3090	4007	7.838	0.2285926
8	5241	441.17524	19242	-482	482	4800	3157	7.92	0.1640682
9	6485	573.68554	20349	-474	474	4980	2900	7.946	0.1425131
10	7428	667.0989	20706	-484	484	4960	2568	7.952	0.124022
11	7653	677.42816	21349	-486	486	3360	2700	7.946	0.1264696
12	7783	661.37016	22234	-486	486	1700	3010	7.926	0.1353782
13	6663	639.86662	20563	-492	492	1780	6010	7.926	0.2922725
14	6489	659.4239	23201	-486	486	1787	12995	8.0125	0.5601052
15	6451	651.412	23241	-488	488	1200		8.01	
16	6200	639.055	23001	-487	487	700		8.02	
17	6100	615.96	23408	-482	482	700		8.01	
18	6019	624.82123	23008	-442	442	667	1400	8.023333	0.0608484
19	5778	508.80463	22758	-470	470	900	3561	7.973333	0.1564724
20	4786	366.337	20140	-486	486	1300	9379	7.875	0.4656902
21	3625	230.54355	17788	-470	470	1400	6200	7.79	0.3485496
22	3488	226.467	16995	-452	452	1150		7.8	
23	3353	251.9847	19779	-486	486	1350	4106	7.85	0.2075939
24	4331	281.3526	24403	-485	485	1550	7548	7.92	0.3093062
25	4321	430.7046	25104	-478	478	2100	12437	8	0.4954191
26	3406	471.7402	25597	-487	487	2000	8433	8.02	0.3294527
27	3935	372.97995	25149	-488	488	1900	7100	7.98	0.2823174
28	3686	269.05103	20704	-489	489	1183	6883	7.85	0.3324478
29	3254	134.1612	12589	-497	497	900	6997	7.58	0.5558027
30	2591	76.024653	9620	-489	489	833	7432	7.386667	0.7725572

Chapter 4

Digester 2

wk	2mn ts in	2mntsout	2mn fs in	MnFS in%	2mnvsin	2mnvsoutw	2FVM/DM	2VM/DM
1	7.074842	4.93306	1.549667	1.42043	5.525176	3.512629	0.7665495	0.6916048
2	7.610016	4.565359	1.740153	1.470976	5.869863	3.094383	0.76269	0.6953026
3	8.160612	4.796858	1.962616	1.476884	6.197996	3.319975	0.7739778	0.7082586
4	8.357745	4.718447	1.994838	1.461784	6.362907	3.256663	0.7603773	0.697658
5	10.2619	4.784247	3.216754	1.525035	7.045142	3.259212	0.661765	0.7000528
6	11.60033	5.51684	4.016254	1.939611	7.584069	3.577228	0.659543	0.641516
7	12.33738	5.679277	4.321432	2.084604	8.015949	3.594673	0.6478856	0.650391
8	10.85438	5.353393	3.653059	1.907134	7.201325	3.446259	0.6647788	0.6302268
9	10.50665	4.803607	3.487453	1.784221	7.019191	3.019386	0.672118	0.6322318
10	11.08996	4.76318	3.684883	1.802291	7.405074	2.960889	0.6707411	0.6669382
11	10.93613	5.148348	3.798073	2.173552	7.138056	2.974796	0.6442092	0.6779852
12	11.56802	4.74211	3.884773	1.834674	7.683242	2.907436	0.6746598	0.5881874
13	14.21652	5.42323	6.180313	1.986536	8.03621	3.436694	0.570764	0.6219126
14	15.49905	8.962223	7.588755	3.823578	7.910297	5.138645	0.535797	0.6440978
15								
16								
17								
18	12.0299	6.579149	4.244422	2.642028	7.78547	3.937122	0.6470797	0.5422335
19	11.2203	6.553994	3.88508	2.366385	7.335218	4.187609	0.6300516	0.5625582
20	10.59734	7.739567	3.934236	3.064034	6.663106	4.675532	0.6256224	0.6162928
21	10.66796	9.417424	3.96576	4.156637	6.7022	5.260788	0.6352104	0.6145814
22								
23	12.83071	8.617432	5.036225	3.21986	7.794481	5.397571	0.6021256	0.5649638
24	13.45619	10.73913	5.013822	4.219791	8.442361	6.519343	0.6221902	0.6386754
25	15.13851	11.98449	6.543623	5.208526	8.594885	6.775958	0.64191	0.6270938
26	15.67582	11.3555	7.152159	5.200152	8.523663	6.155354	0.577325	0.6080158
27	17.74106	13.14712	7.512815	5.759149	10.22825	7.387971	0.7103692	0.6054368
28	14.69439	11.47929	5.801697	5.292282	8.892691	6.187012	0.758336	0.6539384
29	14.98933	10.17908	6.058118	4.564434	8.931207	5.614644	0.7836004	0.7085656
30	14.53169	6.355766	6.309469	2.853066	8.222215	3.5027	0.735135	0.7136675

wk	2meankgvsm3d	est kgvs1	1meankgvsadd	2mean daily ch4/wk		2m3ch4/kgvsadded	2%VS removed
	2.854667	2.92	0.051384	4.587171	1	0.089272	36.35666
1	2.961944	2.92	0.053315	5.096788	2	0.095598	45.96538
2	3.202278	2.92	0.057641	5.836583	3	0.101257	46.37711
3	3.305722	2.92	0.059503	6.475925	4	0.108834	49.07311
4	3.64	3.64	0.06552	7.140816	5	0.108987	54.4695
5	3.918444	3.64	0.070532	8.754895	6	0.124127	54.10028
6	4.141556	3.64	0.074548	8.579264	7	0.115084	56.36147
7	3.720667	3.64	0.066972	8.399939	8	0.125425	53.43055
8	3.626556	3.64	0.065278	6.088533	9	0.093271	58.14019
9	3.825944	3.64	0.068867	7.085656	10	0.102889	61.09025
10	3.688	3.64	0.066384	7.299405	11	0.109957	59.44515
11	3.969667	3.64	0.071454	6.397975	12	0.08954	63.17598
12	4.222444	4.6	0.076004	6.115498	13	0.080463	59.07847
13	4.315333	4.6	0.077676	5.677188	14	0.073088	40.63849
14				5.139929	15		
15				3.580463	16		
16				1.545404	17		
17	4.099222	3.5	0.073786	3.486737	18	0.047255	52.06506
18	3.871222	3.5	0.069682	3.870785	19	0.055549	45.61348
19	3.554444	3.5	0.06398	3.975975	20	0.062144	33.86423
20	3.595722	3.5	0.064723	3.581265	21	0.055332	26.44069
21			0	1.293184	22		
22	4.132722	3.95	0.074389	2.681427	23	0.036046	34.33435
23	4.466333	3.95	0.080394	3.604536	24	0.044836	26.6112
24	4.583667	3.95	0.082506	3.462876	25	0.041971	25.67563
25	4.566611	3.95	0.082199	4.573312	26	0.055637	32.23014
26	5.330722	4.1	0.095953	3.975627	27	0.041433	30.31861
27	4.673722	4.1	0.084127	4.349303	28	0.051699	33.44291
28	4.660611	4.1	0.083891	5.749391	29	0.068534	39.43015
29	4.329389	4.1	0.077929	5.697948	30	0.073117	49.15312

2%ch4	wk	2MnNH4wk	NH32wk	2mnalkwk	1Redoxwk	2-redox	2meanh2swk	2VFA	2mneffpHwk	VFA:TALK1
67.57143	1	1100	41.437	13946	-482	537	700	2010	7.7	0.1441273
65	2	1068	37.669	13885	-481	538	750	2003	7.71	0.1442564
65	3	1087	35.8484	13905	-482	537	700	2020	7.72	0.1452715
65	4	1003.5	28.82344	13744.5	-486	538	750	1995	7.7	0.145149
64.85714	5	2140.8	118.5164	14387.1	-481	535.4	1210	1099	7.75	0.0763879
63	6	3727	226.0811	15636.6	-482	532.8	1780	5000	7.8	0.3197626
64.42857	7	4026.2	277.4495	17957.1	-482	535.4	2910	4100	7.87	0.2283219
64.14286	8	4706.2	255.8051	18599.7	-482	535.6	4550	3804	7.91	0.2045194
65.57143	9	6183.4	396.2083	19635	-474	533	3350	3448	7.89	0.1756048
65.28571	10	7221.4	597.686	19456.5	-484	528.2	1940	2387	7.83	0.1226839
66.57143	11	7711.6	567.9691	19849.2	-486	527	1500	2349	7.89	0.1183423
64.71429	12	7847	456.9783	19568.6	-486	531.4	1140	2418	7.85	0.1235653
62.57143	13	7560.2	536.9115	22383.9	-492	528.6	1280	5883	7.82	0.2628228
64.14286	14	6482.75	319.4797	26005	-486	529	1300	12209	7.81	0.4694866
63.85714	15	6300.3	322.7184	25184.1	-488	533	1000		7.83	
68	16	6008.5	321.435	24991.54	-487	529.2	890.3		7.82	
83.42857	17	5782	344.08	24582.6	-482	520.5	879.6		7.83	
61.42857	18	5485.667	391.6533	24193.17	-442	527	866.6667	1086	7.82	0.0448887
66.28571	19	5481.333	361.6142	23953.33	-470	524.333	1566.667	4400	7.85	0.1836905
66.85714	20	4485	208.354	24654.5	-486	508.5	950	9100	7.82	0.369101
65.71429	21	4289	245.0024	24790	-470	509	1350	4061	7.8	0.1638161
66.28571	22	4377	255.35	25227	-452	527	800		7.78	
66	23	4417	187.9644	25962.67	-486	509	1083.333	3295	7.75	0.126913
59.14286	24	5056.333	123.408	26671	-485	527.333	1383.333	9163	7.71	0.3435567
63.14286	25	4868.333	220.8141	23806.33	-478	530.333	1833.333	11974	7.83	0.5029755
63.85714	26	3761.5	160.0294	29936.5	-487	533.5	3500	9381	7.9	0.3133633
62.85714	27	5388	135.9406	32399	-488	533	4500	6102	7.69	0.1883391
62.71429	28	4961.667	156.2004	32876.33	-489	534.667	3500	7263	7.75	0.2209188
61.85714	29	4484	154.2612	23508.67	-497	536	3500	6009	7.81	0.2556078
62.85714	30	3852.333	132.0886	21094.67	-489	537	3500	6102	7.8	0.2892674

Chapter 5 - figures 5.1 - 5.8

Week	1 cattle litres CH4	2 cattle	3 silage	4 silage	5 brewery	6 brewery
0	0	0	0	0	0	0
1	0.457104	0.304909	0.414046	0.30092	0.804503	0.886454
2	0.574629	0.429177	0.460025	0.372854	0.606778	0.472374
3	0.323952	0.251837	0.327905	0.259273	0.415508	0.166263
4	0.772928	0.624463	0.746189	0.647669	0.349464	0.263609
5	0.555825	0.867393	0.796405	0.667053	0.766163	0.904763
6	0.182046	0.484835	0.366796	0.302553	0.578137	0.432416
7	0.33494	0.324632	0.228357	0.205712	0.320943	0.274904
8	0.368123	0.284312	0.202632	0.171474	0.191092	0.160754
9	0.351423	0.266785	0.213297	0.180048	0.192333	0.117262
10	0.290614	0.172038	0.188731	0.139964	0.214797	0.127238
11	0.227576	0.127935	0.161783	0.104799	0.252308	0.12387
12	0.161699	0.089555	0.111567	0.129361	0.18081	0.134749
13	0.11815	0.090141	0.103766	0.116853	0.108323	0.123776
14	0.094439	0.097815	0.101508	0.114792	0.083335	0.121437
15	0.07247	0.086007	0.104359	0.112797	0.077689	0.103432
16	0.064917	0.083207	0.086004	0.09099	0.056242	0.085691
17	0.066664	0.087637	0.080085	0.094906	0.055544	0.072803

7 trout	8 trout	9 DAF	10 DAF	11 MSW	12 MSW
0	0	0	0	0	0
0.147864	0.16149	0.62545	0.944865	1.230959	1.384514
0.541182	0.425689	0.479651	0.989462	1.470873	1.320264
3.099775	2.120397	0.289776	0.221311	0.266294	0.380269
4.302887	4.725824	0.739055	0.595341	0.437351	0.535318
0.693209	2.029697	1.362734	1.085724	1.54775	1.028318
0.765735	0.803501	0.353904	0.478994	0.319598	0.346225
0.250066	0.452662	0.321054	0.326908	0.258198	0.28273
0.26531	0.271409	0.277286	0.275703	0.909336	0.446976
0.941219	0.240042	0.13284	0.310215	0.36867	0.317588
0.316364	0.162798	0.126305	0.240376	0.211894	0.262555
0.236521	0.16674	0.121174	0.113846	0.157526	0.230457
0.119663	0.121217	0.115552	0.119838	0.115552	0.175117
0.104084	0.109638	0.097222	0.106859	0.111452	0.129835
0.101668	0.104493	0.102917	0.105698	0.097603	0.14098
0.096589	0.08332	0.09407	0.06396	0.103325	0.136095
0.097412	0.071085	0.089743	0.055471	0.098572	0.12291
0.093604	0.072153	0.093606	0.061947	0.093606	0.118811

Flask	tot. ch4	
1	5.017499	cow
2	4.672676	cow
3	4.693455	silage
4	4.012018	silage
5	5.253971	brewery
6	4.571797	brewery
7	12.17315	trout
8	12.12216	trout
9	5.422341	DAF
10	6.096518	DAF
11	7.798558	MSW
12	7.358962	MSW

Chapter 6 figures 6.1 - 6.15

week	T sol 1 %	F sol 1 %	V sol 1 %	vs/ts	mTSF1wk	mFSF1wk	mVSF1wk	mFVSDS1wk
1	5.26	1.72	3.53	0.67	10.02261	2.3200839	7.7025257	0.7685005
2	5.47	1.75	3.72	0.68	10.310947	2.4617388	7.8492082	0.7612555
3	5.23	1.65	3.58	0.68	10.159755	2.3924623	7.7672924	0.7644932
4	5.33	1.62	3.71	0.70	10.481306	2.7808549	7.7004516	0.7356112
5	5.42	1.71	3.71	0.69	10.130393	2.483894	7.6464987	0.7540719
6	5.69	1.27	4.43	0.78	9.7115369	2.7270234	6.9845135	0.718304
7	5.92	1.82	4.10	0.69	11.079573	2.3574772	8.7220956	0.7872273
8	6.73	1.94	4.79	0.71	11.259006	2.3598696	8.899136	0.7904481
9	5.94	1.73	4.22	0.71	11.146931	2.3973782	8.7495528	0.7849544
10	5.61	1.76	3.85	0.69	10.910777	2.2826667	8.6281101	0.7908034
11	6.41	1.74	4.67	0.73	11.157355	2.0302361	9.127119	0.8179569
12	6.82	1.88	4.94	0.72	11.256544	2.0991057	9.1574381	0.8135133
13	6.50	1.85	4.64	0.71	12.502957	1.7346928	10.768264	0.8611047
14	6.92	1.73	5.19	0.75	12.80711	1.6318012	11.175309	0.8726832
15	9.21	2.43	6.78	0.74	12.63767	1.625276	11.012394	0.8713513
16	9.54	2.35	7.19	0.75	11.084194	1.6812936	9.4029006	0.848365
17	8.63	2.00	6.64	0.77	10.926786	1.6038696	9.3229163	0.8529897
18	8.02	1.83	6.20	0.77	11.503849	1.7482076	9.7556411	0.8481305
19	7.68	1.74	5.94	0.77	12.329891	1.7581177	10.571773	0.8573848
20	7.04	1.55	5.49	0.78	12.400237	1.7557806	10.644456	0.8583716
21	7.09	1.49	5.60	0.79	12.011074	1.6495875	10.361486	0.8626613

week	D1ch4/wk	1 CH4/d	D1%ch4	vs/ts f1	1m3ch4/kgvs add	kgvsm3	1%VS red	1%VS red
1	67.769404	9.6813434	70.00	0.768515	0.1466389	5.1350171	54.117344	54.117344
2	62.312033	8.9017191	70.00	0.76125	0.1323107	5.2328055	52.597576	52.597576
3	107.55527	15.365039	69.50	0.7645157	0.2307867	5.1781949	53.919131	53.919131
4	113.02002	16.145717	68.00	0.7346843	0.2446177	5.1336344	51.842072	51.842072
5	99.678292	14.239756	68.57	0.7548077	0.2172635	5.0976658	51.43196	51.43196
6	104.86236	14.980338	69.71	0.7191975	0.2502259	4.6563423	36.643002	36.643002
7	184.0226	26.288943	61.33	0.7872231	0.3516406	5.8147304	53.040246	53.040246
8	185.51951	26.502787	66.33	0.7904016	0.3474485	5.9327574	46.191755	46.191755
9	207.0223	29.574615	63.43	0.7849293	0.3943484	5.8330352	51.819549	51.819549
10	213.84485	30.549264	64.57	0.7907879	0.4130778	5.7520734	55.362586	55.362586
11	215.13257	30.733224	63.57	0.8180361	0.392845	6.084746	48.868714	48.868714
12	220.37243	31.481776	63.33	0.8135213	0.4010809	6.1049587	46.031133	46.031133
13	273.24882	39.035546	59.20	0.8612574	0.422923	7.1788428	56.877593	56.877593
14	267.2074	38.172486	61.80	0.8725863	0.3985086	7.4502057	53.555634	53.555634
15	197.87635	28.26805	54.00	0.8713943	0.2994752	7.341596	38.46793	38.46793
16	188.92957	26.989938	63.00	0.8483161	0.3348782	6.2681143	23.504698	23.504698
17	138.22873	19.746962	61.67	0.8532167	0.344969	6.2147955	28.791646	28.791646
18	138.98573	19.855104	62.00	0.8480328	0.3314729	6.5032563	36.488762	36.488762
19	187.1145	26.730643	51.83	0.8574101	0.4118065	7.0473024	43.770439	43.770439
20	208.48436	29.78348	52.00	0.8584075	0.4557048	7.0957539	48.427253	48.427253
21	206.29383	29.470546	49.83	0.8626611	0.4632312	6.9071217	45.951992	45.951992

week	mnpH1wk		mnVFA1	VFA:TAlk 1	NH4 (1)	NH31
1	7.688	15171.2	1734.104	0.1143024	2303.186	77.86426
2	7.706	16722.8	2774.5665	0.1659152	2276.753	80.13341
3	7.728	17584.8	2427.7457	0.1380593	2319.045	85.734
4	7.738	16435.467	2080.9249	0.1266119	2329.618	88.06852
5	7.718	15171.2	2060.1156	0.1357912	2292.612	82.88494
6	7.704	14740.2	2136.416	0.1449381	2324.332	81.44299
7	7.568	13332.267	2409.5376	0.1807298	2852.985	73.66112
8	7.606	14007.5	3045.0867	0.2173897	2852.985	80.24067
9	7.724	13835.1	2816.185	0.2035536	2863.558	104.9231
10	7.628	14740.2	2670.5202	0.1811726	2773.687	81.9653
11	7.606	13490.3	2938.7283	0.2178401	2868.845	80.68674
12	7.622	14136.8	2635.8035	0.1864498	2868.845	83.64206
13	7.562	13906.933	4745.0867	0.341203	2833.425	72.17342
14	7.438	11723.2	5895.9538	0.5029304	2731.395	52.56774
15	7.308	12197.3	8469.4682	0.6943724	2905.851	41.6287
16	7.414	15947	7827.7457	0.4908601	3069.733	55.95072
17	7.488	12068	7675.1445	0.6359914	3143.745	67.75523

18	7.46	13792	5861.2717	0.4249762	2977.852	60.23935
19	7.456	13044.933	7182.8324	0.5506224	2879.418	57.72292
20	7.296	11435.867	7817.341	0.683581	2912.335	39.84399
21	7.226	9826.8	8982.659	0.9140981	3125.875	35.27966

Chapter 7 figures 7.1- 7.17

week	2%VSRed	T sol 2 %	F sol 2 %	V sol 2 %	vs/ts2	kgvsm3d	mTSF2wk	mFSF2wk	mVSF2w
1	57.904354	4.9102711	1.7059993	3.2042718	0.652517	5.0745894	10.016468	2.4045838	7.6118
2	52.898825	5.4469716	1.7521931	3.6947786	0.6782872	5.2295632	10.288975	2.4446303	7.8443
3	53.097165	5.2013272	1.7116797	3.4896475	0.6705179	4.9601089	10.305116	2.8649528	7.4401
4	54.731853	5.1291317	1.6009251	3.5282066	0.6880729	5.1960106	10.24878	2.454764	7.794
5	51.15762	5.4937788	1.7631067	3.7306721	0.6804881	5.0921244	10.130414	2.4922277	7.6381
6	46.091006	5.7269587	1.7257171	4.0012416	0.6979747	4.9481435	10.779904	3.3576883	7.4222
7	57.686235	5.5775164	1.7873912	3.7901252	0.6795202	5.9714613	11.82891	2.8717181	8.957
8	49.543301	6.592321	1.9973957	4.5949253	0.69693	6.0711137	11.654071	2.5474002	9.1066
9	45.141097	6.9478417	2.0041642	4.9436775	0.7111322	6.0077487	11.638428	2.6268055	9.011
10	36.633156	7.3751866	1.9060375	5.4691491	0.7410403	5.7539545	11.022068	2.391136	8.6309
11	33.085442	7.9274597	2.1865238	5.7409359	0.7241274	5.719668	10.814673	2.2351707	8.5795
12	36.439497	7.6462508	2.1442543	5.5019965	0.7192827	5.7708757	10.927037	2.2707238	8.6563
13	32.004375	8.7130815	2.4881261	6.2249554	0.7181116	6.1032901	11.405936	2.2510005	9.1549
14	3.7730167	12.700763	3.6209093	9.0798535	0.7168038	6.2905803	11.63548	2.1996092	9.4358
15	11.026888	11.380754	2.5906102	8.7901443	0.7733218	6.5863675	11.763017	1.8834662	9.8795
16	0	10.13935	2.1754776	7.9638725	0.7849642	5.0268779	9.4188304	1.8779287	7.5409
17	3.1509067	9.0066695	1.8622972	7.1443723	0.7927383	4.917491	9.2359692	1.8591606	7.3768
18	6.6055305	9.064632	2.0034709	7.0611611	0.7786816	5.039994	9.5650008	2.0044235	7.5605
19	15.349313	8.986975	2.1255287	6.8614463	0.763472	5.4033145	10.574635	2.4690348	8.1056
20	24.388545	7.9477865	1.9181195	6.029667	0.7584773	5.3159489	11.109453	3.1349113	7.9745
21	31.251127	7.4671755	1.9758318	5.4913437	0.7349795	5.4121347	11.120182	2.5288238	7.98

week	2m3ch4/kgvs add	mALK2wk	mnVFA2	VFA:TALK 2	mnPh2wk	NH4 (2)	NH32
1	0.1411034	14912.6	1734.104	0.1162845	7.708	2398.343	84.79122
2	0.1296317	17067.6	2427.7457	0.1422429	7.716	2271.466	81.75433
3	0.2575496	17412.4	2427.7457	0.1394263	7.72	2308.472	83.83203
4	0.2542512	15918.267	2080.9249	0.1307256	7.73	2297.899	85.33237
5	0.2536886	15860.8	2035.8382	0.1283566	7.714	2287.326	81.95807
6	0.2329372	14826.4	2002.89	0.1350894	7.704	2382.484	83.48059
7	0.1989979	13102.4	3076.3006	0.2347891	7.556	2467.068	61.99715
8	0.2688889	13447.2	4163.5838	0.3096246	7.568	3249.476	83.89811
9	0.2834673	14438.5	5819.9306	0.4030842	7.58	3260.049	86.47773
10	0.2169864	14654	5826.6821	0.3976172	7.504	3175.464	70.95998
11	0.2534244	14481.6	3156.0694	0.2179365	7.476	3143.745	65.94062
12	0.3094368	15573.467	5008.185	0.3215845	7.484	3339.347	71.3227
13	0.2024347	15228.667	5505.9191	0.3615496	7.382	3328.774	56.42257
14	0.1294998	17550.32	11728.994	0.6683066	7.26	3497.943	44.92301
15	0.0915312	16809	12992.705	0.7729612	7.114	3492.656	32.1459
16	0.1398462	15056.267	9810.4509	0.6515859	7.258	3466.224	44.31327
17	0.2475631	15085	5826.5896	0.3862506	7.572	3270.622	85.20866
18	0.1806896	16205.6	4552.0231	0.280892	7.636	3174.225	95.50229
19	0.1518984	16033.2	4807.1792	0.2998266	7.518	3038.014	70.07034
20	0.2753732	15587.664	5438.1503	0.3488752	7.466	3112.026	63.81456
21	0.2669302	15300.221	6880.9249	0.4497271	7.39	3265.335	56.36163

Chapter 8 - Experiment 2

	Total MethaneProd / [l]				Total BiogasProd / [l]				%CH4			
	Fl 1&2	Fl 3&4	Fl 5&6	Fl 7&8	Fl 1&2	Fl 3&4	Fl 5&6	Fl 7&8	11&2	3&4	5&6	7&8
1	0.10834736	0.1182	0.1189	0.1182	0.3612433	0.3940	0.39642931	0.394	29.993	29.993	29.993	29.992
2	0.256294641	0.2845	0.2873	0.2819	0.8545208	0.9484	0.95782614	0.94	29.993	29.993	29.993	29.992
3	0.540766817	0.5994	0.6121	0.6113	1.2610087	1.3985	1.42198184	1.410	69.983	69.983	69.983	69.982
4	0.869634562	0.9605	0.9912	0.997	1.7309376	1.9144	1.96366638	1.961	69.982	69.982	69.982	69.982
5	1.249306404	1.3726	1.4212	1.4221	2.2734992	2.5033	2.57810572	2.569	69.978	69.978	69.978	69.977
6	1.58440975	1.7175	1.779	1.78	2.7523582	2.9961	3.08950859	3.080	69.98	69.98	69.98	69.979
7	2.00448761	2.1461	2.2285	2.1929	3.3539878	3.5977	3.71463932	3.675	69.823	71.247	71.899	69.444
8	2.206776562	2.3623	2.4666	2.4005	3.6437266	3.9013	4.04576936	3.974	69.818	71.241	71.893	69.439
9	2.350561413	2.5084	2.5509	2.5497	3.8450281	4.1026	4.16280513	4.175	69.784	71.25	71.901	71.521
10	2.485628305	2.6382	2.6778	2.6857	4.033571	4.2817	4.33720792	4.359	69.786	71.252	71.903	71.523
11	2.606654655	2.7887	2.8495	2.8673	4.198547	4.4891	4.57288736	4.604	73.557	71.252	71.903	71.523
12	2.737742791	2.9338	3.0416	2.9968	4.368073	4.6727	4.81775782	4.769	77.329	79.018	78.453	78.577
13	2.853663366	3.0153	3.1224	3.0797	4.517986	4.7758	4.92082302	4.874	77.327	79.017	78.452	78.576
14	2.944529849	3.071	3.1851	3.1461	4.635496	4.8463	5.00073013	4.959	77.328	79.018	78.453	78.577
15	3.01354831	3.1415	3.2579	3.2262	4.724752	4.9356	5.09468400	5.062	77.328	79.018	77.134	77.294
16	3.067752283	3.2006	3.3249	3.3022	4.794852	5.0103	5.18114026	5.160	77.326	79.016	77.132	77.292
17	3.125917939	3.2749	3.4013	3.3951	4.870073	5.1044	5.27986812	5.280	77.328	79.018	77.134	77.294
18	3.198618032	3.364	3.4887	3.5262	4.964091	5.2172	5.39268906	5.449	77.328	79.018	77.134	77.294
19	3.267716579	3.4458	3.5745	3.6451	5.053450	5.3207	5.49145507	5.600	77.328	79.018	96.706	79.074
20	3.308932362	3.4735	3.6006	3.6828	5.123970	5.4053	5.57137762	5.715	58.446	32.704	32.704	32.703
21	3.508142387	4.1743	4.5024	4.6516	5.346334	6.6922	7.22727884	7.494	89.587	54.459	54.459	54.459
22	3.644145974	5.1779	5.6796	5.7739	5.534433	8.0541	8.82254770	9.065	70.342	73.701	73.795	71.423
23	3.74249023	6.0776	6.7158	6.7332	5.670626	9.2751	10.2267415	10.40	70.339	73.698	73.791	71.420
24	3.841638117	7.0901	7.7512	7.7426	5.797471	10.515	11.4858021	11.63	78.164	81.637	82.237	82.316
25	3.927537261	8.0904	8.8934	8.8512	5.907371	11.740	12.8747421	12.98	78.162	81.635	82.234	82.313
26	4.03042749	8.9002	9.9141	9.9734	6.039005	12.732	14.1158664	14.34	78.164	81.637	82.237	82.315
27	4.10216126	9.2595	10.51	10.748	6.135059	13.173	14.8561831	15.30	74.681	81.579	80.461	80.980
28	4.216968176	9.6775	10.892	11.344	6.288791	13.685	15.3313567	16.03	74.68	81.578	80.459	80.978
29	4.372813437	9.9507	11.409	11.969	6.497496	14.020	15.9735264	16.81	74.672	81.57	80.451	80.971
30	4.481735564	10.054	11.711	12.301	6.636638	14.139	16.3293631	17.2	81,716	87.054	84.936	85.438
31	4.600537645	10.158	11.836	12.532	6.788212	14.258	16.4763444	17.47	81.72	87.059	84.94	85.442
32	4.707968865	10.261	11.96	12.644	6.925225	14.377	16.6224911	17.60	81.718	87.056	84.938	85.439

33	4.866213845	10.397	12.15	12.8	7.126590 6	14.532 8	16.8467389 7	17.78 7	81.718	87.057	84.938	85.440 6
34	4.957711751	10.469	12.256	12.898	7.259270 2	14.624 3	16.9794186	17.90 6	71.444	79.522	79.843	80.239 2
35	5.051453997	10.557	12.366	12.988	7.394975 2	14.734 7	17.1174236 5	18.01 6	71.447	79.525	79.846	80.242 2
36	5.119929956	10.652	12.491	13.097	7.493955 3	14.854 4	17.2739504 1	18.15	71.447	79.525	79.846	80.242 2
37	5.202834708	10.74	12.602	13.187	7.613536 6	14.964 8	17.4119287 7	18.26	71.447	79.525	79.846	80.242 2
38	5.29020472	10.838	12.719	13.284	7.742453 4	15.093 7	17.5684706 6	18.38 4	68.631	75.993	75.284	76.683 9
39	5.481883158	11.035	12.943	13.467	8.012254 7	15.351 9	17.8682498 5	18.62 4	70.675	76.102	74.574	76.289 5
40	5.553699225	11.112	13.025	13.537	8.113376 4	15.453 1	17.9785643 9	18.71 6	70.675	76.102	74.574	76.289 5
41	5.655121407	11.21	13.128	13.632	8.256188 5	15.582 1	18.1167696 9	18.84	70.675	76.103	74.575	76.290 2
42	5.740351794	11.296	13.211	13.704	8.380537 2	15.701 8	18.2319073 9	18.93 9	67.313	72.197	71.329	71.05
43	5.844692021	11.376	13.306	13.801	8.532519	15.812 3	18.3654671 3	19.07 3	67.313	72.197	71.329	71.05
44	5.901617578	11.439	13.375	13.872	8.615386 1	15.899 8	18.4621454 3	19.17	67.313	72.197	71.329	71.05

Chapter 8 - Experiment 2

t	daily MeanBioGasProd. / [l/d]				daily MeanMethaneProd. / [l/d]				
	Fl 1&2	Fl 3&4	Fl 5&6	Fl 7&8	Fl 1&2	Fl 3&4	Fl 5&6	Fl 7&8	
1	0.3468	0.3783	0.3806	0.3783	0.104	0.113	0.114	0.113	
2	0.4467	0.5021	0.5084	0.4944	0.134	0.151	0.152	0.148	
3	0.4468	0.4948	0.5102	0.5174	0.313	0.346	0.357	0.362	
4	0.4782	0.525	0.5513	0.5608	0.335	0.367	0.386	0.392	
5	0.5445	0.591	0.6166	0.6096	0.381	0.414	0.431	0.427	
6	0.5473	0.5632	0.5845	0.5845	0.383	0.394	0.409	0.409	
7	0.5589	0.5589	0.5808	0.5524	0.39	0.398	0.418	0.384	
8	0.2858	0.2994	0.3266	0.2948	0.2	0.213	0.235	0.205	
9	0.1858	0.1858	0.108	0.1858	0.133	0.135	0.078	0.138	
10	0.1588	0.1508	0.1469	0.1548	0.114	0.109	0.107	0.115	
11	0.2568	0.3229	0.3669	0.3816	0.188	0.234	0.267	0.283	
12	0.1666	0.1805	0.2407	0.162	0.129	0.143	0.189	0.127	
13	0.1395	0.0959	0.0959	0.0981	0.108	0.076	0.075	0.077	
14	0.1414	0.0848	0.0961	0.1018	0.109	0.067	0.075	0.08	
15	0.0846	0.0846	0.089	0.0979	0.065	0.067	0.069	0.076	
16	0.0718	0.0766	0.0886	0.1006	0.056	0.061	0.069	0.078	
17	0.0729	0.0912	0.0957	0.1163	0.056	0.072	0.074	0.09	
18	0.085	0.102	0.102	0.153	0.066	0.081	0.079	0.119	

	4	5	5	7					
19	0.0894	0.1035	0.0988	0.1505	0.069	0.082	0.086	0.119	
20	0.094	0.1128	0.1066	0.1536	0.055	0.037	0.035	0.05	
21	0.2231	1.2914	1.6617	1.7851	0.2	0.703	0.905	0.972	
22	0.1714	1.2413	1.4539	1.4322	0.124	0.915	1.073	1.023	
23	0.1325	1.188	1.3662	1.3068	0.096	0.875	1.008	0.933	
24	0.1314	1.2849	1.3044	1.2703	0.103	1.049	1.073	1.046	
25	0.1099	1.2253	1.3889	1.3469	0.086	1	1.142	1.109	
26	0.1316	0.992	1.2411	1.3634	0.103	0.81	1.021	1.122	
27	0.1052	0.4823	0.8107	1.0467	0.079	0.393	0.652	0.848	
28	0.1481	0.4936	0.4577	0.709	0.111	0.103	0.368	0.574	
29	0.1599	0.2565	0.4919	0.592	0.119	0.209	0.396	0.479	
30	0.1629	0.1389	0.4166	0.4566	0.128	0.121	0.354	0.389	
31	0.1599	0.126	0.1551	0.2859	0.125	0.11	0.132	0.243	
32	0.1461	0.1267	0.1559	0.1413	0.115	0.11	0.132	0.12	
33	0.1681	0.1299	0.1872	0.1528	0.132	0.113	0.159	0.13	
34	0.1606	0.1107	0.1606	0.1439	0.111	0.088	0.128	0.118	
35	0.1376	0.112	0.1399	0.112	0.095	0.089	0.112	0.091	
36	0.0917	0.1108	0.145	0.1236	0.063	0.088	0.116	0.101	
37	0.1239	0.1144	0.1429	0.1144	0.086	0.091	0.114	0.093	
38	0.1267	0.1267	0.1539	0.1222	0.086	0.096	0.116	0.095	
39	0.2467	0.2361	0.2741	0.2193	0.175	0.18	0.204	0.167	
40	0.1277	0.1277	0.1393	0.1161	0.091	0.097	0.104	0.089	
41	0.1371	0.1238	0.1327	0.1194	0.097	0.094	0.099	0.091	
42	0.1388	0.1337	0.1285	0.1105	0.095	0.097	0.092	0.08	
43	0.1412	0.1027	0.1241	0.1241	0.097	0.074	0.089	0.09	
44	0.0897	0.0947	0.1047	0.1047	0.062	0.068	0.075	0.076	

Chapter 8

Experiment 1 figures 8.2 and 8.4

Day	Dig1,2ch4/d	dig 3,4	dig 5,6	dig 7,8		cum 1,2	cum 3,4	cum 5,6	cum 7,8
1	0	0	0	0					
2	0.02	0.02	0.02	0.01	1	0	0	0	0
3	0.02	0.02	0.02	0.01	2	0.02	0.02	0.02	0.01
4	0.08	0.08	0.08	0.03	3	0.04	0.04	0.04	0.02
5	0.16	0.16	0.16	0.09	4	0.12	0.12	0.12	0.05
6	0.22	0.22	0.22	0.12	5	0.28	0.28	0.28	0.14
7	0.28	0.28	0.28	0.18	6	0.5	0.5	0.5	0.26
8	0.31	0.31	0.31	0.24	7	0.78	0.78	0.78	0.44
9	0.28	0.28	0.28	0.28	8	1.09	1.09	1.09	0.68
10	0.25	0.25	0.28	0.31	9	1.37	1.37	1.37	0.96
11	0.22	0.22	0.22	0.32	10	1.62	1.62	1.65	1.27
12	0.19	0.19	0.22	0.26	1	1.84	1.84	1.87	1.59
13	0.19	0.19	0.2	0.22	12	2.03	2.03	2.09	1.85
14	0.18	0.18	0.19	0.2	13	2.22	2.22	2.29	2.07
15	0.42	0.38	0.43	0.32	14	2.4	2.4	2.48	2.27
16	0.36	0.4	0.5	0.24	15	2.82	2.78	2.91	2.59
17	0.41	0.52	0.68	0.22	16	3.18	3.18	3.41	2.83
18	0.43	0.62	0.72	0.22	17	3.59	3.7	4.09	3.05
19	0.32	0.62	0.7	0.19	18	4.02	4.32	4.81	3.27
20	0.23	0.43	0.66	0.2	19	4.34	4.94	5.51	3.46
21	0.19	0.24	0.64	0.2	20	4.57	5.37	6.17	3.66
22	0.22	0.21	0.57	0.18	21	4.76	5.61	6.81	3.86
23	0.24	0.2	0.3	0.2	22	4.98	5.82	7.38	4.04
24	0.23	0.23	0.25	0.13	23	5.22	6.02	7.68	4.24
25	0.26	0.25	0.25	0.13	24	5.45	6.25	7.93	4.37
26	0.1	0.27	0.27	0.1	25	5.71	6.5	8.18	4.5
27	0.1	0.2	0.24	0.1	26	5.81	6.77	8.45	4.6
28	0.08	0.09	0.28	0.08	27	5.91	6.97	8.69	4.7
29	0.08	0.1	0.08	0.12	28	5.99	7.06	8.97	4.78
30	0.08	0.08	0.1	0.08	29	6.07	7.16	9.05	4.9
31	0.06	0.05	0.07	0.08	30	6.15	7.24	9.15	4.98
32	0.05	0.06	0.06	0.05	31	6.21	7.29	9.22	5.06
33	0.05	0.06	0.06	0.05	32	6.26	7.35	9.28	5.11
					33	6.31	7.41	9.34	5.16

mean cod loading		cum methane		%COD red.
8.8		5.16		32.1
9.6		6.31		39.2
19.7		7.41		40.9
29.3		9.34		42.5