HIGH SOLIDS ANAEROBIC DIGESTION OF THE PUTRESCIBLE FRACTION OF MUNICIPAL SOLID WASTE

by

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ABSTRACT

Anaerobic digestion is increasingly becoming essential for treating the organic fraction of municipal solid waste (MSW) according to the growing 'energy from waste' recycle concept. Over the last decade, efforts have been made to control the anaerobic digestion of the putrescible fraction of municipal solid waste in engineered reactors, rather than continuing with 'free' digestion in landfill sites. This way of increasing treatment efficiency can be achieved with significantly reduced retention time (days rather than years) and enables the recovery of valuable energy from waste without biogas emissions into the atmosphere, which cause adverse greenhouse effects.

Three basic approaches have been explored for the anaerobic treatment of MSW: (a) conventional 'low solids' slurry digestion; (b) two-phase digestion; and (c) high solids 'dry and semi-dry' digestion. The advantages of high solids digestion processes include high loading rates, and high yields of biogas and methane. Anaerobic digestion at high solids content is also reported to reduce capital and operating costs through smaller reactor volume.

Different reactor design configurations have been applied at full-scale and their performance evaluated. Commercial plants which use a high solids digestion process, recycle a portion of the digested solids residue in addition to the liquid from the digested residue. However, the exact recycling ratio and data concerning the recycling impact on the stability and performance of the digestion process, are not well documented in the

literature. Also, it is recognised that mixing is important to enhance anaerobic digestion but little research has concentrated on the impact of mixing on continuous or semi-continuous high solids anaerobic digestion systems.

The main aim of this research was to evaluate the potential methane production in the stabilisation of the putrescible fraction of MSW using two novel reactor designs. A vertical sequential reactor (VSR) was used to assess the effects of digested recycle ratio (DRR) and leachate recycling (LR) and a horizontal rotary reactor (HRR) was used to evaluate the impact of mixing on the digestion of the PFMSW. Experiments were conducted in both batch and semi-continuous mode using three 70 l reactors, under mesophilic conditions (35°C) and high total solids content.

Process performance was assessed using various waste parameters for solid waste and leachate treatment. Regarding solid waste treatment, VS removal, biogas and methane production and yields were the main parameters used for assessment, among several others. Accordingly, COD, VFA, pH, alkalinity, NH_3-N, TKN etc. have been some of the parameters used to monitor leachate quality. Furthermore, internal biological activity in the VSR was assessed using the observed VFA concentrations and degradation under different operational conditions (DRR and LR).

Initially, batch experiments were carried out in order to evaluate the first start-up of high solids digestion. Furthermore, they provided seed digested residues for the subsequent semi-continuous studies, in addition to providing essential information regarding ultimate process efficiency in

terms of methane yield and VS removal. Also, rapid start-up batch experiments were used to determine the required RT for semi-continuous studies.

Optimum DRR and LR were determined with the use of the VSR semi-continuous process. A DRR of 0.5 was found to be optimum in terms of volumetric methane production, while LR2 (3.5 ℓ leachate recycle) provided a desirable economical option, because of its lower liquid requirements. HRR gave limited indicatory results expressing high treatment potential for high solids anaerobic digestion of the putrescible fraction of MSW.

Finally, a mathematical model was developed for optimising the VSR operational conditions, utilising data produced under semi-continuous conditions.

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LIST OF ABBREVIATIONS

COD	chemical oxygen demand
C/N	carbon to nitrogen ratio
DRR	digested recycle ratio
FCOD	Filtered chemical oxygen demand.
HRR	horizontal rotary reactor
LR	leachate recycle
MSW	municipal solid waste
NH_3-N	ammonia nitrogen
OLR	organic loading rate
rpm	rotation per minute
RT	retention time
TCOD	total chemical oxygen demand
TKN	total Kjeldahl nitrogen
TS	total solids
TVFA	total volatile fatty acids
VCR	vertical conical reactor
VFA	volatile fatty acids
VS	volatile solids
VSR	vertical sequential reactor

NOMENCLATURE USED FOR MODELLING

B	dimentionless Contois equation Kinetic parameter
DRR	digested recycle ratio (mass recycle/mass total waste)
F	volumetric fresh refuse feed (m^3/d)
F_T	total volumetric feed entering the reactor (m^3/d)
K	Chen-Hastimoto kinetic parameter, dimensionless
K_w	proposed Kinetic parameter for liquid concentration (kg/kg total mass)
L	leachate recycle ratio (mass leachate/mass total waste)
M	biomass concentration at reactor effluent (kg/m^3)
M_o	biomass concentration at reactor inlet (kg/m^3)
R	wet volumetric recycle feed (m^3/d)
S	substrate concentration at reactor effluent (kg/m3)
S_o	substrate concentration at reactor inlet (kg/m^3)
S_F	substrate concentration in raw refuse feed (kg/m^3)
V	reactor total volume (m^3)
W	liquid concentration in the reactor (kg /kg total mass)
Y	biomass yield constant (kg biomass produced /kg substrate converted)
θ	retention time (d)
μ	specific biomass growth rate (1/d)
μ_m	maximum biomass specific growth rate (1/d)

CHAPTER 1

INTRODUCTION

Increased production of municipal solid wastes (MSW) accompanied with environmental and economic problems facing the traditional methods of disposal have resulted in tremendous efforts to find alternative methods of disposal. In the UK., at present, more than 85% of all domestic wastes, around 20 million tonnes per year, are disposed of to sanitary landfills, about 10% is incinerated and only around 5% is recovered for recycling. The UK government has set a target for recycling of around 50% of recyclable household refuse by the year 2000 (Dunn et al., 1994).

MSW can be separated into different fractions by mechanical and magnetic methods. Sorting municipal solid wastes to separate the different fractions is an important step towards an integrated waste management approach, where suitable treatment can be applied to each fraction of the waste. This separation allows for recovery of valuable recyclable materials such as metals, paper and glass, which makes recycling the best disposal option for MSW. However, the vegetable and putrescible fraction of MSW, which may reach up to 30% of UK domestic refuse (Barton, 1987), still has to be disposed of. At present, this is usually dealt with in landfills. However, landfilling requires a large area and may cause contamination of underground water. In addition, there is the difficulty of finding new landfill sites. The other common disposal method for MSW in the UK. is incineration. This option also has its problems, such as low calorific value of the organic fraction of MSW, and the possibility of air pollution. Incineration also requires high investment, especially with stringent emission control, and has high running costs.

The increased cost of energy in the mid 1970s, and the desire to be less dependent on non-renewable fossil fuel sources, resulted in world-wide research into alternative sources of energy. Heat recovery from MSW is one approach receiving increasing attention. Dent et al. 1988, estimated the potential available energy through landfill gas utilisation, direct incineration and RDF production and combustion at approximately 1% of the UK's primary energy requirement. Another potential solution to the disposal problem of the organic fraction of MSW is anaerobic digestion. This option also has economic and environmental advantages, which include the generation of methane, the production of compost which can be used as a soil conditioner, the stabilisation of the wastes, and the elimination of odour and pathogens.

The conventional stirred tank anaerobic digestion method is traditionally used for sewage sludges and animal wastes with total solids concentration of 3 to 8%. This digestion process can be used for the organic fraction of municipal solid wastes, if the wastes are diluted first to less than 10% total solids concentration (De Baere et al., 1987). Addition of a large volume of water or sewage sludge makes the process less effective, due to the high investment and running costs for larger reactors. It also increases the cost of heating and post-treatment, and more equipment is required to handle the diluted materials.

The conclusion of a study carried out by Warren Spring Laboratory, in the late 1970s, confirmed that the digestion of the diluted organic fraction of MSW was not economically viable (Le Roux and Wakerley, 1978). This negative conclusion led to the low profile given to research on anaerobic digestion of MSW (Coombs and Coombs, 1989). However, the development of successful high solids full-scale plants, such as those

introduced by Valorga and Dranco, has renewed interest in the anaerobic digestion technique.

Difficulties associated with the conventional slurry digestion process and the fact that methane fermentation occurs naturally in landfills, have resulted in greater interest in digestion at high solids concentration. Most of the recent literature on this subject has indicated an increased tendency towards the use of dry anaerobic digestion systems. Dry anaerobic digestion takes place at total solids content of more than 25% (De Baere et al., 1987). Digestion at higher solids content reduces the capital and operating costs through smaller reactor volume, higher loading rate and limited addition of water or sewage sludge. In addition, biogas production is increased.

Wujcik, (1979), stated that possible disadvantages of dry anaerobic digestion include difficulty in providing a homogeneous substrate mixture. Internal mechanical mixing is usually used in the conventional anaerobic digestion process; however, the maximum solids content which can be mixed effectively is around 8% TS. Above this level, mixing becomes very difficult and pockets of dry substrate may develop, thus reducing the overall decomposition rate. Mixing also improves contact between organisms and substrates and increases the ability of the bacteria to obtain nutrients.

Even when no reactor internal or external mixing is applied, dry anaerobic digestion still requires the recirculation of a portion of the digested materials, and/or a sufficient amount of liquid pressed from the final digested materials. The recirculation of the innoculum of digested residue, which also provides good buffering conditions, requires mixing with the

MSW before loading into the reactor. The digested residue, the incoming feed, and the liquid obtained by pressing the rest of the digested residue are mixed together before loading.

In general, there has been little research into the applicability of the dry anaerobic digestion method to the putrescible fraction of MSW in the UK. Furthermore, none of this research found in the literature so far evaluates mixing effects on the high solids anaerobic digestion process.

The aim of the present research was to investigate the feasibility of high solids digestion of the putrescible material which is produced by using the Dano drum as a separation and pulverisation method. For this purpose, two different 70-litre reactors were developed to treat the putrescible fraction of MSW. The first reactor, which was a horizontal rotating reactor, was used to evaluate the effect of external mixing on the digestion process during batch and semi-continuous experiments. The second reactor, which was based on a sequence of chamber units, was used to optimise the various tested variables of the process, in terms of methane production and volatile solids reduction efficiencies. Only manual mixing was applied to the second reactor prior to loading each chamber unit. Finally, for the evaluation of aerobic post-treatment of the final digested materials that were produced during the semi-continuous operation from both reactors, a forced-air composting vessel was developed.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction.

Municipal solid waste generated in the UK is estimated to be between 26 and 30 million tonnes per year, from which approximately 13 to 20 million tonnes are of domestic or household waste origin (Dangerfield, 1989; Landy, 1987; Mosey et al., 1994). For typical UK solid waste, the putrescible fraction is reported to be in the range between 15 and 30% (Crawford and Smith, 1985; Lawson, 1988; Barton, 1987; Saw et al., 1992; Wheeler, 1994). The putrescible fraction is also reported to be lower during winter than in summer. Tables 2.1 and 2.2 give the composition of MSW and its classification according to size in the UK. Table 2.3 shows the methods of treatment and disposal of municipal solid waste in the UK.

Biological treatment is widely accepted as the best available treatment option for the low calorific value organic fraction of MSW. This biological treatment includes aerobic composting and anaerobic digestion. The anaerobic digestion process usually involves three main steps, as follows:
i) Pre-treatment step, where the organic fraction of the MSW is separated from the rest of the materials that might be good for recycling. Mechanical and source separation techniques are the main pre-treatment methods used by existing commercial plants. Source-separation of the organic fraction might be the best refuse sorting option because it would reduce the pre-treatment cost, and because it would give a better quality end product due to minimum heavy metal and plastic contamination.

Table 2.1 Composition of MSW in the UK (% wet weight) (Source: Barton, 1987).

	% wet weight
Fines	10 - 40
Vegetable and putrescible	15 - 30
Paper/card/wood	20 - 40
Rags	3 - 5
Metal	6 - 8
Glass	7 - 9
Plastic	6 - 9
Other (e.g. rubber, wood and non-ferrous metals)	3 - 10
Moisture	25 - 40

Table 2-2 MSW classification according to size in the UK.

Size Ranges (mm)	Compositional Classes
0 - 10	Putrescible
10 - 20	Paper and card
20 - 40	Plastic film
40 - 80	Dense plastic
80 - 100	Textiles
160 + separated fractions	Miscellaneous combustibles Miscellaneous non-combustibles Glass Fessous metals non-fessous metals Fines

Source: Coombs (1989), based on Warren Springs Laboratory classification

Table 2.3 Methods of Treatment and Disposal of Municipal Solid Waste in the UK (Dangerfield, 1989).

Disposal/Treatment	%
Landfill without treatment	79
Incineration	6
Compacting/shredding/bailing	13
Reclamation and other methods	2

ii) The digestion step, where the organic fraction of MSW is fermented to obtain energy in term of methane gas and a certain degree of stabilisation dependent on the retention time and the type of process.
iii) Post-treatment, which might involve aerobic treatment to further stabilise the end product. Prior to that, the digested materials are pressed and dried. The aerobic post-treatment step combines the advantages of both biological treatments.

Refuse is separated into organic and non-organic fractions to obtain the putrescible and combustible materials. The separation equipment separates the refuse materials on the basis of size, density or magnetic properties. Removal of large objects and inert materials from raw refuse is important in order not to cause operational problems in the digestion process and to obtain a high efficiency performance. A typical separation system usually includes size reduction to assist in screening; magnetic separation for recovery of ferrous metals; screening to remove inorganic fines; screening to remove oversize objects; and separation of the intermediate size inorganic objects such as cans and stones (Pfeffer, 1987). Coombs and Coombs (1989) listed the advantages of sorting the refuse, prior to biological treatment, as follows:
i) Reduction of reactor size and handling equipment requirement.
ii) Improvement of the AD process performance.
iii) Improvement of the control of the environmental conditions such as pH and temperature
iv) Reduction of the energy requirements for heating and mixing.
v) Recovery of useful recycled materials.

Refuse volume reduction can be achieved by shredding or pulverisation. The shredding method is used to reduce the refuse particle size and utilises

a flail or hammer mill to smash the incoming refuse. Hammer mill pulverisation has a significant disadvantage because the following separation of smashed inert materials becomes impossible with any mechanical or physical method.

Hence, in order to obtain a high quality compost end product, refuse separation and screening through a rotary drum is more suitable for biological treatment. This pulverisation method is a wet process that is mainly carried out in a Dano horizontal rotating drum where the refuse travels through the drum and falls into a double rotary screen which separates the materials into two grades (above and below 38 mm). The materials which are larger than 38 mm consist of large inorganic elements not capable of being broken down by biological treatment processes. The fine materials below 38 mm are, however, suitable for the biological treatment processes.

2.2 Anaerobic Digestion.

2.2.1 Basic Microbiology and Biochemistry.

Anaerobic digestion involves the degradation of organic matter to methane and carbon dioxide by a mixed population of interacting microbial bacteria in the absence of oxygen. Fermentative, obligate H_2 producing (proton-reducing), and methanogenic bacteria are the three major metabolic groups of microorganisms which are responsible for methane fermentation (Barlaz et al., 1989). These species of bacteria operate in a consortium and are involved in numerous interspecies activities (Chynoweth, 1987). Complex organic substances are anaerobically digested in a multi-stage process. Fig. 2.1 illustrates the anaerobic methane fermentation process and the different microbial populations involved.

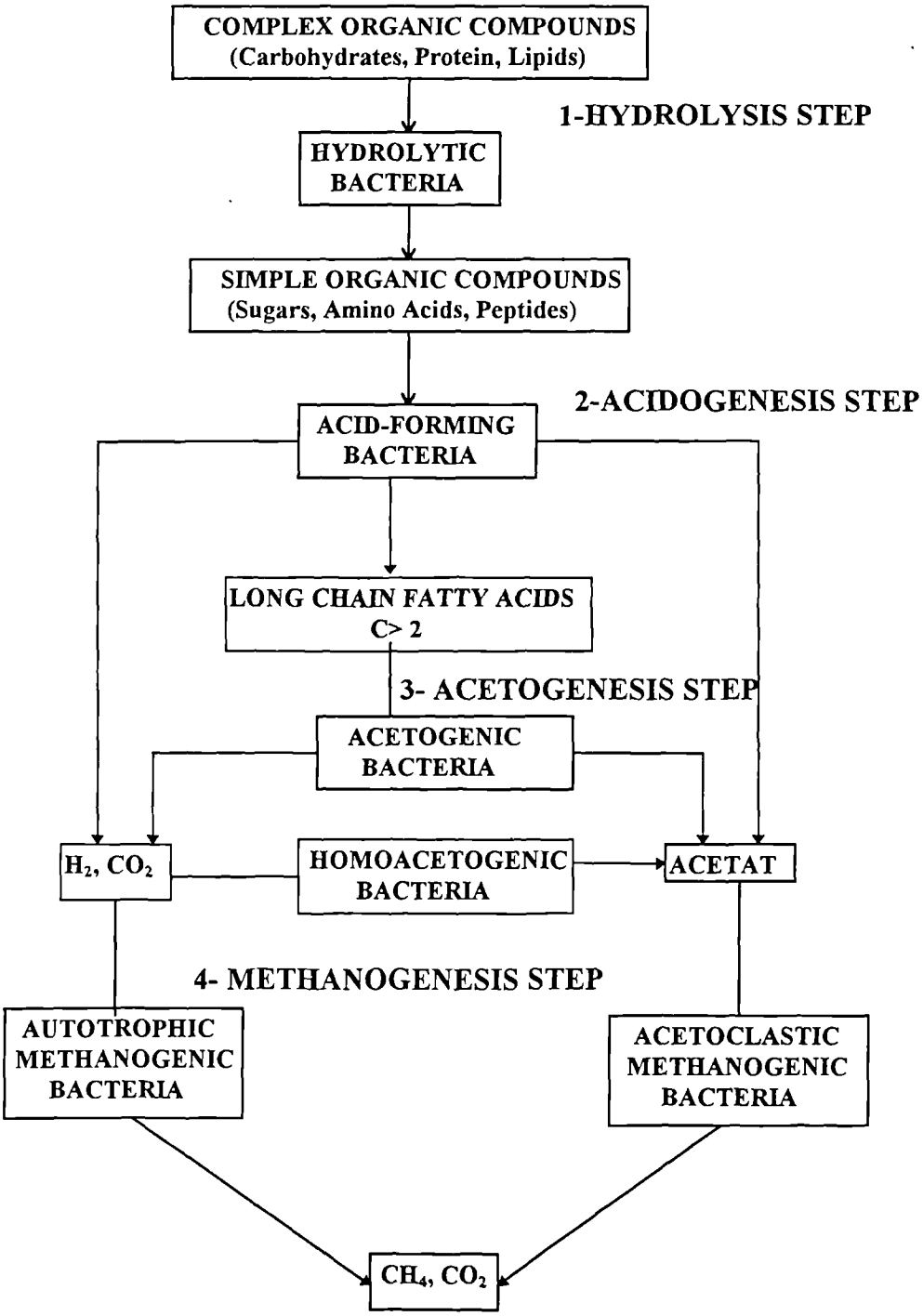


Fig. 2-1 Schematic Diagram of Anaerobic Methane Fermentation Process and the Different Microbial Populations Involved.

The metabolic stages are hydrolysis, acidogenesis (fermentation), acetogenesis and methanogenesis (Kirsop, 1984; Klass, 1984):

i) Hydrolysis and Fermentation.

Complex organic materials, such as cellulose, hemicellulose, proteins and lipids are converted by hydrolytic bacteria to monomeric compounds which can be utilised by the organisms. A subsequent fermentation step converts these monomeric compounds into free sugars, alcohols, short-chain volatile fatty acids, hydrogen and carbon dioxide and other neutral substances (De Baere et al., 1987; Mata-Alvarez and Cecchi, 1992). Fermentative bacteria require CO_2 and an organic acid as carbon sources and ammonia as a nitrogen source (Novaes, 1986).

ii) Acetogenesis.

During this stage, acetogenesis occurs and the organic acids produced are converted into H_2 and acetate by the acetogenic bacteria. The conversion of organic acids with more than two carbon atoms into acetic acid and H_2 is carried out by proton-reducing bacteria (Glauser et al., 1987). In addition, a part of the available H_2 and CO_2 is converted into acetate by the homoacetogenic bacteria that catalyse back reactions among other known groups of bacteria (Novaes, 1986; Boone and Mah, 1987). The obligate proton-reducing bacteria convert longer chain carboxylic acids, such as propionate and butyrate (approximately 50% of the biodegradable COD is fermented to these two acids), and alcohol to acetate, hydrogen and carbon dioxide (Boone, 1984; Barlaz et al., 1989; Coombs and Coombs, 1989). *Syntrophomons wolfei* bacteria oxidise octanoic, heptanoic, caproic, valeric and butyric acids to acetic and propionic acids, in addition to the generation of large quantities of hydrogen gas which is utilised by methanogenic bacteria (Blakey, 1990). Acetic and propionic

are the main substrates for the methane forming bacteria. While acetic acid can be consumed directly by the methanogenic bacteria, the propionic acid produced by *Syntrophomons wolfei* bacteria, or directly by other anaerobic bacteria, is converted by a slow-growing bacterium, *Syntrophobacter wolinii*, to acetic acid (Blakey and Maris, 1990; Dunn et al., 1994). The obligate proton-reducing bacteria can only function at a low partial pressure of hydrogen. These bacteria can only function at hydrogen concentrations of about 10^{-4} to 10^{-5} bar (Schink and Friedrich, 1994). At low partial pressure of H_2, the formation of organic compounds such as acetate is thermodynamically favoured. If the partial pressure of H_2 is maintained at a high level, only products such as propionate and some other organic acids, lactate and ethanol are formed (Zehnder, 1978). The partial pressure of hydrogen is recommended to be maintained below 10^{-4} bar for the conversion of propionate to acetate (Senior and Balba, 1990).

iii) Methanogenesis.

Acetate, hydrogen and carbon dioxide are the most important substrates to be utilised by the methanogens. Acetoclastic and Autotrophic are the two main methanogenic bacteria producing of methane. *Methanosarcina* and *methanothrix*, are the only known acetoclastic methanogenic bacteria able to produce methane from acetic acid. However, almost all of the methanogenic bacteria can utilise hydrogen and carbon dioxide (Archer and Kirsop, 1990). The methanogenic step produces methane mainly from the following reactions:

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$$

$$CH_3COOH \rightarrow CH_4 + CO_2$$

The second reaction (acetoclastic) is responsible for approximately 70-75% of the methane produced in the anaerobic digestion process, while the first reaction, through the autotrophic bacteria path, produces most of the remaining total methane generated (Kirsop, 1984; Glauser et al., 1987; Dunn et al., 1994).

The percentage flow of the energy content through the anaerobic digestion process was illustrated by McCarty (1982), as shown in the following Figure:

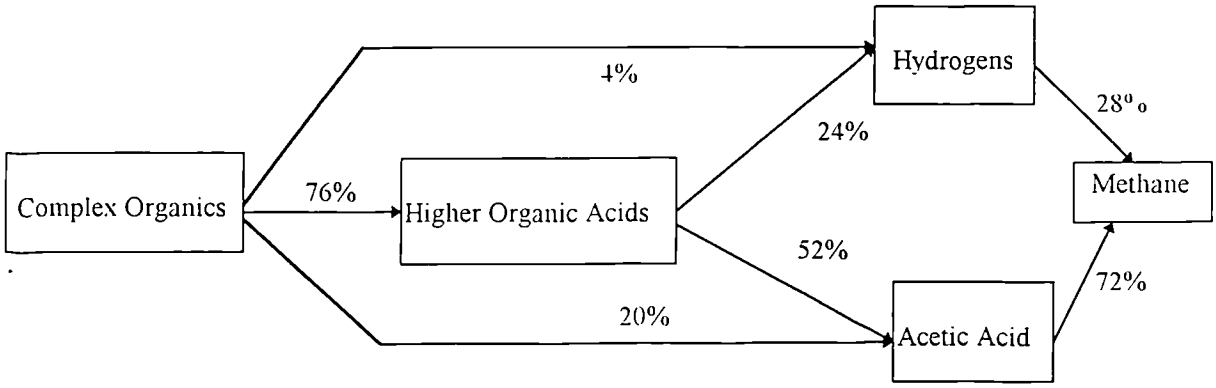


Fig. 2.2 Percentage Flow of the Energy Content Through the Anaerobic Digestion Process

2.2.2 Parameters Affecting the Anaerobic Digestion Process.

Control of the operating parameters during anaerobic digestion, in order to establish and to maintain the optimum environmental conditions for the methanogenic bacteria, is required to maintain a high efficiency process. Control of these parameters will speed up the microbial activities which help to obtain maximum biogas yields in as short a retention time as possible. These parameters are:

i) Oxygen Sensitivity.

The toxicity of oxygen to obligate anaerobes may be due to the toxic products that are formed by the interaction of oxygen with cells and media or by the oxygen acting as an oxidant (Morris, 1975). A stable digestion of complex organic wastes was considered by Dirasian et al. (1963) to be possible when redox potential is between -490 and -550 mV, whereas the optimum was found to be between -520 and -530 mV. This optimum range was reported in other work as well (Malina, 1992).

Despite the fact that many of their key enzymes are extremely unstable in air, methanogens are reported to survive in air and to recover quickly when returned to a reduced environment. In fact, many methanogens can survive exposure to air for several hours or longer without losing viability, thus there is no need to avoid exposing the anaerobic process to oxygen as strictly as early reports suggested (Jarrell, 1985). Kiener and Leisinger (1983) found that exposures to air for up to 30 hours did not affect the ability of three strains of methanogenic bacteria to survive, namely, *Methanobacterium thermoautotrophicum*, *Methanobrevibacter arboriphilus* and *Methanosarcina barkeri*. They reported that oxygen caused no or only recoverable damage in these bacteria up to this critical time of contact. However, longer exposure killed the bacteria rapidly. A

longer exposure time to oxygen was reported by Fields and Agardy (1971) to occur before the failure of the digestion process. They found that methane production, in batch fed raw sludge digestion, ceased only after 69 hours of oxygen addition (total of 1330 mg of oxygen per litre of reactor). Further more, Pirt and Lee (1983) concluded that, in contrast to the commonly reported requirement for a complete exclusion of oxygen, the introduction of traces of oxygen can enhance methane production by bacterial digestion of algal cells. The rapid utilisation of oxygen by facultative bacteria, associated with the first stage of the digestion process, can maintain a low redox potential. In addition, these facultative organisms could have a role in supplying growth factors for the methanogenic bacteria. The redox potentials usually return to normal within a few hours after exposure to air (Van Den Berg et al., 1976).

ii) Moisture Content.

MSW is considered to be too dry for anaerobic digestion (Wujick and Jewell, 1980). Therefore, for efficient anaerobic digestion, water has to be added to ensure adequate moisture level. When digesting at low moisture content, less contact between substrate and the bacteria occur. On the other hand, increasing moisture content over its optimum level raises investment and running costs due to the need for larger reactor volume, more handling and loading equipment and post-treatment of the residue. Therefore, running the reactor over the optimum moisture level or near the total solids upper limit should be avoided. The feasibility of achieving efficient methane production at low moisture content was first investigated at Cornell University using agricultural feed and laboratory scale batch reactors. The findings of this study were reported by Jewel (1980); and Wujick and Jewell (1980). Jewel reported significant methane production rates at total solid contents up to 40% (60 % moisture content), provided

pH control and adequate bacterial innoculum and acclimatisation occurs. However, the rate of digestion was affected at total solids content higher than 32.5%. Wujick and Jewell concluded that methane production was affected at total solids content between 30 and 35%; while acid production was affected only above 55% TS. De Baere and Verstraete (1984a) reported, as well, that inhibition of methane producing bacteria is likely to occur at total solids of 40% or higher. On the other hand, Klein and Rump (1987) reported that anaerobic digestion was possible with a total solids content of 40%. Furthermore, anaerobic digestion of the organic fraction of MSW was reported by Mosey et al. (1994) to proceed reliably at digestate total solids contents of up to 50 %. They also found that the optimum digestate solids content for high solids anaerobic digestion was between 25 and 35% TS (65-75% moisture content). Furthermore, most of the commercial and pilot scale plants for dry anaerobic digestion run at total solids between 30 and 35% or even higher (40% TS) in the case of the Valorga pilot plant (France) and Kwu-Fresenius (Germany) (Klein and Rump, 1987).

For high biogas and methane yields, the digestion process should be run with low total solids content. Wellinger et al. (1992) studied the influence of dry matter content on the anaerobic digestion of MSW. Their experiments demonstrated that the gas yield increased with increasing moisture content of the reactor contents with an optimum process total solids of 13% at a retention time of 30 days and 35°C temperature. The results of different batch experiments to evaluate the moisture contents between 55 and 80% were reported by Senior et al. (1990b). They found that methane production increased with moisture content up to 75% , however, a further increase to 80% moisture content resulted in a reduction of methane production. On the other hand, De Walle and Chian

(1979) found that in order to maximise gas production in sanitary landfill, a moisture content above 75% is required.

Wujcik (1979), stated that volatile acid levels were affected by the moisture content of the substrate. He found that volatile acid levels, at total solids more than 35 percent (65% moisture content), were very high, thus necessitating the addition of buffer materials to maintain a pH level over 6.3. A maximum volatile acids concentration of 33 g/l was measured at 55 percent total solids. Above that level, acids production declined, to reach around 14 g/l as acetic acid at 70 percent total solids reactor. The hydrolysis of organic solids seems to proceed at moisture contents above 40 percent. In contrast, Senior et al (1990) observed that the highest total volatile fatty acid (TVFA) concentrations were recorded with the 75% moisture content samples. However, maximum solids level for stable mesophilic anaerobic digestion of the organic fraction of MSW was found to be approximately 36% TS, by Rivard et al. (1990), despite applying mechanical mixing and optimising other environmental conditions such as pH and nutrient levels.

iii) Temperature.

Anaerobic digestion can be operated under either mesophilic (20-45°C) or thermophilic (50-65°C) conditions. The temperature used has to be relatively constant to maintain the maximum gas production rate. The optimal temperature might differ depending on the nature and composition of the wastes and the type of digester used.

Different optimal temperatures have been reported in the literature for anaerobic digestion of the organic fraction of MSW. Kirsop (1984) reported that optimal temperature for most of the pure cultures of

methanogenesis is in the range between 35 and 40°C. On the other hand, Mata-Alvarez and Cecchi, (1992) reported optimal temperature values in the range of 33 to 37°C for the mesophilic and 53-58°C for the thermophilic. A higher mesophilic optimal value of 41°C was found by Hartz et al. (1982). Pfeffer (1974) also found the optimum temperature to be 42°C for mesophilic conditions and more than 60°C for thermophilic conditions. However, under mesophilic conditions, when the temperature reaches 43°C, gas production decreases significantly, and gas production stops when the temperature reaches the range of 45 to 55°C (Pfeffer, 1974; Lettinga, 1980). Kasali and Senior (1989) obtained the same results with anaerobically digested refuse obtained from a landfill at Glasgow (UK) at 40% moisture content They found that increasing the temperature from 40°C to 55°C resulted in inhibition of the anaerobic process. This phenomenon might indicate the conversion of mesophilic activity to thermophilic activity able to function slowly in the 43 to 55°C temperature range.

Most of the literature reported that thermophilic digestion make a shorter retention time and higher biogas and loading rates possible. Comparison of both mesophilic (35°C) and thermophilic (55°C) conditions in pilot digesters processing, a high solids concentration showed that the average gas production was 20 to 25% higher in thermophilic than mesophilic conditions (Marique et al., 1989). Cooney and Wise (1974) obtained an average gas production which was 50% higher under thermophilic than under mesophilic conditions at 30 days retention time. Pfeffer (1978) also found a 60% increase in gas at thermophilic rather than mesophilic conditions for the same retention time. Operating under thermophilic conditions (55°C) was reported to reduce the retention time to an optimum of 10 days, compared to 15 days under mesophilic conditions (35°C)

(Bonhomme and Pavia, 1986). Mosey et al. (1994) also observed higher biogas production and a better quality end product under thermophilic temperature (55°C) compared to mesophilic (35°C).

A conflicting result was obtained by Glauser et al (1987), where a similar gas yield under both mesophilic and thermophilic conditions was produced at 18 days retention time. De Baere et al. (1985) found that there was no significant difference between mesophilic and thermophilic conditions up to a loading rate of 17.2 kg COD/m^3 reactor per day. However, above this level an increase in loading rate of at least 25% could be achieved under thermophilic conditions. The increase in heat requirement under thermophilic conditions and the high sensitivity to sudden changes in loading rate and temperature, or to inhibitors, especially oxygen and nitrate, might outweigh the advantages of a shorter retention time or higher loading and gas production rates (Glauser et al., 1987; Marique et al., 1989; Rimkus et al., 1982). Under mesophilic conditions, anaerobic digestion can resist a sharp temperature fluctuation in the range of 10 to 45°C for up to one day (Lettinga, 1980; Kirsop, 1984). In laboratory scale experiments using wastes obtained from Dranco pilot plants, Van Meenen et al. (1988) studied temperature fluctuation under thermophilic conditions. Their findings indicate that there is no detrimental influence in increasing the temperature from 55 to 63°C. However, when the temperature dropped from 63.5 to 20°C for a short time, it was very difficult to achieve recovery back to full activity.

iv) VFA, pH and Alkalinity.

These three parameters are interrelated parameters of the AD process. VFA is one of the most important monitoring parameters in the anaerobic digestion process. High concentrations of VFA are often associated with

an unstable anaerobic process and are the first sign of a stressed reactor (McCarty and McKinney, 1961). Low pH values usually coincide with high VFA concentrations. Adequate alkalinity is important to minimise the effect of VFA accumulation. The addition of buffer materials might be essential to restore and to maintain a neutral pH value if the VFA concentrations exceed the buffering capacity of the anaerobic digestion system.

a) VFA

High concentrations of VFA have been reported to cause stress in the microbial population and lead to complete process failure. Furthermore, an increase in acetate level indicates a problem with the methanogenic population. The accumulation of VFA concentrations might occur temporarily as a result of overloading, organism washout, ineffective mixing and temperature upset, or might cause a permanent imbalance in the anaerobic digestion process if caused by toxic conditions (McCarty and Brosseau, 1963). Acetate, also, can accumulate rapidly under nutrient deficiency (Speece, 1983). Since around 70% of the methane gas is formed from acetic acid, conversion from acetate to methane must occur to keep the acetate at a low level to increase the available free energy for the anaerobic oxidation of intermediate volatile fatty acids such as propionate and butyrate (Hill et al., 1987; Hickey and Switzenbaum, 1991). The possibility of product inhibition of propionate degradation by acetate was reported in the literature (Hobson and Shaw, 1976; Boone and Xun, 1987). Mawson et al. (1991) observed that the rate of propionic acid utilisation was reduced by approximately 50% when the added acetic acid level increased from 500 mg/l to 2000 mg/l. Hill et al. (1987) used seventy reported observations from the literature to develop a relationship between acetic and propionic acids levels as an indication of the stability of the

anaerobic digestion process. They suggested that, for anaerobic digestion of animal manure, a propionic to acetic acid ratio greater than 1.4, or acetic acid levels more than 800 mg/l, indicate imminent digester failure. Ghosh (1984, 1987) suggested that accumulation of butyrate to a high concentration of more than 3 g/l could be indicative of the onset of end-product inhibition. In his experiment with the digestion of cellulosic refuse at 25% TS, an accumulation of high VFA concentrations (20 g/l) inhibited the hydrolysis-acidification process when acetic, propionic and butyric acid concentrations were higher than 8, 6.5 and 3.5 g/l, respectively. Inhibition of the hydrolysis step was also reported to occur when the pH was between 5.5 and 7.0 and the volatile acids reached a maximum of 20-30 g/l (DE Baere et al., 1985), or 50 to 60 g/l as COD (Ten Brummeler et al., 1988; Ten Brummeler and Koster, 1989), at pH between 5.5 and 7.0. The inhibition of methanogenesis has been attributed to the action of un-ionised acids (UVFA`s). The un-ionised VFA concentrations, which are a function of pH and total VFA concentrations, inhibit methanogenesis at low concentrations. Kroeker et al. (1979) reported inhibition when the UVFA concentrations were in the range of 30 to 60 mg/l while Mawson et al. (1991) observed 50% inhibition of methane formation when the UVFA`s concentrations reached 14 mg/l.

On the other hand, McCarty and McKinney (1961) found that accumulation of acetic acid at concentrations of more than 10 g/l was not toxic to methane forming bacteria. McCarty and Brosseau (1963), also, concluded that a sudden increase in acetic and/or butyric acids concentrations to 6 g/l , at neutral pH values, stimulates the anaerobic digestion in pure culture experiments. They also found that a very short period was required for acclimatisation of a propionic acid concentration of 3 g/l. However, a sudden increase of propionic acid concentrations,

even as high as 8 g/l as acetic acid, initially hinders gas production for about a week before normal gas production resumes. They also found that this high propionic acid concentration appeared to inhibit the acid-forming rather than the methane-forming bacteria. The accumulation of iso-butyrate in the digestion mixed liquor resulted in an immediate drop in the rate of methane production and the pH. Di San Marzano et al. (1981) reported that propionic acid accumulation not exceeding 3g/l appeared harmless for the reliability of the anaerobic digestion process. Furthermore, Jarrell and Saulnier (1987) observed no inhibition of pure methanogenic cultures at 70 g/l propionic acid concentration. Lin et al. (1986), also, reported that methanogenesis occurred normally up to a feed of a mixed substrate of acetic, propionic and butyric acid concentrations of 70 g/l as COD.

b) pH and Alkalinity.

The mixed population of interacting microbial bacteria involved in the anaerobic digestion process have different optimum pH values. Hence, the optimum pH range has to be suitable for all types of bacteria involved in anaerobic digestion. Different values have been given for the most effective pH range required for the growth of methanogenic bacteria. Farquhar and Rovers (1973) stated that the optimal pH range is between 6.4 and 7.2, while an optimal pH range between 6.8 and 7.4 was reported by Zehnder (1978). McCarty (1964b) reported that the optimum pH range is between 7.0 and 7.2, and that methane production can proceed successfully as long as the pH is maintained between 6.6 and 7.6. The optimum pH for growth of most species of methanogenic bacteria is reported to be around 7 by Zehnder et al. (1981) and Kirsop (1984). Huser et al. (1982) found that, for the *Methanothrix soehngenii* type of methanogenic bacteria, the optimum pH is in the range of 7.4 to 7.8 and

methane formation occurred within a range of 6.8 to 8.2, while Zinder and Mah (1979) found that the optimum pH is around 6 for some methanogenic species.

A pH of below 6.2 or more than 7.6 can be toxic to methane forming bacteria (Pfeffer, 1978). Anaerobic digestion is suppressed at pH levels between 5 and 6 and the low pH inhibits acidogenic conversion of the substrates. The sensitivity of methanogenesis to pH values below neutral is a result of toxic action of undissociated organic acids, which freely permeate the cellular membrane of microorganisms at pH values between 5 and 6 (Kirsop, 1984; Switzenbaum et al., 1990). Pfeffer (1978) indicated that buffer should be added if the pH drops below 6.6. Sodium bicarbonate is reported to be the best supplement to adjust waste with low pH values (McCarty, 1964a). Ten Brummeler and Koster (1989) found that sodium bicarbonate gives the best result for controlling pH in the optimum range of 6.8 - 7.4, whereas calcium carbonate was not sufficient to maintain an acceptable pH level. A similar result was obtained by Jewell et al. (1981). Due to the high cost of buffer and the possibility of toxic effects if a large amount is used, initial tests are needed to determine the optimum buffer concentration to be added. Addition of 2.5% sodium bicarbonate (equivalent to 84 mg per g dry weight refuse), was reported by Kasali et al. (1989) to promote methanogenic bacteria by a factor of six. However, addition of 5% $NaHCO_3$ caused inhibitory effects on both the methanogenic and acidogenic bacteria. For the upper limit of pH values, Seagren et al. (1991) recommended a pH level below 8.1 for successful anaerobic digestion of high pH industrial wastes. They also observed that only methanogenic bacteria appeared to be inhibited at a pH level above 8.1, while, acetogenic, hydrolytic and fermentative bacteria were able to function at this high pH value. On the other hand, Clark and

Speece (1971) found that a pH above 9 halted methane production, thus inhibiting the methanogenic bacteria. This inhibition might be the result of ammonia toxicity at this high pH value.

Addition of buffer materials might be necessary to maintain a suitable pH level for the anaerobic digestion process. However, the addition of excessive amounts is economically undesirable and might also be toxic to the anaerobic digestion process.

The buffering capacity in the anaerobic digestion process is provided by the reaction of ammonium ions with bicarbonate ions to form an ammonium bicarbonate buffer at around pH 7. Adequate alkalinity indicates that the process has a good buffering capacity. Sufficient bicarbonate alkalinity is required to maintain a good buffering capacity in the anaerobic digestion process.

At a pH of between 6 and 8, bicarbonate alkalinity is the major component of the total alkalinity. The pH level falls to around 6 when the bicarbonate alkalinity falls below 500 mg/l (Fannin, 1987). For well operated municipal digesters, the VFA to alkalinity ratio should be maintained between 0.1 and 0.3 (US-EPA, 1976). Alkalinity is usually determined by titration with acid to a pH of 4.5; and it is recommended to be in the range of 2500-5000 mg/l (Saw 1988). Ripley et al. (1986) found that a ratio of intermediate alkalinity, (titration endpoint of pH from 5.75 to 4.3), which approximates VFA alkalinity, to partial alkalinity (titration to pH 5.75), which gives the bicarbonate alkalinity, should be kept below 0.3 for the successful digestion of poultry manure.

v) Nutrients and Toxic Compounds.

a) Nutrient Requirements.

Adequate nutrients are very important for the growth of methane forming bacteria. Nitrogen is the major nutrient required for microbial growth. Other nutrient requirements for the stimulation of methane production include sulphur, and trace metals. Speece (1985) listed the nutrients in decreasing order of importance, as follows: nitrogen, sulphur, phosphorus, iron, cobalt, nickel, molybdenum, selenium, riboflavin and vitamin B_{12}. He also reported that methane production can occur even if not all of these nutrients are present. However, with proper nutrients, the utilisation rates of the anaerobic digestion process can be increased by a factor as high as 15 (Speece, 1987a). Therefore, in order to maintain a very efficient anaerobic digestion process, nutrients may have to be added. The nitrogen requirement is reported to be around 6 kg per 1000 kg of COD or 1 kg per 60 m^3 of methane produced (Speece and Parkin, 1987); while phosphorus requirement is around 15% of the nitrogen requirement (Speece and McCarty, 1964). For optimal methane production a carbon:nitrogen ratio (C/N) between 20:1 and 30:1 is required (Hawkes, 1980; Ten Brummeler and Koster, 1989; Stafford et al., 1980). Mata-Alvarez and Cecchi (1992) suggested a C/N/P around 75:5:1, with trace elements such as Fe, Co, Mo, vitamins etc., for optimal growth rate of the methanogenic bacteria. However, anaerobic digestion is possible up to C/N ratio of 45:1, with digester failure only being reported to occur when C/N ratio reaches 52:1 (Stafford et al., 1980; Renzo, 1977). The phosphorus content of municipal solid waste is low and this element must be added to maintain stable microbial growth (Pfeffer, 1978). Phosphorus should be maintained at N/P ratio of 5:1 (Lettinga, 1980; Pfeffer, 1974).

b) Toxic Compounds.

Nitrogen can be related to both nutrients and toxicity. Many important nutrients become toxic at high concentrations. Cell growth can only proceed at optimal rates if there are suitable nutrients within the process. Methanogenic bacteria, as mentioned earlier, utilise the ammonium ion as a main nitrogen source (Zehnder, 1978). In the high solids anaerobic digestion process, where less water is available for dilution, the potential for ammonia inhibition and salt toxicity is increased. Ammonia toxicity is pH related. At high pH values above 7.5, the equilibrium shown in Eq. 2.1 is shifted to the right, where ammonia in the form NH_3 predominates, which is inhibitory at much lower concentration than the ammonium ion NH_4 (Wujick and Jewell, 1980).

$$NH_4^+ \rightleftharpoons NH_3 + H^+ \qquad (2.1)$$

There are conflicting reports of the effect of ammonia nitrogen concentrations above 1500 mg/l (Bhattacharya and Parkin, 1989). Hobson and Shaw (1976) observed that total ammonia partly inhibited growth and gas production at 3 g/l and caused complete inhibition of the bacteria at 4 g/l. These results agree with those of McCarty (1964) who stated that at any digester pH, 3 g/l ammonia-nitrogen inhibited digestion, while concentrations below 3 g/l were inhibitory only at pH values between 7.4 and 7.7. However, Lettinga (1980) reported that a stable mesophilic digestion process can be maintained at 5 g/l, provided the system has been allowed to acclimatise. In fact, with acclimatisation, higher ammonia nitrogen concentrations were reported not to cause toxicity to the anaerobic digestion process. For instance, Kroeker et al. (1979) reported that ammonia nitrogen up to 7 g/l and even higher values between 8 and 9

g/l (Parken and Miller, 1982), were found to be not toxic to the methanogenic bacteria.

Free ammonia was recommended by De Baere et al. (1984) to be kept below 80 mg/l. McCarty and McKinney (1961) concluded that free ammonia concentration over 150 mg/l was severely toxic to the anaerobic digestion process. However, Kroeker et al. (1979) reported that the anaerobic digestion process can function even at high free ammonia concentration of around 350 mg/l provided that initial acclimatisation of the methanogenic bacteria occurred.

Despite the fact that traces of heavy metals provide essential nutrients required to stimulate the anaerobic digestion process, high heavy metals concentrations can be toxic to methogenic bacteria. The toxicity of heavy metals increases in the following order: iron < cadmium < zinc < chromium < lead < copper < nickel (Mosey and Hughes, 1975; Hayes and Theis, 1978). McCarty (1964b) listed the stimulatory and inhibitory concentrations of alkali and alkaline earth-metal salts such as sodium, potassium, calcium and magnesium for the anaerobic digestion process as in Table 2.4. Van Meenen et al. (1988) found that sodium of more than 8 g/kg resulted in almost total inhibition of methane production in high solids anaerobic digestion. However, acclimatised methanogenic bacteria can tolerate toxicity many levels higher than unacclimatised methanogens. Furthermore, studies reported by Speece and Parkin (1983) and Speece (1987b) indicated that the toxicity of pH, various petrochemicals, ammonium, sulphide, copper, oxygen, cyanide and chloroform was reversible, and that methanogenic bacteria have significant potential for acclimatisation to both chronic and sporadic exposure to these toxicants. Significant variation in the toxicity concentration levels have been reported

in the literature, due to the complexity of the subject. Most toxicity studies have ignored the effects of antagonism, synergism, acclimatisation and complex reactions (Speece, 1987b).

Table 2.4 Alkali and Alkaline-Earth Cation Effects on the Anaerobic Digestion Process (after McCarty, 1964b).

Cation (mg/l)	stimulatory	moderately inhibitory	strongly inhibitory
Sodium	100-200	3500-5500	8000
Potassium	200-400	2500-4500	12000
Calcium	100-200	2500-4500	8000
Magnesium	75-150	1000-1500	3000

2.2.3 Organic Fraction Stabilisation.

Waste stabilisation is achieved by destroying the biodegradable fraction of MSW and lowering the C/N ratio. Municipal Solid Waste typically contains 40-50% cellulose, 10-15% lignin, 5-12% hemicellulose, 4-5% lipids and 2-4% protein (Barlaz et al., 1989; Clausen and Gaddy, 1987). Whereas lignin is not degradable, the rest of these compounds have different rates of breakdown. Cellulose takes weeks to break down, hemicellulose and protein have a faster rate (days). Lipids (fats, oils and grease) have a high energy value and become fluid at a temperature slightly above ambient, subsequently increasing the liquid content of the refuse (Pfeffer, 1992). Proteins are nitrogenous compounds that provide a valuable source of nutrients for the biodegradation of refuse. The C/N ratio decreases as carbon is converted to biogas. A C/N ratio less than 18 is considered adequate for a stabilised residue (De Baere et al., 1985).

2.2.4 Gas Yield.

Stabilisation has a direct relation with methane gas production. McCarty (1964a) showed that the theoretical methane production of 0.348m^3/kg of COD removed was obtained from complete stabilisation at standard temperature and pressure. The potential biogas production can be estimated by multiplying the VS by the theoretical specific gas yield (Coombs and Alston, 1988).

The two common methods of estimating the potential gas yield (VS and COD) are not accurate, due to the need for a large dilution (at least 100 times) to determine the COD value in the laboratory, which results in unreliable data (Chen and Hashimoto, 1978). Meanwhile, in the VS potential gas yield method, lignin is highly volatile but not degradable in the anaerobic digestion process. In addition, the easily degradable compounds are destroyed during the laboratory tests to determine the total solids (TS%) value at 105°C. Bill (1963) recommended a lower temperature for VS testing (75°C) to obtain more accurate results. Chandler et al. (1980) developed the following equation to predict the value of the biodegradable fraction of MSW:

Biodegradable fraction = 0.83 - (0.028) x lignin content of VS%

2.2.5 Digester Design and Operation.

The digester size is determined by the solids content and the retention time of the process. The digester should be designed to optimise retention time and run at the highest feasible solids concentration. The maximum loading rate depends on solids concentration, retention time, temperature and the quality of feed used. Raw refuse should be sorted to obtain the organic fraction and to reduce the particle size, which helps to speed up the digestion process. Smaller particle size and the removal of inert wastes

allow for higher organic loading rate. Higher solids concentration reduces the reactor volume and cost and allows for higher loading rate. Short retention time is possible if the sale of compost (with further aerobic post-treatment) is the main objective of the process. However, a longer retention time is required if biogas production or waste disposal are the main goals of the process. For the organic fraction of municipal solid waste, minimum HRT is around 12 days for a digester operating under mesophilic conditions, while a good design value is around 14 days retention time (Cecchi and Mata-Alvarez, 1989). Anaerobic retention times of less than 12 days were reported by Vinzant et al. (1990) to cause unstable digestion at 37°C, despite maintaining optimum nutrients and pH levels. Traverso and Cecchi (1988) found that the optimum hydraulic retention time for the organic fraction of MSW is between 14 and 15 days in a completely mixed reactor. In semi-dry anaerobic digestion of the mechanically sorted organic fraction of MSW, operated under thermophilic conditions and 20% TS, the critical levels of organic loading rate (OLR) and retention time of 20 kg TVS per m^3 per day and 6 days, respectively, were reported by (Cecchi et al., 1992).

Van Velsen and Lettinga (1980) found that the minimum retention time required for the anaerobic digestion process is independent of the feed concentration. Therefore, higher loading rate should be obtained by increasing the feed concentration rather than decreasing the retention time. However, exceeding the upper allowable loading limit (overloading) or a large sudden increase of the organic substrate loading can cause formation of both hydrogen and volatile fatty acids (VFA) at a rate faster than the methanogenic bacterial consumption.

The organic loading rate was reported by De Baere et al. (1985) to depend on the digestion process operating temperature. A loading rate of 21.4 kg COD/m^3 reactor per day was possible at thermophilic temperatures , while a loading rate over 17.2 kg COD/m^3 reactor per day was found by De Baere and Verstraete (1984b) to decrease the performance of the dry anaerobic digestion process under mesophilic operating conditions. In order to reduce the VFA resulting from overloading, Stafford et al. (1980) suggested to stop loading the reactor and/or to increase the reactor temperature. However, Van Meenen et al. (1988) found that reactivating unbalanced dry anaerobic reactor with a high amount of VFA, was best achieved by regularly feeding the reactor, despite the high amount of VFA.

i) Addition of Sewage Sludge.

Addition of sewage sludge is desirable to improve nutrient levels in MSW and as a seed in the start up of the anaerobic digestion process. Sewage sludge also contributes to the stability of the digestion process and to the fertiliser value of the end product (De Baere and Verstraete, 1984a). However, Klein and Rump (1987) concluded that sewage sludge should not be added to the anaerobic digestion process due to the possibility of heavy metal contamination of the end product. In their experiments, dry anaerobic digestion of the organic fraction of municipal solid waste with a total solids up to 40% was possible without the addition of sewage sludge. Also, based on Refcom experience, the addition of sewage sludge was found to be not essential for the continuous anaerobic digestion of municipal solid waste (Legrand et al., 1989), since, in the continuous process, recycling the liquid obtained from the digested residue replaces the use of sewage sludge.

ii) Type of Digester Operation.

There are mainly three types of digester operation:

a) Batch Operation.

With this type of operation, a constant volume of feed, mixed with an innoculum (e.g. from previous digestion operation), is added to the digester with no addition or withdrawal during the retention period. The retention time depends on gas production; when this ceases the process is considered to be completed. This type of operation is inexpensive and very simple. However, batch reactors result in low productivity (slow reaction rates and low gas yields) due to repeated start ups.

b) Continuous Operation.

With this type of operation, feed to the reactor is continuous, and the withdrawal of the digested residue is also continuous. This type of operation requires a smaller digester but more equipment for loading, mixing and unloading is needed.

c) Semi-continuous Operation.

With this type of operation, a given volume of digested residue is withdrawn at regular intervals, and replaced with an equal volume of incoming feed. This type of operation gives more time to adjust the refuse and might prove to be more flexible than continuous operation (Glauser et al., 1987).

iii) Mixing.

Mixing improves the contact between microorganisms and substrates, and influences the ability of the bacteria to obtain nutrients (Bonhomme and Pavin, 1986). Mixing enhances the reliability of the process by ensuring

rapid dispersion and maximum exposure of the incoming feed to the microorganisms. Mixing is also required to eliminate any isolated pockets or dead reactor zones and to maintain a uniform temperature throughout the reactor (Noone, 1990). There are three methods for mixing the anaerobic digestion of the organic fraction of municipal solid wastes:

a) internal mechanical mixing.

b) gas recirculation.

c) recirculation of digested residue (external mixing).

Internal mechanical mixing is usually applied for the CSTR conventional anaerobic digestion process; however, a maximum solids content which can be effectively mixed is around 8% TS. Above this level, mixing becomes very difficult. Gas recirculation, where pressurised gas is released in different sections of the reactor, appears to be more effective for dry anaerobic digestion than mechanical mixing. The Valorga pilot and commercial plant at La Buisse and Amiens, France, are applying gas recirculation techniques for mixing the reactor contents. However, for dry anaerobic digestion the mechanism by which gas recirculation occurs is not clear and not well documented. Also, for dry anaerobic digestion, recirculation of the digested residue requires mixing before loading into the reactor. The digested residue, incoming feed and liquid obtained by pressing the rest of the digested residue are mixed together before loading.

iv) Start-Up.

The most common method to start up a continuous dry anaerobic process is to fill the reactor with innoculum (digested materials or sewage sludge). After a short adaptation period, the innoculum materials are replaced by adding a high solids content feed at a low daily loading rate until a desirable solids content is reached. No experimental data are given in the literature for the start up of the commercial continuous dry anaerobic

digestion of municipal solid waste. For instance, in the case of Dranco, De Baere and Verstraete (1984b) reported the need for adjusting the Dranco pilot plant during the first start up due to accumulation of VFA. However, they did not explain how that was accomplished. For the start up of the dry batch digestion of the organic fraction of municipal solid wastes, the addition of a high amount of methanogenic seed and buffer is essential, to prevent unbalanced digestion (Buivid et al., 1981; Ten Brummeler and Koster, 1989). Partial aerobic composting can be applied to remove the easily degradable materials. Ten Brummeler and Koster (1990) found that at least 19.5% of the volatile solids should be converted to prevent the imbalance of the dry anaerobic digestion process. However, approximately 40% of the potential methane yield was lost in the process.

2.2.6 State of the Art of Anaerobic Digestion of MSW.

There are three main techniques for digesting the organic fraction of municipal solid waste for the purpose of energy recovery and compost production:

i) Conventional completely mixed digestion.

ii) Two-phase digestion.

iii) Single-stage high solids digestion.

i) Conventional Completely Mixed Digestion.

The conventional digestion method is traditionally applied for sewage sludge and animal wastes with total solids concentration of 3 to 8%. This digestion process can be used for the organic fraction of municipal solid wastes, if the wastes are diluted first to less than 10% total solid concentration. De Baere et al. (1987) estimated that 6 to 10 m^3 of water needs to be added per ton of the organic fraction to reduce the total solids

content from 55 to 5 % TS. Addition of a large volume of water or sewage sludge makes the process less effective for the reasons already discussed.

The main practical problems with a large-scale application of the conventional digestion process are the formation of a hard scum layer at the top of the reactor and the build up of hard materials around the mixing equipment. A proof of concept facility, Refcom (Fig. 2.3) was operated in Pompano Beach, Florida, from 1978 to 1985. The system had two 1260 m^3 reactors with the capacity to handle up to 21 tons of refuse derived fuel (RDF) per day. The total biogas yield was about 0.34 m^3/kg of VS added under thermophilic conditions (58 to 60°C). This biogas yield corresponds to approximately 75% destruction of volatile solids at a retention time of between 6 and 26 days. The system was planned to be operated at a total solids concentration between 6 and 8%, however, mixing and hard scum formation limited the digester to be operated at only 3 to 4.79% TS. The project was shut down in 1985 due to problems in the sorting line, feeding preparation and the mechanical stirrers in the digesters, in addition to financial difficulties (Cecchi and Mata-Alvarez, 1992). The results of 10 periods of steady state operation, at various retention times and total solids concentrations before the plant closure, were used as a basis for a detailed systems and economic analysis for a 400 tonne per day plant. The conclusion of these studies indicated that the Refcom system can be economically run at 8 to 10% TS. Operating the plant at 10% total solids (TS), reduces the reactor volume and increases the process capacity from 21 to 50 tons/day (Isaacson et al., 1987; Legrand et al., 1989). This conclusion was based on two similar plants. The Broni plant, Italy, which is the largest conventional CSTR anaerobic digestion process for municipal solid waste in Europe, and the Biomet plant at Sundbyberg,

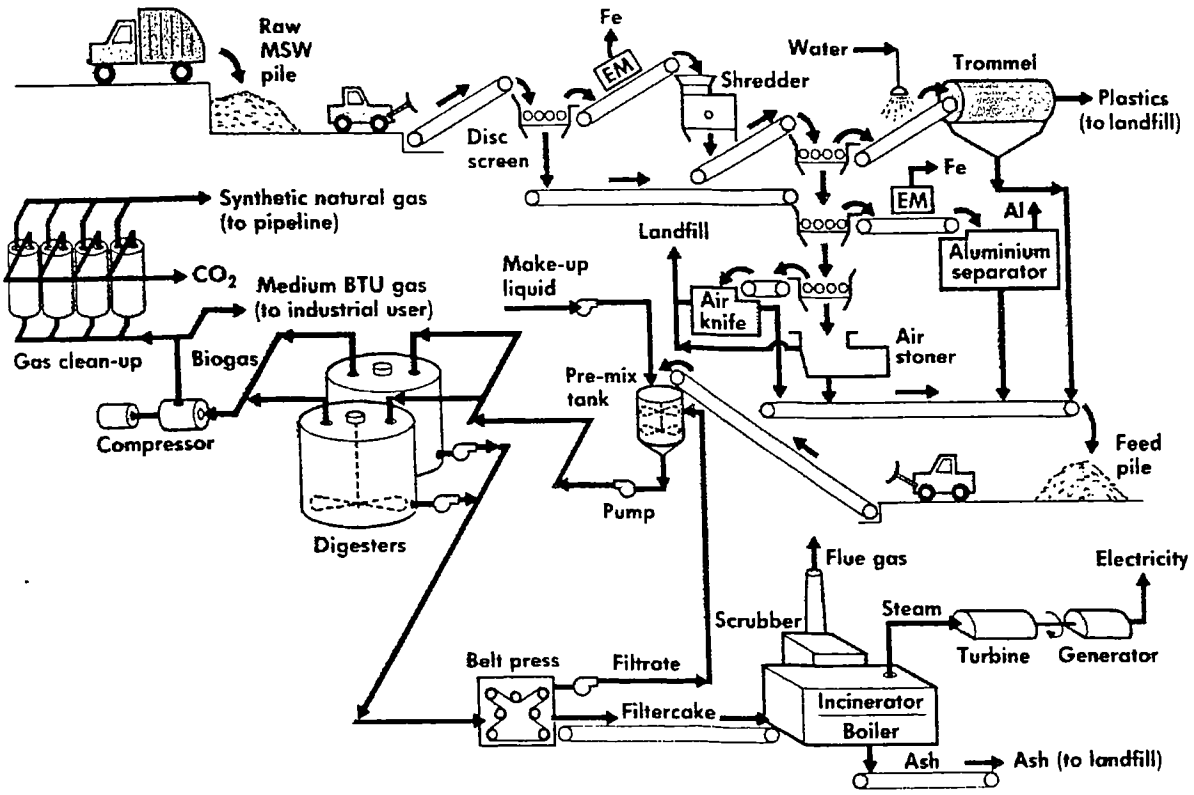


Fig. 2.3 Refcom Flow Diagram
(Source: Coombs 1990)

Sweden. The Broni plant treats a mixture of sewage sludge and the organic fraction of MSW with total reactor volume of 2000 m^3. Laboratory and pilot scale experiments showed that an organic fraction of MSW to sewage sludge ratio of 1:6.3 gives a feed with a total solids concentration of 10.7%. The total solids concentration inside the completely mixed reactor is 7 to 8 %. The substrate was digested at a loading rate of 5 kg VS/m^3 reactor per day under mesophilic conditions (35°C) and a retention time of 10 days. The methane production was between 1.3 and 1.6 m^3/m^3 reactor per day (Cecchi et al., 1988). The Biomet pilot scale plant has a horizontal reactor with a capacity of 20 m^3. The sorted organic fraction of MSW is mixed with sewage sludge at a ratio of 85 sewage sludge to 15 MSW (TS basis) before loading into the reactor at a feed mixture total solid concentration of 8%. Methane of 0.25 to 0.3 m^3/kg VS added was obtained under mesophilic conditions (38°C) and 25 to 30 days retention time (Szikiszt et al., 1988). Table 2.5 lists existing and under-construction commercial plants for the conventional slurry digestion of the organic fraction of MSW.

ii) Two-Phase Anaerobic Digestion.

The two phase process requires two reactors in series. The first reactor is used to optimise the growth of acid forming bacteria. The second reactor is to optimise methane formation. The leachate obtained from the hydrolysed and acidified reactor is fed to the methane reactor. The concept of two-phase digestion, Fig. 2.4, was developed by Pohland and Ghosh, (1971), while the two phase process for MSW was first promoted by Ghosh and Klass (1978). They used two completely mixed reactors to digest sludge and refuse with an overall retention time of 8 days.

Table 2.5 Commercial Plants for Continuous Conventional Anaerobic Digestion of the Organic Fraction of MSW (after De Jong et al., 1993 and IEA, 1994).

1 - Existing Plants						
Plants	Location	Waste Type	Capacity tonne/year	temperature	Pretreatment	Started Year
Avecom	Vaasa, Finland	Mechnically Separated (MS-MSW), Sewage sludge	40000	Mesophilic	Drum	1990
Italba	Bellaria, Italy	MS-MSW	4000	Mesophilic	Wet Separation	-----
HKV	Herning, Denmark	Source Separated (SS-MSW) and Manure	1500	Thermophilic	Wet Separation	1991
2 -Under-Development Plants						
HKV	Herning, Denmark	SS-MSW and Manure	7000	Thermophilic	Drum/Wet Separation	1994
Snamprogetti	Verona, Italy	MS-MSW	50000	Mesophilic	Drum	----
Wet CSTR	Bro, Sweden	SS-MSW	35000	Mesophilic	Drum	1995

MS : mechanical separated MSW

SS : source separated MSW

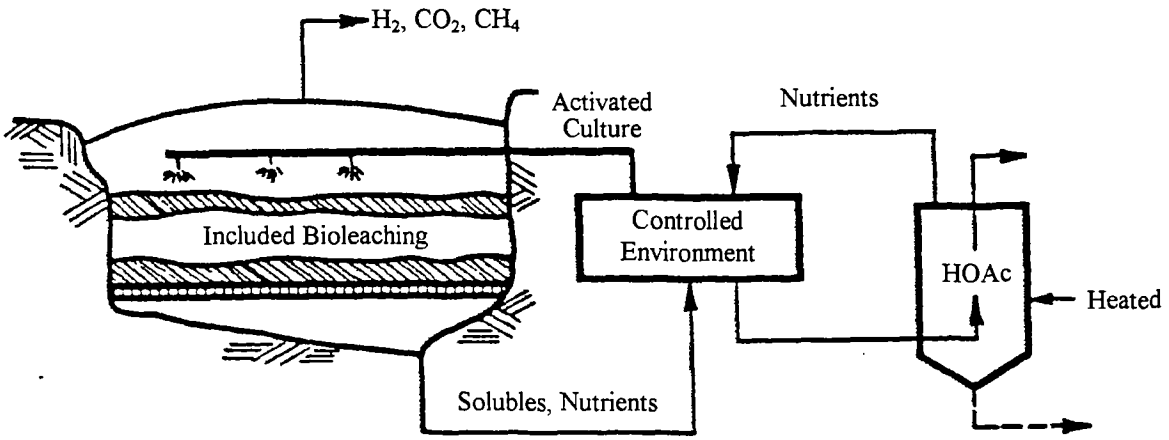


Fig. 2.4 Concept of Two-Phase Digestion.
(Source: Ghosh 1984)

Ghosh (1984; 1987) listed some of the advantages of the two phase compared to the conventional CSTR process:

- ability to handle dry solids,
- minimum feed processing is required,
- slurrification is not necessary,
- no mechanical mixing is required,
- addition of external nutrients is minimised,
- accelerates decomposition of organic wastes,
- ability to conduct fermentation in simple vessels, and
- recovery of volatile acids is possible

There is no clear evidence as yet that two-phase digestion systems, which are more complicated, and consequently more expensive, have definite advantages over one-phase systems (Mata-Alvarez and Cecchi, 1992). The major arguments against two-phase digestion are:

a) it is illogical to separate phases when syntrophic relationships between hydrolytic-fermentative-acidogenic microorganisms and methanogens are necessary to complete anaerobic digestion (Raskin et al., 1995).

b)- the reported performance of the process might be the result of two completely mixed reactors in series compared to one in the conventional stirred single stage reactor (Fox and Pohland, 1991).

The two phase process was reported to face many practical difficulties. The need for two reactors makes the overall volume much higher than the volume of a one-stage process reactor, and increases the equipment requirement for loading and unloading the two reactors. Therefore, high investment, operation and maintenance costs are expected. The operation costs involve controlling the temperature and the optimal pH ranges for both reactors. In addition, the process might face problems with the start

up of the methane reactor and clogging of channel in the percolated reactor (Ten Brummeler et al., 1991). Also, hydrogen in the first reactor must be collected and injected into the second reactor to prevent methane reduction (Kirsop, 1984).

Hofenk et al. (1983) studied two-phase anaerobic digestion of the organic fraction of MSW in a pilot-scale plant. The plant had two batch reactors, the first containing five 60 m^3 acid optimisation reactors. The second had 10 m^3 capacity for methane formation. The process had a retention time of 4 to 6 weeks. The fine materials caused percolation problems in the first reactor. The study concluded that there was no difference in gas production between the one-stage and the two-phase process. This conclusion was confirmed by Glauser et al., 1987, who reported that the two phase separation did not allow the methane yield or the VS reduction to increase significantly compared to a single-stage process.

However, when utilising municipal solid wastes with total solids of 68.6% in a two-phase laboratory scale batch reactor, Ghosh (1987) found that about 81% of the biodegradable volatile solids could be stabilised during three months under mesophilic conditions (35°C). He reported that the overall methane yield of 0.26 m^3/kg VS was obtained after 97 days digestion. Similar results were obtained at the University of Newcastle Upon Tyne where Anderson and Saw (1992) reported that when anaerobically digesting the putrescible fraction of MSW in two 50 litre bench-scale solid bed reactors at 35°C, the digestion process was completed in approximately three months with about 73% VS reduction and an overall methane yield of approximately 0.27 m^3/kg VS added.

Table 2.6 lists existing and under-construction commercial two- phase anaerobic digestion systems. In Germany, a BTA mesophilic two-phase system was developed and tested from 1986-1989 in an R&D plant in Munich (Warth and Schnell, 1989). The methanisation stage is carried out in a high yield methane reactor with 90% conversion of the soluble substrate feed into biogas. At the end of 1991, a 20,000 tonnes/year capacity BTA unit was completed at Helsingor, Denmark. Digestion is carried out for 3 days in two continuously fed phases. Hydrolysis and acidification occurred in the first reactor and methanogenesis in the second reactor. Biogas produced was 120 m^3 per ton of source separated organic waste (vegetable, fruit and garden) with a 65% methane content in the biogas. Digested material is dewatered mechanically and stabilised aerobically for 10 to 12 days (De Jong et al., 1993).

iii) High Solids Anaerobic Digestion.

Difficulties associated with the conventional slurry digestion process and the fact that methane fermentation occurs naturally in landfills result in greater interest towards digestion at high solids concentration. Most of the recent literature indicates an increased tendency towards the use of high-solids anaerobic digestion systems. High-solids anaerobic digestion of MSW includes semi-solid and dry-solid digestion processes. The semi-solid digestion is defined as a digestion process with total solids concentration between 12 and 20% (De Baere and Verstraete, 1984a; Cecchi et al., 1990a), whereas dry anaerobic digestion takes place at total solids content of more than 20-25% (De Baere et al., 1987; Baeten and Verstraete, 1988).

Table 2.6 Commercial Plants for Two-Phase Wet Anaerobic Digestion of Organic Fraction of MSW (Mesophilic Condition).

1 - Existing plants					
Plants	**Location**	**Waste Type**	**Capacity tonne/year**	**Pretreatment Methods**	**Started Year**
BTA	Helsingor, Denmark	SS-MSW	20000	Pulping	1991
	Kaufbeuren, Germany		3000		1992
	Baden, Germany		5000		1993
Paques	Breda, Netherlands	SS-MSW	15000	None	1987
	Balk, Netherlands		1000	Drum/wet	1992
DSD CTA	Plauen, Germany	SS-MSW and Manure	3000	------	1992
2 -Under Developments Plants					
ANM	Ganderkese, Germany	SS-MSW	3000	---	1993
BTA	Karlsruhe, Germany	SS-MSW	6000	Pulping (SS/MSW)	1995
	Kiel, Germany		30000		1995
	Nurnberg, Germany		25000		1995
	Tronoto, Canada		20000		
Paques	Bombay, India	MS-MSW	50000	Drum	---
	Pune, India	MS-MSW	85000	Drum	---
	Leiden, Netherlands	MS-MSW SS-MSW	75000 25000		1996
Two-stage	Boras, Sweden	SS-MSW	12000	Drum	1995

Source: De Jong et al. (1993); IEA (1994).
SS : source separated MSW
MS: mechanical separated MSW

Digestion at higher solids content reduces capital and operation costs through smaller reactor volume, higher loading rate and limited addition of water or sewage sludge. The return of investment increases from 18.4% to 42.5% as feed solids concentration is increased from 10 to 20% (Clausen and Gaddy, 1987). In addition, dry anaerobic digestion helps to increase biogas production. Reactors operating at 30% total solids produce 5 to 6 times more biogas than conventional reactors (De Baere et al., 1985; Beetschen and Cazanave, 1988).

Deboosere et al. (1986) reported that dry anaerobic digestion gives biogas yields 6 to 10 times higher than the conventional process.

The main problems associated with high-solids anaerobic digestion, as stated by Ghosh (1984, 1987), might be related to low moisture content, mass transport limitation, occurrence of an imbalance between volatile fatty acids, poor penetration, diffusion and distribution of microorganisms through the substrate mass. Legrand et al. (1989) suggested that in high solids digestion systems such as Dranco or Valorga, reactor volume is minimised at the expense of higher mechanical complexity and energy usage in materials handling.

Semi-solid digestion systems are similar to the conventional completely mixed slurry type. However, mixing and loading equipment have to be modified to handle the semi-solid substrates. A pilot plant located at Treviso, Italy, is digesting semi-solid substrates. The plant has a 3 m^3 reactor operating under mesophilic conditions (37°C). An "armed anchor stirrer", rotating at 70 rpm. is used as a mixing device and a membrane tank is used to load the feed into the reactor. The process effluent

supernatant was used for feed dilution. The plant at the University of Venice was first run at low total solids (TS) content.

Cecchi et al. (1986) reported that when a stirred semi-continuous reactor at mesophilic temperature and a moisture content of 93.6% was used for the anaerobic digestion of the organic fraction of MSW methane recovery was stable up to a loading rate of 5 kg TVS/m^3 reactor per day at 14 days retention time. On the other hand, when using semi-solid substrates (mechanically sorted) with total solids up to 20%, Cecchi et al. (1990a) found that a loading rate up to 7 kg TVS m^3/day can be digested at HRT of 15 days under mesophilic conditions. They obtained a volumetric methane production of around 0.8 m^3/m^3 reactor per day, specific biogas production of 0.23 m^3/kg TVS added per day, and total volatile solids (VS) removal of approximately 29%. This low conversion of the organic fraction to biogas was attributed to poor substrate quality and the presence of a high percentage of non degradable compounds.

Attempts to digest in dry total solids conditions started as early as the late 1950s. Schulze (1958), reported that methane production is possible at total solids concentration of up to 40% using a mixture of air-dried sewage sludge and actively digesting sludge in a batch experiment. However, high TVFA concentrations were accumulated at the higher total-solids rate. Jewell (1980) initiated the current work on dry digestion by using low cost batch reactors to treat organic and agricultural wastes at a total solids content of up to 40%. The continuous dry anaerobic digestion of the organic fraction of MSW was first investigated by De Baere and Verstraete (1984a & b). They used 40 l laboratory scale reactors operating at total solids between 30 and 35%, and a retention time in the range of 14 to 21 days. Methane production was in the range of 2.1 to 2.8 m^3 CH_4 per

m^3 reactor per day, when a fresh compost obtained from a Dano rotating drum facility was used. The encouraging results obtained from this experiment led to the construction of the Dranco pilot plant.

World-wide, there are several commercial and pilot-scale plants for dry anaerobic digestion of municipal solid wastes in operation or in the planning stage. These high-solids plants are operating in both batch and a continuous digestion modes. The batch operating plants, such as the Biocel process, use a simple procedure where the organic fraction of the refuse is inoculated with digestate from the previous run before it is sealed and left for completion.

During the digestion period, leachate is recirculated through the reactor contents. The continuously-fed digestion reactors are fed once daily (despite being called continuous-operation) with an organic fraction of MSW at a digestate high solids content of 20-40% (IEA 1984; Mosey et al., 1994). Both completely-mixed and plug-flow systems are used with the continuously -fed digestion reactors. The plug flow systems rely on external recycle or some back mixing of a proportion of the outgoing digestate as seed innoculum for the incoming refuse. The continuously -fed digestion processes include: Valorga process (France), Dranco process (Belgium), Kompogas process (Switzerland) and Funnell process (USA). Table 2.7 lists existing and under- construction plants for the commercial dry anaerobic digestion of the organic fraction of MSW.

Table 2.7 Existing and Under-Development Commercial Plants for Continuous Dry Anaerobic Digestion of OF/MSW (De Jong et al., 1993; IEA, 1994).

1 - Existing plants						
Plants	Location	Waste type	Capacity tonne/year	Temperature Type	Pretreatment Type	Started (Year)
Dranco	Gent, Belgium Brecht, Belgium Salzbrg, Austria	Source separeted MSW (SS-MSW)	700 10600 20000	Thermophilic	Drum	1984 1992 1993
Valorga	Amiens, France Papeete, Tahiti Tilburg, Netherlands	Mechanical separated MSW (MS-MSW)	55000 95000 52000	Mesophilic	Drum	1988 1991 (1992) 1993
Kompogas	Rumlang, Switzerland	SS-MSW	5000	Thermophilic	Manual	1992
Funnell	Dinwiddie, Virginia, USA	MS-MSW	20000	Mesophilic	Screen and Handsorting	1994
2 -Under-Development Plants						
Dranco	Cardiff, UK.	MS-MSW	100000	Thermophilic	Drum/wet	1995
Kompogas	Kempten, Germany	SS-MSW	------	Mesophilic	Pulping	1995
Valorga	Mons, Belgium Rouen, France Alicante, Spain	SS-MSW MS-MSW MS-MSW	90000 150000 100000	Mesophilic	Drum	Contracts awarded

2.2.7 Research/Developments for High Solids Batch Digestion.

i) Biocel Process

In the Netherlands, the Biocel batch dry anaerobic digestion process was developed at Wageningen Agricultural University. It was developed as a simple system with low investment and operation costs (Fig. 2.5). The Biocel process has been tested at laboratory-scale and pilot-scale since 1985. Several tests were carried out, at first, to speed up and optimise the first start-up of the batch reactor. At the time, the process was reported to have a retention time between 60 and 90 days at 30 - 35°C and about 55% VS removal (Ten Brummeler et al., 1988). Further studies were carried out by Ten Brummeler and Koster (1990) and Ten Brummeler et al. (1991) to speed up the start-up and to decrease the retention time of the process. They found that the retention time depended on the amount of residue recycled. A retention time of 32 days was achieved when 40% of the digested residue of the substrate was added to the fresh feed (40:60 ratio) and leachate recycling was applied. Methane yield of 221 m^3/kg VS added was obtained under these experimental conditions. A pilot-plant-scale Biocel reactor of 450 m^3 was tested for both VFY (Vegetable, Fruit and Yard) and agricultural wastes with a maximum loading rate of 7 kg VS/m^3 reactor per day. Aerobic post-treatment was also applied to produce compost. Digestion time was 20 days, which was the minimum time required for this process (Ten Brummeler, 1992). Construction started in 1994 for the Biocel commercial plant at Lelystad, Netherlands. This Biocel process has the capacity to digest 35000 tonnes of source separated MSW per year under mesophilic conditions (IEA, 1994).

Biocel Commercial Plant System Description:

After the removal of coarse contaminants, the incoming waste is loaded into a 25 m^3 dosing bunker which feeds the material into a mixing/sieving

unit (200 mm mesh width) where the material is mixed with innoculum before loading into the batch reactor. Magnetic separation steps are carried out before and after the mixing and sieving stage of the process to remove ferrous materials. The loading and unloading equipment, for the 400 to 600 m^3 reactors, is fully automated. The reactors are filled evenly with preheated material by belt conveyors. Digestion takes place at a temperature of about 35°C, a dry matter content of about 35% and a retention time of approximately 22 days. Biogas production is 100 m^3 per tonne with a 55% methane content. Leachate collected at the bottom of the reactor is heated and then recycled to the top of the reactor. Part of the digested material is returned to the mixing drum as innoculum. The remainder is processed to obtain compost (De Jong et al., 1993).

ii) Sebac Leach-Bed Processes.

At the University of Florida, USA, a sequential batch anaerobic composting (Sebac) process was developed for anaerobic treatment of the organic fraction of MSW. Sebac is a three-stage leachate-recycle type process (Fig. 2.6). In stage 1 (new stage), the putrescible fraction of MSW is shredded to about 10 cm before being loaded into the reactor, where it is moistened and inoculated by recycling leachate from stage 3 (old stage). In stage 2 (mature stage) active and balanced digestion (low levels of volatile acids) is operated in a batch mode. Leachate recycling is carried out for 15 min each day between stages 1 and 3. The leachate from the base of the vessel is transferred between established and new batches to provide organisms, moisture, nutrients and removal of inhibitory organic acids produced during the start-up of stage 1.

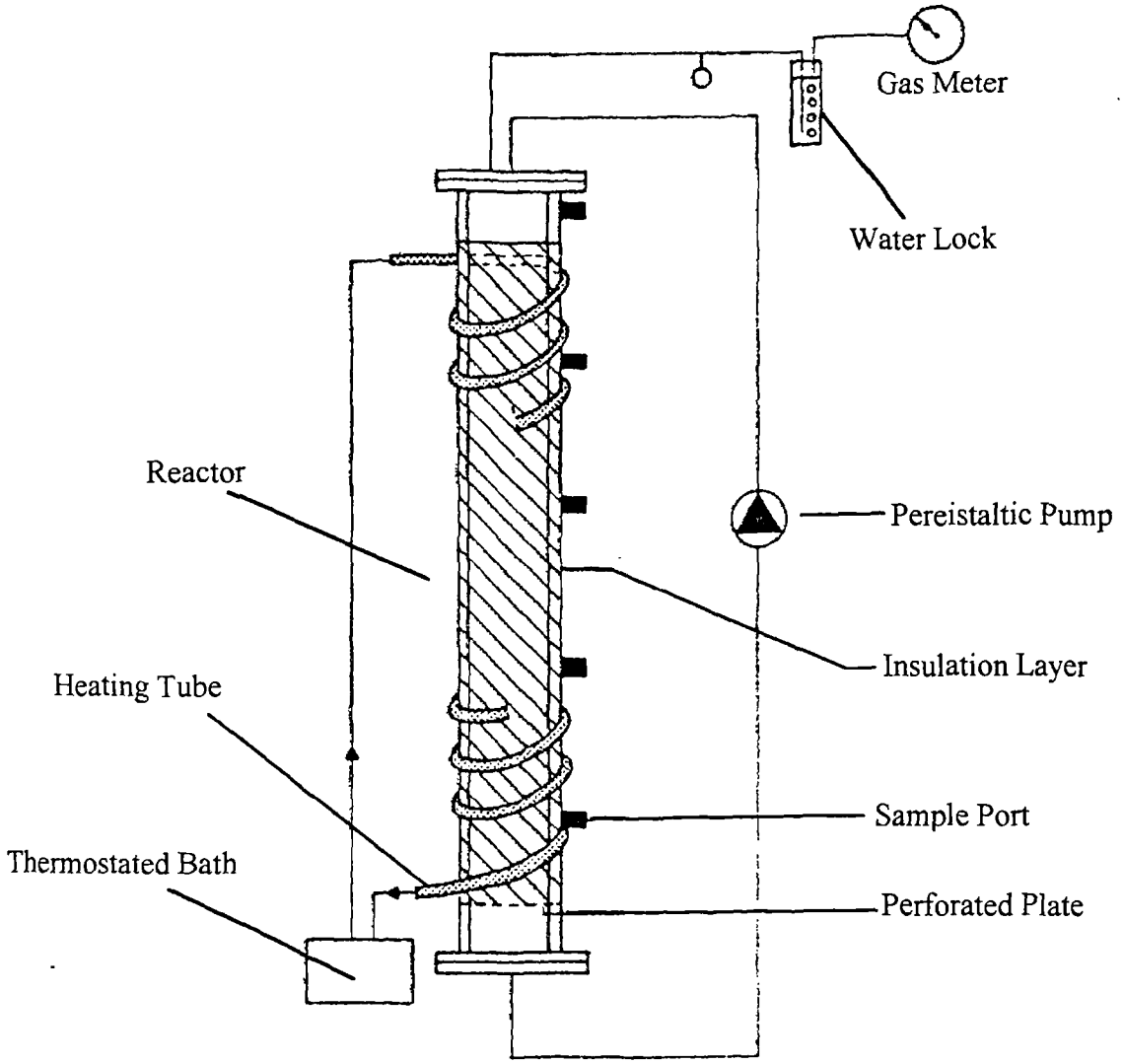


Fig. 2.5 Laboratory-Scale Biocel Reactor.
(Source: Ten Brummeler et al. 1991)

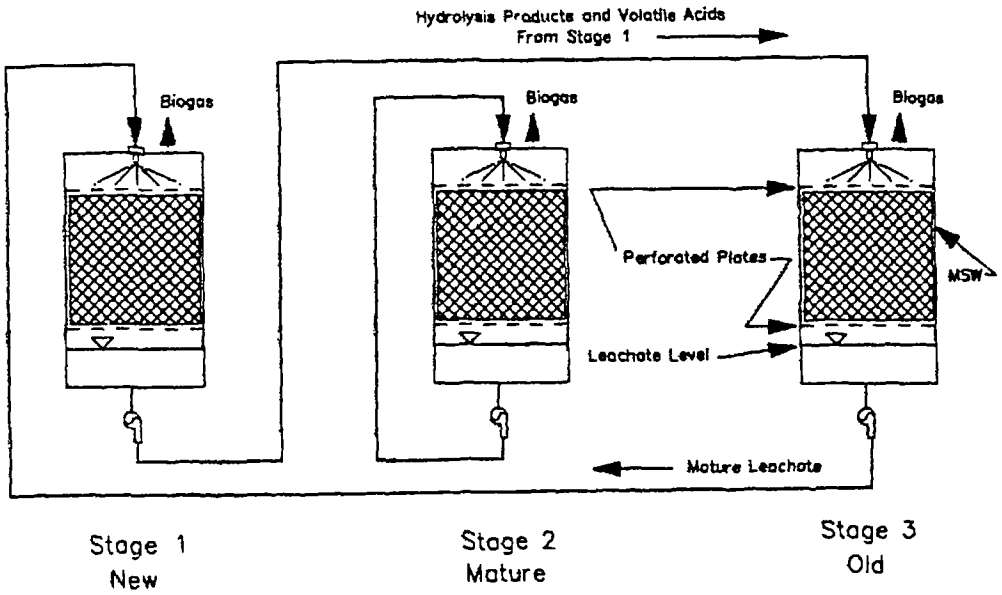


Fig. 2.6 Schematic Diagram of Sebac Process.
(Source: Chynoweth et al. 1991)

The operation and performance of this process, along with the results of 19 trials conducted in a pilot-scale plant, were reported by Chynoweth et al. (1991; 1992). The results of these 19 trials showed that about 50% conversion of organic matter was obtained at an operating temperature of 55°C. This organic conversion corresponds to a methane yield of 0.2 m^3 / kg volatile solids added. Two organic wastes, from different locations and sorting methods, were used in these trials. The shredded organic fraction of MSW was tested in 21 and 42 days runs. For the 21-day run, a mean methane yield of 0.16 m^3/kg VS added and methane production of 1.02 m^3/m^3 reactor per day were achieved. A mean volatile solids reduction of 36% was obtained during the 21 days retention time (7 days at each stage). Meanwhile, the 42-day run had mean methane yield and production values of 0.19 m^3/kg VS added per day and 0.61 m^3 CH_4/m^3 reactor per day, respectively, corresponding to volatile solids reductions of approximately 50%.

Hand sorted organic fraction of MSW, with higher initial VS content, containing mainly paper, yard and food wastes, was tested only in 21 days retention time runs. Mean methane yield of 0.19 m^3/kg VS added and methane production of 1.06 m^3 CH_4/kg VS per day, corresponding to mean volatile solids reduction of 40.6%, were obtained from this hand sorted organic waste. The loading rates corresponding to the 42 and 21 days experiments were approximately 3.2 and 6.4 kg VS/m^3 reactor per day, respectively. Most of the methane was produced in stage 1 The rest of the methane was obtained from stage 2 of the process, while methane content reached more than 50% in the biogas produced.

2.2.8 Research/Developments for High Solids Continuous Digestion.

At present, Valorga and Dranco are the most successful and commonly used commercial plants for continuous dry anaerobic digestion of municipal solid waste. Table 2.7 lists the existing and under construction commercial plants for the continuous dry digestion.

i) Dranco Process.

The Dranco pilot plant, located at Ghent, Fig. 2.7, has a total volume of 56 m^3 and a capacity to handle between 2 and 2.5 ton of the organic fraction of MSW per day. The plant has been in operation since 1984. Mixed garbage as a feedstock was used between 1984 and 1991, and source separated waste since 1991 (Six and De Baere, 1992). The refuse is first shredded and homogenised in a Dano drum for 3 days, after which the separated organic fraction is subjected to sieving through a 22 mm sieve (Van Meenen et al., 1988; Coombs and Coombs, 1989). The sieved organic fraction is then digested for a period of 12 to 18 days. During 3 years operation of the Dranco demonstration plant, steady-state biogas production of 6-8 m^3/m^3 reactor per day with 55% methane and 45% CO_2 was obtained at 55°C temperature. A volatile solids reduction of approximately 55% was achieved at the end of the digestion period (Van Meenen et al., 1988). Other reported results from the Dranco demonstration plant showed that volumetric methane production in the range of 2.75 to 4.4 m^3 CH_4 per m^3 reactor per day was obtained when a loading rate between 10 and 13 kg VS m^3.d was applied. The volumetric biogas production obtained was between 5 and 8 m^3/m^3 reactor per day with 55% methane content at 55°C. The specific methane yield was between 208 and 229 l/kg VS added, corresponding to 50 to 55% organic matter conversion efficiency (De Wilde et al., 1989; Six and De Baere, 1992). These high volumetric biogas and methane production rates were

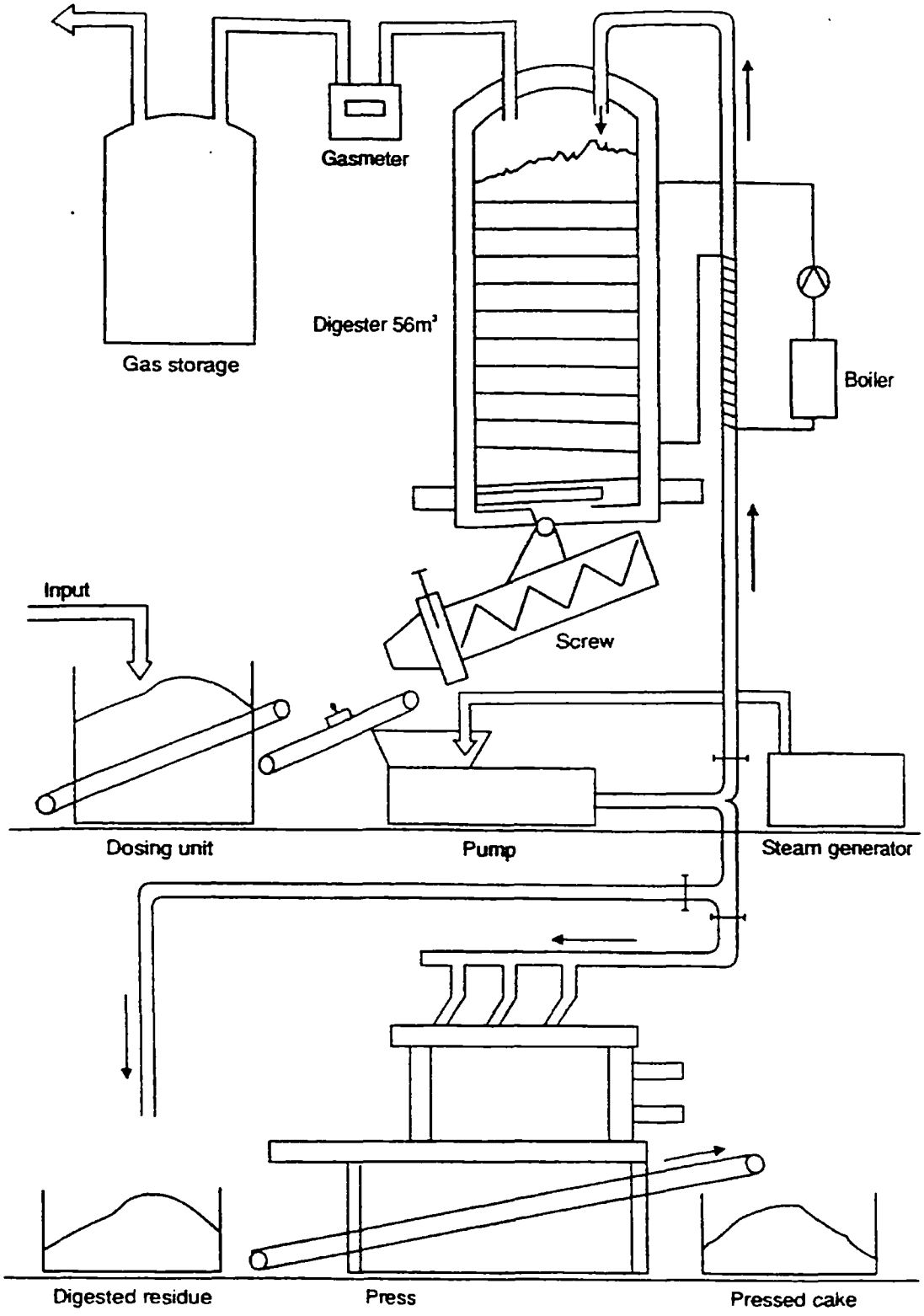


Fig. 2.7 Schematic Diagram of Dranco Demonstration Plant. (Source: Dunn et al. 1994)

achieved at a thermophilic temperature of 55°C. Lower biogas and methane production were obtained under mesophilic operating conditions. De Baere and Verstraete (1984a), De Baere et al. (1985) and Deboosere et al. (1986) reported that when the Dranco process was operated at 35-40°C, total solids content of 25-35% and a loading rate of 10 to 15 kg VS/m^3 reactor per day, the volumetric methane production obtained was in the range of 2.1 to 2.8 m^3 CH_4 / m^3 reactor per day. The required retention time was between two and three weeks. The produced biogas consisted of 50 to 60% of methane. Digested material is removed from the reactor by a screw conveyor. The digested residue with a total solids concentration between 32 and 35% and a pH of 8.2 to 8.5 is dewatered to 60% total solids by a screw press. The press liquid is used to adjust the feed moisture content (Deboosere et al., 1986; Six and De Baere, 1992). For further stabilisation, the dewatered digested materials are subjected to post-digestion aerobic treatment for 2 to 3 days (Baeten and Verstraete, 1988). A higher aerobic post-treatment retention time of 10 days was reported to be used in the Dranco process when digesting the source-separated organic fraction of MSW (Six and De Baere, 1992). Both anaerobic and aerobic steps are carried out at a thermophilic operating temperature of 55°C (Deboosere et al., 1986).

ii) Valorga Process.

In France, the first facility using the Valorga process started in 1984 near Grenoble. The pilot plant had a capacity of 500 m^3 and was capable of processing 16,000 tons of municipal solid waste per year. Raw refuse was sorted at the plant to obtain the organic fraction. The complete Valorga process consists of preparation, digestion, biogas treatment, incineration and refining units. Fig. 2.8 shows three of the main Valorga process units. The Valorga preparation unit consists of storage of raw refuse in a pit,

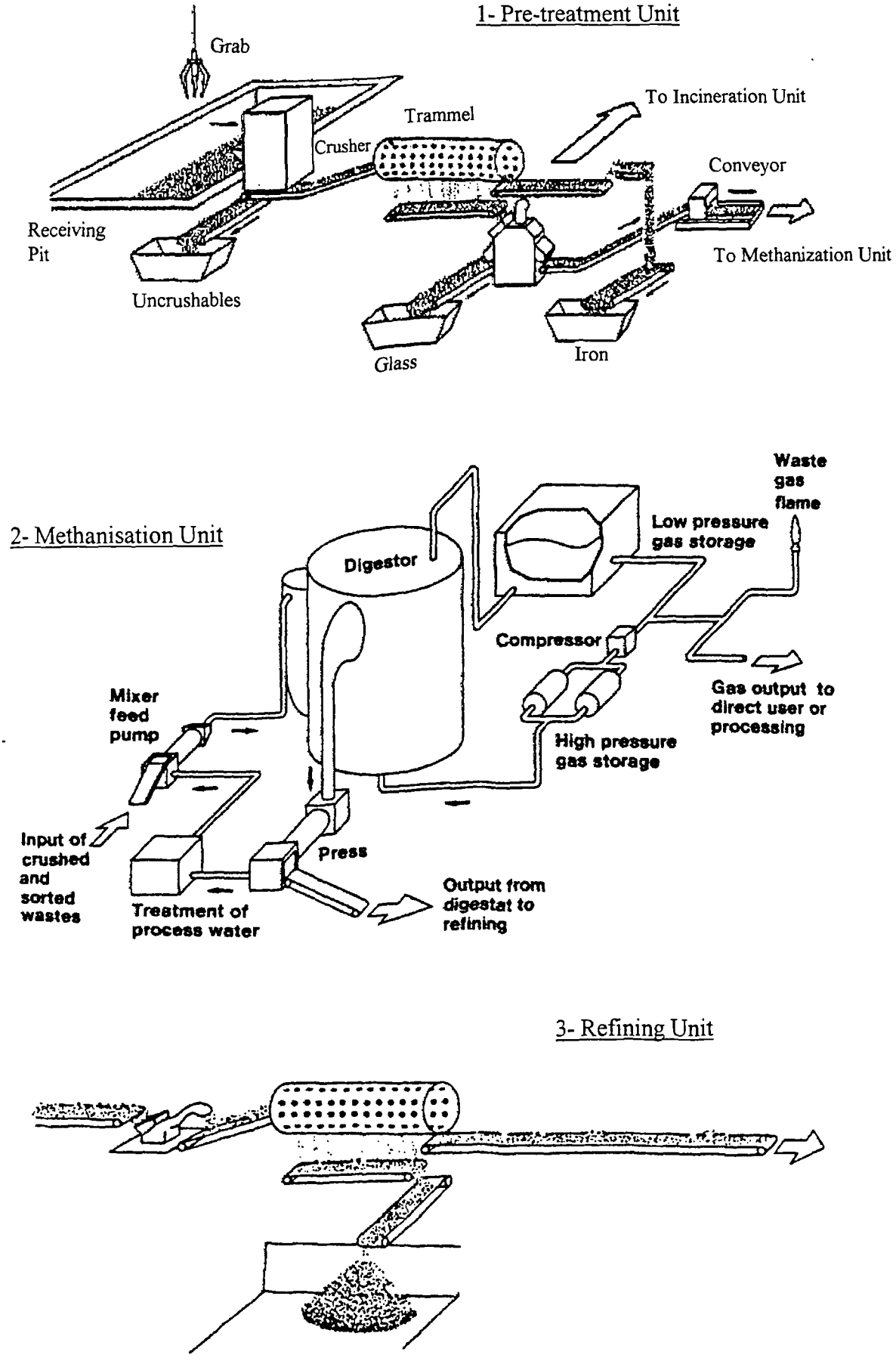


Fig. 2.8 Schematic Diagram of Various Valorga Units.
(Sources: Bonhome and Claquin 1988; Brolin and Dahl 1990)

sorting by particle size, magnetic sorting to remove ferrous metals, and reduction of particle size. The refuse is shredded before the removal of ferrous metals. The waste then passes through a set of three trommels each with a different size mesh. Large objects over 200 mm are landfilled, while the incineration unit is used for waste falling through the 200 mm mesh trommel which contains a combustible refuse-derived-fuel fraction. The sorted organic fraction falling from the 50 mm mesh trommel (16-50 mm in size) is used for digestion. A piston pump loads a mixture of this sorted organic fraction, extracted digested residue, and pressed liquid obtained from processing the digested materials into the reactor on a continuous basis. An equal amount is extracted from the outlet. The contents of the reactor is mixed by the programmed injection of pressurised biogas into different sections of the system (Beetschan and Cazanave, 1988; Bonhomme and Claquin, 1988; Chaize and Bonhomme, 1989). The plant runs under mesophilic conditions (37°C) and total solids content between 35 and 40%. Average biogas yield is 5.5 m^3/day (60% CH_4) with a daily loading rate between 12 and 15 kg organic matter/m^3 reactor per day. Approximately 50% of volatile solids (VS) is converted to biogas in 15 to 20 days retention time (Bonhomme and Pavia, 1986; Zaoui, 1988).

A Valorga commercial plant started up in August 1988 in the city of Amiens. This plant has three 2400 m^3 reactors and processes 55000 tonnes of municipal solid waste per year. The plant operates under mesophilic conditions (35-40°C), a retention time of 17 to 25 days, total solids content between 30 and 35% and a loading rate of 7.5 to 9 kg VS per m^3 reactor per day. The specific methane yield is between 210 and 240 l CH_4 per kg VS added. The average production of biogas is 146 m^3 per ton of sorted MSW. This biogas contains between 50 and 60% methane

with an annual methane mean value of 54%. (Chaize and Bonhomme; 1989; Saint-Joly, 1992; Valorga, 1992). Part of the digested material is pumped to the mixing unit to be used as innoculum. The remaining digested materials are discharged to the dewatering unit. The extracted digested materials containing approximately 24 to 28% total solids are sent to the dehydration presses which raise its dry matter content to 60%. The liquid produced by these presses is used to dilute the material in the mixers (Chaize and Bonhomme, 1989; De Jong et al., 1993). The refining unit helps in upgrading the quality of the digested materials by the separation of burnable materials and the removal of heavy inert metals, glass and plastic.

The Valorga pilot plant is reported to be capable of digesting the sorted organic fraction of MSW at a high dry solids content between 35 and 40% (Bonhomme and Pavia, 1986; Beetschen and Cazanave, 1988). However, the commercial plant digests at a total solids content between 30 and 35%. The optimal digestion was reported by Valorga (1992) to be found between 30 and 35% total solids (TS).

Valorga, as well as Dranco, plants recycle a portion of the digested residue. The exact amount is not revealed in either case. However, Dranco seems to use more recycled residue because mixing is only taking place outside the digester. No information is given either for the degree or effectiveness of mixing or for the movement of solids inside the reactor for both Valorga and Dranco plants

iii) KWU-Fresinuis Demonstration Plant.

In Germany, the KWU-Fresinuis demonstration plant, Fig. 2.9, was developed to optimise dry anaerobic digestion of municipal solid waste.

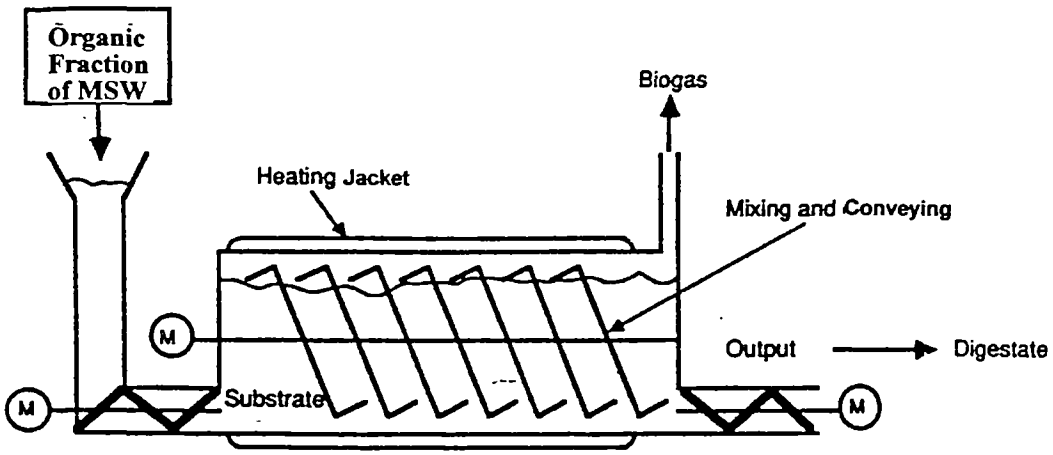


Fig. 2.9 Schematic Diagram of KWU Process
(Source: Klein and Rump 1987)

The feed has a total solids content of 40% (50% organic matter) and no water or sewage sludge has to be added to the process. The plant uses screw mixing and conveying equipment. The biogas production rate is about 5 m^3/m^3 reactor per day (60% CH_4) at 10 days hydraulic retention time and about 50% total volatile solids removal is achieved. Based on the results obtained from this process, a 100 m^3 plant is designed with a capacity to handle 5 tons/day of municipal solid wastes. Klein and Rump (1987) reported that anaerobic digestion was possible with a total solids content of 40% in a 1.2 m^3 horizontal reactor with an internal mixing mechanism. At this total solids and a loading rate of 10 kg VS/m^3 day, the specific methane yield obtained was around 0.300 m^3/ kg VS, while the methane content in the biogas was around 60%. Approximately 50% VS reduction was achieved within 10 days retention time. No information is given regarding the temperature at which the digestion is carried out, start up procedure, or nutrient requirements, especially when no sewage sludge is added.

iv) The Kompogas Process.

In Switzerland, a new system designed to treat solid wastes from 15 to 40% total solids has been developed. The Kompogas pilot plant was tested from 1988 to 1992. A full-scale plant with a reactor volume of 200 m^3 started up in 1992 to treat 3000 tons of source-separated MSW (mainly garden and vegetable wastes). The system includes a shredder to reduce the size of the material to less than 5 cm. The KOMPOGAS process is a horizontal plug flow dry digestion system with a reactor net volume of 15 m^3. The reactor is equipped with a hydraulically driven stirrer for mixing .Also, a part of the digested material is recycled as innoculum (Wellinger et al., 1992; 1993).

The feed materials are buffered, heated and then mixed with leachate to obtain a dry matter content of 30 to 35%. Heat is fed to the reactor by heating the bottom of the reactor with heat from gas engines. After 15 to 20 days, the digested materials are pumped out of the reactor. The residue is aerobically post-composted for five to ten days in a bunker where it is turned fully automatically (De Jong et al., 1993). Wellinger et al. (1993) reported average performance data of the Kompogas pilot plant. Based on 26 days retention time and a loading rate of 8.1 kg VS/m^3.d, at 27% TS and 55°C temperature, and an initial organic feed volatile solids (VS) of 54%, biogas production and yield were 2.7 m^3/m^3 reactor per day and 0.37 m^3/kg VS added, respectively. Methane content of the biogas was 59% and volatile solids (VS) reduction was 35%.

v) High-solids Research in the USA.

In the USA, a pilot-scale plant operated for six months to assist the feasibility of a full-scale commercial plant with a capacity to treat 1,000 tonnes of municipal solid waste per day to be built near San Diego, California. The results confirmed that biogas production at 32% TS is six times the biogas production of conventional digesters. The results also showed the need for further research in the area of solids transfer, mixing and movement in the reactor (Logsdon, 1990). The process, located at the University of California, combined anaerobic and aerobic biological treatment. The first stage of the process was carried out in 2.54 m^3 anaerobic reactors at total solids (TS) between 25 and 30%. The volatile solids (VS) loading rate was approximately 7 kg VS per m^3 reactor per day. During 30 days anaerobic retention time, the reactor contents were mixed mechanically. At the second stage, the digested materials were subjected for 3 days to aerobic composting in two units with a capacity of 0.85 m^3. During this second stage, the total solids of the organic materials

increased to 65% TS. Both anaerobic and aerobic steps were carried out at 55°C. Biogas production of 5 and 5.8 m^3 per m^3 active reactor volume per day was obtained with a methane content between 48 and 52%. The initial VS (82 % of TS) degraded to 63 and 59% after the anaerobic and aerobic treatment, respectively (Kayhanian et al. 1991a, 1991b).

vi) High-solids Research in the UK.

In the UK, a one year study was conducted by Environmental Resources Limited (ERL) for Cardiff City Council to determine the feasibility of building an anaerobic reactor to process 30,000 tons of municipal solid wastes per year (which could be upgraded to 100,000 tonnes/year). The study concluded in 1991 (Bristow, 1991) that anaerobic digestion technology was still under development and considered to be an expensive, risky and largely untested option for treating municipal solid wastes. However, if the Council decided to build the anaerobic digester, the study recommended a dry anaerobic digestion process after sorting the refuse either at source or in a Dano rotating drum system. The cost of disposal by dry anaerobic digestion was estimated to be about £34/ton compared with between £4 and £11/ton for landfill. However, marketing the biogas, scrap metals and digestate is highly feasible for the dry anaerobic digestion. Based on these recommendations, construction of a commercial plant based on the Dranco system was expected to start in 1995 at Cardiff but has been subject to delay. The proposed plant will have a capacity to handle 100,000 tonnes of the putrescible fraction of MSW per year with the pre-treatment by the Dano drum process (IEA, 1994).

Laboratory-scale studies, financed by the Department of Trade and Industry and managed by the Energy Technology Support Unit (ETSU),

were carried out at Warren Spring Laboratory to evaluate and to optimise high-solids anaerobic digestion of the putrescible fraction of MSW. Three different feedstocks were evaluated in 10-litre digestion vessels at high-solids content, and at both mesophilic (35°C) and thermophilic (55°C) temperatures. The feedstocks were a reject fraction from a refuse-derived fuel plant, pulverised waste from a Dano drum and a surrogate MSW that was developed to provide a consistent and reproducible substrate for lab-scale experiments. The fresh feedstock was added to the reactor on a weekly basis (one or two times per week) and manually mixed with the remaining digestate together with a measured quantity of fresh make-up water. The pulverised waste from a Dano drum was found to be the most biodegradable of the three feedstocks tested, and resulted in the highest gas production. At a loading rate of approximately 9 kg/m^3 reactor per day, 20 days retention time and 35 % TS, biogas production of up to 4 m^3/m^3 reactor per day was obtained when operating at 55°C thermophilic temperature. This compared to 2.5 m^3/m^3 reactor per day biogas production obtained at 35°C mesophilic temperature. The methane content in the biogas was 47.3 and 52.4% during the mesophilic and thermophilic runs, respectively.

Under mesophilic operating conditions, at the same loading rate and 19 days retention time, methane yield was around 0.118 m^3 methane per kg VS added and the calculated volatile solids (VS) reduction was 31.2 %. Under thermophilic conditions, higher values of 47.6 to 52.4% volatile solids (VS) reduction and methane yield of 0.205 to 0.224 m^3 methane per kg VS added were reported. Comparing these results with the high-solids commercial plants, lower methane yields and volatile solids reduction at mesophilic operating conditions were reported in this experiment than in

other commercial plants (such as Valorga process) operating at this temperature. Mosey et al. (1994) concluded that high-solids anaerobic digestion can proceed reliably at a digestate solids contents of up to about 50% TS, while the optimum value is closer to 25-35% TS. More details about these experiments can be found in reports published by ETSU (Dunn et al., Kidby and Purdom, Mosey et al. and Wheeler, 1994).

2.2.9 Performance of High Solids Anaerobic Digestion Systems.

It is very difficult to compare the performance of the different systems for anaerobic digestion of the organic fraction of municipal solid wastes because:

(i) of the variability of the organic fraction used (variation of MSW composition, based on seasons and social and cultural behaviour among different countries).

(ii) of the lack of an accepted standard method for solid waste analysis.

(iii) the parameters used for the description of the processes are not defined.

(iv) of the lack of uniformity in presentation (Cecchi et al., 1988).

(v) the published data are often used inadequately to substantiate the reported performance of the digestion process (Dunn et al., 1994).

(vi) data are protected by commercial secrecy.

(vii) of the lack of detailed performance data for the existing commercial plants (Legrand et al., 1989); in addition, the reliability and performance of the process may be overstated for commercial purposes (Coombs, 1990).

The performances of anaerobic digestion processes differ widely due to the varying operational conditions, such as temperature, loading rate and retention time. Table 2.8 gives a summary of the performance of some of systems used for the anaerobic digestion of the organic fraction of MSW. Comparisons of these various digestion systems are listed in terms of organic loading rate, volumetric and specific methane yield and volatile solids reduction.

The data in Table 2.8 show the advantages of high solids digestion processes in terms of high loading rates and volumetric biogas and methane production. Biogas production in these systems is high under both mesophilic and thermophilic conditions compared with the conventional CSTR processes. Volumetric biogas production obtained by Dranco and Valorga can reach up to 5.5 and 8 m^3/m^3 reactor per day, respectively, which corresponds to organic loading rates of up to 15 kg VS/m^3 reactor per day. Much lower biogas production is normally achieved in the case of conventional CSTR processes.

Despite the high volumetric biogas and methane production, high solids digestion processes have low overall conversion efficiencies. Specific methane yields such as 0.21 to 0.24 m^3 CH_4/kg VS added for the Valorga process, and 45 to 55% VS reduction, compare with a methane yield of up to 0.34 m^3/kg VS added and a volatile solids reduction of up to 75% from the Refcom conventional process, indicating the lower conversion efficiencies in the dry digestion systems. Other factors, besides the process moisture content and loading rate, influence these low conversion efficiencies, including such as retention time and the quality of the

Table 2.8 Operating Conditions and Performance for Some MSW Anaerobic Digestion Processes

Process	Valorga	Dranco Demonstration Plant	Dranco Demonstration Plant	University of Venice	University of Venice	BTA	Biomet	UK/ Warren Spring Lab.	Refcom
Type	Dry	Dry	Dry	Slurry	Semi-Dry	Two-Phase	CSTR	CSTR	CSTR
Temperature (°C)	37-40	55	35	35	36	-----	37-42	30-36	60
HRT(days)	15-20	18-21	16-21	14	16	2 - 3	19-27	16-100	6-27
Feed TS (%)	35-40	35%	30-35%	6.4	20	----	7-10	9	4.5-10.3
Loading Rate kg VS/m^3/day	12-15 (14)*	10-13	10-15	4.2-5	6.8	--	2.6	2.9-3.9	2.2-7.1
Specific Gas Yield m^3/kg VS added	------	0.5-0.6	------	0.64	0.23	0.65 - 0.85	0.43	0.45 - 0.44	------
Gas Production m^3/m^3/day	5.5 (4)*	5-8	4 -5	2.6	1.6	------	1.1	0.93 - 1.83	------
Specific methane yield. m^3/kg VS added	0.210-0.240	0.22-0.29	0.164 m^3/kg TS added	------	-------	-----	0.23-0.29	0.27-0.29	0.168-0.343
Methane production m^3/m^3/day	-------	2.75-4.4 (3.33)*	2.1-2.8	1.8	------	----	0.58	------	0.5-1.7
CH_4 (%)	60 (54)*	55	50-60	63	51	70-80	53	60-65	53
VS removal (%)	45-50	50-55	55	63	29	------	41	51-55	44-75
References	Valorga, 1985; Zaoui,1988; Saint-Joly, 1992	De Baere et al., 1987; De Wilde et al., 1989; Six and De Baere, 1992	De Baere and Verstraete, 1984 (a & b); Deboosere et al., 1986	Cecchi et al., 1986	Cecchi et al., 1990a	Warth and Schnell, 1989	Szikriszt et al. 1988; Peres et al. 1992	Le Roux and Wakerley, 1978; Cecchi and Mata-Alvarez, 1992; Commbs and Commbs,1989	Legrand et al., 1989

* mean values

feedstock used. For instance, the indicated retention time of the Valorga process has a lower retention time, 15 to 20 days, than the Refcom required retention time of 27 days. Mata-Alvarez and Cecchi (1992) reported that specific methane production is a measure which indicates the biodegradability of the substrate and the efficiency of the process. High values, around 0.5 m^3 CH_4/kg TVS indicate high biodegradability of waste. On the other hand, values around 0.1 indicate poor biodegradability of the input materials. Under such conditions, further degradation of this feed at longer retention times would be minimal. Table 2.9 gives the specific biogas yields according to VS removed for various anaerobic digestion processes. These data show that similar conversions were obtained for both high solids and slurry types of digestion. Therefore, the presence of a high percentage of non-biodegradable compounds might have contributed to the low reported conversion efficiencies based on total volatile solids (TVS) added.

Another important factor that effects the conversion efficiency, is the methane content in the biogas produced, which tends to increase with increasing moisture content in the process. A methane content of up to 65% was obtained in the CSTR conventional digestion experiment carried out at Warren Spring Laboratory, compared with 54 to 60% obtained in Dranco and Valorga plants. The reason for this higher methane content in CSTR conventional reactors might be due to the dissolution of more CO_2 as the moisture content of the system increases. A portion of the carbon dioxide produced remains in the liquid phase, either as soluble gas or in the form of bicarbonate ion (Pfeffer, 1987).

Table 2.9 Specific Biogas Yields According to VS Removal (Cecchi et al. 1988; 1990a).

Process	Type	Specific Biogas Yield (m^3/kg VS removed per day)
Dranco	Dry	0.8
KWU-Freseinus	Dry	1.0
University of Venice	Semi-Dry	0.8-0.9
Biomet	Slurry	1.0
Warren Spring Laboratory	Slurry	0.9

2.2.10 Summary.

The high solids anaerobic digestion process is increasingly becoming an essential pre-requisite for treating the organic fraction of MSW. The advantages of high solids digestion processes include high loading rates and high yields of biogas and methane. Anaerobic digestion at high solids content is also reported to reduce capital and operating costs through smaller reactor volume.

It is reported that commercial plants which use a high solids digestion process recycle a portion of the digested solid residue in addition to pressed liquid from the final digested residue. However, the exact recycling ratio and data concerning the recycling impact on the stability and performance of the anaerobic digestion process are not well documented in the literature. For instance, the recycled digested solids ratio for the Dranco process was reported by Coombs and Coombs (1989) to be as high as 9 parts digested to 1 part fresh refuse. Legrand et al. (1989) also stated that a substantial portion of the Dranco reactor effluent is recycled. De Baere et al. (1985) reported that the material recycled, in the Dranco process, is mainly the liquid portion which is obtained to inoculate and to adjust the incoming waste. The Valorga process also appears to recycle a portion of the digested residue (Beetschan and Cazanave, 1988; Bonhomme and Claquin, 1988). The exact amounts are not revealed in either case. However, the Dranco process seems to use more recycled residue because mixing only takes place outside the reactor.

The importance of mixing in enhancing the anaerobic digestion process is well recognised in the literature. However, little research on the impact of mixing on continuous or semi-continuous high solids anaerobic digestion systems has been cited in the literature so far. Furthermore, mixing the reactor high solids contents, either inside the reactor or prior to loading it, is not well documented in the literature due to commercial secrecy. In reported data for both Valorga and Dranco plants, no information is given either for the degree and effectiveness of mixing or for the movement of solids through the reactors.

The impacts of mixing, of recycling digested residues and of leachate recirculation on the overall performance of the high solids digestion of the organic fraction of MSW was identified as an important area for further study at the start of this research in early 1992.

CHAPTER 3

PROJECT OBJECTIVES

The main aim of this research was to evaluate the potential methane production and stabilisation of the Dano drum fine putrescible fraction of municipal solid waste using two dry processes. This putrescible fraction was obtained from a refuse treatment plant in Anglesey. The experiments were conducted both batch and semi-continuous mode using three 70 l reactors. All anaerobic reactors (Chapter 4) were run under mesophilic conditions (35°C) and high total solids content. For both the first start-up and in subsequent batch experiments, a horizontal rotary reactor (HRR) and a vertical conical reactor (VCR) were developed. The semi-continuous anaerobic digestion tests were carried out in two reactors:

i) a modified horizontal rotary reactor (HRR), which rotated at 3 rpm to provide the substrates with adequate mixing, and

ii) a vertical sequential reactor (VSR) that consisted of 7 sections and was designed to recycle a large portion of the digested residue.

In addition, a forced air composting reactor was used to aerobically post-treat the final digested residues.

The specific objectives of the study were to :

1) investigate the first start-up of high solids anaerobic digestion of the putrescible fraction of municipal solid waste; and to evaluate the impact of mixing, addition of seed sludge and buffer materials, and recycling of digested residue to accelerate the batch process.

2) evaluate the feasibility of using the horizontal rotary reactor (HRR) in terms of:

- biogas production
- stabilisation of the organic fraction of MSW
- movement of the substrates inside the reactor

3) develop and use a simple and economical lab. scale reactor, the vertical sequential reactor (VSR), for the determination of both the optimum recycling ratio of final digested solids materials (DRR), and the optimum recycled leachate, in terms of methane production, methane yields and volatile solids reduction during semi-continuous operation.

4) monitor the impact of changing operating conditions, such as loading rate and moisture content on the efficiency and stability of the processes.

5) evaluate the impact of forced-air aerobic treatment on the final digested materials.

6) develop a mathematical model for the semi-continuous vertical sequential reactor with a view to optimising overall reactor efficiency.

The scope of this study was to evaluate the high solids anaerobic digestion of the organic fraction of MSW under all of the above stated environmental (35°C) and operational (OLR, TS) conditions. This evaluation was carried out using various reactor designs and two operational modes.

CHAPTER 4

EQUIPMENT DESIGN AND DEVELOPMENT

4.1 Horizontal Rotary Reactor (Batch).

Mixing enhances the performance of the anaerobic digestion process by improving the contact between micro-organisms and substrates, which enables them to obtain carbon and nutrients more rapidly. Mixing by means of rotation was reported to be the method used in aerobic composting plants utilising Dano drum technology, which is probably the most widely adopted rotating drum composting method (Pescod, 1991). However, the application of a rotating drum to anaerobic digestion has to overcome many obstacles, such as extracting biogas and heating the reactor contents while rotating. This innovative approach, used in the present work, tried to overcome such difficulties in laboratory-scale experiments, as well as ensuring adequate mixing.

A cylindrical drum reactor was constructed from PVC and was 1 metre long and 0.3 metres in diameter. During operation, the reactor was rotated at 3 rpm around a shaft positioned at the centre of the drum, as indicated in Fig. 4.1 and 4.2. A variable speed AC motor (Crompton Parkinson) was used to drive a V-Belt drive consisting of two pulley wheels and a V-Belt. The first pulley wheel was bolted to an end plate on the reactor and the second was keyed into the gear box unit. The motor was attached to a gear box which controlled the speed of rotation at 3 rpm.

Biogas was collected through 3 millimetre holes located under fine mesh at both ends of the shaft inside the drum. A gas sealing joint

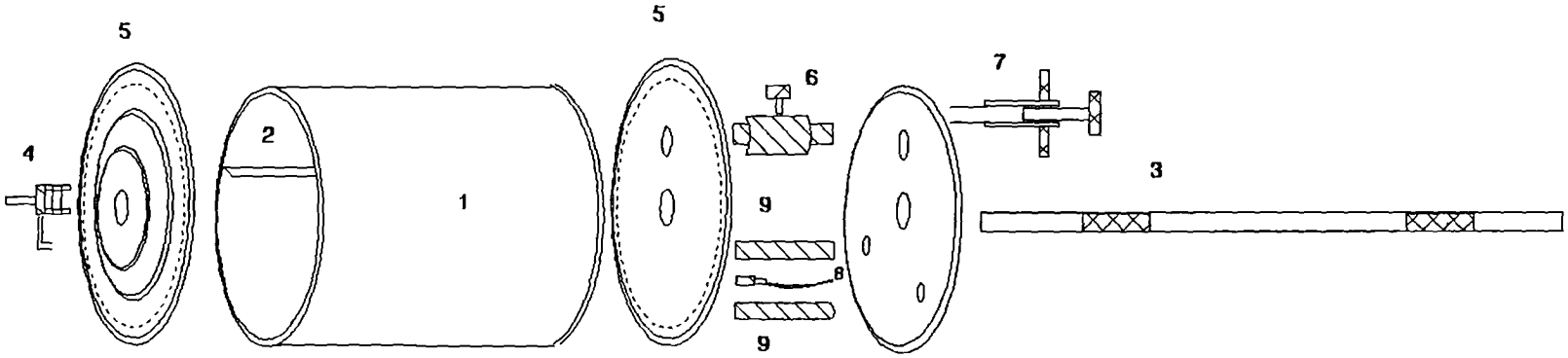


Fig. 4.1 Detailed Reactor Design of Horizontal Rotary Reactor (Batch)

1. P.V.C. Drum (1*O.3m diameter)
2. Two Parallel Fins
3. Shaft with 2.3mm Holes Under Mesh
4. Gas Sealing Joint
5. Drum End Plate
6. Ball Valve
7. Sample Extracting Rod
8. Gas Connecting Pipe
9. Holders

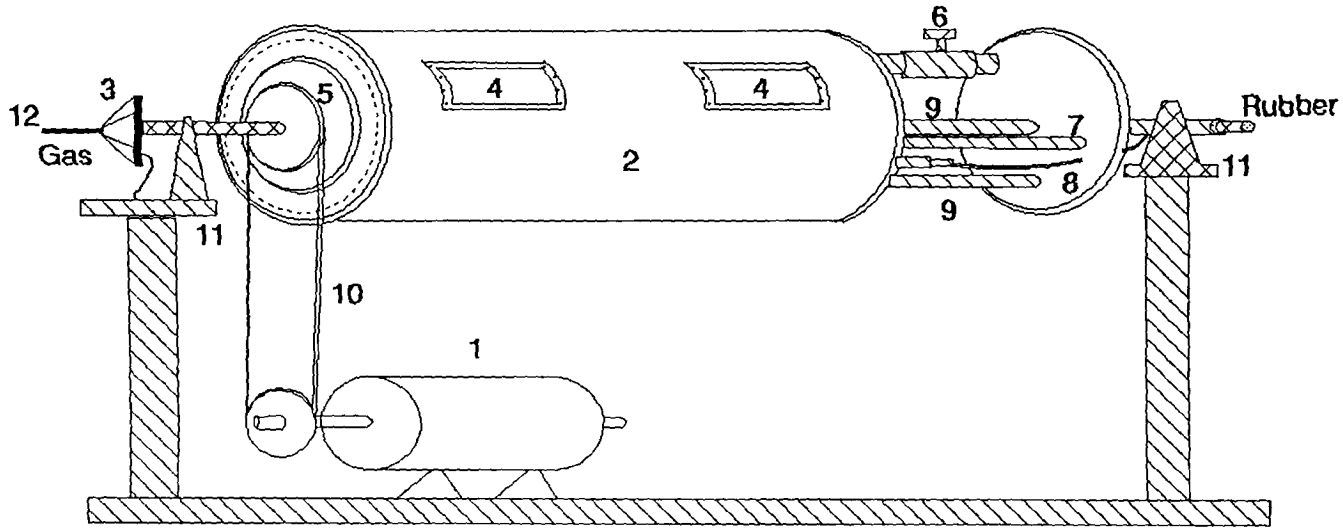


Fig. 4.2 Horizontal Rotary Reactor

1. A.C. Variable Speed Motor & Reduction Gear Box
2. P.V.C. Drum (1m long, 30cm diameter)
3. Gas Sealing Joint
4. Stainless Steel Cover (300*250mm)
5. Pulley Wheel & "O" Ring Seals
6. Ball Valve
7. Shaft
8. Gas Connecting Pipe
9. Holders (Supporters)
10. V-belt Drive
11. Bearing Mounting
12. Gas Outlet

enabled the transfer of gas whilst the reactor was rotating (Fig. 4.3). The joint consisted of a bearing-housing and a sealed bearing inside the housing. The housing was attached to a fixed point, which enabled the shaft to rotate and the gas to be collected. The reactor had an effective volume of 30 litres because the capacity available was only the volume beneath the shaft, in order not to block the gas path. Due to blockage of the vent holes at later stages of the experiments, the gas was collected through a ball-valve that was first sealed by a rubber bung. During the batch experiment, a weekly digesting solids sample was taken by a Sample Extracting Rod.

4.1.1 Sample Collection Device.

Samples of digested solid materials were taken through the ball-valve by a stainless steel sample rod (Fig. 4.4) with a plunger which was retracted when the rod was inserted to collect the sample. The external part of the rod moved through two oil seals to prevent air entering the reactor. There were also two oil seals in a housing before the ball-valve.

The plunger was completely sealed against the inside of the hollow rod when the rod was inserted into the drum via the ball-valve. When the plunger was extracted, it created a vacuum which collected the sample. The rod was then extracted initially only as far as the end of the ball-valve, which then closed, after which the rod was extracted further and removed.

4.1.2 Difficulties Associated with the Horizontal Rotary Reactor.

The electrical wiring for the thermal blanket controlling the temperature

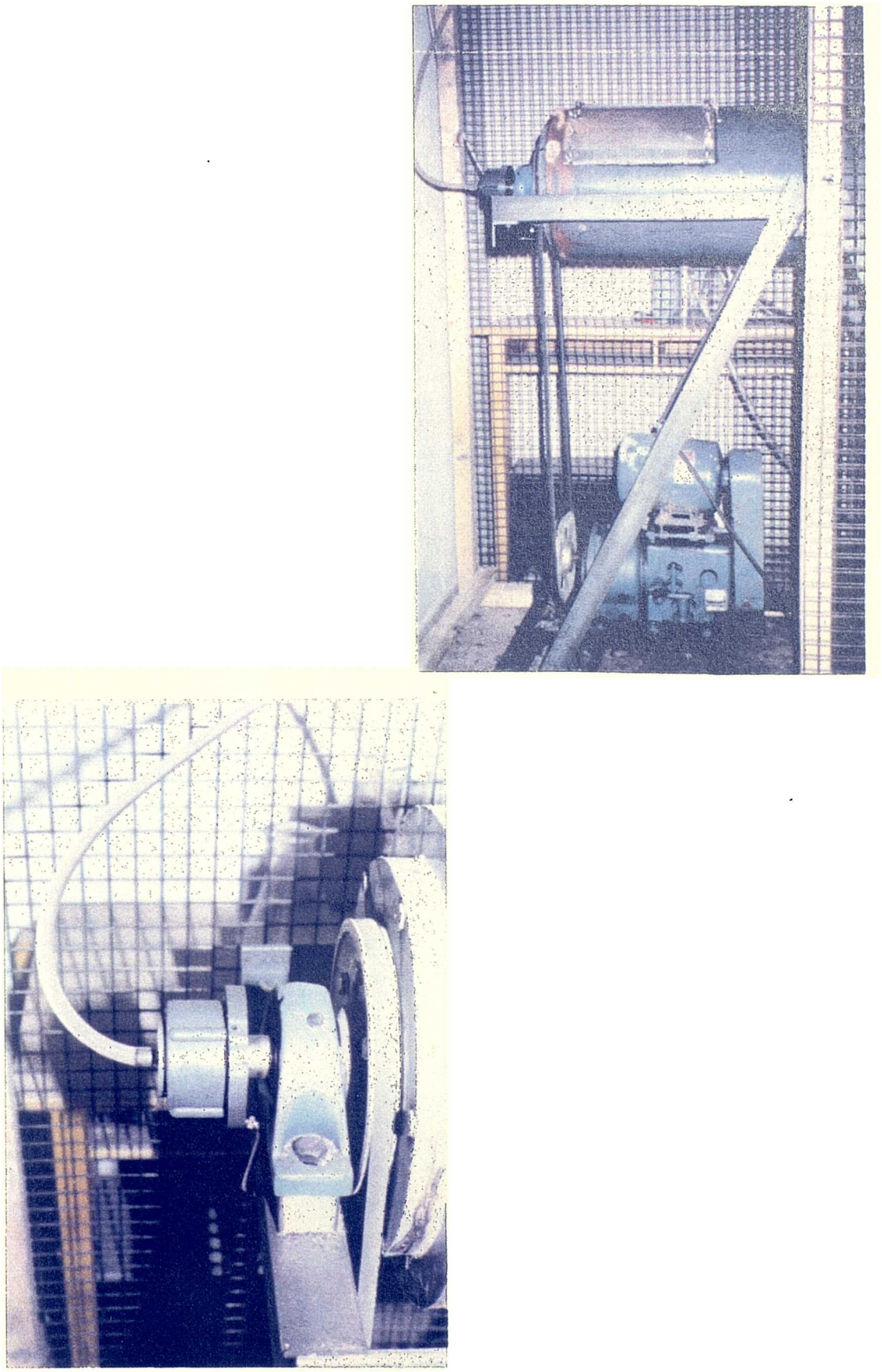


Fig. 4.3 The Gas Sealing Joint and Biogas Outlet

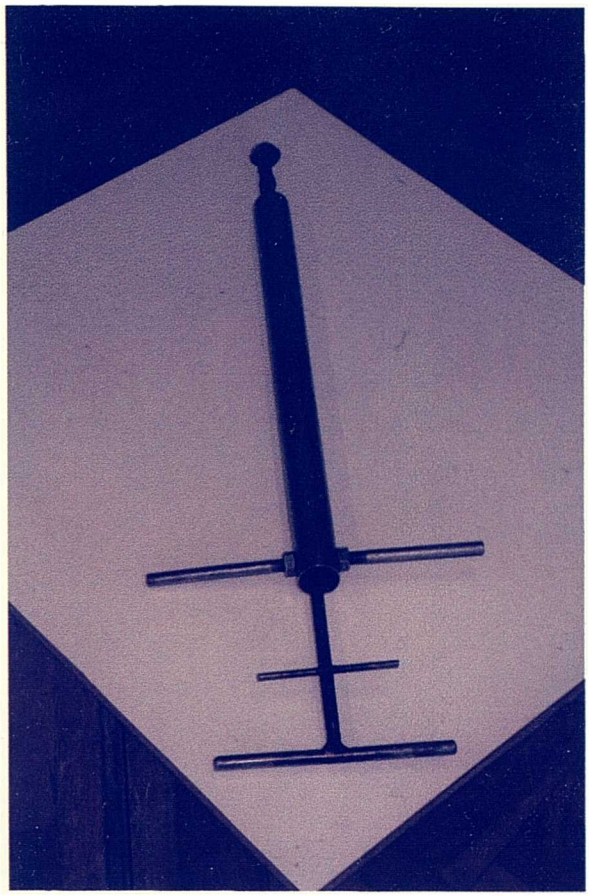
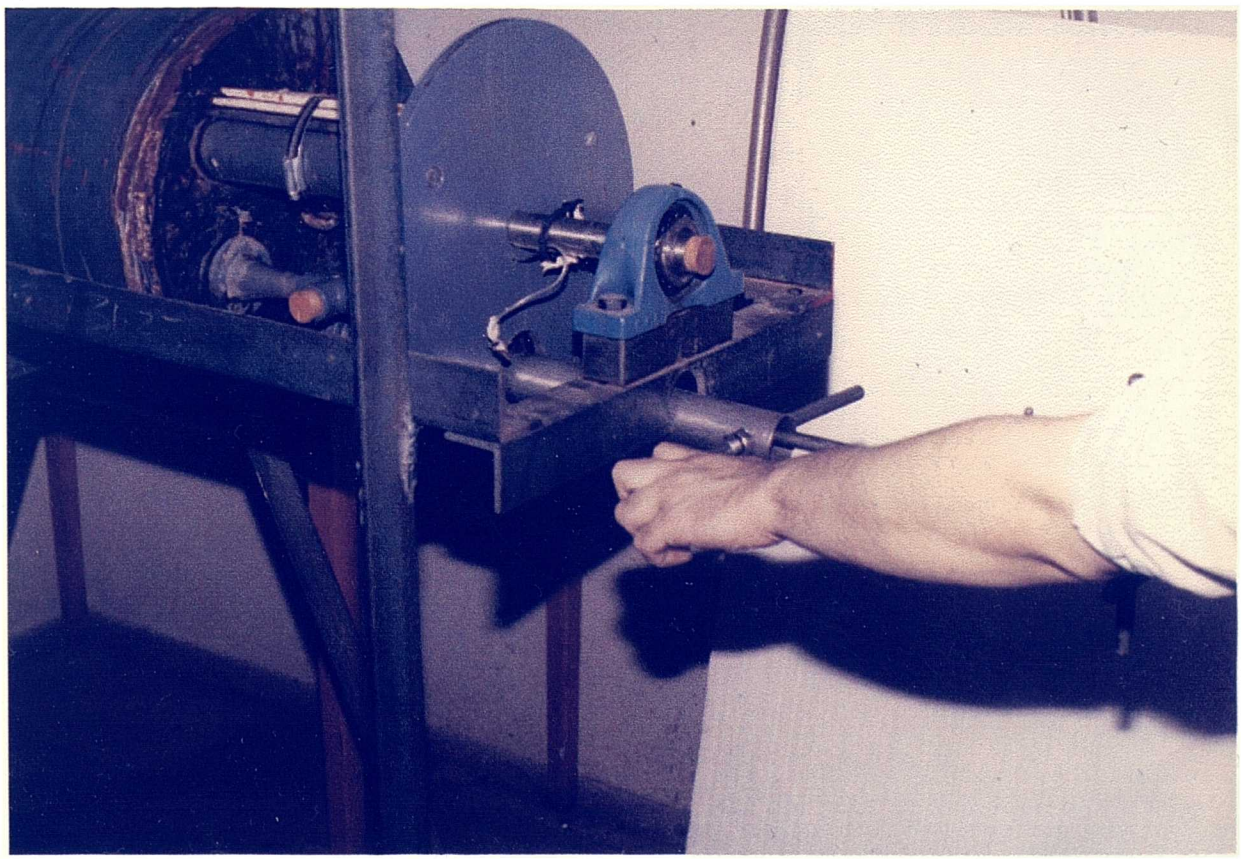


Fig. 4.4 Sample Extracting Rod



while the drum was rotating, proved to be very difficult to manage. The solution was to operate the reactor in a room controlled at a temperature of 35°C. There was frequent blockage of gas outlet (holes) due to the glutinous nature of the digested solids materials.

4.2 Horizontal Rotary Reactor (Semi-Continuous).

This reactor was basically the same as the design used in the batch experiment, except for the modifications stated below:

Due to frequent blockage of the gas outlets (holes) at the shaft, a connecting pipe was fitted from the side wall of the drum to the external part of the shaft and, in addition, the mesh covering the holes was removed.

For samples taken during the semi-continuous experiment, loading and unloading apertures were constructed to make sampling more feasible (Fig. 4.5). Samples were taken by a Sample Collecting Chamber which was fitted and sealed with rubber. The front side of the Sample Collecting Chamber had a transparent viewing window to enable removal of the aperture, sample removal and aperture replacement (Fig. 4.6). Meanwhile, nitrogen gas was injected through a tube at the top of the Sample Collecting Chamber to flush out air that might have entered during the sampling procedure.

4.3 Vertical Conical Reactor.

This reactor was developed to compare it, as a non-mixed reactor, with the horizontal rotary reactor. It was also developed to evaluate the

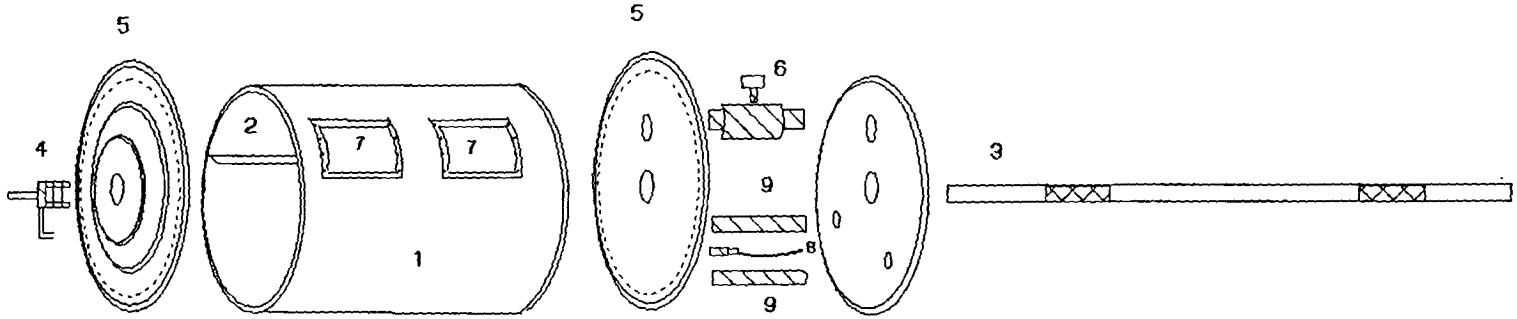


Fig. 4.5 Detailed Design of Horizontal Rotary Reactor (Semi-Continuous)

1. P.V.C. Drum (1*0.3m diameter)
2. Two Parallel Fins
3. Shaft with 2.3mm Holes Under Mesh
4. Gas Sealing Joint
5. Drum End Plate
6. Ball Valve
7. Stainless Steel Cover
8. Gas Connecting Pipe
9. Holders



Fig. 4.6 Sample Collection Chamber for the Semi-Continuous Phase of the Horizental Rotary Reactor Research

suitability of a conical shaped reactor for a high solids anaerobic digestion process.

The PVC Conical Reactor was 1 metre long and 0.3 metres in diameter. The conical shape at the bottom of the unit was to guide the solid material towards the neck of the vessel without creating a dead zone in the lower corners of the reactor (Fig. 4.7).

The provision of two gate valves in sequence at each end of the reactor was to prevent air from entering during loading and unloading the reactor. Only one valve was opened at a time whilst the other was closed.

Design Problems.

The movement of solid materials from the vertical conical reactor proved to be very difficult, even when applying pressure with Nitrogen gas, due to the glutinous nature of the materials. Leakage of gas occurred in the early stages and prevented the gas from being collected. The source of the leak could not be detected at the time. Only after dismantling the reactor, a crack was found in the inner wall, which might have been the result of applying too much pressure to move the solid materials. At the time, the decision was made to continue with the experiment to obtain stable digested materials to be used in further tests, whilst developing the Vertical Sequential Reactor which allowed for enhanced solid materials movement. It took more than 5 months to design, develop and construct the Vertical Sequential Reactor to be used in the semi-continuous mode. This type of reactor proved to be more suitable for the digestion of waste with low total solids content.

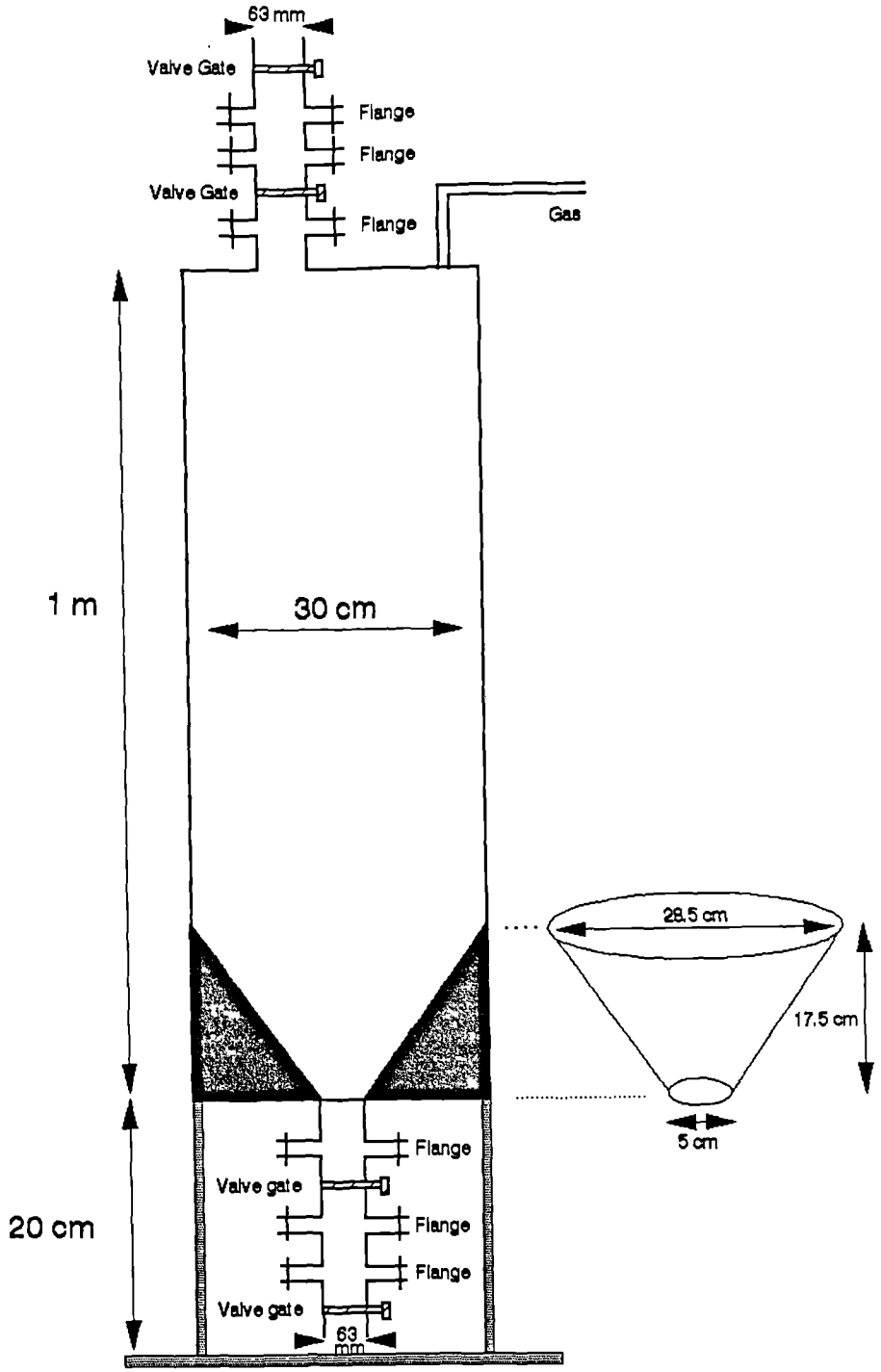


Fig. 4.7 Schematic Layout of Vertical Conical Reactor

4.4 Vertical Sequential Reactor.

This novel vertical sequential reactor was designed and developed for the following reasons:

-To enable a practical semi-continuous operation which allowed for easier movement of the reactor solids content to overcome the solids movement difficulties that were experienced with the previously described vertical conical reactor.

-To facilitate compartment stages of the anaerobic digestion process for the purpose of studying the internal activities of biodegradation.

-To determine the actual solids retention time.

-To accommodate simultaneous leachate treatment within the same unit.

This reactor consisted of six PVC cylindrical chamber units (containers) with each container having a capacity of 6.4 litres, with a 9 litre leachate collection container located at the base of the reactor. The chamber unit (Fig. 4.8) had a 12 millimetre mesh held by an extension of the flange at the base of the unit and a rod insertion point which enabled the chamber to be lifted by lifting gear.

The chamber units were joined together with 12 bolts located at 5 centimetre intervals in the flanges at each end of all the units. The units were sealed with rubber rings. The reactor was held in place by guiding and lifting rods on either side of the steel frame housing (Fig. 4.9).

Each run comprised a cycle of six units with a sequence cycle continuing for 24 days. In order to remove the last container, five of the chamber

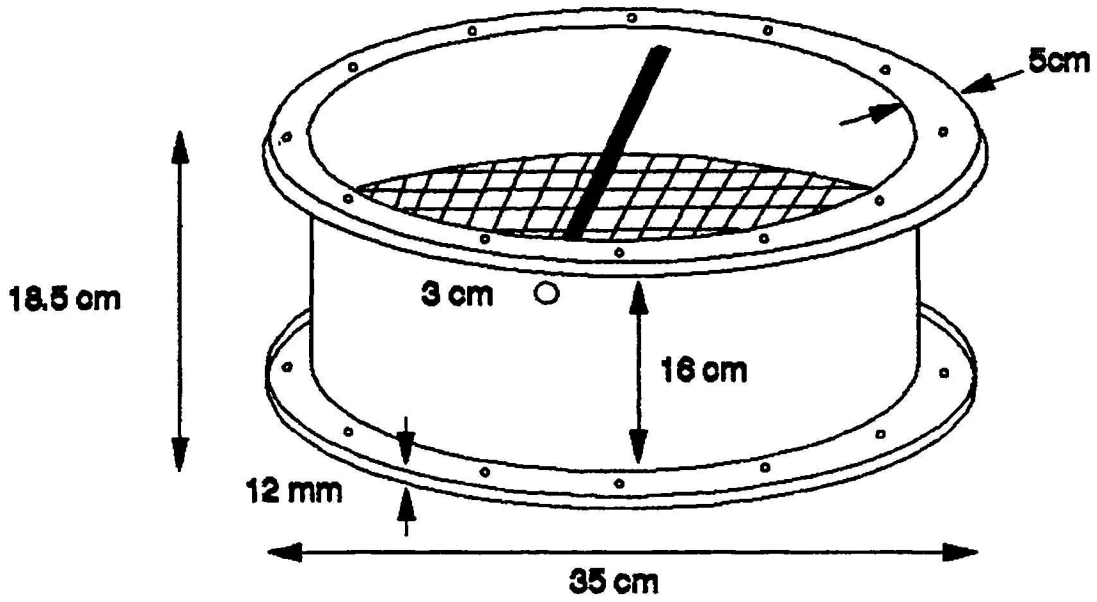




Fig. 4.8 Cylindrical Chamber Unit with Mesh Base



Fig. 4.9 Components of the Vertical Seqential Reactor

units had to be lifted by lifting gear located on either side of the steel frame. In-turn chamber 6 became chamber 1 and so on. The gas was collected from the top of the reactor via a pipe leading to a gas meter after it had passed through a water-trap.

This reactor provided a simple and economical method for the movement of high solids content materials at this scale of operation. It also produced a leachate without the need for pressing equipment.

Operating Procedure.

The following procedure was carried out once every 4 days for a complete cycle of 24 days (Fig. 4.10):-

1. . The 12 bolts in both ends of the sixth (last) chamber unit were unlocked.

2. . The lifting rod was placed in the centre hole of the fifth unit.

3. . The guide rod was placed in the centre hole of the first unit.

4. . The unit was raised upwards by the lifting gear (Jack).

5. . The sixth unit (24 days retention time) was removed.

6. . The leachate was drained from the base unit.

7. . The lifting gear was reversed (downwards).

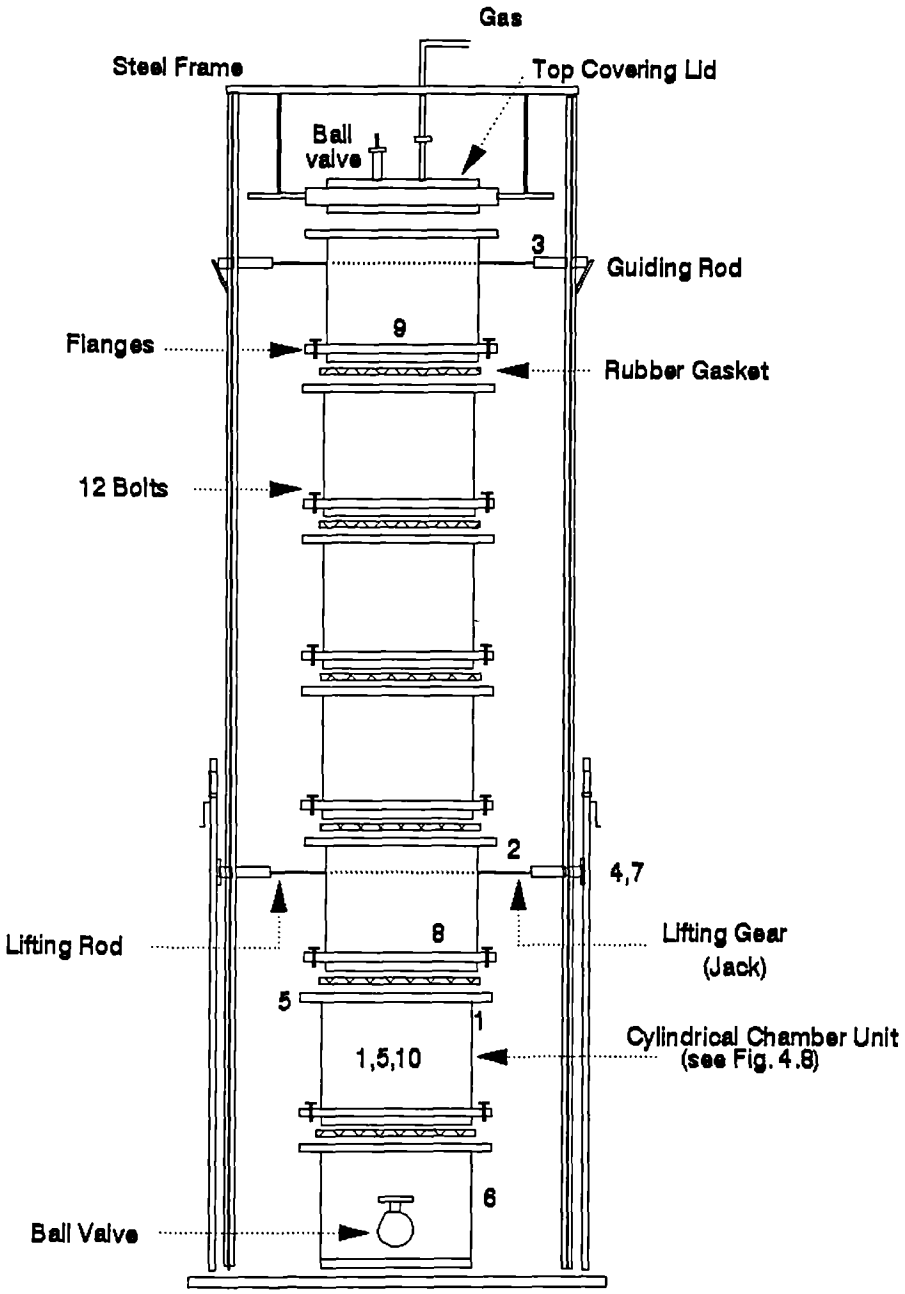


Fig. 4.10 Schematic Layout of

Vertical Sequential Reactor

8. The fifth unit was bolted to the base.

9. . A solids sample was taken from the first unit (4 days retention time).

10. The sixth unit was replaced, after loading, at the top of the reactor.

11. The reactor was sealed with the top cover lid.

12. The reactor was flushed with Nitrogen gas for ten minutes to flush out the air.

13. The gas meter was connected 2 hours after loading.

4.5 Forced-Air Composting Reactor.

The forced-air composting reactor was constructed of PVC and was 1 metre long and 0.3 metres in diameter (Fig. 4.11). Near the base of the reactor was a perforated plate with 3 millimetre holes in a radial pattern which allowed the air to pass through. The air passed through a gate valve located under the perforated plate which also assisted in the removal of liquids that resulted from dewatering of the material prior to starting the composting. Air passed out through a thin pipe from the top lid of the reactor to a flow meter. The air flow rate was fixed at 1.7 cubic metres per day. Three thermometers were installed in the reactor, two separate

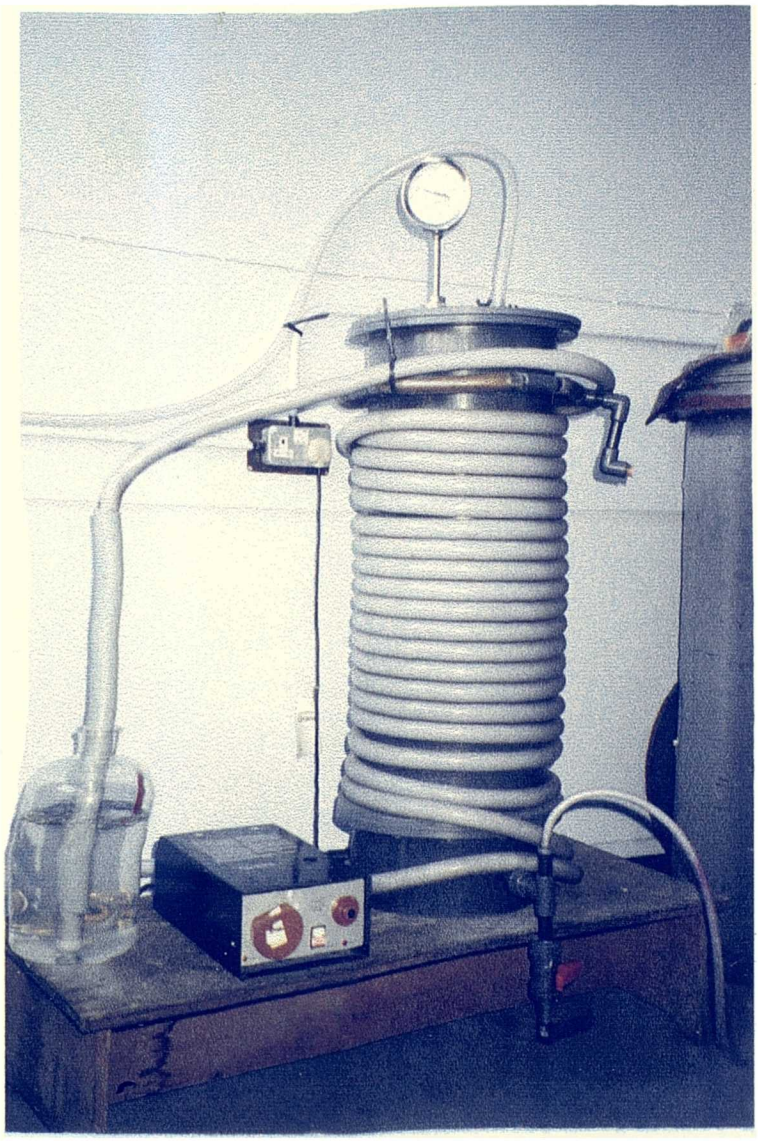


Fig. **4.11** Forced Air Composting Reactor

thermometers near the base and one at the top of the reactor, housed inside an insert pipe (Fig. 4.12). Around the reactor, a thermal jacket was wrapped to maintain the reactor temperature at 35°C.

4.6 Heating System.

In order to maintain the room temperature at 35°C, a heating system was installed. The heating system consisted of a 3Kw convector heater which was controlled by an Omrone 5C temperature controller. The temperature sensor was a 100Ω resistance thermometer. A variable transformer was used to power a small coiled heater which warmed the air intake to the room, so that external fluctuations did not affect the room temperature.

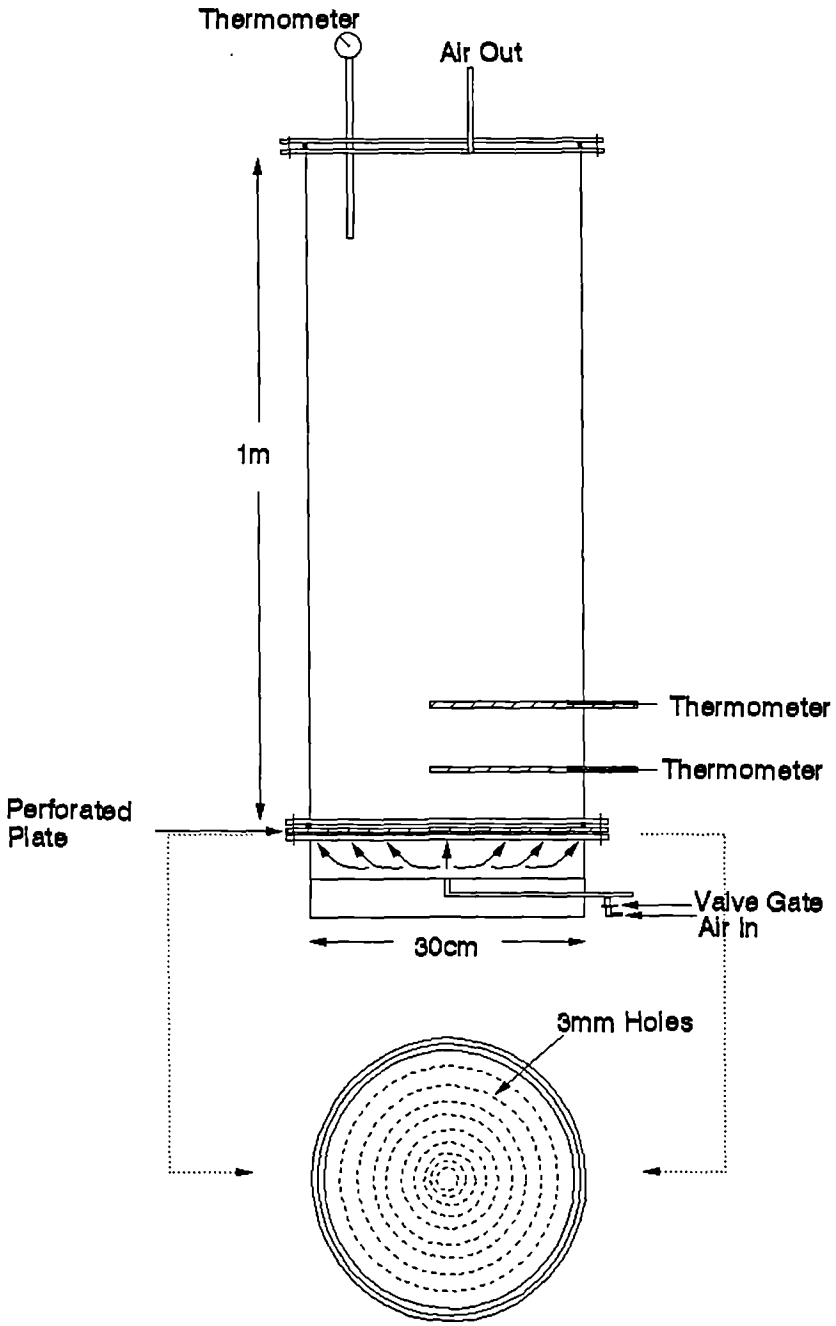


Fig.4.12 Schematic Layout of Forced Air Composting Reactor

CHAPTER 5

MATERIALS AND METHODS

5.1 The Source of the Organic Fraction of MSW.

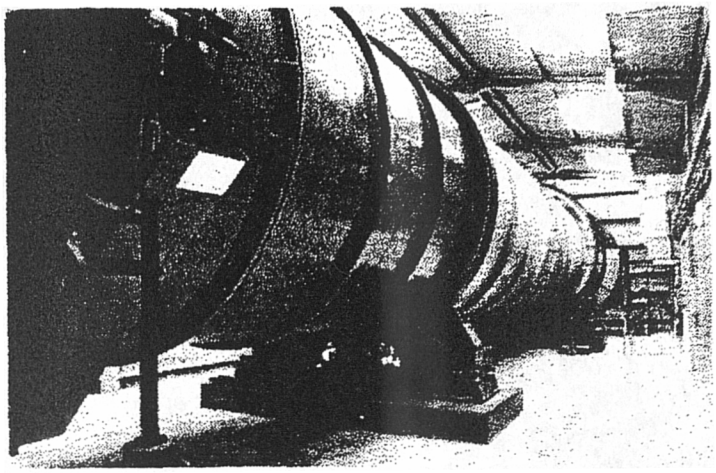
The organic fraction of MSW was obtained from a refuse treatment plant at Anglesey (Fig. 5.1). At the time when samples were collected, the plant was operated as follows:

- The bulky items not suitable for pulverisation were removed manually from the received refuse.
- The rest of the waste was fed into a hydraulic ram feeder located directly in line with the Dano pulverising drum
- The raw refuse was loaded into the drum by means of a hydraulically-operated push-plate.
- The Dano drum consisted of a horizontal steel drum 24 metres long by 3.79 meters internal diameter. and rotated at approximately 3.5 rpm.
- Water was added to the refuse to soften the paper and cardboard. The constant collision of harder materials with the softer materials and contact with the walls of the pulveriser broke down the refuse into small fragments.
- The refuse travelled through the drum over a period of 4 - 6 hours and fell into a double rotary screen which separated the materials into two grades (above and below 38 mm). The materials which were larger than 38 mm consisted of large inorganic components not capable of being broken down (Anglesey Borough Council Brochure, 1988).

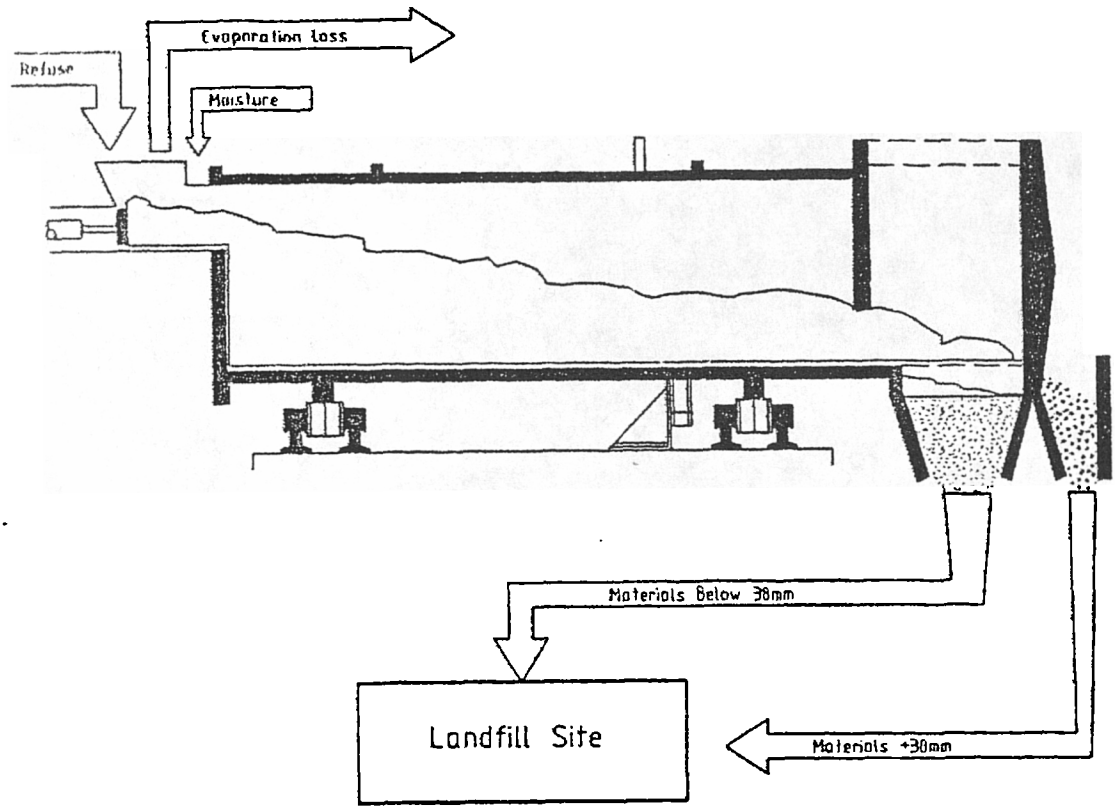
The fine materials less than 38 mm particle size were the subject of this research. Table 5.1 gives the approximate composition of these fines

Table 5.1: The Approximate Composition of Dano Fines According to Particle Size (Anglesey Borough Council, 1988).

Particle Size (mm)	Weight (%)	Organics (%)	Glass (%)	Plastics (%)	Others (%)
<38 to ≥23	2.86	0.66	1.2	0.44	0.57
<23 to ≥18	4.81	2.6	1.2	0.47	0.54
<18 to ≥11	14.52	9.6	3.59	0.35	0.98
<11 to ≥6	29.92	25.57	2.65	0	1.7
<6	47.88	47.09	0.79	o	0
Total	100	85.54	9.42	1.26	3.78



View of Dano Drum



Screen and Conveyors

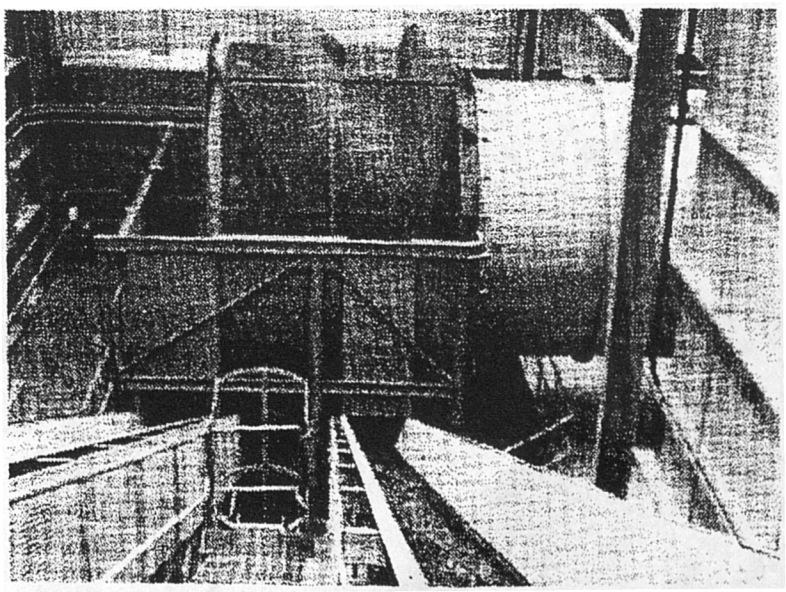


Fig. 5.1 Refuse Treatment Plant at Anglesey

(relative to particle size), which were separated manually at the Anglesey Plant, using a sample of around 3.2 kg obtained during the winter season.

5.2 Source of Seed Sludge.

The digested sludge that was used as an inoculum during the initial start-up of the processes was obtained from Barkers Haugh Sewage Treatment Works, Durham, and was collected from the recycling pumps. A further preparation of the collected digested sludge was subsequently needed, due to some operational problems that were encountered at the treatment plant at that time. The digested sludge was centrifuged at 2000 rpm for 30 minutes (MSE, GF.8). It was then placed into two five-litre reactors inside a room with temperature controlled at 35°C for three days. Around 20 grams of whey powder was fed to each bottle daily. A stirrer was used to mix the contents of each reactor. By the end of the third day, the methane content of the biogas reached more than 70%.

5.3 Feed Stock Preparation.

Three shipments (around 60 kg each) of the pulverised materials were collected to be used in the initial testing and in the batch experiments. Prior to the start of the semi-continuous operation, an arrangement was made with the plant manager at Anglesey to mail a weekly shipment of 20 kg of refuse placed in a plastic bag inside a sealed container. The transportation time was 2-3 days. The refuse was then put through a 12 mm mesh sieve to collect large glass, stones, plastics, metals, and other inert particles. Fig. 5.2 shows samples of both used and rejected portions of the received refuse. The sieved refuse was packed in plastic bags and stored at 4°C until loaded into the reactors. Unfortunately, early in the





A: Rejected

B: Used



Fig. 5.2 Sorting of the Pulverise Materials (A: Rejected, B: Used)

experiment, the plant in Anglesey was closed down and a shipment of around 400 kg had to be collected and stored in a freezer. Before use, a bag of refuse was defrosted for two days at 25°C. After defrosting, the whole bag was sieved and weighed to obtain the required amount for feeding the reactors. The rest of the sieved refuse was kept in the cold room to be used for later loadings. The fine pulverised materials received were very difficult to separate into different components. The rejected part (after sieving) was in the range of 20 to 30% of the total wet weight received. The remaining refuse contained up to 10% small stones and glass particles that could not be removed; it was only after the sieving of the ash that they were recovered. Table 5.2 gives the approximate physical composition of the refuse sample sorted once during the initial testing period, using 10 kg of refuse.

The mean moisture content, throughout the project, was 58% of the total refuse weight, with a range between 53 and 62%. The nature of the refuse changed with season. During spring and early summer more vegetable materials were present. As the waste was collected mainly from farming communities, it included plant and animal waste as well as domestic waste.

5.4 Sampling Procedures.

Different sampling procedures were used throughout this work, due to the variety of samples and experiment types involved. A summary of the sampling procedures, according to reactor type, is given below.

Table 5.2 Approximate Physical Composition of the Refuse Sample Sorted during the Initial Testing Period of this Study

Constituent	Percentage Weight (wet)
Fine Organic (Food and Vegetable)	68.6
Glass	15.4
Papers	5.5
Plastics	2.3
Other (Metals, Bones, Stones, etc.)	8.2
Total	100

5.4.1 Samples from the Horizontal Rotary Reactor.

Batch run.

A sample of around 50 grams of solids was extracted weekly for analysis.

Semi-Continuous run.

A sample of 100-150 grams of solids was taken from the inlet aperture, and about 300 grams from the outlet aperture. The contents of this reactor were very heterogeneous due to good mixing, therefore a small sample (even less than the 50 grams that was taken) was considered adequate

5.4.2 Samples from the Vertical Conical Reactor (Batch Run).

Because of design limitations, only leachate samples were collected. About 100 ml of leachate was obtained weekly.

5.4.3 Samples from the Vertical Sequential Reactor (Semi-Continuous).

Both solids and leachate samples were obtained from this reactor every four days. Solids samples around 400 grams were taken from the last chamber (24 days RT), and between 100 and 150 grams from the first chamber (4 days RT). At the same time, leachate samples of around 150 ml were taken from the base unit. At the end of each run during the second phase (leachate study), approximately 150 grams of solid sample were taken from chamber units 1 to 5 for different retention time analyses.

5.5 Solids Sample Preparation.

Two different water extraction methods were applied in this work to obtain liquid that could be used in the analyses. The first method used the wet solids directly , while the second method used the dry solids that were diluted with known amounts of distilled water. Because of the time and

equipment limitations involved in handling many samples at once, it became clear that this second method was needed, to preserve the samples.

5.5.1 Water Extract from Wet Solids Samples.

To extract liquid from the wet solids sample, an equal amount of distilled water was added to the wet solids sample. The sample was then mixed manually for about five minutes and pressed by a garlic pressing device prior to filtering. The filtered liquid obtained was then used to carry out the analyses for VFA, pH, and Ammonia-Nitrogen. For VFA determination during the batch HRR study, this was the principal method used.

5.5.2 Water Extract from Dry Solids Samples.

After removing the stones and the glass from the sample solids the dried solids were blended, to improve the homogeneity and representative character of the sample, in a Moulinex blender for about 20 seconds. The sample was then passed through a fine sieve to obtain powder form materials and to remove as much inert matter as possible. Most of the sample was extracted with water, the rest was used as solids for total COD, TKN and solids elemental analyses. For total COD determination, ten to twelve milligrams of powder form solids were used directly as a sample. For TKN and elemental analyses (C, N, H), the required amount for sampling was also taken from the powder form solids. Several authors have used the principle of water extraction for the analyses of dry solid samples of compost, as an indication of the potential leachate quality.(Hirai et al., 1983; ETCL, 1989).

In the present study, the following procedures were performed to obtain the liquid from dry solids samples :

- A known amount of distilled water (150-900 ml) was added to a known amount of dry weight (20-120 grams).
- The sample was shaken and mixed for 24 hours in a sealed bottle by an orbital mixer (Denlex).
- The sample was then left to settle for half an hour before filtration.
- The filtered liquid was then used to carry out the required analyses for VFA, pH, Filter COD and Filter P.

The water extract from solids samples method was found to be not suitable for the determination of ammonia-nitrogen, due to heat related evaporation of ammonia during total solids determination.

5.6 Analytical Methods and Procedure

The analyses were carried out according to Standard Methods (1989). Table 5.3 gives a summary of the parameters and analytical methods and a list of the instruments that were used for the analysis. The main instruments used and their description are presented in Appendix A1.

5.6.1 Total Solids Content.

Total solids content was determined by drying five duplicate samples to constant weight at 105°C in an oven. The time required for drying varied from 18 to 24 hours. The difference in weight between the initial sample and dried sample divided by the initial sample weight, represents the total solids in the sample (%).

Table 5.3 Summaries of the Parameters and Analytical Methods, and List of Instruments Used for the Experimental Analyses.

Parameter	Method	Instrument	Frequency	
			Batch	Semi-Con.
Total Solids	Gravimetric	Oven (103°C)	Weekly	2X/week
Volatile Solids	Gravimetric	Furnace (550°C)	Weekly	2X/week
COD	Dichromate Reflux	Reflux Apparatus	Weekly	2X/week
pH	Glass Electrode	Corning pH meter	Weekly	2X/week
Volatile Fatty Acids	Gas-Liquid Chromatography	Pye UNICAM 304	Weekly	2X/week
Ammonia - Nitrogen	Distillation/Titration	Kjeldahl Apparatus	Weekly (Both)	
Total Nitrogen	Distillation/Titration	Kjeldahl Apparatus	Weekly (Both)	
Phosphate	Ascorbic Acid	----------	as Required	
Metals	Atomic Absorption	PYE UNICAM with SP9 Computer	Occasionally (Leachate)	
Gas Production	Gas Meter	Alexander Wright Wet Gas Meter	Daily (Both)	
Gas Composition	Gas Chromatograph	Becker 403 Chromatograph	Daily (Both)	
Element (C, N & H)	Solids Elemental Analyser	Carlo Erba 1106	Occasionally (Both)	

5.6.2 Volatile Solids.

Total volatile solids analysis was performed by burning the oven dried sample to a constant weight of ash by heating at 550°C in a furnace. The temperature of the furnace was increased gradually to prevent the loss of ash by sudden ignition of the sample. The difference in weight between the dried sample and heated sample, divided by the weight of the dried sample, represents the total volatile solids in the sample (%).

5.6.3 Density.

The density was determined by placing the wet solid materials into a pre-weighed container with a known volume. The weight of the solid materials sample, divided by the container volume, represents the wet solid density (kg/m^3).

5.7 Calculations for the Conversion of the Results to mg/g.

5.7.1 Calculations for the Wet Solid Samples.

The calculation procedure was as follows:

i) A known weight of the sample was pressed to obtain the liquid using a garlic presser.

ii) Standard Methods (1989) was used to obtain the result in mg/l

iii) After the determination of the total solids of the samples (as a fraction of 1), the concentration of the samples was calculated as follows:

$$S_C = \frac{S_W * TS}{S_W * (1 - TS) + D_w} \qquad (5.1)$$

Where, S_C = sample concentration (mg/l),

S_W = sample weight (g),

TS = total solids of the sample (as a fraction of 1),

(1 - TS) = moisture content of the sample (%),

D_W = Distilled water (ml)

iv) The result in mg/l was converted to mg/g, using the following equation:

$$R\ (mg/g) = \frac{R\ (\frac{mg}{l})\frac{1l}{1000ml}}{S_C(\frac{g}{ml})} \qquad \textbf{(5.2)}$$

Where, R is the result of the analysis.

5.7.2 Calculations for the Dry Solids Water Extract Method.

i) The sample concentration S_C was calculated according to the initial dilution (g/ml). For example, from the procedure in section 5.5.2, 150 ml of distilled water was used to dilute 20 grams of dried solids sample.

ii) After obtaining the results, the analysis for the filtered liquid (mg/l), equation 5.2, was used to convert the results to mg/g.

CHAPTER 6

START-UP AND BATCH EXPERIMENTS

6.1 Start-Up and Operation of a Batch Process Using the Horizontal Rotary Reactor.

6.1.1 Introduction.

The stability of the process depends upon the start up of the reactor, when an equilibrium between the acidogenic and methanogenic phases has to be achieved. For the start up of dry batch digestion of the organic fraction of municipal solid wastes, the addition of a high amount of methanogenic seed, such as digested sludge, and buffer to prevent unbalanced digestion is essential, with a recommended initial buffer to feed ratio of 0.025-0.2 (Buivid et al., 1981; Ten Brummeler and Koster, 1989). Rapid degradation of the easily degradable materials, which form at least 9% of the VS in municipal solid waste, causes an imbalance in the dry anaerobic digestion process (Ten Brummeler and Koster, 1990). The imbalance occurs due to rapid formation of lactic and acetic acids which results in a pH drop. Acid formation starts within 2 hours when the organic fraction of municipal solid waste is digested at 35% TS without the addition of a methanogenic seed to the process (Ten Brummeler et al., 1991). The amounts of methanogenic seed and buffer required depend on the nature of the organic materials in the waste. Initial testing or further addition might be required.

The parameters used to measure the stability of the digested materials include volatile solids (VS), volatile fatty acids (VFA), and the carbon to nitrogen (C/N) ratio. Digested materials with volatile solids reduction of

around 55% and a volatile fatty acids concentration of less than 1 g/l as COD are defined by Ten Brummeler et al., (1988, 1991) as an adequate indicator of the completion of the digestion process. A carbon to nitrogen ratio of less than 20 is considered an indicator of process stability. De Baere et al. (1985), specified a C/N ratio of less than 18 for a stabilised compost. However, the C/N ratio as well as total VFA reduction depends on the initial values in the waste materials. Diaz et al. (1994), stated that this indication value of less than 20 does not apply to materials such as manure with initial lower C/N ratio. He also recommended an addition of nutrients when the C/N ratio is 40. The same argument can be applied for a given indication value for TVFA

6.1.2 Objectives.

The objectives of this batch test were to:

i) evaluate the horizontal rotary reactor (HRR) design.

ii) study the start-up and the performance of a batch process of dry anaerobic digestion of Dano pulverised refuse at 35% TS using the HRR.;

iii) obtain stable digested materials to be used in the semi-continuous experiments.

6.1.3 Operating Parameters.

i) Volatile Solids Utilisation.

The method used for the determination of VS reduction was based on the actual weight measurements of the initial wastes and the final digested materials. The VS reduction can then be calculated after the determination of VS content in both cases.

ii) Specific Biogas and Methane Yields.

Biogas and methane yields were calculated according to the initial volatile solids weight of the fresh refuse feedstock.

$$SMY_a = \frac{Q_{CH}}{R_W . TS . VS} \qquad (6.1)$$

Where,

SMY_a is specific methane yield (m^3/kg VS added),

Q_{CH} is methane production (m^3), and

R_W is refuse total wet weight (kg).

Also, biogas and methane yields were calculated according to the lost VS weight (kg) using to the following equation:

$$SMY_r = \frac{Q_{CH}}{VS_I - VS_F} \qquad (6.2)$$

Where,

SMY_r is specific methane yield (m^3/kg VS removed),

VS_I and VS_F are initial and final Volatile Solids (kg), respectively.

iii) Total and Filtered COD %.

Total and Filtered COD percentage Losses were calculated according to the following equation:

$$\text{Percentage COD Loss (\%)} = \frac{\text{Initial COD (mg / g)} - \text{Final COD (mg / g)}}{\text{Initial COD (mg / g)}} * 100 \qquad (6.3)$$

6.1.4 Experiment.

The Horizontal Rotary Reactor (Section 4.1) was loaded, through the Ball-Valve, with 18 kg of pulverised solid waste mixed with 4.6 kg seed sludge and 400g buffer materials. Table 6.1 gives the characteristics of the different components of the feed materials used to start-up the process. The reactor was then flushed with nitrogen gas for approximately 10 minutes.

6.1.5 Results and Discussion.

The initial start-up period showed a high increase in the concentration of volatile fatty acids and low pH values, which indicated a period of unbalance in the digestion process. These phenomena might have been the result of a lag or acclimatisation period for the methanogenic microorganisms to adapt to the new environment.

The initial pulverised materials used had a low pH value of 5.9 and a high concentration of TVFA of up to 15.9 mg/g (16.7 mg/l as COD). This concentration consisted of 51% acetic acid, 21% propionic acid, 13% n-butyric acid and 10% n-valeric acid. This might have been due to a relatively long transportation time (2-3 days) while the material was stored in a sealed container. This long transportation time allowed start-up of the digestion process and a high production of TVFA, especially during summer. Ten Brummeler et al. (1991) reported that, for the organic fraction of MSW, acid formation started within 2 hours under anaerobic conditions. Calculation to obtain VFA concentrations as COD equivalent values can be found in Appendix B2.

Table 6.1 Characteristics of the Initial Loading Materials Used for Start-Up of the HRR.

Feed Materials	Parameters	Units	Values
Refuse	Weight	kg	18
	moisture Content	% Weight	58
	Total Solids	% Weight	42
	Volatile Solids	%TS	64
	Total COD	mg/g	860
	Filter COD	mg/g	82.5
	Carbon	%TS	39.85
	Nitrogen	%TS	1.17
	Hydrogen	%TS	3.8
	C/N	--	34
	TCOD/TVS	---	1.34
Seed Sludge	Weight	kg	4.8
	Moisture Content	% Weight	97
	Total Solids	% Weight	3
	Carbon	%TS	40.76
	Nitrogen	%TS	4.91
	Hydrogen	%TS	5.76
	C/N	--	8.3
	Seed/Feed	wet weight	0.26
Buffer	NH_4HCO_3 Sodium Bicarbonate	g/kg TS	53
Mixture	TS	% Weight	35.2
	pH	----------	7.1

After addition of the seed sludge and sodium bicarbonate buffers, the pH of the mixture was 7.1. However, the pH dropped to 6 after one week and this was caused by a sudden accumulation of TVFA concentration. Despite the addition of the buffer materials and the seed sludge at start-up time, the initial period of the experiment showed a high increase in TVFA concentration and a drop in pH. The use of a higher quantity of seed sludge might have reduced the lag period. However, this higher sludge content would have resulted in the TS of materials in the process being lower than the required 35 %TS. Also, the addition of more buffer to control pH values might have caused toxicity to methanogenic bacteria due to the increase of Na^+ in the process.

This trend of TVFA increasing and low pH value continued up to the end of the second week of operation, when the highest value of TVFA was observed. The TVFA reached a value around 42 g/l as COD (55.6 mg/g), as shown in Fig. 6.1 and 6.2, respectively. This value was less than that reported to inhibit hydrolysis of organic compounds when the pH was between 5.5-7.0 and the volatile acids reached a maximum of 20-30 g/l (De Baere et al., 1985), or 50 to 60 g/l as COD (Ten Brummeler et al., 1988; Ten Brummeler and Koster, 1989), at pH between 5.5 and 7.0. Conversion of VFA Concentrations from mg/l to mg/g is given in Appendix B3.

The TVFA decreased in the batch reactor slowly over the next three weeks. At the same time, the pH started to increase until it stabilised near neutral values after five weeks of operation, as seen in Fig. 6.3. A period of high biogas production of up to 40 l/d was observed in the first four days of the experiment, with biogas composition of mainly carbon dioxide

Fig. 6.1 VFA (mg/g) Relative to Time for the First Start-up of HRR

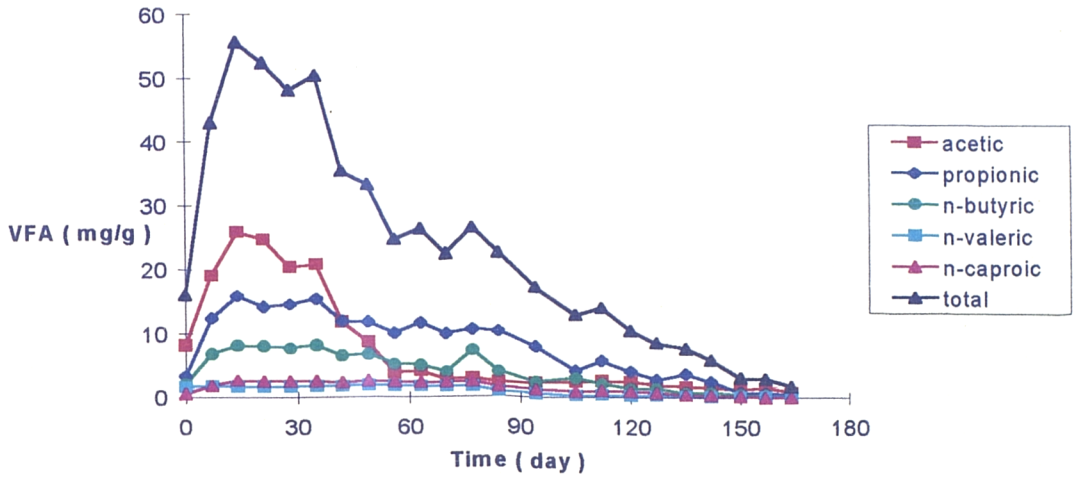


Fig. 6.2 VFA (g/l as COD) Relative to Time for the First Start-up of HRR

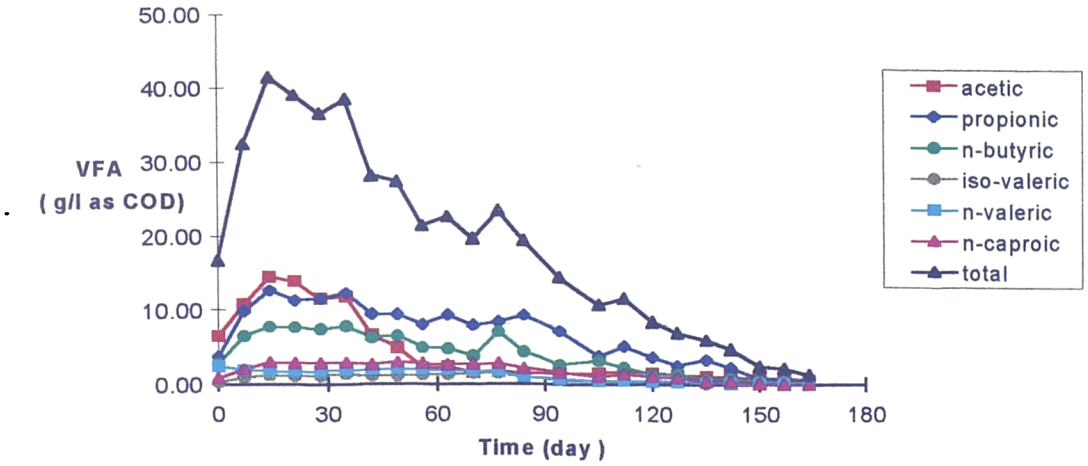
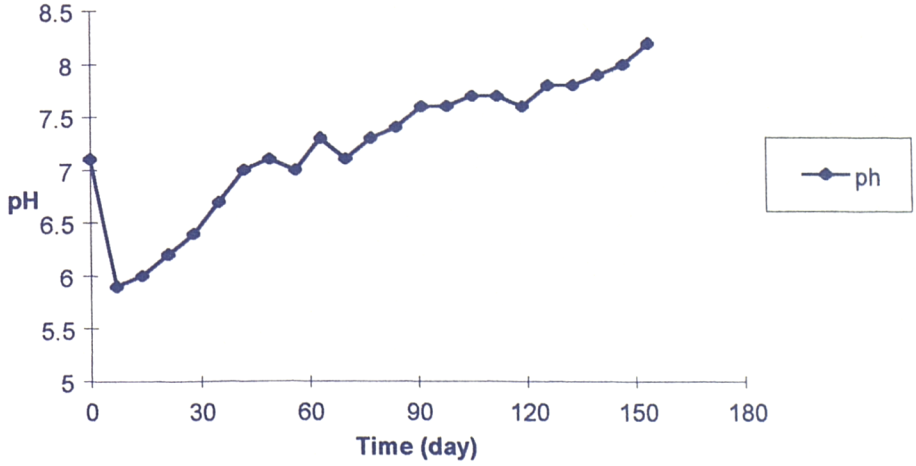


Fig. 6.3 pH Relative to Time for Batch HRR Experiment



and nitrogen. Biogas production dropped at day five to 7 l/d and remained within the range of 4 to 10 l/d until day 33 when it started to increase. Meanwhile, a methane content in the biogas of almost 10% was reached within a week of operation. The low biogas production recorded in this period might have been the result of the sudden increase of propionic acid concentration. McCarty and Brosseau (1963), reported that a rapid increase in propionic acid concentration, to levels of 3 to 8 g/l, hindered gas production for up to one or two weeks before it returned to normal production (Section 2.4.4).

The methane content of the biogas increased gradually with time, as seen in Fig. 6.4, while carbon dioxide tended to decrease. A decrease of about 20% of acetic acid concentration was noticed between day 14, when the maximum value of 25.9 mg/g (14.6 mg/l as COD) was reached, and day 35. Then, a sudden increase of methane content in the biogas, up to 37%, occurred. The peak biogas and methane production period was between day 66 and day 90 and lasted for 24 days. On day 71, gas production reached the highest level during this period (29 l/day), with a methane content of 56%. This period coincides with neutral pH values and rapid reduction of TVFA concentration. Actually, a rapid decrease of acetic acid concentration of about 85% was observed between days 35 and 66. At the same time, a significant reduction of butyric acid and propionic acid concentrations occurred (39% and 22% reduction, respectively). This relates to a continuation of the increase in pH, which reached 7.3 in the ninth week. Faster degradation of propionic and butyric acid concentrations occurred after acetic acid concentration reached values

around 1.5 g/l as COD(2.3 mg/g) after 11 weeks of operation. The effect of acetic acid accumulation on the rest of the short chain TVFA has been discussed in Section 2.3.3 of the literature review chapter.

From day 91 to day 105, gas production decreased rapidly. This coincides with the degradation of a significant amount of TVFA during the previous peak period and reduction of the organic matter available for consumption by the methanogenic bacteria. This period was followed by stable biogas production up to day 141, after which gas production dropped below 10 l/day. At the end of the experiment, day 165, biogas production had reduced to around 2 l/day. The final TVFA was around 1.3 g/l as COD (1.7 mg/g). This value is near to what has been reported as an indication of a stable digested material.

A specific biogas yield of around 0.52 m^3/kg volatile solids added, and a methane yield of about 0.255 m^3/kg VS added, were accumulated during the course of the experiment, as seen in Fig. 6.5. Methane content of the biogas produced had a mean value of 52.6% (excluding the initial acclimatisation period). The theoretical methane yield, as reported by Molnar and Bartha (1988), is 0.5 m^3/kg VS removed. In terms of COD removal, the methane yield should be 0.35 m^3/kg COD removed (Keefer and Urtes, 1962; De wilde et al., 1989). The methane yield obtained in this experiment was 0.453 m^3/kg VS removed and around 0.336 m^3/kg COD removed, which was equal to about 90 % and 96 % of the theoretical methane yield as VS and COD removal, respectively.

Fig. 6.4 Biogas Composition Relative to Time for the Start-up of Dry Batch HRR Experiment.

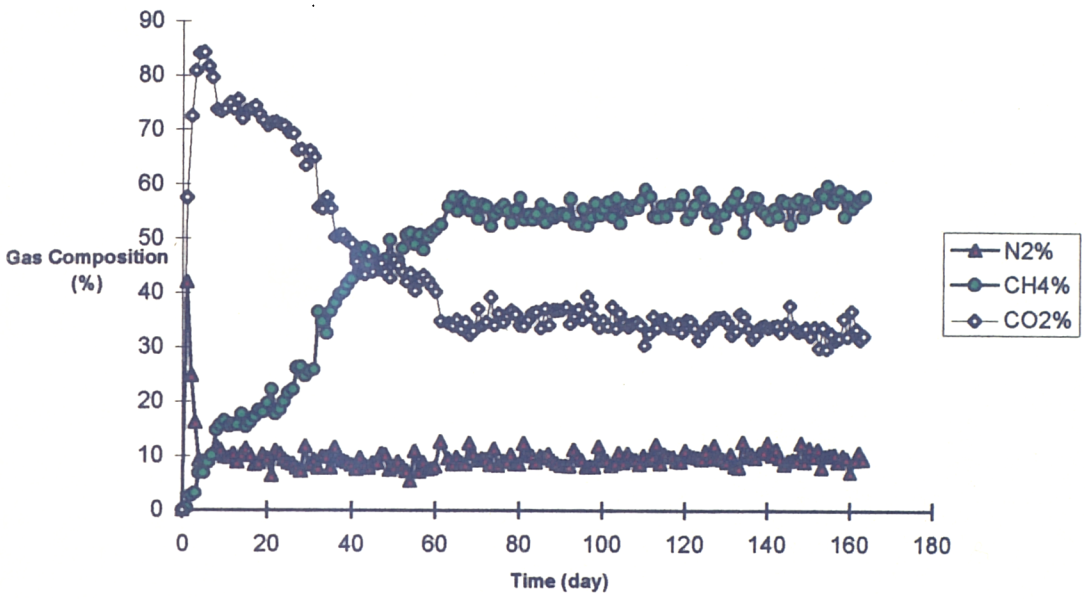


Fig. 6.5 Total Cummulative Biogas and Methane Production for Batch HRR

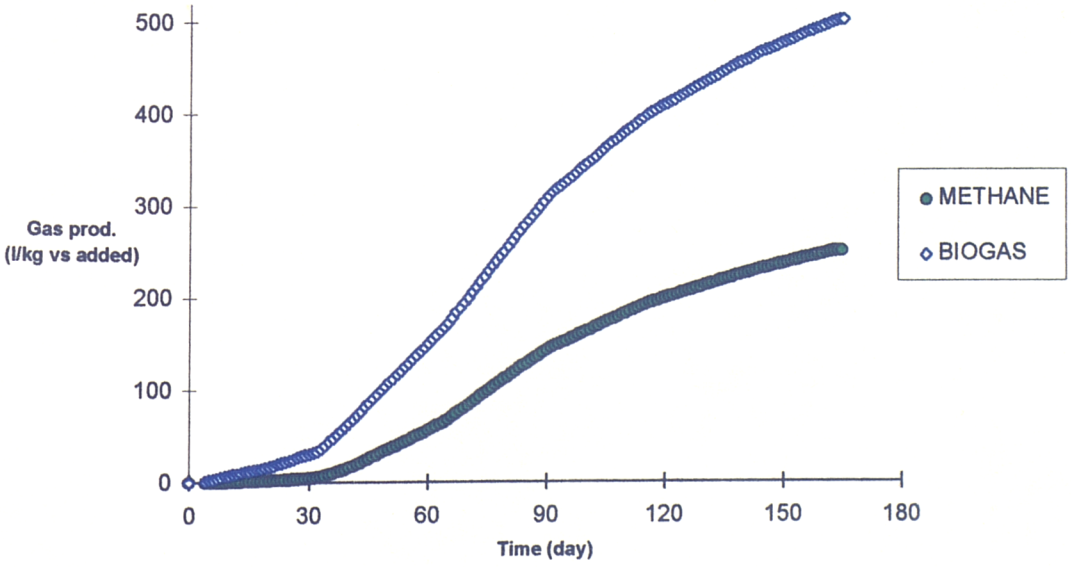


Table 6.2 shows the characteristics of the digested materials at the end of the batch run. The digested materials had a pH value of 8.3 and ammonia-nitrogen concentration of 2500 mg/l. The process performance is given in Table 6.3. At the end of the experiment, volatile solids reduction reached around 56%, which indicated completion of the digestion process. However, it took more than five months to achieve that. Total COD dropped from 860 mg/g to 590 mg/g, while filtered COD dropped from an initial value of around 82 mg/g to a final value of about 22 mg/g, a percentage drop of 31.4% and 73% for TCOD and FCOD, respectively. The final TCOD value of 590 mg/g was much below the acceptable value of 700 mg/g at which composted materials are suggested (Finstein et al., 1986). The C/N ratio showed a reduction of approximately 35%, where it reached a value of 26 at the end of this experiment. This C/N ratio was close to the range of 15 to 25 that was reported by Pescod (1991) for the final composted materials. However, it was higher than the upper C/N ratio range of 5 to 20 that was reported by Hirai et al. (1983) and Finstein et al. (1986) for a well-composted material.

6.1.6 Conclusions on the Batch HRR Study.

The findings of this experiment can be summarised as follows:

i) Successful start-up of the HRR was achieved using a seed sludge to feed refuse ratio of 0.26 (0.02 dry) and 53 grams of sodium bicarbonate per kg of refuse total solids.

ii) Despite the addition of the buffer materials and the seed sludge at start-up time, the initial period of the experiment showed a high increase in TVFA concentrations and a drop in pH, when the TVFA reached a value around 42 g/l as COD (55.6 mg/g).

Table 6.2 Characteristics of the Digested Materials at the End of the Batch Run

Parameters	Units	Values
Total Solids	% Weight	32.4
Volatile Solids	% TS	44
Total COD	mg/g	590
Filter COD	mg/g	22
Carbon	%TS	28
Nitrogen	%TS	1.07
Hydrogen	%TS	2.06
C/N	Ratio	26
TCOD/VS	----	1.34
pH	----	8.3
Ammonia-N	mg/l	2500

Table 6.3 HRR Performance at the End of the Batch Run

Parameters	Values
Total Solids Reduction (%)	36
Volatile Solids Reduction (%)	56
Specific Biogas Yield	
m^3/kg VS added	0.52
Specific Methane Yield:	
m^3/ kg VS added	0.255
m^3/ kg VS removed	0.453
m^3/ kg COD removed	0.336
Mean Methane Content (%)	49
CH_4 Content from day 35*	52.6

* Excluding the initial acclimatisation period solids reduction reached

iii) Despite continuous mixing of the reactor at 3 rpm, it took more than five months to complete the digestion process.

iv) Stable digested materials, in terms of VS reduction and final TVFA concentrations, were obtained with final VS reduction of 55.6% and final TVFA concentration of around 1 g/l as COD.

v) At the end of the experiment, volatile solids reduction reached around 56%, while a specific methane yield of about 0.255 m3/kg VS added (0.453 m^3/kg VS removed) was accumulated.

6.2 First Start-Up and Operation of a Batch Process Using VCR.

6.2.1 Introduction.

Another type of reactor design, the Vertical Conical Reactor, was developed to be operated and evaluated in a long-term batch experiment. Compared with the previous HRR batch experiment (Section 6.1), this design was tested for a higher seed/feed ratio, in addition to a lower TS content and less added buffers.

6.2.2 Objectives.

The objectives of this test were:

i) To evaluate the VCR design;

ii) To obtain stable digested materials to be used in the follow-up experiments;

iii) To evaluate a seed/feed ratio of 0.49, with lower TS and less added buffers than before.

6.2.3 Experiment.

Table 6.4 gives a summary of the characteristics of the initial feed materials used for start-up of the VCR (Section 4.3).

6.2.4 Results and Discussion.

Due to a crack in the inner wall of the reactor (Section 4.2), no data on gas production or gas composition could be collected. However, data collected from leachate samples (weekly basis) and solids samples (obtained at the initial and final stages of the experiment) were used to describe the performance of the process.

The highest TVFA value reached was around 8.2 g/l as COD after 20 days of operation, as seen in Fig. 6.6,. This low TVFA value, compared to the highest value of 42 g/l as COD obtained during the HRR batch run, might be attributed to many factors that resulted in a shorter acclimatisation period, such as high seed to feed ratio and preparation of the seed sludge in order to make it adapt to the new environment, as explained in the experimental section. The addition of a higher amount of digested sewage sludge as an innoculum, to test for a higher innoculum to feed ratio, resulted in an increase in the moisture content of the reactor materials (70%).

One of the most important factors was the lower total solids used in this experiment. Many authors associate high concentration of TVFA with increase of total solids in the anaerobic digestion process. Jewell et al. (1982) and Wujcik (1979) reported a trend of increasing TVFA concentrations with decreasing moisture content. They found that, at 30%

Table 6.4 Characteristics of the Initial Feed Materials Used for Start-Up of the VCR.

Materials	Parameters	Units	Values
Refuse	Weight	kg	20.5
	Moisture Content	% weight	58.4
	Total Solids	% Weight	41.6
	Volatile Solids	% TS	67
	Total COD	mg/g	890
	Filter COD	mg/g	78
	Carbon	% TS	41.5
	Nitrogen	% TS	1.15
	Hydrogen	% TS	4.55
	C/N	Ratio	36
	TCOD/TVS	Ratio	1.32
Seed sludge	Weight	kg	10
	Moisture Content	% weight	94
	Total Solids	% Weight	6
	Carbon	% TS	38.7
	Nitrogen	% TS	5.28
	Hydrogen	% TS	4.67
	C/N	Ratio	7.34
	Seed/Feed	Ratio	0.49
Buffer	NH_4HCO_3 Sodium Bicarbonate	g/kg TS	40
Mixture	TS	% Weight	30
	pH	----------	7.3

TS, the reaction rate was similar to almost all rates at higher moisture levels. However, a large change in the rate of the reaction between solids contents of 30% and 35% was observed. The highest TVFA concentrations reached in their batch experiments on the influence of water on cow manure digestion was more than 30 g/l at around 55 %TS. The maximum TVFA concentrations reached around 10 g/l when the process total solids were about 30%. Also, De Baere et al. (1985), and Ten Brummeler et al. (1988) reported that high TVFA accumulation, which reached up to 45 g/l as COD, occurred at dry fermentation (35% TS) when pure refuse was used. However, lower TVFA maximum values were obtained when using higher innoculum and adding buffer materials.

In this work, moisture content cannot be considered as the sole reason for TVFA accumulation. The higher innoculum ratio used in the latter case increased the methanogenic activity, which helped with the consumption of TVFA produced. Therefore, the higher innoculum ratio used prevented the high values of TVFA experienced in the first batch study. The initial pH of the loading mixture was 7.3; however, it dropped to 6.4 after 4 days of operation before it started to increase. A neutral pH value of 7.0 was obtained after two weeks of operation (Fig. 6.7).

It should be emphasised that because of the design limitation of the VCR, no mixing was carried out during the course of this experiment, apart from the initial manual mixing prior to reactor loading. Also, there was no leachate recirculation during this stage of the experiment, therefore there was no homogeneity of the reactor contents. Consequently it is reasonable to hypothesize that stratification of the biological activities occurred and

Fig. 6.6 VFA Values Relative to Time for the First Start-up of VCR Experiment

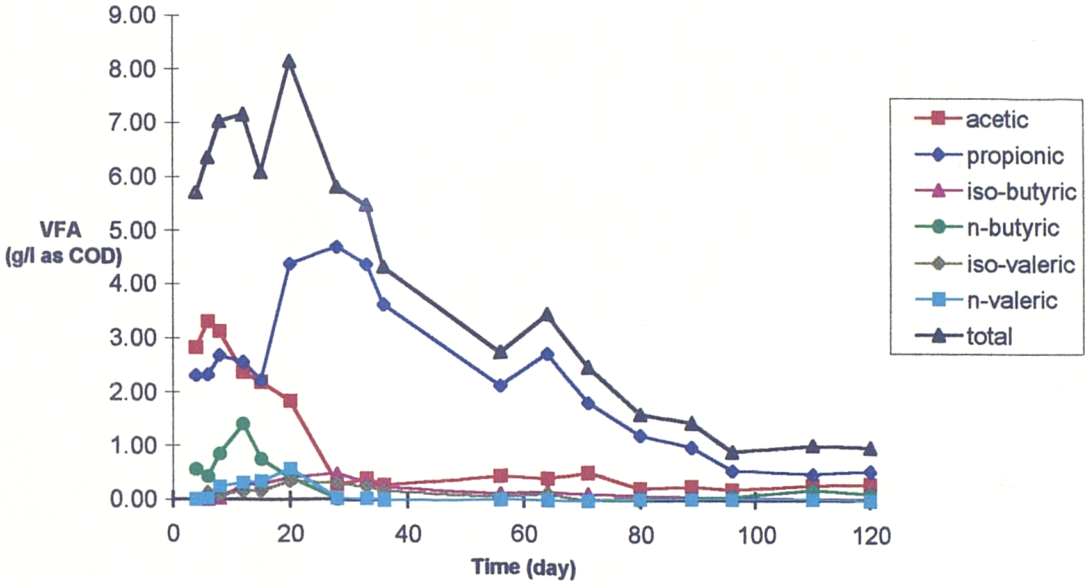
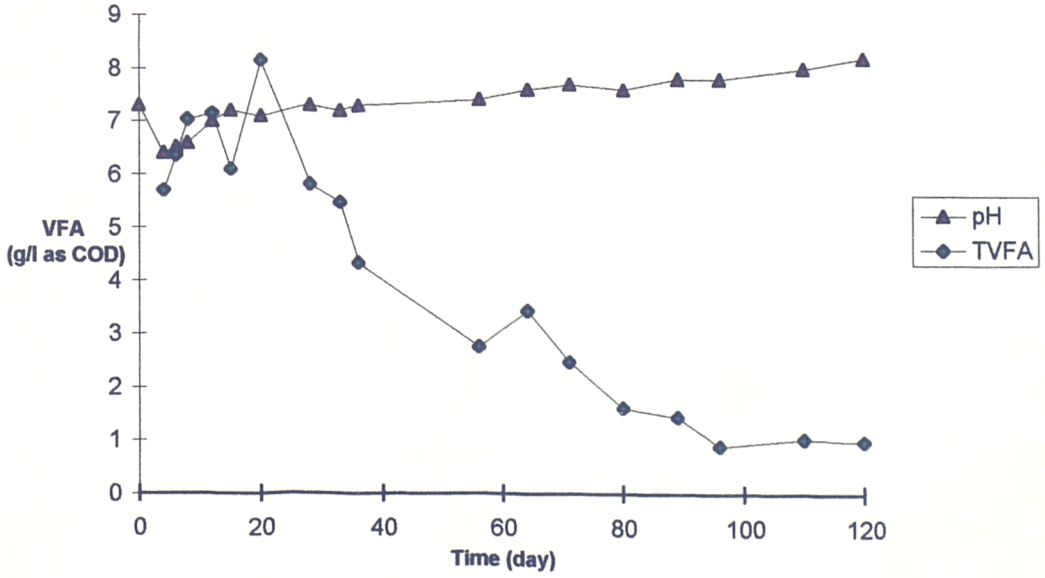


Fig. 6.7 VFA and pH Values During VCR Batch Experiment



that the leachate sample was not representative of the whole reactor contents.

The increase in the innoculum to feed ratio in this experiment might explain the high pH values of the initial start-up period, compared to the batch HRR run. The final digested materials were mixed together and more than 1 kg of sample was taken for the final analyses of this run. Table 6.5 shows the results of these analyses. After five months of operation, Volatile Solids reduction was around 52.6% and TVFA of less than 1 g/l as COD was reached. The final C/N ratio was 27, this represented a decrease of approximately 25% from the original feed refuse C/N ratio and only 4% higher than the final C/N ratio that was obtained at the end of the batch HRR experiment. The final pH values for leachate and digested solids materials were 7.9 and 8.2, respectively.

6.2.5 Conclusions on the Batch VCR Study.

The findings of this experiment can be summarised as follows:

i) The design of the VCR was not practical for operation at high solids concentration, due to the difficulties of solids movement and mixing.

ii) The digested materials obtained after five months were of adequate stability and comparable with the final materials of the batch HRR study;

iii)- The use of a high S/F ratio of 0.49, thus lower TS (30%), seemed to have a positive effect on the acclimatisation period, despite using less buffer.

Table 6.5 Characteristics of the Digested Materials at the End of the Batch VCR Run.

Parameters	Units	Values
Total Solids	**% weight**	**28**
Moisture Content	**% weight**	**72**
Volatile Solids	**% TS**	**49**
VS Reduction	**%**	**52.6**
TCOD	**mg/g**	**620**
FCOD	**mg/g**	**28**
Carbon	**% TS**	**30.8**
Nitrogen	**% TS**	**1.13**
Hydrogen	**% TS**	**2.9**
C/N	**Ratio**	**27.2**
pH	**-----**	**8.2**
Leachate		
pH	**------**	**7.9**
NH_3-N	**mg/l**	**1040**

6.3 Batch Experiments with Digested Materials as an Innoculum Using the Vertical Sequential Reactor (VSR).

6.3.1 Introduction and Objectives.

After the first start-up of the batch process, further studies were considered necessary to evaluate the retention time required for the follow-up semi-continuous experiments. In addition, information on biogas production could be obtained, when using fresh refuse to digested materials at a ratio of 30:70 (wet weight). The advantages expected when using a high ratio of digested materials and fresh organic wastes to start the anaerobic digestion process include the acceleration of the digestion process, a short lag period and an adequate buffering capacity to maintain a balanced operation. After completion of the previous batch experiment using the VCR, the reactor contents were transferred to the newly constructed Vertical Sequential Reactor (VSR). At that stage, no gas production could be measured from this digested material.

6.3.2 Operating Parameters.

Volatile Solids Utilisation:

The use of recycled digested materials as an innoculum makes direct and straightforward determination of volatile solids reductions quite difficult. This happens especially when running continuous or semi-continuous operations with recycled digested materials. At this stage of the experiment, it was very important to evaluate various methods for calculating VS reduction. The methods used for the determination of VS reduction were based on:

a) the actual weight measurements of the initial wastes and the final digested materials (same as Section 6.1.3). This method is suitable mainly for laboratory and small-scale experiments.

b) the mass balance of the process, which is described in Appendix B1.

c) the accumulated biogas and methane yields. Only an estimated value was obtained when adopting this method, since only the theoretical biogas yield of cellulose, which represents the highest portion of the domestic refuse, was used (Mosey et al., 1994).

d) the percentage loss of the VS content between the initial and final VS%.

All of the above mentioned methods depend on the accuracy of the VS determination procedure. Further discussion of these methods is given in Chapter 7, where appropriate.

Other operating parameters were the same as Section 6.1.3.

6.3.3 Equipment.

The Vertical Sequential Reactor (VSR), which was designed for semi-continuous operation, was used to carry out these batch experiments. A detailed description of this unit is given in Chapter 4 (Section 4.3).

6.3.4 Experiment.

Two consecutive runs were conducted with a fresh refuse to digested materials at a ratio of 30:70 (wet weight). Two runs were carried out as follows:

i) Run 1.

The final digested materials (Table 6.5) from the first start-up of the Vertical Conical Reactor were used as an innoculum to start-up this experiment. The innoculum material was mixed with 6 kg of putrescible waste (42% TS and 64% VS) and 4 litres of leachate that was also obtained from the previous experiment, in addition to 2 litres of tap water. The mixture was then loaded into the reactor.

ii) Run 2.

After completion of the first run, the digested materials were applied as an innoculum to initiate the second run. The putrescible waste used in this run had 40% TS and 68% VS. The same amounts of fresh waste, leachate and tap water were applied to this run as in the previous one.

6.3.5 Results and Discussion.

i) Biogas and Methane Production.

Biogas production lasted 29 and 25 days for runs 1 and 2, respectively. Fig. 6.8 and 6.9 show the accumulated biogas and methane yields, and also illustrate the methane content in the biogas for these two runs. During the first run, the methane content in the biogas increased gradually from 12%, after one day of the experiment, to 50%, after 9 days. From day 11 onwards, the methane content in the generated biogas was between 55 and 60%. This relates to the peak biogas production of 33 l/day, which was recorded on the same day (11). A significant drop in biogas production was observed at day 19, when the level dropped from 31 l/day to 22 l/day. Thereafter, biogas started to decrease rapidly until gas production ceased after 29 days of operation.

Fig. 6.8 Accumlated Biogas and Methane Yields and Methane content for Batch Run 1.

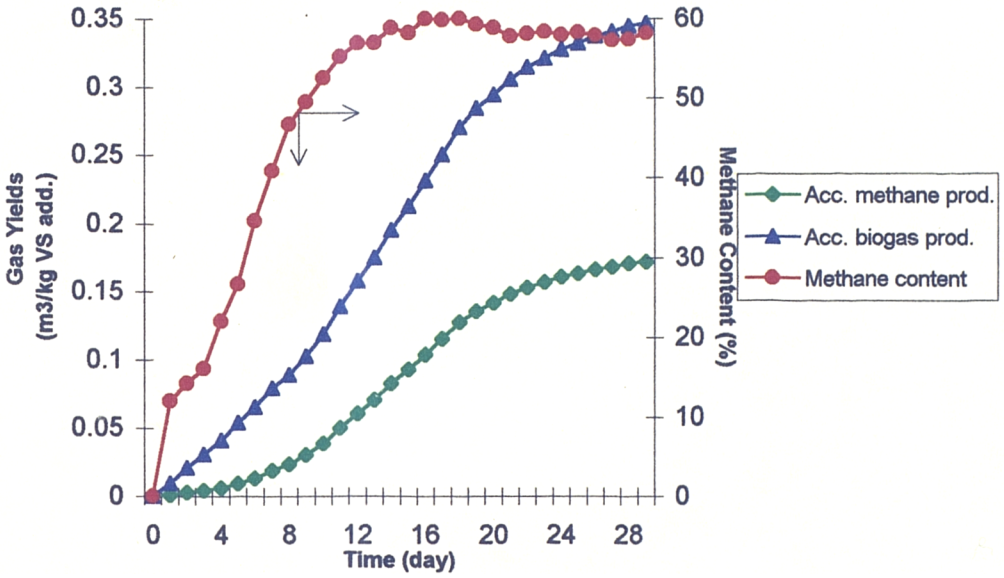
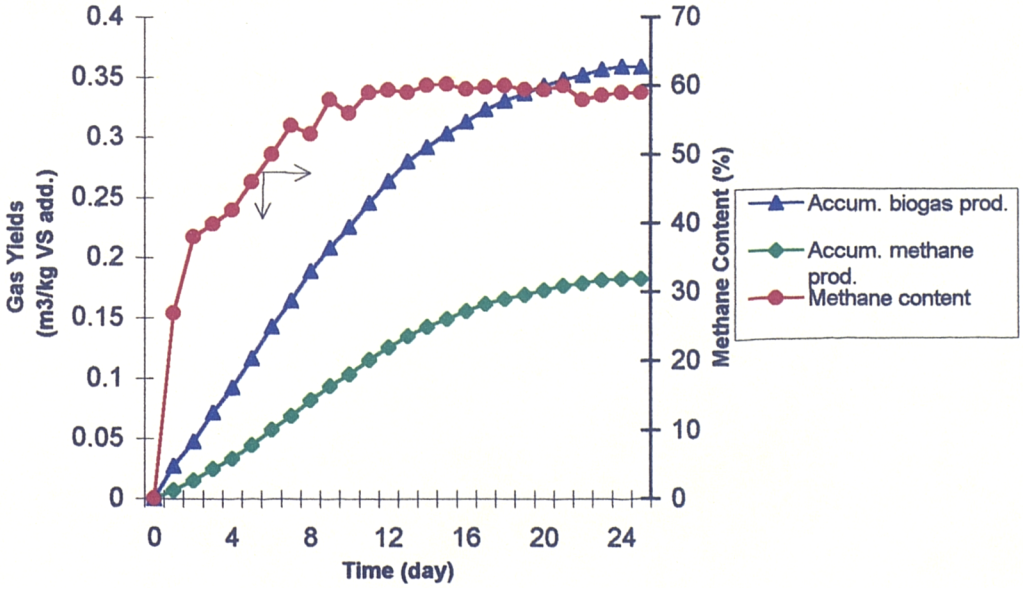


Fig. 6.9 Accumlated Biogas and Methane Yields and Methane Content for Batch Run 2.



During the second run the methane content of the biogas increased from 27%, after one day of the experiment, to 50% at the end of the sixth day. A lower lag period was observed in this run, which indicated the rapid build-up of active microorganisms. The methane content of the biogas ranged between 55 and 60% during the period from day 9 to the end of this run. Peak biogas production of 44 l/day was observed at day 6. Gas production started to decrease from day 13, when it was 28 l/day, to 20 l/day at day 14. A second drop was observed at day 17, when biogas production dropped from 18 l/day to 12 l/day. From day 17 onwards, biogas production dropped rapidly until it ceased altogether at day 25. The methane content of the biogas during run 2 was higher in the initial period than in the first run. Thus, the lag period was less in run 2. Methane yields of 0.173 and 0.183 m^3/kg VS added, corresponding to volatile solids reductions of 40.6% and 45%, were obtained in runs 1 and 2, respectively. Table 6.6 gives a summary of biogas and methane yields that were accumulated during these two runs.

Table 6.6 Summary of Biogas and Methane Yields.

		Run 1	Run 2
Specific Biogas Yield	**m^3/kg VS add.**	0.345	0.349
Specific Methane Yield	**m^3/kg VS add.**	0.173	0.183
	m^3/kg VS rem.*	0.426	0.407
Mean Methane Content	%	50	52.4

* Based on actual weighing method.

ii) Characteristics of the Final Digested Materials.

The characteristics of the final digested solids materials and the corresponding leachate quality at the end of each run are given in Tables 6.7 and 6.8, respectively. Table 6.7 shows also the final digested solids materials of the VCR batch run.

Table 6.7 Characteristics of the Final Digested Solid Materials.

		VCR Run	Run 1	Run 2
Total Solids	% of weight	28	31.4	30.2
Volatile Solids	% TS	49	51	53
pH	--	8.2	8.2	8.3
Total COD	mg/g	620	620	630
Filter COD	mg/g	28	27	22
Filter TKN	mg/g	------	1.74	1.23
Filter P	mg/g	------	0.57	0.42
Total Carbon	% TS	30.8	--	32
Total Nitrogen	% TS	1.13	1.13	1.176
Total Hydrogen	% TS	2.9	--	1.75
C/N	---	27.2	--	27

Table 6.8 Characteristics of the Leachate at the End of Each Run.

		Run 1	Run 2
pH	-------	7.7	7.8
Total COD	mg/l	6500	7000
Filter COD	mg/l	5900	6420
Ammonia-N	mg/l	986	1069
Total-N (TKN)	mg/l	1206	1157
Phosphorus	mg/l	210	189
Alk. End Point 4.5	mg $CaCO_3$/l	4500	4800

iii) pH and VFA.

Total VFA concentrations were examined for both the leachate and solids samples at the end of both runs. The results are reported in Tables 6.9 and 6.10 for run 1 and run 2, respectively. At the initial start-up, acetic acid concentrations were over 90% , while propionic acid concentrations were only around 4 % of the refuse total VFA concentrations.

Table 6.9 VFA Concentrations and pH Values for Batch VSR Run 1

	Initial Refuse Solids (mg/g)	Final Digested Solids (mg/g)	Final Leachate (mg/l as COD)
Total VFA	7.5	1.5	632
Acetic Acid	7.1	0.68	366
Propionic Acid	0.3	0.2	175
N-butyric Acid	0.1	0.1	26
pH	5.3	8.2.	7.7

Table 6.10 VFA Concentrations and pH Values for Batch VSR Run 2

	Initial Refuse Solids (mg/g)	Final Digested Solids (mg/g)	Final Leachate (mg/l as COD)
Total VFA	8.3	1.69	561
Acetic Acid	7.6	1.08	381
Propionic Acid	0.4	0.13	135
N-butyric Acid	0.1	0.06	18
pH	5.1	8.3	7.8

The reported leachate pH values at the end of both runs were obtained after filtering the leachate. Different pH values for total and filtered samples were observed throughout the various phases of this project, where higher values were obtained for the filtered samples (+ 0.3-0.5). The reasons for this might have been the loss of carbon dioxide during filtration. Digested solids pH values were higher than leachate pH values; this might be explained by the lower TVFA concentrations present in the solids samples of the final digested materials. The high pH values obtained for the final digested materials, for all batch runs in this work, were within the range of reported pH values for similar types of feedstock and process. The reported pH values of the dry anaerobic digestion process for the organic fraction of MSW were in the range between 8 and 8.5 (De Wilde and De Baere, 1990; Coombs and Coombs, 1989; Van Meenen et al., 1988).

At the end of both runs, the leachate TVFA concentrations were much lower than 1 g COD/l, which is the level at which Ten Brummeler et al. (1992) considered the dry anaerobic digestion process to be completed. The significant decrease in biogas production coincided with the decrease of TVFA concentrations, indicating that the hydrolysis of organic compounds had become rate limiting.

iv) Volatile Solids Conversion Efficiencies.

Table 6.11 shows the results, based on various calculation methods, for the determination of volatile solids reduction for both runs. For batch experiments, with no solid samples withdrawn from the reactor, the actual weighing method was selected as the basis for reporting the specific gas

Table 6.11 Summary of the VS Conversion Efficiencies for Runs 1 & 2

Method	Units	Run 1	Run 2
VS Reduction:	%		
Actual weighing		40.6	42.2
Mass balance		39	44.5
Theoretical biogas		43.4	45
Percentage lost		20	22
TVFA reduction	%	80	79.6
FCOD reduction	%	70	76
TCOD reduction	%	22	25

and methane yields. It was also used to evaluate the other methods of estimating the VS reduction in anaerobic digestion processes. The VS conversion efficiencies were similar to those reported by others with similar high solids processes. Molnar and Bartha (1988) reported 42% VS reduction at 30 days retention time.; while Chynoweth et al. (1992) obtained volatile solids reductions of 45% at a residence time of 21 days when operating the SEBAC process at a thermophilic temperature of 55°C.

The calculations of the conversion efficiencies for both total and filtered COD were based on the percentage loss between the initial feedstock and final digested materials values. The initial refuse feedstock, for run 1, had a FCOD of 90 mg/g. A percentage reduction of around 70% was obtained at the end of run 1 to reach 27 mg/g, while a percentage reduction of 76% was obtained at the end of the second run. Total COD removal efficiencies were about 22% percentage reduction for run 1, and 25% for run 2. Final TCOD values, for both runs, were below the compost acceptable level of 700 mg/g (Finstein et al., 1986).

6.3.6 Conclusions on the Batch VSR Study.

The findings of these experiments can be summarised as follows:

i) The use of digested residue as an innoculum accelerated the start-up of the digestion process when a recycled digested material to fresh refuse ratio of 0.7 (wet weight) was adapted.

ii) A retention time of 25 days was required for completion of this dry batch anaerobic digestion experiment, which was carried out at 30% initial total solids.

iii) Methane yields of 0.173 and 0.183 m^3/kg VS added, corresponding to volatile solids reductions of 40.6% and 45%, were obtained in runs 1 and 2, respectively. Compared with the methane yield which was obtained in the long batch experiment using the HRR, around 68% of the potential methane yield (0.255 m^3/kg VS added) was recovered from run 1; while, for run 2, the methane yield amounted to 72% of the potential methane yield.

CHAPTER 7

VERTICAL SEQUENTIAL REACTOR-SEMI-CONTINUOUS STUDIES

7.1 Introduction.

The slow growth rate of the methanogenic bacteria requires an efficient means of maintaining a high level of viable biomass in the reactor. Anaerobic digestion of high solids organics between 30 and 40% TS is inhibited by the accumulation of high TVFA concentrations (Wujuik and Jewell 1980). As stated earlier in Section 6.1, for the digestion of the organic fraction of municipal solid wastes, the addition of a high amount of methanogenic seed, such as digested sludge, and buffer to prevent unbalanced digestion is recommended (Buivid et al., 1981; Ten Brummeler and Koster, 1989). Recycling of the effluent fraction of the reactor to dilute the incoming wastes was found to improve the buffering capacity of the digestion process and this, therefore, enhanced the stability of the process (Cecchi et al., 1990c). In addition to the provision of innoculum and alkalinity to the reactor contents, liquid from dewatering the reactor effluent helps to conserve water and heat and provides nutrients (Legrand et al., 1989). Leachate recycling during the digestion period is used, as well, to maintain a uniform moisture content and redistribute the soluble substrate (TVFA) and methane bacteria throughout the mass of MSW within the reactor contents.

Ten Brummeler et al. (1991) found that higher recirculation of the digested organic fraction helped to shorten the sub-optimal conditions during the start-up of dry anaerobic digestion. A retention time of 36 days was

required for the completion of the batch digestion process when they applied 40% digested materials as an innoculum to start up the mesophilic dry anaerobic digestion at a TS of 35%. They attributed the shorter Dranco retention time to the use of high digested solids to fresh organic fraction ratio. Hence, the solids retention time, in such high solids digestion, is determined by the recirculation of the innoculum digested materials.

7.2 Objectives.

In this work, the impact of various digested to fresh refuse ratios, as well as different leachate recycling levels, on the VSR semi continuous operation was examined. Phase one of this study evaluated the effect of several digested recycle ratios (DRR) on the semi-continuous high solids anaerobic digestion operation. Three DRR values of 0.75 (DRR1), 0.5 (DRR2) and 0.33 (DRR3) were examined during this first phase of the VSR semi-continuous experiment. The DRR values were lowered by increasing the organic loading rate of the process. One of the main objectives of this phase was to determine the optimum experimental DRR in terms of volumetric methane production, organic loading rate and process conversion efficiencies (methane yield, VS and COD reductions).

In the second phase of this study, the effect of different process moisture contents, through leachate recycle variation, was investigated at fixed DRR value. Leachate recycled volume was reduced successively from an initial 6 (LR1) to 3.5 (LR2), 1.5 (LR3) and 0.8 (LR4) litres, and this accordingly reduced the moisture content of the process. Meanwhile, the DRR remained at 0.5 (wet weight basis) throughout this experiment.

The specific objectives, for both phases of the experiment, were to evaluate the impact of DRR(OLR) and LR (TS) variation on:

i) the biogas and methane production and yields,

ii) the process efficiencies in terms of VS, TCOD and FCOD reductions,

iii) the quality of the final digested materials produced,

iv) the internal reactor microbial activities by using VFA results in terms of mg/g and mg/l as COD, pH, FCOD and acidification levels at different reactor depths, and

v) the quality of leachate (drained liquid) generated.

7.3 Operating Parameters.

7.3.1 VS Reduction.

Two different methods for calculating VS reduction, reported in Section 6.3.2, were used for the semi-continuous experiments. These methods were based on:

i) actual weight measurements by weighing the components of the chamber units'contents at the initial feeding time and after the 24 days cycle. The reduction in VS can then be calculated after the determination of VS content in both fresh refuse and final digested residue. The following equation was used to calculate the VS reduction:

$$VS\ Reduction(\%)=\frac{VS\ \text{Weigh Loss}}{VS\ \text{Fresh Feed}}*100 \qquad (7.1)$$

ii) mass balance equation (same as Section 6.3.2, Appendix B-1).

7.3.2 Organic Loading Rate (OLR).

Organic loading rate calculations were based on grammes VS fed per litre of chamber unit volume per day of a complete cycle. The available volume of the chamber unit was approximately 6.5 litres. A retention time cycle of 24 days was fixed throughout the experiment. Therefore,

$$OLR = VS\ fed\ (g) / 6.5\ l / 24\ days \qquad (7.2)$$

7.3.3 Digested Recycle Ratio(DRR).

The DRR was calculated according to the following equation:

$$DRR = DR / (F + DR) \qquad (7.3)$$

Where, DR = Digested recycled materials (kg),

F = Fresh refuse used (kg).

For practical reasons, the DRR was mixed on a wet weight basis at the time of loading. The DRR was then recorded using both wet and dry weight bases after determination of the total solids content for both refuse and digested materials.

7.3.4 Specific Biogas and Methane Yields.

Mean values of biogas and methane production per mean kg VS added values were used in Eq. 6.1 and 6.2 to determine the specific biogas and methane yields.

7.3.5 Total and Filtered COD %.

Total and filtered COD percentage losses were calculated according to Eq. 6.3.

7.3.6 Steady State Conditions.

Steady state conditions were considered to have been reached when stable biogas production and stabilised efficiency parameters were obtained. The variation of biogas and methane production between loading intervals should remain relatively stable for at least one to two retention time periods. Steady state conditions were defined by Pfeffer (1987) as the period when the standard deviation of biogas production of less than 10% of the average is obtained. To determine this steady state period, both biogas volumetric production and specific yields were observed.

7.4 Equipment.

A detailed description of the Vertical Sequential Reactor (VSR), that was designed for semi-continuous operation, is given in Chapter 4 (Section 4.4).

7.5 Refuse Characteristics.

All experiments up to the end of LR3 run used refuse obtained from Anglesey Refuse Treatment Plant. However, because of the closure of this plant and the exhaustion of all of the stored refuse, the last experiment of phase 2 (LR4) was carried out with putrescible refuse obtained from Salford, Greater Manchester, Refuse Treatment Plant, which applied the same Dano drum technique. The difference between the two types of

refuse used was that the Salford refuse came from an urban catchment area, whereas the Anglesey refuse was collected from a fairly rural area.

A total of 6 bags, 20 kg each, was obtained from the Salford plant. One bag was rejected because it was considered not suitable for anaerobic digestion. The rejected refuse contained materials of a fluffy type, with a TS of 71%, VS of less than 24%, TCOD of 350 mg/g, high pH value of 7.7 and very low TVFA concentration (0.9 mg/g). This refuse was much drier than that from Anglesey. Only six 500g samples of Salford refuse were analysed compared to at least 30 samples for Anglesey refuse. The physical composition for these two types of putrescible fraction of MSW is shown in Tables 7.1 and 7.2.

7.6 Experimental Procedures.

The procedure for operating the VSR was described in Section 4.4 of this work. The semi-continuous experiments were carried out directly after the end of the second batch run (Section 6.3). Leachate was mixed manually with the incoming fresh refuse and the recycled materials. The free liquid drained through the mesh at the bottom of the chamber units and thus carried the TVFA downward through the more mature digested residue stages, where the TVFA was consumed by methanogenic bacteria. In addition to its role as an innoculum, the leachate provided the newly incoming feed with nutrients and buffering capacity. Recycling the digested solids residue and drained leachate was the only means of providing buffering capacity for pH control and an additional nutrient source.

Table 7.1 Anglesey Refuse Characteristics During VSR Semi-Continuous Experiment.

Parameters*	Mean	Range	Standard Dev.
TS (%)	42.7	39.0-48.5	2.9
VS (% TS)	63	58-67.5	4.0
TCOD (mg/g)	789	730-843	24.4
TCOD/TVS	1.25	1.2-1.34	--
FCOD (mg/g)	63.2	50-73	5.1
TKN (% TS)	1.02	0.9-1.24	0.16
Phosphorus (% TS)	0.042	0.033-0.05	-- --
Elemental Analyses			
C (% TS)	38.41	35-41.6	2.86
N (% TS)	1.26	1.03-1.63	0.25
H (% TS)	3.75	2.7-4.8	1.13
C/N	31.4	25-40.3	6.4
Density wet w. (kg/m^3)	545	525-577	27.8

Table 7.2 Salford Refuse Characteristics During LR4 Experiment.

Parameters*	Mean	Range	Standard Dev.
TS (%)	51	49-53.8	1.6
VS (%)	49.2	47.5-51.4	1.5
TCOD (mg/g)	602	590-620	12.6
TCOD/TVS	1.22	1.17-1.25	-----
FCOD (mg/g)	43.7	40-48	1.4
TKN (%)	0.9	0.73-1.04	0.13
Elemental Analysis			
C (% TS)	32	31-33.41	1.7
N (% TS)	1.36	1.28-1.45	0.12
H (% TS)	3.24	2.3-4.4	1.6
C/N	23.4	23-24.2	0.9
Density wet w. (kg/m^3)	460	-----	-----

(*) For elemental analyses, 3-5 samples were used, while at least 6 samples were used for the rest of the parameters in table 7.2, while a minimum of 25 was used in Table 7.1.

A fixed retention time of 24 days was maintained throughout the experiment. This retention time was determined from the result of the two previous batch runs (Section 6.3).

7.7 Sample Collection.

The sampling procedure is described in Section 5.4.3

7.8 Analytical Methods Used.

The dry solids water extract method was applied for the following analyses: pH, FCOD, VFA, TKN, P and Heavy metals. These analyses, in addition to those for ammonia nitrogen and alkalinity, were conducted on the leachate samples. Conversion of results from mg/l to mg/g for the water extract from dry solids samples method is given in Appendix B4.

Dry powdered solids samples were used to determine TCOD and for the elemental analysis (C:N:H). During the steady-state conditions, at least 6 samples were used to evaluate each of the parameters monitored unless otherwise stated, with the exception of biogas and methane production and yields, where at least 24 samples were used.

7.9 Results and Discussion of Phase 1 (Digested Recycle Ratio, DRR).

7.9.1 Biogas and Methane Production.

Table 7.3 presents, for steady state conditions, biogas and methane yields with the corresponding DRR ratio and OLR. Fig. 7.1 and 7.2 show the daily biogas and methane production and biogas composition during the DRR experiment. The digested solids recycle ratio (DRR) phase lasted for approximately 200 days.

Table 7.3 Steady-State Biogas and Methane Production and Yields Relative to OLR and DRR.

Parameters	Units	Values	DRR1	DRR2	DRR3
Digested Recycle	Wet Weight	Mean	0.76	0.5	0.33
Ratio (DRR)	Dry Weight	Mean	0.685	0.4	0.265
	g VS / day	Mean-SD*	91.7 ± 3.19	159.3 ± 3.41	198.8 ± 1.32
		Range	86 - 97.9	147.4 - 173.2	196 - 200
Loading Rate	kg VS/m^3/d	Mean-SD	2.4 ±0.08	4.1 ±0.24	5.2 ±0.06
		Range	2.23 - 2.54	3.9 - 4.5	5.1 - 5.3
	kg VS/m^3/ 4 days	Mean	9.6	16.4	20.8
Biogas	l/day	Mean-SD	37.3 ± 3.34	61.92 ± 4.81	54 ± 4.16
Production		Range	32-44	54-71	47-60
Biogas	m^3/m^3 reactor./day	Mean	0.971	1.615	1.4
Production	m^3/m^3 A.** vol./day	Mean	1.24	2.06	1.8
Methane	l/day	Mean-SD	19.52 ± 0.91	32.13 ± 1.48	24.6 ± 1.34
Production		Range	17.9-21.33	29.2-34.9	22.4-26.7
Methane	m^3/m^3 reactor/day	Mean-SD	0.508 ± 0.02	0.832 ± 0.04	0.64 ± 0.036
Production		Range	0.467 - 0.55	0.757 - 0.91	0.585 - 0.70
Methane	m^3/m^3 A** vol./day	Mean-SD	0.65 ± 0.03	1.06 ± 0.05	0.819 ± 0.05
Production		Range	0.599-0.711	0.969 - 1.164	0.75 - 0.89
Specific Biogas	m^3/kg VS added	Mean	0.406	0.39	0.272
Yield	m^3/kg VS removed	Mean	0.837	0.834	0.732
Specific	m^3/kg VS added	Mean	0.213	0.202	0.124
Methane Yield	m^3/kg VS removed	Mean	0.438	0.433	0.333
CH_4 Content		Mean-SD	52.6 ± 3.06	51.9 ± 3.17	45.6 ±
	% of Biogas	Range	48.1 - 57.8	45.1 - 55.4	37.5 - 49.6
CO_2 Content		Mean-SD	38.9 ±2.6	40.5 ±2.56	46.4
		Range	35.2 - 44.3	34.6 - 45.5	41.2 - 51.5

(*) Standard deviation.
(**) based on active reactor volume of approximately 30 litres.

Fig.7.1 Daily Biogas and Methane Production during DRR Study (Phase 1)

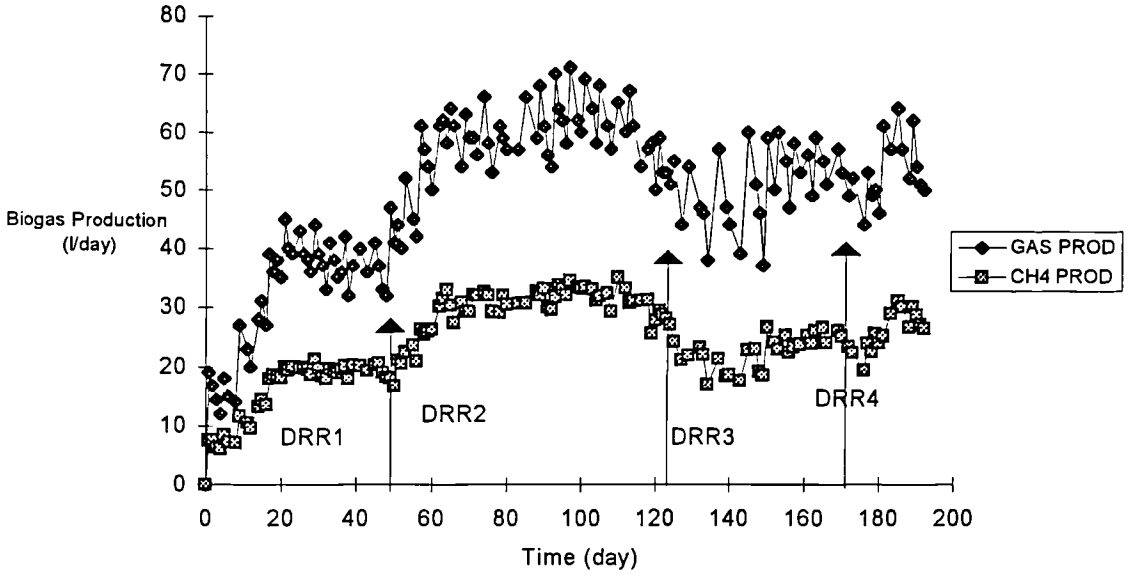
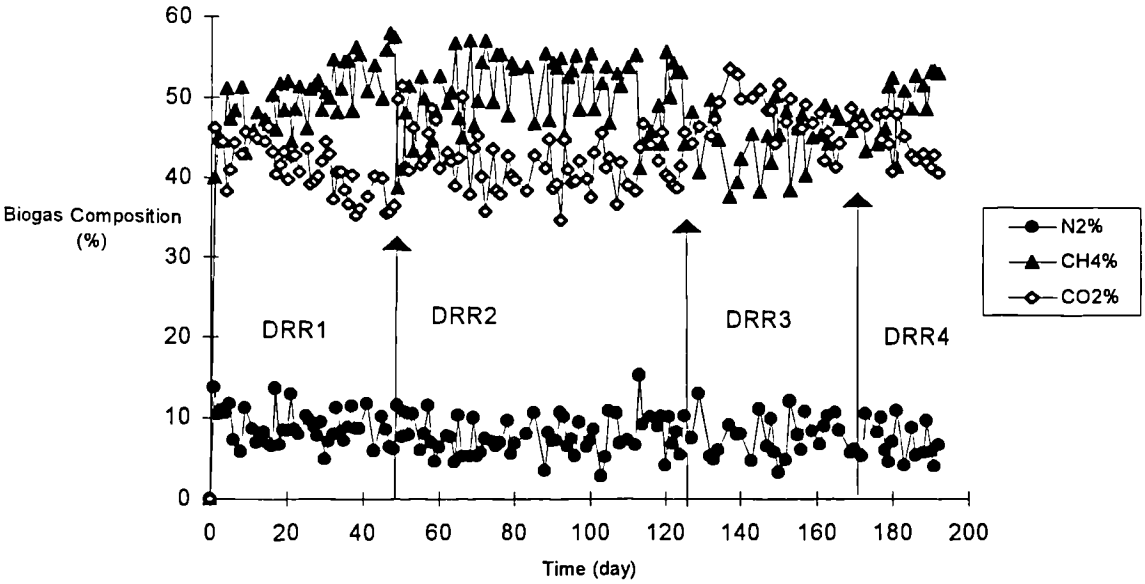


Fig. 7.2 Biogas Composition during DRR Study (Phase 1)



At DRR1 (0.76) and organic loading rate of 2.4 kg VS per m^3 reactor per day, biogas production increased gradually to reach a maximum of 44 l/day, which corresponds to 21.3 l of CH_4/day, after 29 days of operation. These values were close to the DRR1 mean biogas and methane production of 37.3 and 19.5 l/day, respectively. Steady-state conditions, for the DRR1 run, were considered from day 17 onwards when biogas and methane production reached 39 and 17.9 l/day, respectively. Methane content in the biogas produced reached approximately 50% after only 4 days of operation, while mean biogas composition during this run was 53% methane and 39% CO_2. On the other hand, mean volumetric biogas and methane production values were approximately 0.971 and 508 m^3 per m^3 reactor per day, respectively. A methane yield of approximately 0.213 m^3/kg VS added was achieved during DRR1 run.

From day 48, at the start-up of DRR2 run, the organic loading rate was increased to 4.1 kg VS per m^3 reactor/day. This OLR increase resulted in a significant increase in the volumetric methane production, by approximately 64 %, compared to DRR1 run to reach 0.832 m^3 CH_4 per m^3 nominal reactor volume per day. Steady-state conditions for the DRR2 run were considered from day 64 onward. Maximum biogas and methane production of 71 and 34.4 l/day, respectively, were obtained at day 97 of the experiment. Despite the increase in volumetric methane production, the specific methane yield was lower in DRR2, by approximately 5%, than in the DRR1 runs due to the higher methane content in the biogas in the latter case.

On day 124 of the experiment, the digested recycle ratio was reduced to 0.33 by increasing the OLR to 5.2 kg VS per m^3 reactor per day. Steady-state conditions, for DRR3 run, were considered from day 149 onwards, and also at day 149 maximum biogas and methane production of 60 and 27.1 l/day, respectively, were obtained. During this DRR3 run, a decline in biogas and methane production was observed compared to the previous run of DRR2. Volumetric methane production decreased by approximately 23% to reach a mean of 0.64 m^3 per m^3 reactor per day. However, this DRR3 volumetric methane production was higher than that obtained in the DRR1 run by approximately 21%.

High CO_2 content in the biogas produced was experienced in the DRR3 run, up to 51.5%, with a mean value of 46.4%. This high CO_2 led to a decline in the methane content from 52 %, in the DRR2 run, to 45.6%. Mean methane yield during this run was 0.124 m^3/kg VS added, which represented a decrease of approximately 41% from the DRR1 run value. A sizeable reduction in the process performance was observed during the DRR3 experiment. However, there was no complete process failure due to the sufficient retention time that was used for both solids (24 days) and leachate (4 days).

On day 172 of the experiment, at the start-up of the DRR4 run, the operational conditions of DRR2 were re-established and the system performance increased gradually towards that previously experienced during the DRR2 run. The DRR4 run was operated only for one RT cycle of 24 days, so it was not allowed to reach steady state conditions due to

lack of time and because only limited raw materials were available. Table 7.4 presents some indicatory results of the performance of this DRR4 run.

Biogas and methane production resumed directly after loading the reactor, with apparently little or no effect on the methanogenic bacteria to the air (oxygen) exposure for approximately 30 minutes loading time. The low impact of air exposure on the digestion process, throughout VSR semi-continuous experiments, was attributed to:

i) The nature of the reactor contents where the wet compacted solids residues meant that little or no air could disturb the inner reactor contents, apart from the first chamber unit.

ii) The exposure time (30 minutes) was not sufficient to cause any permanent damage to the methanogenic bacteria.

However, it seemed that longer exposure time (up to 6 hours during sample collection from all chamber units at the end of DRR2 run) did adversely affect the methanogenic activities. The 6 hours air exposure period was much lower than the 30 and 69 hours that were reported by Kiener and Leisinger (1983), and Fields and Agardy (1971), respectively, as the threshold for the survival of the methanogenic bacteria. The process took around 4 days to recover fully.

Biogas production varied mostly between the first and the fourth day after loading the reactor, throughout the study. Biogas production tended to follow a pattern which showed that the highest biogas production value was usually obtained directly one day after loading the reactor and that the lowest value was obtained after four days from loading. However,

Table 7.4 Biogas and Methane Production and Yields duringt DRR4 Experiment

Parameters	Units	Values	DRR4
Digested Recycle Ratio (DRR)	Wet weight	Mean	0.5
	Dry weight	Mean	0.42
Loading Rate	g VS / day	Mean-SD	144 ± 3.89
		Range	138.6 - 147.7
	kg VS/m^3/d	Mean-SD	3.75 ± 0.05
		Range	3.6 - 3.8
	kg VS/m^3/ 4 days	Mean	15
Biogas Production	l/day	Mean-SD	55 ± 5.76
		Range	46-64
Methane Production	l/day	Mean-SD	27.62 ± 2.26
		Range	24-31
Methane Production	m^3/m^3 reactor/day	Mean-SD	0.726 ± 0.06
		Range	0.67 - 0.808
Methane Production	m^3/m^3 active	Mean-SD	0.927 ± 0.078
	reactor/day	Range	0.802 - 1.03
Specific Biogas Yield	m^3/kg VS added	Mean	0.38
Specific Methane Yield	m^3/kg VS added	Mean	0.193
CH_4 Content	% of Biogas	Mean-SD	49
		Range	41 - 53
CO_2 Content		Mean-SD	43.8
		Range	39 - 46.2

methane production was relatively stable during the same period. The reason for this stable methane level, was that the methane content in the biogas produced tended to increase with time, in contrast to biogas production which had a considerable decline during the same period. The lowest methane percentage was recorded usually after one day, while the highest value was found to occur on the fourth day after loading the reactor, so the increase in biogas production had no effect on methane production. Due to the oscillation of the biogas production throughout this study that was relevant to the sequence of the process operation, the data had to be assessed upon the corresponding day of biogas collection.

The mean specific methane yields for DRR1 and DRR2 of 0.213 and 0.202 m^3 CH_4/kg VS added, respectively, were close to (DRR2) or within the range (DRR1) of the reported methane yield values by similar high solids anaerobic digestion processes, such as the Dranco process (208 to 229 l CH_4 /kg VS added), and the Valorga process (210 to 240 l CH_4 /kg VS added) (De Wilde et al. 1989; Saint-Joly, 1992).

A typical specific biogas yield according to VS removal was reported by Cecchi et al. (1988; 1990a) to be between 0.8 and 1.0 m^3/kg VS removed per day in the anaerobic digestion of the organic fraction of MSW. Therefore, the specific biogas yields obtained during DRR1 and DRR2 of 0.837 and 0.834 m^3/kg VS removed per day, respectively, were within this reported range. Methane contents in the biogas produced during these two runs were approximately 53 and 52% for DRR1 and DRR2 runs, respectively. These values were within the reported range of 50 to 60%

methane content in the biogas that was reported for high solids digestion processes (De Baere and Verstraete, 1984b; Saint-Joly, 1992)

The highest obtained volumetric methane production of 0.832 m^3 CH_4 per m^3 reactor volume per day in DRR2 run, agreed with the reported volumetric methane values under similar operating conditions (OLR, temperature and moisture content). At a loading rate of up to 7 kg VS per m^3 reactor per day and a retention time of 15 days under mesophilic conditions, Cecchi et al. (1990a) obtained a volumetric methane production of around 0.8 m^3 per m^3 reactor per day and specific biogas production of 0.23 m^3/kg TVS added per day in a semi-dry anaerobic digestion of the organic fraction of MSW process.

The maximum OLR of 5.2 kg VS per m^3 reactor per day, applied at DRR3 run, was much lower than the maximum OLR values that were reported by the existing high solids digestion systems, such as Dranco and Valorga, despite the fact that a slightly higher retention time was used in this study. However, the VSR process had a different loading mode than the one reported by such commercial systems. Therefore, it was operated as a four day batch-fed system of actual OLR of 21 kg VS /m^3 fed every four days, which was higher than the maximum allowable OLR for daily batch-fed processes such as Dranco and Valorga. So, the initial impact of this high actual OLR might be the reason for the decrease in performance of the process during the DRR3 run. Biogas and methane production and yields as a function of every four days' organic loading rate are illustrated in Fig. 7.3 and 7.4, respectively. At DRR2, the mean actual organic loading rate was 16.4 kg VS per m^3 reactor every four days (20.4 kg COD per m^3

Fig. 7.3 Volumetric Biogas and Methane Production Relative to Organic Loadig Rate for the DRR Experiment.

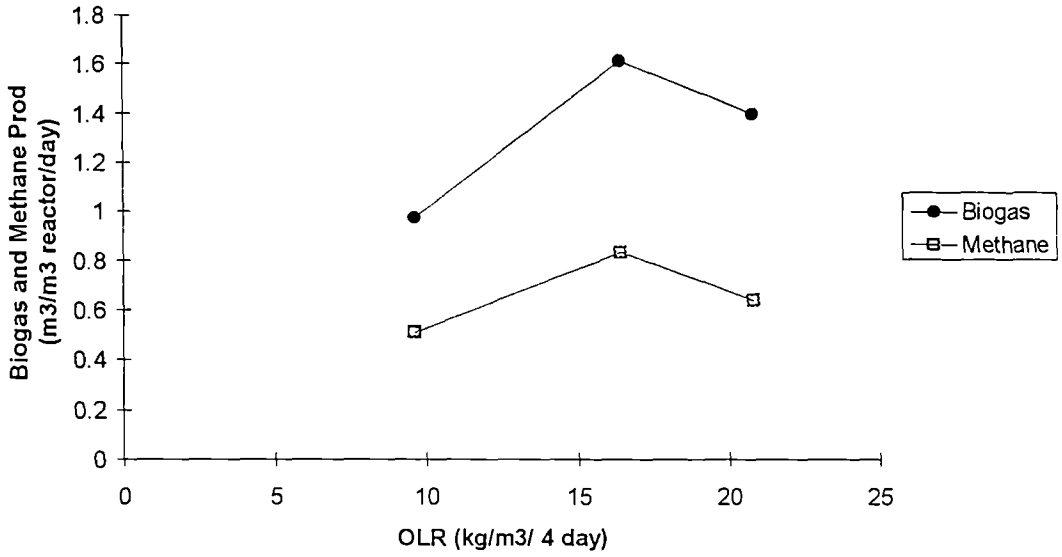
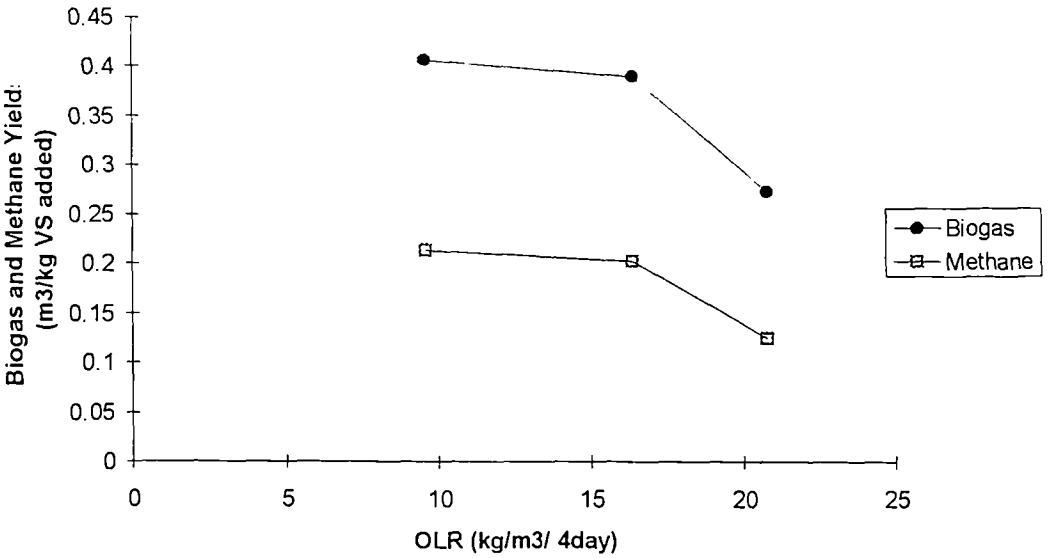


Fig. 7.4 Biogas and Methane Yields Relative to Organic Loading Rate during DRR Experiment.



reactor per 4 days) of the process. This value was higher than the maximum "allowed" organic loading rate of 17.2 kg COD per m^3 reactor per day under mesophilic operating conditions that was reported by De Baere et al. (1985).

The volumetric methane production values were much higher when using the active reactor volume which was estimated to be approximately 30 l for the calculation, in which 0.65, 1.06 and 0.819 m^3 CH_4 per m^3 active reactor per day were obtained for DRR1, DRR2 and DRR3, respectively.

7.9.2 Process Efficiencies.

i) Characteristics of the Final Digested Materials.

The final characteristics of the digested residues were found to be dependent on the effect of both DRR and the variation of the initial refuse composition. A brief description of these refuse variations is given in Table 7.5, where an analytical breakdown of refuse characteristics used in Phase 1. Table 7.6 gives the characteristics of the final digested residues for all DRR runs. Figs. 7.5 and 7.6 illustrate the feed mixture, the digested residues after four days and the final digested residues.

Total solids (TS) of the final digested residues remained relatively stable throughout this phase of the operation. During this DRR study with fixed leachate recycling, the final digested materials had a mean total solids value of approximately 29 % (71 % moisture content). This stability of total solids occurred despite the variation in DRR values, thus different organic loading rates, and might be the result of the four days gap between

Table 7.5 Analytical Breakdown of Refuse Characteristics Used in Phase 1

Parameters	Units	DRR1	DRR2	DRR3	DRR4
VS	% of TS	64.2	62.8	63.8	63.4
TCOD	mg/g	807	786	780	758
FCOD	mg/g	64.0	59.6	65.7	63.4

Table 7.6 Characteristics of the Final Digested Residue during DRR Study

Parameters		DRR1	DRR2	DRR3	DRR4
TS (%)	Mean	29.4 ±0.4	29.2 ±0.6	28.8 ±1.0	29.3 ±0.8
	Range	27.8-30.6	28.6-30.8	28.3-29.6	28.3-30
VS (%)	Mean	48.8 ±0.9	47.2 ±1.1	52.6 ±1.0	46.8 ±0.3
	Range	48-50	46-49.5	51-53.2	46-47
TCOD	Mean	567 ±8.1	551.8 ±18	618.1 ±8.2	515.6 ±10.5
(mg/g)	Range	560-578	520-590	553-640	500-522.5
FCOD	Mean	19.9 ±1.4	18.6 ±1.5	25.8 ±1.6	17.7 ±1.1
(mg/g)	Range	17.9-21	16-21	24-27	16-19
TKN (%)	Mean	1.05 ±0.15	1.1 ±0.13	0.92 ±0.09	------
	Range	0.8-1.2	0.9-1.27	0.83-1.01	
C* (% TS)	Mean-SD	28.7 ±0.9	29 ±11.77	31.6 ±2.46	27.6
	Range	27.8-29.5	27-30.4	28.7-33	27.3-28.2
N* (% TS)	Mean-SD	1.19 ±0.11	1.3 ±0.07	1.136 ±0.1	1.2
	Range	1.08-1.31	1.23-1.36	1.05-1.23	1.18-1.24
H* (% TS)	Mean-SD	2.68 ±0.25	3.1 ±o.6	2.41 ±0.88	1.9
	Range	2.4-2.93	2.51-3.37	1.75-3.42	1.7-2.1
C/N*	Mean-SD	24.2 ±1.6	22.1 ±0.6	27.7 ±1.18	22.9
	Range	22.4-25.8	21.7-22.85	26.8-29.1	22-24

(*) For elemental analyses (C:N:H) at least 3 samples were used at each run, whereas between 6 and 8 samples were used at each run of this experiment.

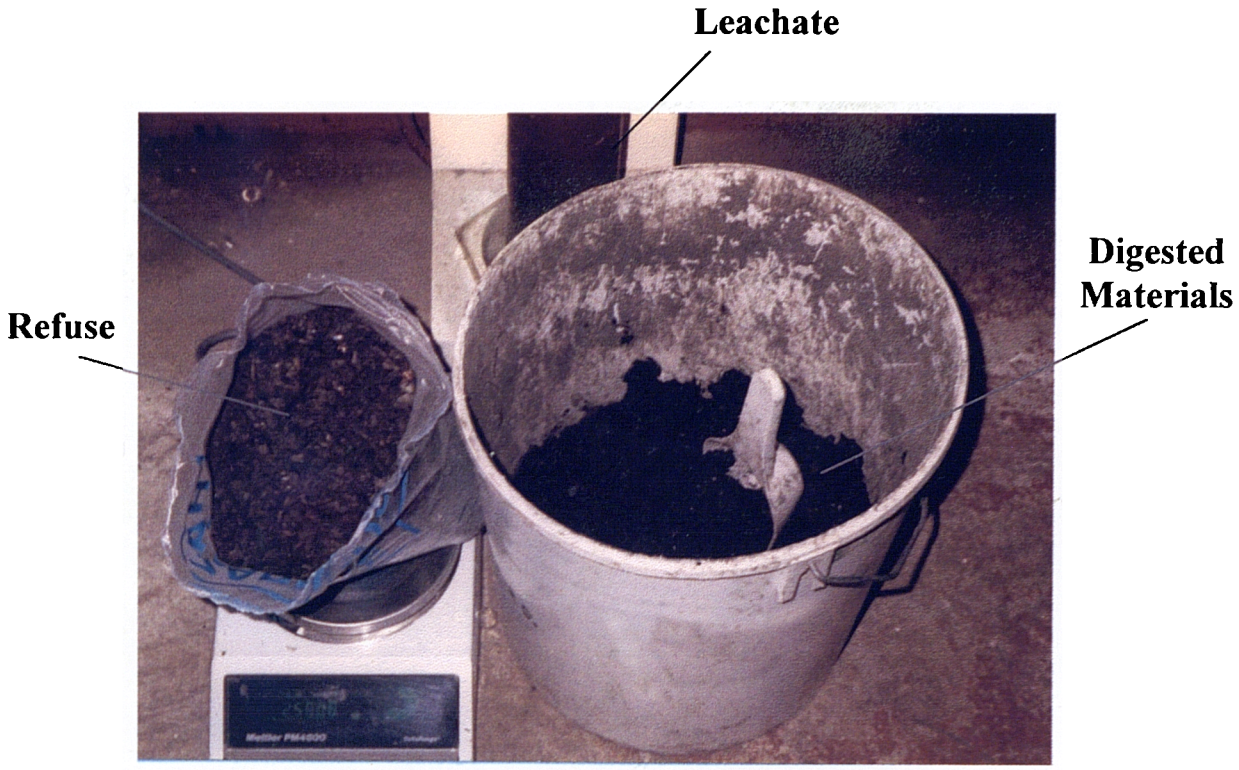


Fig. 7.5 Feed Mixture for VSR



Fig. 7.6 First (4 Days RT) and Sixth (24 Days RT) Chamber Units

feeding which was sufficient for the excess liquid to be drained up to this moisture level.

The final digested solids residues had a VS content (% of TS) of approximately 49, 47 and 53% for DRR1, DRR2 and DRR3, respectively. These VS values were within the range reported for the Dranco end product (Humotex) which has a VS (% TS) of 44 to 53% (De Wilde et al., 1989) and for the Valorga final product VS (% of TS) of 40 to 52% (Beetschen and Cazanave, 1988, Saint-Joly, 1992).

The C/N ratio showed a percentage reduction of 23, 30 and 12% for DRR1, DRR2 and DRR3, respectively. However, the final C/N ratio did not reach the recommended range of 5 to 20 for well composted materials (Hirai et al. 1983; Finstein et al., 1986).

Contrary to the expected decrease of total nitrogen during the digestion process, due to bacterial intake, a slight increase of N to a mean value of 1.3% was observed, compared to putrescible feed N of a mean of 1.26% at DRR2. This trend of slightly higher total nitrogen after 24 days of operation than the initial refuse values at DRR1 and DRR2 runs, was also observed when the direct solids TKN determination method (Section 5.5.2) was applied. Insignificant reduction was observed during the DRR3 run. Mean total nitrogen values of 1.05, 1.1, 0.92% were obtained in the product from DRR1, DRR2 and DRR3, respectively, compared with a mean of 1.02% that was obtained for the initial refuse used. This apparent increase in nitrogen relative to dry weight, as previously indicated by

Stentiford and Dodds (1992), does not express an overall increase in nitrogen but a decrease in VS.

ii) Removals and Reductions.

Table 7.7 presents the process performance efficiencies during the DRR phase in relation to VS, TCOD and FCOD reductions. Method b (Section 6.3.2) is widely used for the determination of VS reduction due to its simplicity and because of the practical difficulty associated with the determination of the more realistic method a (i.e. additional equipment for weighing and handling the materials). All of the results obtained by either method (a and b) fell in the same range as obtained by the other method. For ease of comparison to the literature, the VS reduction values defined by method b are used for any further assessment.

The highest VS reduction of 49% (mean value) was achieved at the DRR1 run. VS reduction in DRR2 was only 4% lower than in DRR1. However, significant decreases of 24% and 20% compared to DRR1 and DRR2, respectively, were observed for DRR3.

The VS reduction obtained in the first two runs of this phase were within the reported typical values of VS reduction in the high solids anaerobic digestion of the organic fraction of MSW processes. De Wilde et al. (1989) reported that the final Dranco product (Humotex) had a 50 to 55 % conversion efficiency, while Saint-Joly (1992) reported a 47% VS reduction for the Valorga process. This reduction was sufficient for the end product to be used as an organic soil conditioner. However, the VS reduction obtained in this work was less than the 55% VS removal that was set as the stability criterion for anaerobic digestion processes (Section

6.1). This fact, in addition to the values obtained for the C/N ratio, showed the need for further post-treatment if the digested residues were to be fully stabilised.

Table 7.7 Performance Efficiencies in Terms of VS, TCOD and FCOD during Phase 1

Reduction (%)	Values	DRR1	DRR2	DRR3	DRR4*
Measured VS	Mean-SD	52.3 ±3.34	49.4 ±3.65	37.8 ±2.73	48.2 ±4.3
Reduction (Method a)	Range	48.5 - 55	41.3 - 53.4	34.2 - 41	45 - 53.8
Calculated VS	Mean-SD	48.6 ±2.66	46.6 ±3.4	37.1 ±1.32	50.4 ±1.3
Reduction (Method b)	Range	45.2 - 52	40.2 - 52	35 - 39	49.2 - 52
TCOD (% loss)	Mean-SD	29.7 ±2.3	29.8 ±2.9	20.4 ±2.0	32.6 ±2.2
	Range	26.8-33.3	23-33	7-22.4	31.6-35.81
FCOD (% loss)	Mean-SD	69.8 ±3.3	68.5 ±4.2	60.6 ±3.6	72.2 ±2.7
	Range	64.5-74	60-74.2	57.8-64.7	69.6-75

(*) All of this run samples were obtained after the start of the second phase.

For TCOD reduction, the same percentage loss of 30% was obtained for both DRR1 and DRR2 runs. A drop of 31% occurred at DRR3 compared to the DRR1 run. The highest FCOD percentage loss of 70% was achieved in the DRR1 run, while DRR2 was only 2% lower than this value. FCOD removed in DRR3, however, was 13% less than in DRR1.

High reduction efficiency (VS, TCOD and FCOD) in DRR4 was the result of the additional 28 days retention time. During this period, no leachate recycling was applied and the reactor contents were not disturbed by loading the reactor.

7.9.3 VFA , pH, NH_3-N and the Internal Reactor Contents.

i) VFA, pH and NH_3-N for DRR Final Digested Residues.

Table 7.8 shows refuse VFA during the DRR study. Refuse VFA consisted mainly of approximately 87% acetic, 5% propionic, 1.8% iso-butyric, 1.5% n-butyric and 1.3% iso-valeric acids.

Table 7.9 gives the VFA concentrations, pH and NH_3-N for the final digested residue of the DRR phase of the VSR semi-continuous experiments. At the early stage of DRR1, final digested residue TVFA concentration was approximately 1.7 mg/g, and decreased gradually to reach around 0.1 mg/g at the end of this experiment. The mean value of TVFA concentration was 0.6 mg/g with a range of 0.1 to 0.8 mg/g during the steady state period. Acetic acid was always the major component, constituting at least 60% of the total VFA in the final digested materials for all runs during this phase.

VFA concentrations remained below 1 mg/g during the DRR2 experiment, with a mean value of approximately 0.7 mg/g. However, a sharp increase in VFA concentrations was observed during the DRR3 run, rising to up to 2.7 mg/g at the end of this experiment with a mean value of around 2.48 mg/g. This increase coincided with a decrease in pH which had a mean value of approximately 7.6 compared with mean pH values of 8.24 and 8.1 for DRR1 and DRR2 runs, respectively. These final digested residue pH values, obtained in the DRR1 and DRR2 runs, were similar to the pH values that were reported to occur during the optimal digestion in the Dranco process of pH 8.0 (De Baere et al., 1985) or even much higher pH values between 8.2 and 8.5 (Deboosere et al., 1986; De Baere et al., 1987).

Table 7.8 Refuse VFA, pH and NH_3-N during Phase 1.

Parameters*	Mean	Range	SD
pH	5.77	5.3-6.1	0.29
NH_3-N (mg/l)	267	122-428	86
NH_3-N (mg/g)	0.38	0.14-0.74	0.19
VFA (mg/g)			
acetic	10.10	7.6-12.9	2.1
propionic	0.60	0-1.4	0.4
iso-butyric	0.21	0-0.54	0.22
n-butyric	0.17	0-0.63	0.2
iso-valeric	0.15	0-1.2	0.4
Total	11.74	9.4-14.3	1.8

(*) Samples number = 12 to 20

Table 7.9 TVFA, pH and NH_3-N of the Final Digested Residue during Phase 1

Parameters	DRR1	DRR2	DRR3
pH	8.24 (8.1-8.3)	8.10 (7.8-8.3)	7.58 (7.4-7.7)
VFA (mg/g)			
acetic	0.37 (0.1-0.5)	0.4 (0-0.68)	1.5 (1.46-1.6)
propionic	0.06	0.10 (0.1-0.2)	0.60 (0.5-0.7)
iso-butyric	0.03	0.03	0.10 (0-0.2)
n-butyric	0.07	0.01	0.05
iso-valeric	0.04	0.12 (0.1-0.2)	0.13 (0.1-0.2)
Total	0.6 (0.14-0.6)	0.7 (0.3-0.9)	2.48 (2.2-2.7)
NH_3-N (mg/g)	2.43 (2.09-2.64)	2.03 (1.55-2.36)	1.50 (1.2-1.66)
NH_3-N (mg/l)	1022 (915-1086)	826 (665-945)	622 (494-692)

The numbers in parentheses represent the range of at least 6 data (6-12).

Ammonia-nitrogen tended to rise with an increasing digested solids recycle ratio (DRR), with means of 1022, 826 and 622 mg/l for DRR1, DRR2 and DRR3, respectively.

The second most dominant acid varied from n-butyric in DRR1, to iso-valeric in DRR2, to propionic acids in DRR3. The three major acids in the residue were above 88% in DRR1, 94% in DRR2 and 93% in DRR3, so they almost fully represented the TVFA samples. Propionic acid was the second in (DRR3) and the third in (DRR1 and DRR2). The fact that propionic was the second largest concentration in the DRR3 run (where it comprised 25% of the final VFA, as opposed to 11% in DRR1 and 15% in DRR2), suggested that the DRR3 run required an extension (more RT) to digest the VFA to a level equal with the DRR1 and DRR2 runs.

ii) Internal activities study.

a) VFA, pH and NH_3-N.

In order to observe the reactor contents through different stages in fermentation, the VSR consisted of several chamber units, each one representing four days' retention time. For the DRR phase of the VSR semi-continuous operation, as mentioned previously, samples were taken from the first chamber unit which represented day 4 of the 24 days cycle. In this section, phase-separation was evaluated with the use of VFA as an indicator of the internal conditions affecting the performances of the favourable acetogenic and methanogenic bacteria.

Table 7.10 gives VFA, NH_3-N concentrations and pH in the digesting waste for day 4 (four days after loading the reactor) of the various DRR

Table 7.10 TVFA, pH and NH_3-N of day 4 during DRR Phase Experiments

Parameters	DRR1	DRR2	DRR3
pH	7.35 (7.2-7.5)	7.16 (6.9-7.4)	6.35 (6.0-6.6)
NH_3-N (mg/l)	1.57 (1.2-1.85)	1.11 (1.0-1.23)	0.93 (0.86-0.97)
NH_3-N (mg/l)	698 (529-821)	572 (455-811)	431 (422-446)
VFA (mg/g)			
acetic	3.89 (2.1-5.6)	3.92 (2.47-5.9)	1.8 (0.83-4.0)
propionic	2.68 (1.0-4.33)	3.96 (2.1-4.8)	14.6 (12-17.9)
iso-butyric	0.04	0.05	0
n-butyric	2.0 (1.1-3.5)	1.47(0.1-3.4)	1.5 (0.4-3.0)
iso-valeric	0.07	0.14	0.5
n-valeric	0.12	0.13	0.4
Total	8.84 (6.0-11.7)	9.72 (7.4-12.1)	19.1 (16.0-22.2)
propionic/acetic	0.69	1.01	8.33
acetic/n-butyric	1.95	2.67	1.20
propionic/n-butyric	1.34	2.69	9.73

Values between parentheses represent the range of at least 10 samples

stages. Acetic and propionic were the only two acids, out of the eight acids analysed (including iso- and n-caproic), which showed any significant variation with decreasing DRR values (increasing OLR). In the DRR1 run, acetic acid was 31 % higher than propionic acid, while in DRR2 similar values were obtained for both acids, with a marginal preponderance (1%) of propionic acid. However, a sharp increase in propionic acid was observed from the start of the DRR3 experiment. The mean propionic acid concentration of 14.6 mg/g was approximately 88% higher than the mean acetic acid concentrations that were produced during this run. pH values as low as 6.0 (mean of 6.35) were measured during DRR3, which indicated more favourable conditions for acidogenic bacterial growth (Alexiou and Anderson, 1994). This low pH was in contrast to the optimum pH values of 7.3 and 7.2 that were obtained during the DRR1 and DRR2 runs, respectively. These optimum pH values were reported to enhance the growth of methanogenic bacteria (Zehnder, 1978).

Acetic, propionic and n-butyric acids constituted 94 to 97% of the TVFA, so they may be taken as fully representing the VFA of the samples. The ratios of acetic/propionic and propionic/n-butyric (mostly the former) showed an obvious shift of anaerobic internal activities, probably due to unfavourable conditions for acetogens and methanogens. Therefore, there was inhibition of major acid conversion to acetic acid and further to methane. The fact that acetic acid in the DRR1 and DRR2 runs were almost equal seems to indicate that this was the maximum degradation level that methanogens could achieve during this four days, independent of DRR. Also, the increase in propionic acid with the subsequent increase in

the digestion rate of butyric acid (equal values in DRR1 and DRR2 runs), proved that acetogenesis reached its maximum degradation capacity, independently of DRR. Therefore, only acidogenic bacteria are capable of acting further to increase the propionic acid (with any further increase in OLR) until they inhibit their own activities by high H_2 concentrations. Hence, the DRR3 loading is an OLR indicating potential failure, if OLR is further increased without changing other operational conditions to establish stability (i.e. adding alkalinity to maintain pH, increasing the retention time and/or the temperature).

b) Acidification.

For further evaluation of the acidogenic phase, a method for interpretation of VFA and COD results was applied in this work. Alexiou and Anderson (1994) and Alexiou et al. (1994a) suggested the following Eq. for the assessment of the overall acidogenic phenomenon:

$$\text{Acidified COD (\%)} = \left[\frac{\text{COD of VFA (mg / g)}}{\text{Filtered COD (mg / g)}}\right] * 100 \qquad (7.5)$$

Table 7.11 gives the calculated acidified COD (acidification) results for phase one of the VSR semi-continuous experiment. Acidification level increased by approximately 40% from an initial refuse value of 20.3% after four days of operation during the DRR1 run. However, the acidification dropped below 5% by the final day (day 24) of this first run. Despite the fact that a further acidification increase of approximately 49% from the initial refuse value had occurred during day 4 of the DRR2 run, the acidification level of the final digested solids was similar to the final DRR1 result. This low acidification level indicated that the system was

Table 7.11 Calculated Acidification Results for Phase 1 (mean values).

i-Refuse

Parameters	Refuse
TVFA (mg/g as COD)	12.8
FCOD (mg/g)	63.2
Acidification (%)	20.3

ii-Day 4

Parameters	DRR1	DRR2	DRR3
TVFA (mg/g as COD)	12.3	13.6	27.6
COD (mg/g)	37	34	52
.Acidification (%)	33.4	40	53

iii-Day 24 (Final Digested Residues)

Parameters	DRR1	DRR2	DRR3
TVFA (mg/g as COD)	0.98	0.93	3.26
FCOD (mg/g)	20	18.6	26
Acidification (%)	4.9	5.0	12.5

capable of handling the increase of OLR (DRR value of 0.5) efficiently, and that the DRR1 run was underloaded for the applied reactor conditions.

The maximum acidification level was found to occur during DRR3 run, in response to decreasing the DRR value to 0.3 and increasing the organic loading rate, as stated in Section 7.3 of this chapter. This maximum acidification value of 53% was higher than the raw refuse acidification by approximately 62%. Acidification during this run was slightly over the acidified matter range of 40 to 50% which Alexiou et al. (1994b) recommended should not be exceeded when feeding a methanogenic reactor in the two phase process in order to avoid digestion failure. This recommended range was obtained for the two-phase anaerobic digestion of industrial wastewater. However, high acidification values, up to 60%, have been experienced in this work without failure in the digestion process. Acidification levels of DRR1 (33.4%) and DRR2 (40%) were within or lower than this recommended range, and this would enhance the establishment of stable acetogenic and methanogenic activities in two-phase applications.

At the end of the DRR3 run, the final digested acidification value was 12.5% which was much higher than the 5% value that was obtained in the first two runs of this phase (DRR1 and DRR2). This indicated once more that, in DRR3, the organic matter could not be fully digested in the given retention time.

7.9.4 Leachate Characteristics.

i) Leachate volume.

Tap water was added to the leachate in order to maintain it at the desired level. The variation of the incoming refuse total solids and also the fact that samples were regularly taken during digestion were the reasons for the different amounts of tap water required throughout the study.

Despite the fact that DRR varied during Phase 1, total solids (TS) remained relatively stable, as mentioned previously in this chapter. The real difference was the amount of drained liquid found at the end of the four days intervals between loading the reactor. Table 7.12 gives the respective data.

Table 7.12 Total Liquid Added During Phase 1.

Type of Liquid Added	DRR1	DRR2	DRR3
Drained liquid (l)*	5	4.5	4.3
Range	(4.7-5.2)	(4.2-4.6)	(4.1-4.5)
Tap water (l)	1.0	1.5	1.7
Range	(0.8-1.3)	(1.4-1.8)	(1.5-1.9)

(*) After sampling

ii) Leachate Filtered COD.

Fig. 7.7 shows leachate FCOD relative to time during the DRR experiment. After the DRR1 experiment had run for 48 days, leachate FCOD dropped by approximately 48% to reach 2700 mg/l at the end of this run. During the DRR2 run, leachate FCOD varied between 2200 and 3100 mg/l, with a mean value of 2580 mg/l. This quasi-steady state reflected the level of non-biodegradable FCOD existing in the raw

materials, which varied with loading. However, an increase in FCOD values was observed with increasing loading rate, reaching a mean value of 3300 mg/l during the DRR3 run.

iii) VFA, pH and Alkalinity.

Leachate movement allowed for the removal of high TVFA concentrations from the first two top-chamber units (days 4 and 8). Leachate then travelled through the more mature stages in the following lower chambers of the reactor; where the methanogenic bacteria were active and readily consuming the incoming TVFA.

Fig. 7.8 shows leachate TVFA during the DRR study. High TVFA concentrations were observed at the start of the semi-continuous phase up to the 12th day of the experiment. From that day onwards, a rapid degradation of TVFA concentrations occurred, which reached a level below 100 mg/l as COD (14-81 mg/l), after 32 days from the beginning of this experiment. This low leachate TVFA concentration remained throughout the DRR1 and DRR2 runs. However, a slight increase of leachate TVFA concentration of up to 120 (mean of 90) mg/l as COD was observed during DRR3 run. This increase was much lower than expected, as other indicators (i.e. VS reduction, biogas and methane yields) showed lower conversion efficiency in this run. This might have been due to the fact that drained liquid remained for four days at the bottom of the reactor; which might have allowed the TVFA to be consumed by methanogenic bacteria in the liquid.

A slight increase in leachate propionic acid concentration of up to 62 mg/l was observed during DRR3 run. The only sign of a stressed reactor that could be derived from this VFA data was that the propionic to acetic acid ratio (mean 1.0; maximum 1.8) approached the 1.4 level suggested by Hill et al. (1987) as an indication of the stability of the anaerobic digestion process. A greater propionic to acetic acid ratio than this 1.4 could indicate imminent reactor failure. Mean propionic to acetic acid ratios of 0.26 (up to 0.5) and 0.31 (up to 0.63) were obtained during the DRR1 and DRR2 runs, respectively. TVFA obtained from the solids samples (water extract methods), showed much higher TVFA concentrations in the DRR3 run than in the DRR1 and DRR2 runs.

The acidification level in leachate samples, as shown in Fig. 7.9, reached up to 20% on day 8 of the experiment. However, a significant drop of more than 90%, from the initial acidification level, was observed at the end of the DRR1 run, to reach a level below 1%. This low acidification level remained for most of the DRR2 run (mean of 1.3%). A marginal increase of only up to 3.3% (mean of 3%) had occurred in the DRR3 run. Low TVFA concentrations and acidification levels indicated that most of the organic matter present in the leachate samples was consumed by the methanogenic bacteria and that mostly non-biodegradable COD remained in the system.

Fig. 7.10 shows pH in the leachate samples during phase 1 of the Semi-continuous experiment. Similar pH values, which ranged between 7.6 and 7.9, were obtained during the first two runs (DRR1 and DRR2). Lower pH, with a mean of 7.4 (7.3 to 7.6) was obtained during the DRR3 run.

Fig. 7.7 Leachate FCOD during DRR Study (Phase 1)

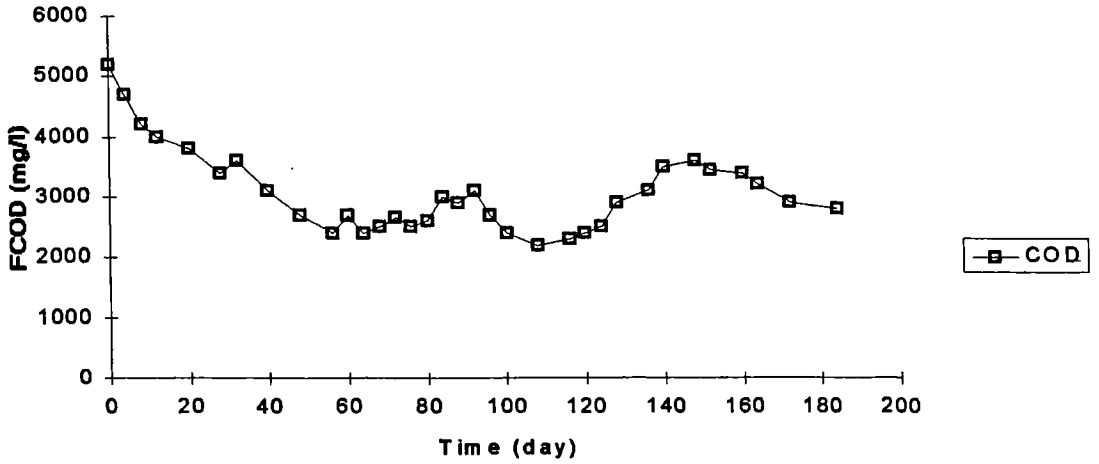


Fig. 7.8 Leachate VFA Concentrations during DRR Study

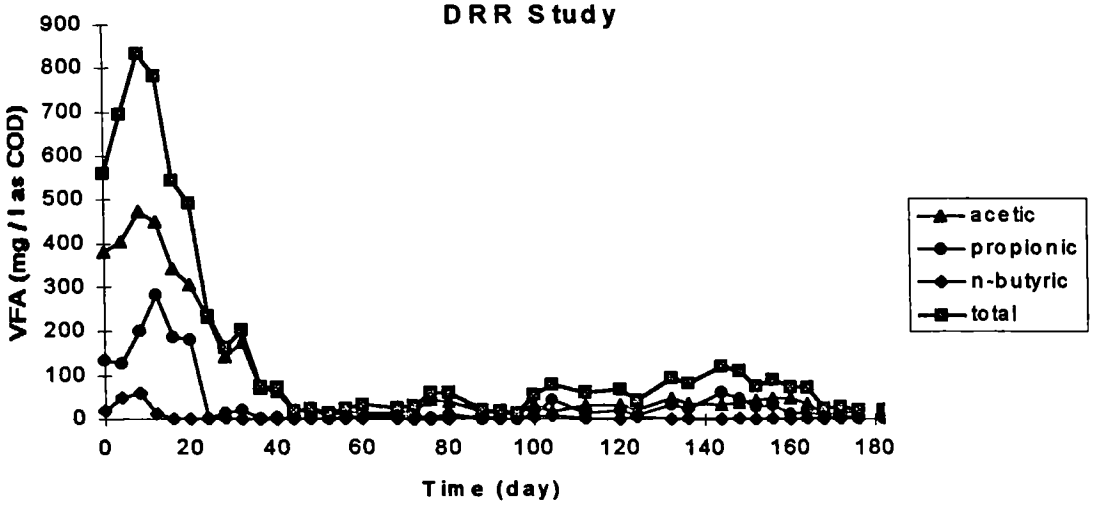
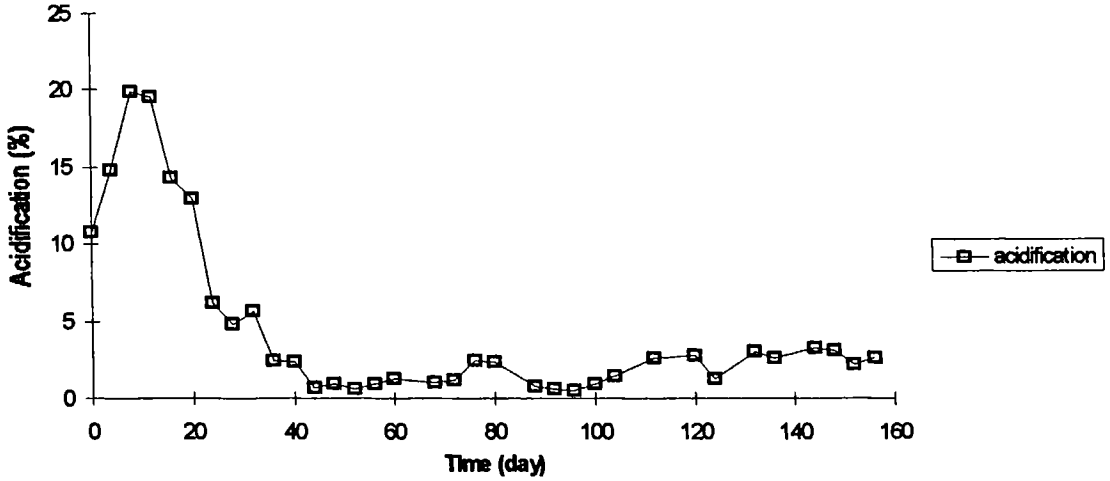


Fig. 7.9 Leachate Acidification Results during Phase 1 Experiments



These pH values were obtained by measuring pH directly after collecting the leachate samples and before filtering them. However, a pH between 7.9 and 8.1 was obtained throughout the VSR semi-continuous study when measuring pH after filtering the leachate samples.

During this phase, the total alkalinity (end point 4.5) was in the range of 4600 to 6320 mg/l, with the highest value being observed in the DRR1 run and the lowest in the DRR3 run.

iv) TKN and NH_3-N.

Fig. 7.11 indicates the concentrations of total nitrogen (TKN) and ammonia nitrogen in the leachate samples during Phase 1. Ammonia nitrogen represented approximately 87, 90 and 85% of the total nitrogen that was found in the leachate samples for DRR1, DRR2 and DRR3, respectively.

The highest NH_3-N concentration of 1100 mg/l was observed during the DRR1 run, during which a mean NH_3-N concentration of 1011 mg/l was obtained. Ammonia nitrogen concentrations lower by approximately 25 and 31%, compared to the previous run, were observed in the DRR2 and DRR3 runs, respectively. The reason for this low ammonia nitrogen and total nitrogen values might have been that the process was well established at this stage, with a healthy bacterial population using ammonia nitrogen as a main nutrient source for growth. However, this reason might not be applicable to the DRR3 run, where a mean NH_3-N concentration of 702 mg/l was obtained. On the contrary, high organic loading rate and

Fig. 7.10 Leachate pH during DRR Study (Phase 1)

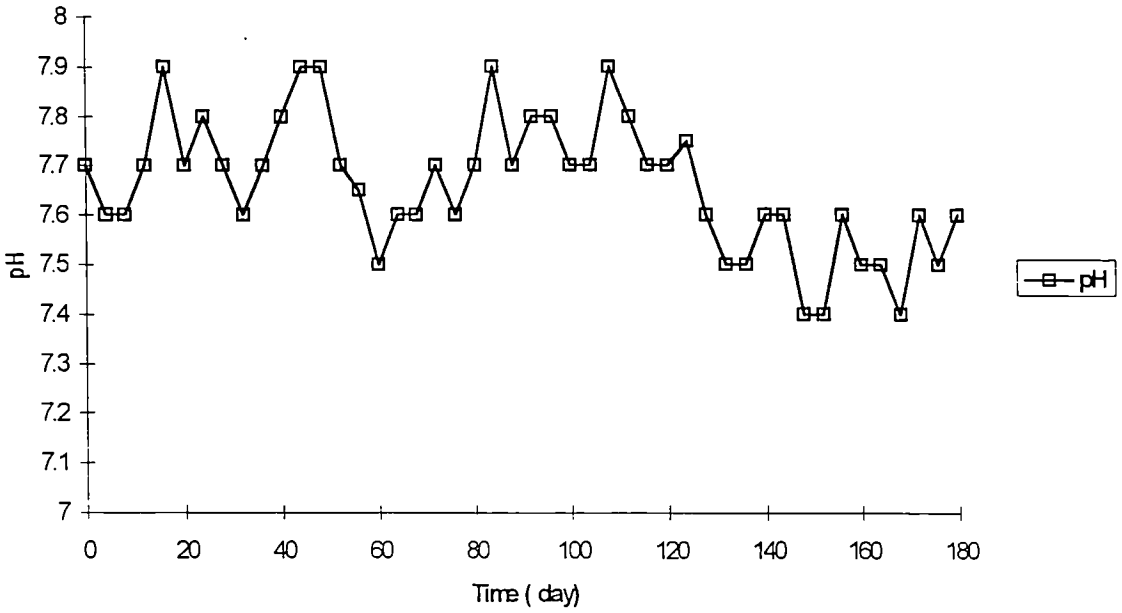
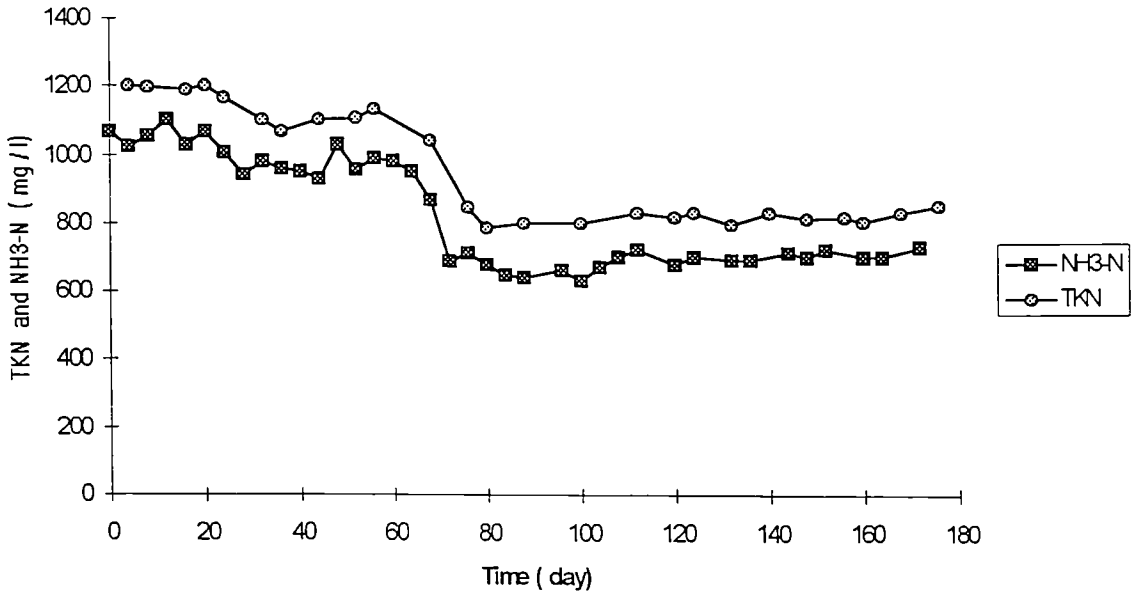


FIg. 7.11 Leachate Total and Ammonia-Nitrogen during Phase 1



low DRR ratio, which resulted in decreased process performance, might be attributed to this low NH_3-N concentration during the DRR3 run.

7.10 Results and Discussion of Phase 2 (Leachate Recycle, LR, Study)

7.10.1 Biogas and Methane Production.

Table 7.13 gives, for steady state conditions, biogas and methane results relative to leachate recycling (LR). Fig. 7.12 and 7.13 illustrate the daily biogas and methane production and biogas composition during the second phase of this experiment, which lasted 160 days.

The results of LR1 have been given previously as the DRR2 run. Each experiment of this phase (LR2 to LR4) lasted for approximately 54 days. Steady-state conditions were considered to have been reached from days 21, 81, and 129 onwards, when biogas (methane) production reached 54 (24.4), 45 (22.3) and 35 (16.5) l/day, for LR2, LR3 and LR4, respectively. The organic loading rate remained relatively stable throughout this phase, within a range of 3.7 to 4.1 kg VS per m^3 reactor per day (mean values for all LR runs).

Maximum biogas production of 65 l/day, corresponding to 32.6 l CH_4 per day, was obtained on day 33 of LR2, compared to 71 (biogas) and 34.4 l/day (methane) for the LR1 run. However, maximum daily biogas production values of 55 l (25.7 l of CH_4)and 39 l (17.3 l of CH_4) litres were obtained on day 105 of LR3 and on day 137 of LR4, respectively. Mean volumetric methane production was 0.832, 0.763, 0.588 and 0.387 m^3 CH_4 per m^3 nominal reactor volume per day for LR1 to LR4 runs,

Table 7.13 Steady-State Biogas and Methane Production and Yields during Phase 2.

Parameters	Units	Values	LR2 * 3.5 litres	LR3 1.5 litres	LR4 0.8 litres
Loading Rate	g VS / day	Mean-SD	153.9 ± 5.6	152.2 ± 5.15	142.5 ± 4.32
		Range	149 - 165.4	146 - 160	136.2 - 149
	kg VS/m^3/d	Mean-SD	4 ± 0.156	3.95 ± 0.135	3.7 ± 0.09
		Range	3.9 - 4.3	3.8 - 4.17	3.5. - 3.8
	kg VS/m^3/ 4 days	Mean	16	15.8	14.8
Biogas Production	l/day	Mean-SD	56.3 ± 5.1	44.3 ± 4.7	32.47 ± 3.58
		Range	48-65	38-55	28-39
Biogas Production	m^3/m^3 reactor/day	Mean	1.466	1.15	0.845
	m^3/m^3 active reactor/day	Mean	1.87	1.47	1.08
Methane production	l/day	Mean-SD	29.3 ± 2.01	22.6 ± 1.91	14.86 ± 1.22
		Range	26-32.6	19.54-25.7	13-17.3
Methane Production	m^3/m^3 reactor/day	Mean-SD	0.763 ± 0.053	0.588 ± 0.049	0.387 ± 0.03
		Range	0.674-0.849	0.509-0.67	0.34-0.45
Methane Production	m^3/m^3 active reactor/day	Mean-SD	0.977 ± 0.07	0.752 ± 0.063	0.495 ± 0.04
		Range	0.862-1.087	0.651-0.857	0.435-0.576
Specific Biogas Yield	m^3/kg VS added	Mean	0.37	0.291	0.225
	m^3/kg VS removed	Mean	0.809	0.681	0.684
Specific Methane Yield	m^3/kg VS added	Mean	0.192	0.151	0.105
	m^3/kg VS removed	Mean	0.421	0.348	0.313
Percent CH_4	% of Biogas	Mean-SD	52.2 ± 2.44	50.8 ± 2.12	46.6 ± 2.82
		Range	47.65-55.8	46.7-54	41.4-50
Percent CO_2		Mean-SD	39.42 ± 1.73	41.23 ± 1.66	44.2 ± 3.4
		Range	35.7-42.1	38-45.44	39-49.2

* LR1 (6 litres) is shown in Table 7.3 as DRR2

Fig. 7.12 Daily Biogas Production during Leachate Variation Experiment (phase 2)

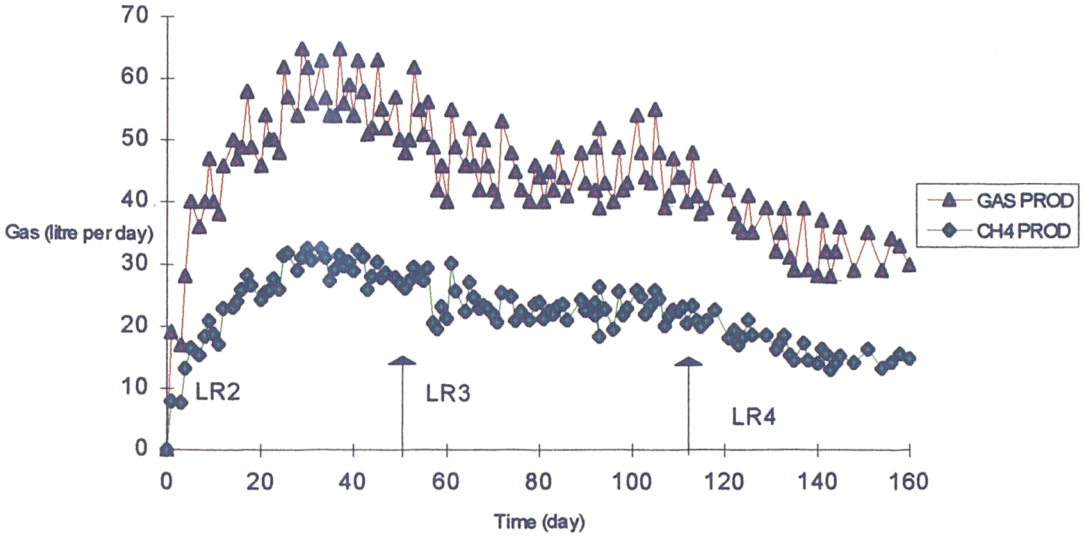
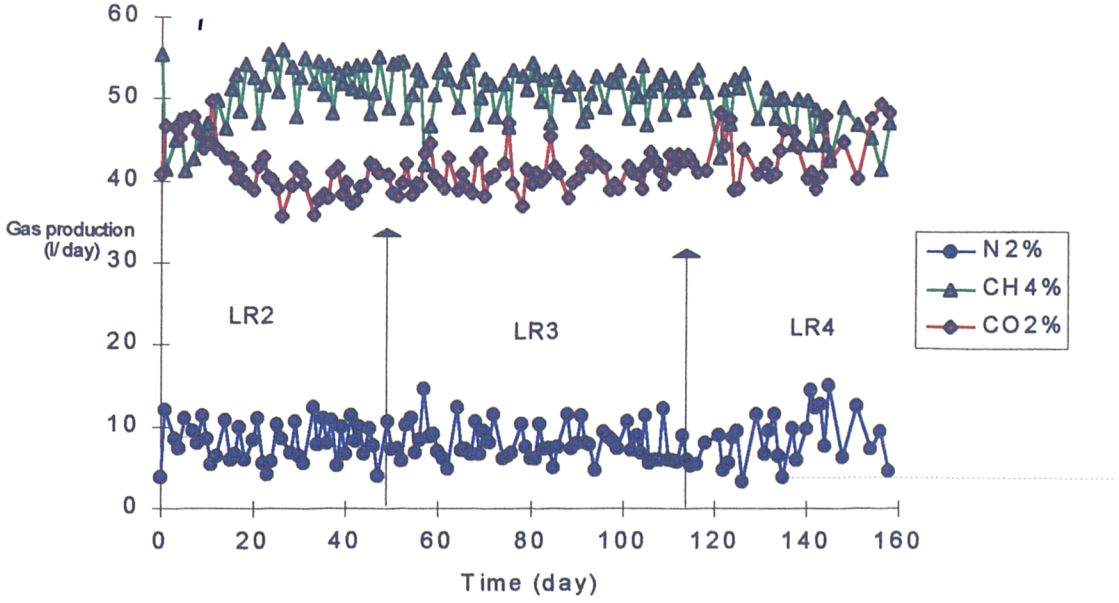


Fig. 7.13 Gas Composition during Leachate Study (Phase2).



respectively. The volumetric methane production values were 22% higher when using the active reactor volume for the calculation.

Reducing the level of the recycled leachate affected both the production and the composition of the biogas produced during this phase. Biogas production decreased by 9, 28.5 and 47.6%, while methane production decreased by 8.8, 29.7 and 53.7%, for LR2, LR3 and LR4, respectively, compared to the LR1 run. Comparison of the reduction in biogas and methane production, showed that a marginal difference between them was observed for the LR2 run. However, for the LR3 and LR4 runs, methane had a more sharp decline than biogas production due to high carbon dioxide content in the biogas, with decreasing moisture content. Similar percentages of CH_4 (52%) and CO_2 (40%) were obtained for the LR1 and LR2 runs. Methane content in the biogas showed a decrease of approximately 3 and 11% for the LR3 and LR4 runs, respectively, compared with the previous two runs, in contrast to the CO_2 percentage in the biogas which increased by approximately 5 (LR3) and 11% (LR4).

Specific methane yield was similar during the LR1 and LR2 runs, where only 5% reduction had occurred in the latter to reach 0.192 m^3/kg VS added. A more significant decline, of approximately 25% and 48%, was observed when further reducing the process moisture content (recycled leachate), in the LR3 and LR4 runs, respectively. The insignificant difference between the LR1 and LR2 runs, in terms of methane production and yield, despite decreasing leachate recycling by 42%, made the latter more attractive in relation to reducing the operational cost and the reactor volume.

Biogas yield according to VS removal, for LR2 run, showed a reduction of less than 3% compared to LR1, to reach a mean value of 0.809 m^3/kg VS removed. This value was within the typical specific biogas yield range of 0.8 to 1.0 m^3 per kg VS removed. A significant reduction of approximately 19%, in terms of VS removal, was observed in the LR3 and LR4 runs. This reduction followed the lowering of the moisture content of the process by reducing the recycled leachate level. Mean methane yields based on VS removal illustrated a reduction of approximately 3%, 20% and 28% for LR2, LR3 and LR4, respectively, compared to the LR1 result of 0.433 m^3/kg VS removed.

Higher biogas and methane yields, according to VS removed rather than VS added, indicate the presence of a relatively low percentage of biodegradable matter in the putrescible fraction of MSW. On the other hand, low values of biogas and methane yields based on both VS removed and added indicate a decrease in the overall performance efficiency of the anaerobic digestion process with time during this phase of study. At the LR4 run, low biogas and methane yields were obtained according to both kg VS removed and added, compared with the previous Phase 2 runs (mainly the LR1 and LR2 runs). These low yields indicated that the effect of reducing the system moisture content, rather than the low refuse biodegradable fraction, was the main reason for the results observed in this run.

Biogas production followed the same pattern as the one described in the previous section, where the highest and the lowest biogas production was

obtained after one and four days, respectively, from first loading of the reactor.

7.10.2 Process Efficiencies.

i) Final Digested Residues Characteristics.

Table 7.14 presents an analytical breakdown of refuse characteristics used in Phase 2, while Table 7.15 gives the characteristics of the final digested residues during this phase.

Total solids of the final digested residues are usually less than the initial total solids of the feedstock, due to the effect of hydrolysis on the organic matter. The final digested residues of the Dranco process have a total solids content between 30 and 35%, while feed has between 35 and 40% TS. The Valorga process has feed and effluent total solids of 35 to 40 and 35%, respectively. The similar initial feed to final effluent total solids was attributed to the occurrence of continuous compacting and dewatering due to the pressure from solids residues piled high in the reactors (Deboosere et al. 1986; De Baere et al. 1987; Legrand et al., 1989). In this work, the total solids in the final digested matter were used to evaluate the process, rather than the initial total solids of the feedstock, which were expected to be higher, to minimise the effect of the addition of a high amount of leachate prior to loading the first chamber unit of the reactor. Mean total solids in the digested residue of approximately 29, 31, 33 and 36% for runs LR1 to LR4, respectively, were obtained during this phase.

As mentioned in the previous Section, methane production decreased significantly with the drop in the moisture content of the process. This reduction was more evident at the 33% (LR3) and 36% TS (LR4) runs,

Table 7.14 Analytical Breakdown of Refuse Characteristics Used in Phase 2 .

Parameters*	Units	LR1	LR2	LR3	LR4
VS	% of TS	62.8	62.6	60.9	49.2
TCOD	mg/g	786	790	760	602
FCOD	mg/g	59.6	64.2	61.5	43.7

(*) Mean values

Table 7.15. Characteristics of the Final Digested Residue during Phase 2.

Parameters	Values	LR1 (DRR2)	LR2	LR3	LR4
TS (%)	Mean-SD	29.2 ±0.6	30.9 ±1.0	32.6 ±0.9	36 ±1.1
	Range	28.6-30.8	30.3-32	32-34	35-38.6
VS (%)	Mean-SD	47.3 ±1.1	47 ±1.1	48.3 ±2.7	40.2 ±1.8
	Range	46-49.5	45-48.8	47-52	39-43.2
TCOD (mg/g)	Mean-SD	551 ±18.2	550 ±13.1	563.3 ±23.4	492.7 ±15.5
	Range	520-590	530-570	540-590	470-501
FCOD (mg/g)	Mean-SD	18.6 ±1.5	19.6 ±0.9	22.5 ±2.7	22.7 ±1.2
	Range	16-21	18-20	19-26	21-25
C (% TS)	Mean-SD	29 ±11.77	28.46 ±1.36	29.9 ±1.4	25.8 ±1.16
	Range	27-30.4	27.4-30	28-31.1	24.5-26.8
N (% TS)	Mean-SD	1.3 ±0.07	1.24 ±0.06	1.175 ±0.06	1.26 ±0.06
	Range	1.23-1.36	1.2-1.3	1.1-1.24	1.23-1.33
H (% TS)	Mean-SD	3.1 ±0.6	2.21 ±0.69	3.1 ±0.33	3.39 ±0.21
	Range	2.51-3.37	1.73-1.9	2.78-3.25	3.1-3.6
C/N	Mean-SD	22.1 ±0.6	22.89 ±0.56	25.5 ±1.77	20.3 ±1.1
	Range	21.7-22.85	22-23.3	24.1-27.9	19.5-21.6
Density	kg/m3	1233	1130	980	800

where methane reductions of approximately 30% and 54% were noted, respectively, compared to the 29% TS in (LR1) run. However, a marginal methane reduction of approximately 9% was observed at 31% TS (LR2) compared with the 29% TS run. These results agreed with the finding of Wujcik (1979) and Jewell (1980) that a significant reduction in the rate of methane production occurred at total solids content above 32%.

The final digested solids residues had a mean VS content (% of TS) of 47.3, 47, 48.3 and 40.2% for LR1, LR2, LR3 and LR4, respectively. The C/N ratio showed a percentage reduction of 30, 27, 19 and 14% for LR1 to LR4 runs, respectively. However, only the C/N ratio of the LR4 run reached the recommended range of 5 to 20 for well composted materials, despite the low C/N percentage reduction value, due to the low initial refuse C/N ratio used during this run.

ii) Removals and Reductions.

Table 7.16 presents the process performance efficiencies during LR phase in relation to VS, TCOD and FCOD reductions. The effect of lowering leachate recycling between LR1 and LR2 had only a marginal decrease in terms of VS removed with only 3% reduction in the latter. For the LR3 run, VS decreased by approximately 9%, from the LR1 value; however, a higher decrease of 16% was obtained for this VS drop when comparing VS reduction results according to method b of VS determination. A sharp decline in VS reduction of approximately 28% (compare to LR1) was notable at LR4 run, when the final digested residues had total solids of more than 36%. These results agreed with the finding of Wujcik (1979)

who reported a significant reduction of the overall anaerobic digestion process efficiency when the moisture content of the system decreased.

Table 7.16 Performance Efficiencies (VS, TCOD and FCOD Removal) during Phase 2.

Reduction (%)	Values	LR1	LR2	LR3	LR4
Measured VS (Method a)	Mean-SD	49.4 ±3.65	47.8 ± 2.18	41.6 ± 2.53	37.5 ± 2.09
	Range	41.3 - 53.4	45 - 51.7	38.2 - 45.1	34.4 - 40
Calculated VS (Method b)	Mean-SD	46.6 ±3.4	45.2 ± 3.11	42.7 ±3.3	33.3 ± 2.37
	Range	40.2 - 52	41 - 48.8	37.6 - 46	30.5 - 36
TCOD (% loss)	Mean-SD	29.8 ±2.9	30.4 ±2.0	25.8 ±3.9	18.2 ±1.9
	Range	23-33	28.2-34	22.7-29	16.5-20.3
FCOD (% loss)	Mean-SD	68.5 ±4.2	69.4 ±1.9	63.2 ±4.3	48.8 ±3.2
	Range	60-74.2	67-71.9	56.6-67.2	44.0-51.0

The VS reduction obtained in the LR2 run was close to the reported typical values of VS reduction, which were discussed in Section 7.9.1 (i), in the high solids anaerobic digestion of the organic fraction of MSW processes. However, as in the case of the DRR1 and DRR2 (LR1) runs, the obtained VS reduction was less than the 55% VS removal, that was set as the stability criterion for the anaerobic digestion processes (Section 6.1). Also, the values and percentage reduction of the C/N ratio showed the need for further post-treatment of the digested residues, in this phase as well as in Phase 1, to be fully stabilised.

For TCOD reduction, the percentage loss in LR2 was similar to the LR1 value of 30%. Drops of approximately 11% and 39 % were observed at LR3 and LR4, respectively, compared to the LR1 run. In relation to FCOD, the highest percentage loss of approximately 69% (mean value)

FCOD, the highest percentage loss of approximately 69% (mean value) was obtained in both the LR1 and LR2 runs. FCOD showed a drop of approximately 9% for LR3 and 29% for LR4, compared to the LR1 run.

7.10.3 VFA, pH, NH_3-N, and Internal Reactor Contents During Phase 2.

i) VFA, pH, and NH_3-N.

The final digested solids residue prior to the start of Phase 2 had a pH of 8.3, TVFA concentration of approximately 0.3 mg/g (0.34 mg/g as COD), FCOD of 14.2 mg/g and acidification level of 2.3%. Tables 7.17 to 7.20 give VFA, pH, NH_3-N, FCOD and Acidification results for runs LR1 to LR4 of the leachate recycle phase of the VSR semi-continuous operation.

Fig. 7.14 to 7.21 show the VFA concentrations results in terms of mg/g and mg/g as COD for all runs of Phase 2. Despite the fact that the TVFA concentration (mg/g) after 4 days of operation indicated a decrease by approximately 17% from the initial refuse TVFA, the mg/g as COD results showed that an actual increase of approximately 6% had occurred during this period. The same trend of decreasing TVFA (mg/g) and increasing TVFA (mg/g as COD) was also observed during LR2, LR3 and LR4. High propionic acid concentrations, observed at day 4, resulted in higher TVFA concentrations (mg/g as COD). At the end of 4 days of operation, the propionic acid concentrations increased by 85%, 96%, 95% and 88% for runs LR1, LR2, LR3 and LR4, respectively. In contrast, a significant drop in the acetic acid concentrations was observed at the end of day 4 of the operation. The acetic acid reductions were 62%, 80%, 79% and 50% for LR1, LR2, LR3 and LR4, respectively. The mean pH values were between 7.2 and 7.34 (optimum for methanogenic bacteria growth) for the

Table 7.17 VFA, pH, NH_3-N , FCOD and Acidification Results for LR1 Experiment of the VSR Semi-Continuous Operation.

Time	pH	NH_3-N	VFA (mg/g)			VFA (mg/g as COD)	FCOD	Acidification
days	----	mg/l	Acetic	Propionic	TVFA	TVFA	mg/g	%
0*	5.8 (5.3-6.1)	267	10.2	0.6	11.7	12.8	63.2	20.2
4	7.2 (6.9-7.4)	572	3.9 (2.47-5.9)	4.0 (2.1-4.8)	9.7 (7.4-12.1)	13.6	34	40
8	7.3	----	0.8	4.6	5.8	8.6	30	28.8
12	7.8	----	0.2	0.7	1.0	1.4	24	6.0
16	8.0	----	0.6	0.1	0.8	0.9	22	4.2
20	8.1	----	0.6	0.0	0.7	0.8	19	4.1
24**	8.1 (7.8-8.3)	826	0.4 (0-0.7)	0.1 (0.1-0.2)	0.7 (0.14-0.6)	0.93	18.6	5.0

* Refuse

** Final digested residue

Values between parentheses represent the range of at least 6 samples.

Table 7.18 VFA, pH, NH_3-N , FCOD and Acidification Results for LR2 Experiment of the VSR Semi-Continuous Operation.

Time	pH	NH_3-N	VFA (mg/g)			VFA mg/g as COD	FCOD	Acidification
days	----	mg/l	Acetic	Propionic	TVFA	TVFA	mg/g	%
0*	6.1 (5.8-6.4)	267	9.2 (7.4-11.3)	0.2 (0.0-0.6)	9.7 (7.8-11.7)	10.6	62	17.2
4	7.28 (7.1-7.7)	670	1.8 (1.0-2.3)	5.6 (4.1-6.0)	8.5 (7.4-9.1)	12.6	38	33.1
8	7.2	---	3.4 (	3.9	8.2	11.3	35	32.4
12	7.8	---	2.2	0.6	3.5	4.7	25	18.7
16	8.0	---	0.6	0.2	1.7	2.7	22	12.4
20	7.7	---	0.7	0.1	1.2	1.7	19.8	8.6
24**	8.0 (7.8-8.3)	940	0.5 (0.3-0.7)	0.2 (0.0-0.4)	0.82 (0.5-1.0)	1.1	19.6	5.6

* Refuse

** Final digested residue

Values between parentheses represent the range of at least 6 samples.

Table 7.19 VFA, pH, FCOD, NH_3-N and Acidification Results for LR3 Experiment of the VSR Semi-Continuous Operation.

Time	pH	NH_3-N	VFA (mg/g)			VFA mg/g as COD	FCOD (mg/g)	Acidification (%)
days	----	mg/l	Acetic	Propionic	TVFA	TVFA	-----	--------
0*	6.1	----	9.2	0.2	9.7	10.6	63.2	16.8
4	7.34 (7.2-7.4)	977	1.9 (1.3-2.4)	4.4 (3.2-5.7)	7.8 (6.7-9.6)	11.3	37.1	30.5
8	7.6	943	1.9	3.5	6.6	9.5	34.0	28.0
12	7.7	1144	2.8	0.4	4.1	5.4	26.0	20.9
16	7.9	1393	0.8	0.2	2.2	4.0	26.0	15.4
20	8.0	1361	1.8	0.3	2.7	3.5	21.0	16.7
24**	7.9 (7.7-8.1)	1400	1.0 (0.9-1.1)	0.2 (0.1-0.3)	1.6 (1.4-1.9)	2.1	22.5	9.5

* Refuse

** Final digested residue

Values between parentheses represent the range of at least 6 samples.

Table 7.20 VFA, pH, NH_3-N, FCOD and Acidification Results for LR4 Experiment of the VSR Semi-Continuous Operation.

Time	pH	NH_3-N	VFA (mg/g)			VFA mg/g as COD	FCOD	Acidification
days	----	mg/l	Acetic	Propionic	TVFA	TVFA	mg/g	%
0*	6.9 (6.6-7.3)	130	3.8 (2.4-4.5)	0.3 (0.1-0.5)	4.6 (2.6-5.8)	5.6	43	13
4	7.6 (7.4-7.9)	595	1.9 (1.5-2.4)	2.5 (2.2-2.8)	5.4 (5.1-6.0)	7.7	33	23.4
8	7.8	630	1.2	0.9	4.1	6.7	30	22.2
12	7.9	735	2.1	0.3	3.1	4.0	27	15
16	8.0	1015	0.5	0.1	0.8	1.1	23	4.9
20	8.0	1050	0.1	0.1	0.4	0.7	24	3.1
24**	8.1 (7.9-8.2)	1225	0.08	0.04	0.3 (0.1-0.6)	0.5	22.7	2.2

* Refuse

** Final digested residue

Values between parentheses represent the range of at least 6 samples.

Fig. 7.14 VFA Concentrations (mg/g) for LR1 Run.

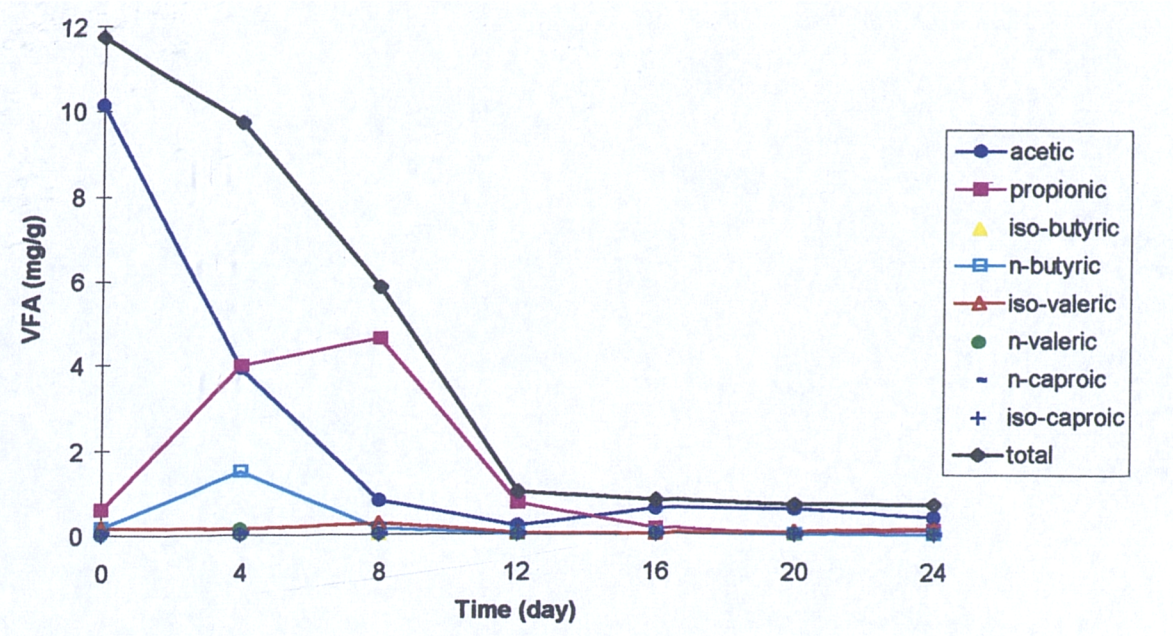


Fig. 7.15 VFA Concentrations (mg/g as COD) for LR1 Run.

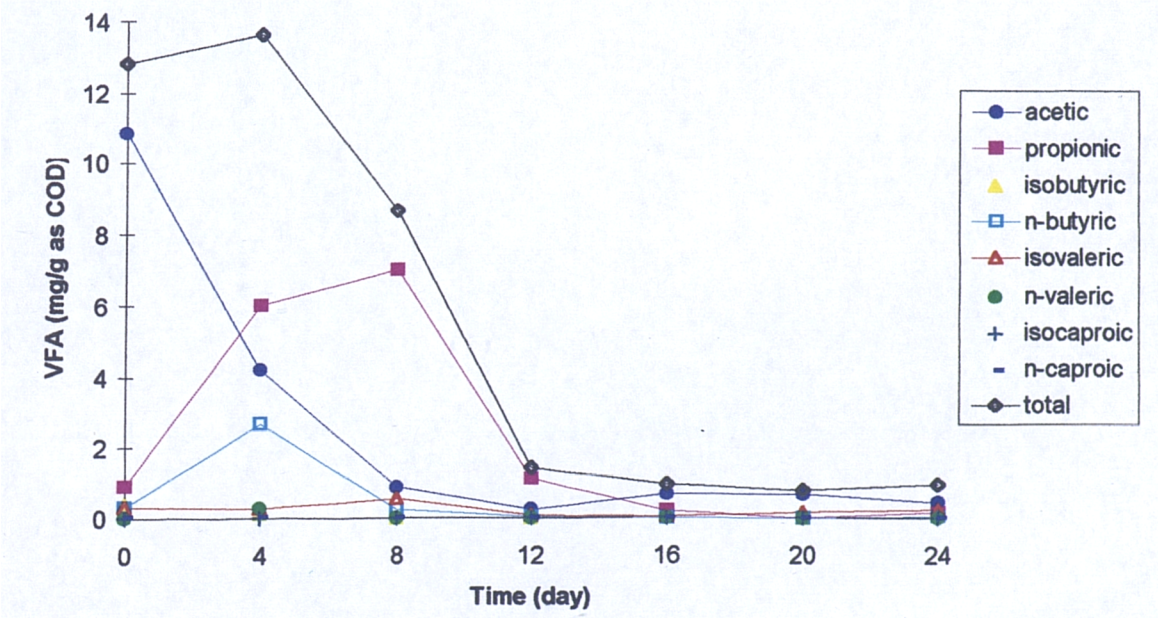


Fig. 7.16 VFA Concentrations (mg/g) for LR2 Run.

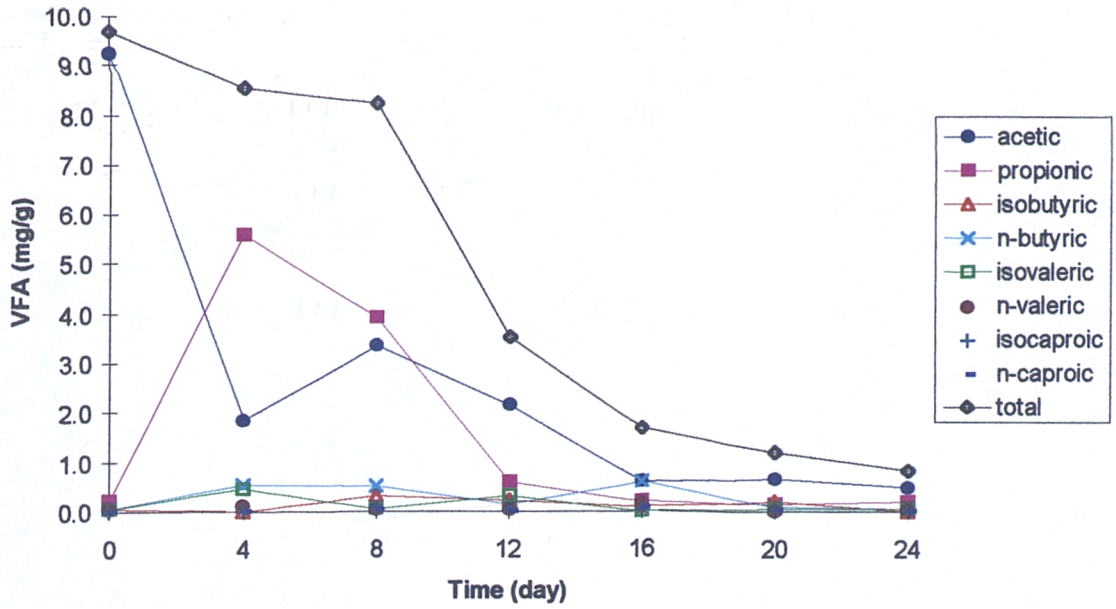


Fig. 7.17 VFA Concentrations (mg/g as COD) for LR2 Run.

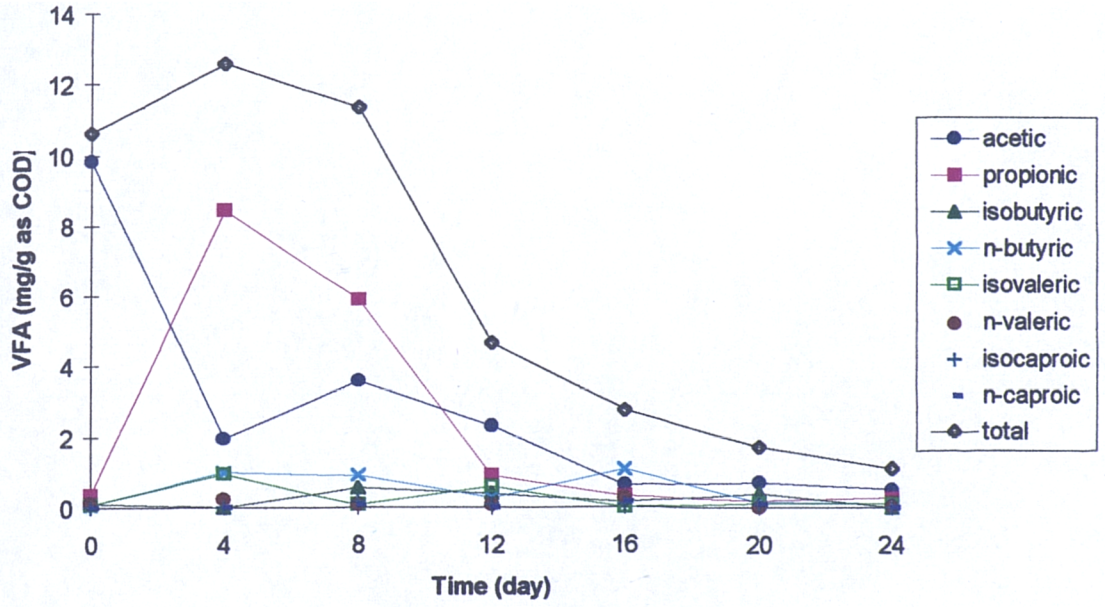


Fig. 7.18 VFA Concentrations (mg/g) for LR3 Run.

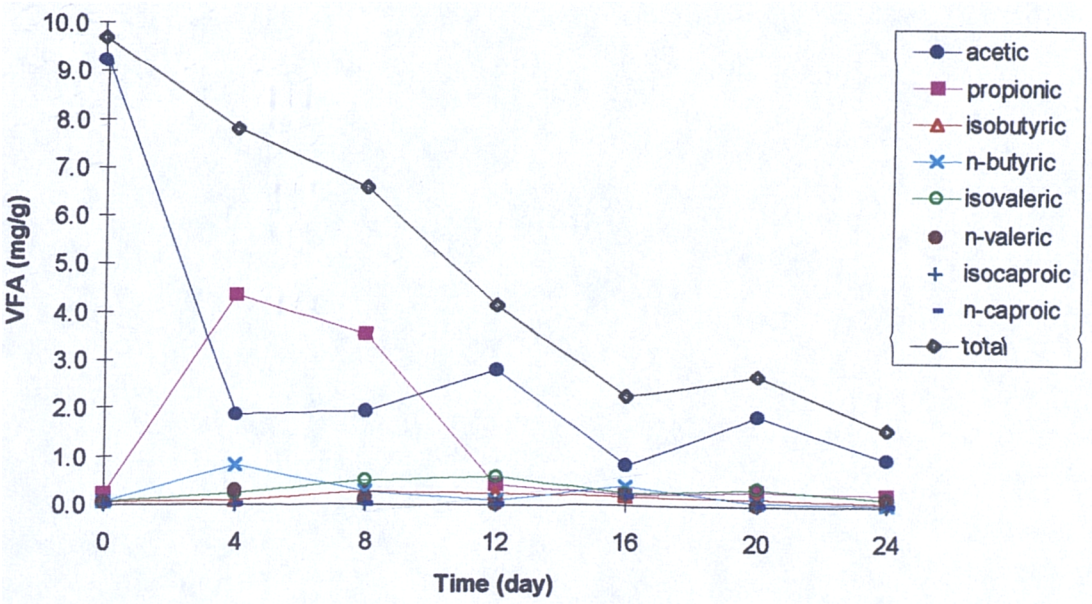


Fig. 7.19 VFA Concentrations (mg/g as COD) for LR3 Run.

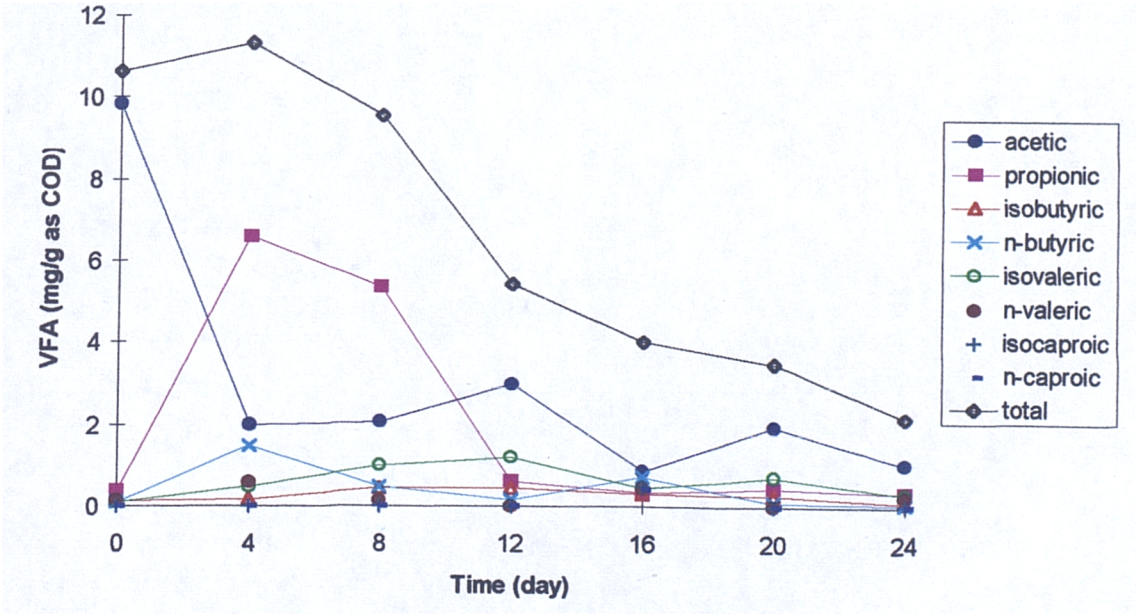


Fig. 7.20 VFA Concentrations (mg/g) for LR4 Run.

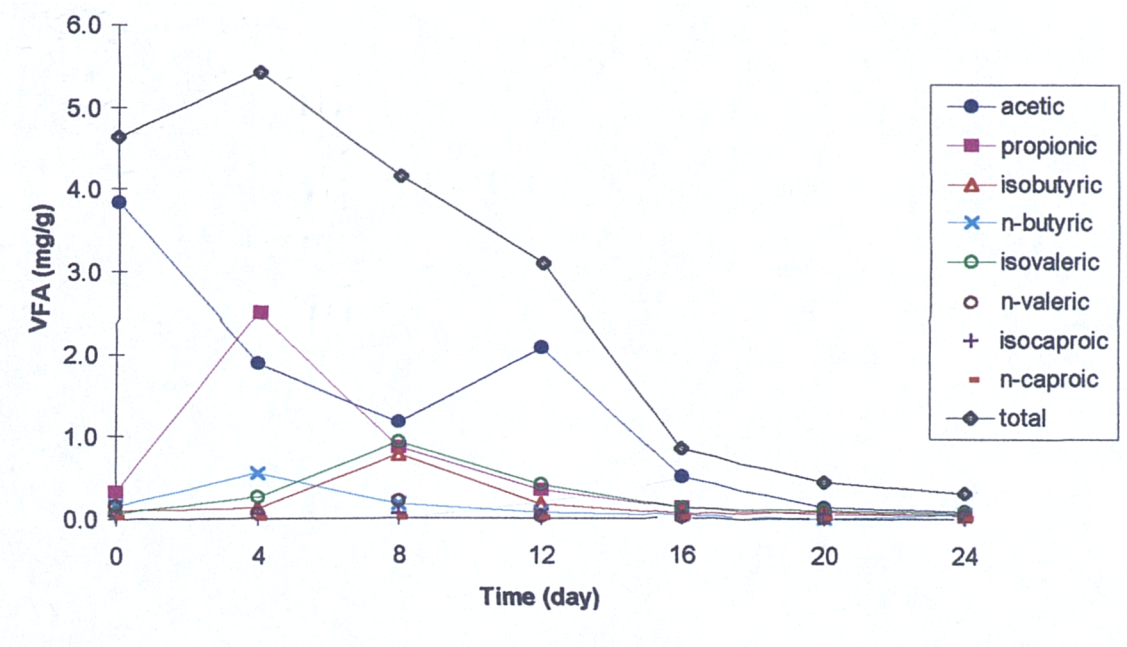
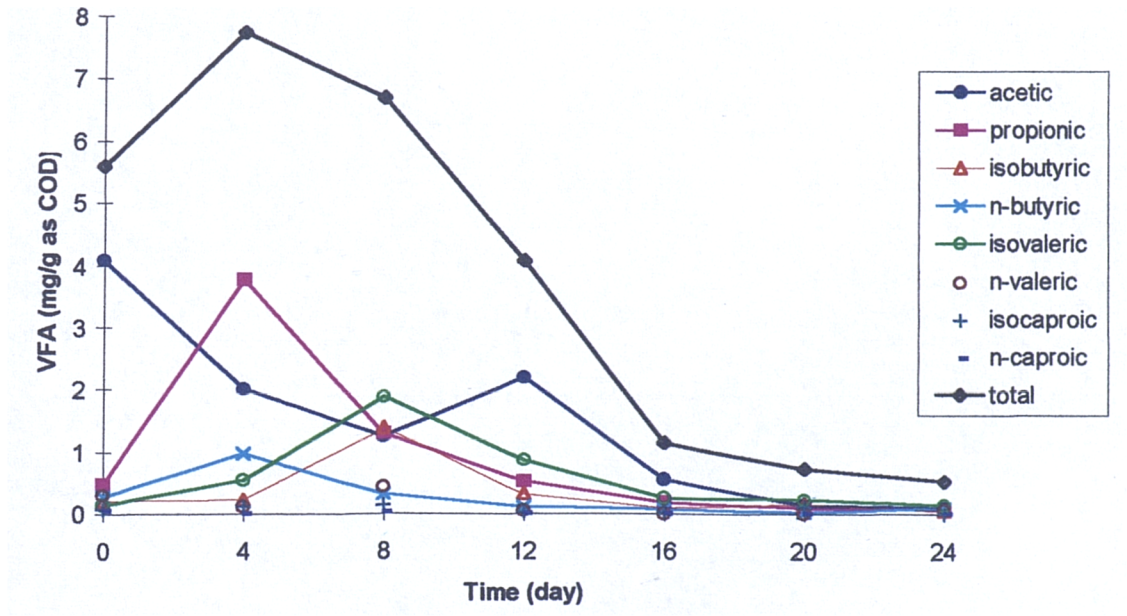


Fig. 7.21 VFA Concentrations (mg/g as COD) for LR4 Run.



(LR2), 38% LR3 and 24% LR4 were obtained from day 8 to day 12. The mean pH values, at the end of day 12, were 7.8, 7.8, 7.7 and 7.9 for LR1, LR2, LR3 and LR4, respectively.

It seemed that all of the organic matter had acidified by day 8, while acetogenesis finished by day 12 (there were no changes in acetic acid concentrations after day 12) of the LR1 run. During this run, the process was stable from day 16 onwards.

In the LR2 run also, all of the organic matter acidified by day 12, while acetogenesis finished around day 20. In the LR3 run, almost all organic matter had acidified by day 20 to 24, while acetogenesis might have been finished by day 24.

Finally, in the LR4 run, all organic matter acidified by day 12 to 16, while acetogenesis finished by day 16. The fact that the waste was rapidly (and possibly completely) acidified was also shown by the peaks created in day 4 for both graphs (7.20 and 7.21), whereas the peak appears only in the mg/g as COD graphs for the LR1, 2 and 3 runs. Therefore, the low organic matter in the refuse used during this run, LR4, was not gradually acidified as in LR1 to LR3 runs, but rapidly acidified, as the biomass was then adapted to handle higher concentrations of organic matter.

Final digested residues for LR1, LR2 and LR4 (due to low initial organic matter) had TVFA concentrations below 1 mg/g level, which indicated stable digested materials. The TVFA concentrations were 0.7 mg/g (0.9 mg/g as COD), 0.8 mg/g (1.1 mg/g as COD) and 0.3 mg/g (0.5 mg/g as

COD) for LR1, LR2 and LR4, respectively. The only exception was the LR3 run, where a TVFA concentration of 1.6 mg/g (2.1 mg/g as COD) was obtained at the end of the 24 days retention time. pH values, for the four runs, were stable within 7.9 to 8.1 (mean values).

Ammonia-nitrogen seemed to increase, with few exceptions, relative to retention time throughout the course of this study. Ammonia-nitrogen has been reported to increase with decreasing digestion process moisture content (Wujick and Jewell, 1980). This trend was evident for LR runs 1 to 3, where ammonia-nitrogen increased from 826 mg/l (LR1) to 1400 mg/l (LR3) with decreasing leachate (liquid) recycling level. However, a mean ammonia-nitrogen concentration of 1225 mg/l was obtained during the LR4 run despite a further decrease in leachate recycling level. This low concentration might have been be due to lower protein content in the Salford putrescible fraction than in the Anglesey product. The maximum ammonia-nitrogen concentration, which was obtained in the LR4 run, was far less than the reported inhibitory level (McCarty, 1964b; Hobson and Shaw, 1976; Bhattacharya and Parkin, 1989).

ii) Acidification.

Acidification values at the various levels of the VSR process show the phase-separation within a single stage plug flow reactor. High acidification values in the first four days of operation indicated the hydrolysis and acidogenic steps of the anaerobic digestion process. Fig. 7.22 shows acidification levels relative to time for all of the Phase 2 experiments. The LR1 run acidified rapidly at the beginning and was steady after day 12. In the LR1 to LR4 runs similar acidification levels occurred between days 4 and 8, with a sharp decrease in LR2 acidification from day 8 to day 12 and

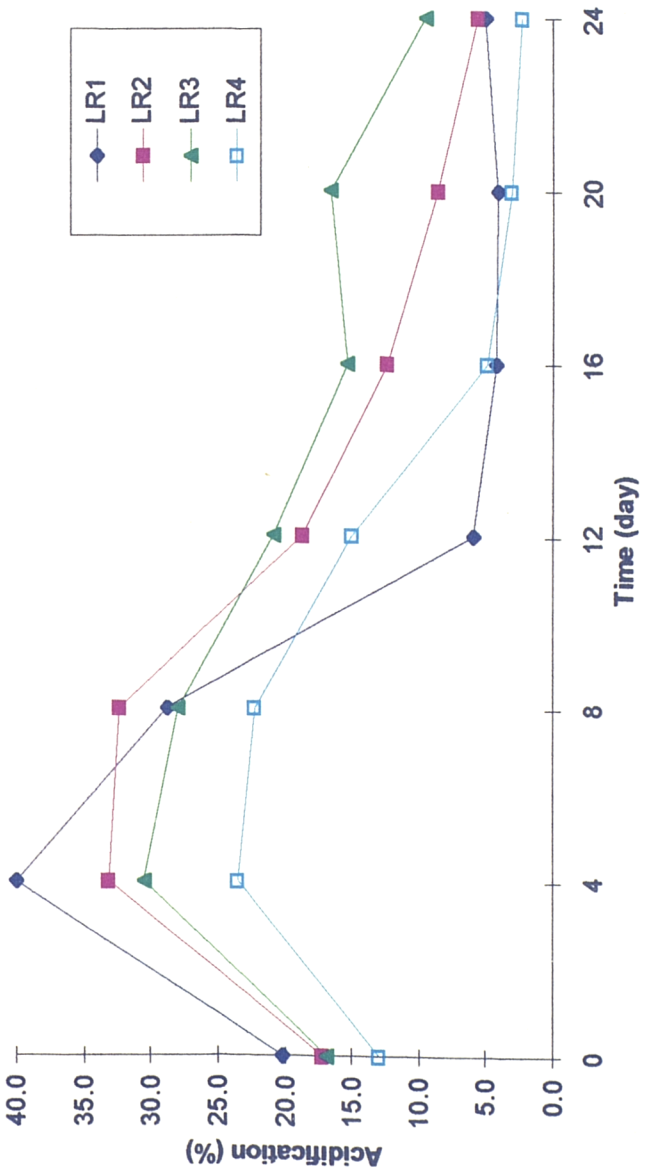


Fig. 7.22 Acidification during Phase 2 of VSR Semi-Continuous Experiment.

further reduction after 24 days. Similar sharp but gradual decreases were observed for the LR3 and LR4 acidification levels, the difference in the case of the LR4 run was that there was little organic matter and a continuous gradual decrease in acidification occurred up to day 24. The LR3 run seemed to face more difficulty in acidifying completely all the organic matter and had a second peak on day 20, after which it might have decreased and completely stabilised all organic matter if more retention time had been allowed.

During runs LR1 to LR4, acidification peaked at day 4 in all cases. In the LR4 run, acidification peaked at only 23%, while the other runs showed much higher values. This low acidification value might have been the result of both low refuse VFA concentrations (low organic matter) and low moisture content of the system in this run. In fact, when examining day 4 VFA and acidification results for LR1 to LR3, it seems that both of these parameters tended to increase with increasing moisture content in the system. The highest increase had occurred in LR1 run where acidification had increased at day 4 by approximately 49.5%, whereas in LR3 a lower acidification level of 48% was obtained. Further decrease in moisture content resulted in a decrease for both VFA and acidification values. LR3 acidification level increased from the initial acidification of the refuse by only 45%. These results agreed with the finding of Ghosh (1984) and Kasali (1986) who reported that increasing the moisture content of the refuse stimulated the acidogenesis activities.

Acidification level dropped from day 4 to day 8 by 28, 2, 8 and 14% for LR1, LR2, LR3 and LR4, respectively. The most significant drop was at

LR1 where most of the acetic acid from day 4 was consumed. The results of the first 8 days of operation indicated that hydrolysis and acidogenesis were the two predominant steps up to the end of the 8th day of operation.

From day 12 onwards, hydrolysis seemed to stop and the process was controlled by the acetogenic and methanogenic steps. In the LR1 run, acidification reached a stable level of 6% and during further digestion, up to day 24, an acidification level of only 4 to 5% was obtained. This day 12 result indicated that operating at this retention time might be possible under LR1 operational conditions. In the LR2 run, the 5% acidification level was obtained at only day 24 of the process. However, an acidification level of approximately 8% was obtained at the end of 20 days of operation.

The final acidification level of LR3 (9.5%) showed that a longer retention time might be required to obtain the 5% acidification level which seemed a good indicator for the stability of the high solids anaerobic digestion of the organic fraction of MSW.

Despite the low efficiencies that were obtained in the LR4 run, in terms of methane yield, VS and COD reductions, the acidification level, unexpectedly, was lower than the 5% indicator level from the end of day 16. Actually, the final digested residue in this run reached the lowest acidification level of the entire study. The reason for this might have been the nature of the waste received during this run. The Salford refuse contained much lower VFA concentrations (less organic matter) than the refuse obtained from Anglesey.

The operational conditions in the LR1 run can be considered as a close approximation to the leach-bed two-phase process, while the operational conditions in the LR3 run as the single stage, with gradual sequences between phases. The LR1 operational conditions should be used if the system is required to cope with high VFA load (sufficient alkalinity). On the other hand, LR3 operational conditions should be used if the system is dealing with low organic matter refuse (such as the waste used in the LR4 run).

7.10.4 Leachate Characteristics.

i) Leachate volume.

Table 7.21 gives the total liquid added (recycled drained liquid and tap water) during phase 2 of this semi-continuous experiment. In the LR4 run, mainly tap water was used to adjust the Salford refuse to obtain total solids close to the Anglesey refuse. As this practice did not allow for hardly any excess liquid to be recycled, the LR4 run could be assumed to simulate the case of the Anglesey refuse without recycling.

Table 7.21 Total Liquid Added During Phase 2 of VSR Semi-Continuous Experiment.

Type of Liquid Added	**LR1**	**LR2**	**LR3**	**LR4***
Drained Liquid (l)	**4.5 (4.2-4.6)**	**2.8 (2.5-3.0)**	**0.7 (0.4-0.9)**	**0.0**
Tap water (l)	**1.5 (1.4-1.8)**	**0 8 (0.5-1.0)**	**0.8 (0.6-1.2)**	**0.8 (0.7-1.0)**

(*) Approximately 80 to 100 ml of drained liquid was mainly used for analysis.

ii) Leachate Filtered COD.

Fig. 7.23 shows leachate FCOD against time over the period of the LR experiment. During the LR2 run, leachate FCOD varied between 2170 and 2620 mg/l, with a mean value of 2424 mg/l. This quasi-steady state, as explained previously in the case of the LR1 (DRR2) run, reflected the level of non-biodegradable FCOD existing in the raw materials.

An increase of FCOD value to reach a mean value of 2947 (2740-3120) mg/l coincided when the amount of total liquid added during the LR3 run decreased. However, a further decrease in the volume of the total liquid during the LR4 run did not cause an increase in FCOD value due to the low organic matter in the refuse used in this run. During this run, mean FCOD value of 2314 mg/l , with a range of 2000 to 2650 mg/l, was obtained.

iii) VFA, pH and Alkalinity.

Fig. 7.24 illustrates leachate VFA concentrations during the LR study. A low TVFA concentration of 11 mg/l as COD was observed prior to the start-up of the LR2 run. TVFA increased gradually to reach up to 80 mg/l as COD during this run, which had a mean TVFA of 45 mg/l as COD. The maximum TVFA concentration of 126 (mean of 105) mg/l as COD was obtained on day 72 of the LR3 run, when only 1.5 litres of total liquid were added. The final run, LR4, with low initial TVFA concentrations, had a mean TVFA of 80 mg/l as COD and a range between 51 and 111 mg/l as COD. These low TVFA values indicated that the four days leachate retention time was sufficient for the degradation of VFA for all of the runs evaluated.

Propionic to acetic acid ratios were below 1.0 which indicated a stable anaerobic digestion process, in relation to leachate quality, throughout the course of this experiment. Acidification, as well, remained low with mean values of 2.6, 3.7 and 3.2% for the LR2, LR3 and LR4 runs, respectively.

Fig. 7.25 indicates pH in the leachate samples during phase 2 of the semi-continuous experiment. These mean pH values were 7.7, 7.6 and 7.7, corresponding to pH values after filtration of 8.0, 7.8 and 7.9, which were obtained for the LR2, LR2 and LR4 runs, respectively.

Fig. 7.26 shows the total alkalinity at pH end point of 4.5. Mean total alkalinity values of 5670, 7200, 8260 and 7150 mg/l were obtained for the LR1, LR2, LR3 and LR4 runs, respectively. These total alkalinity values were higher than the range of 2500 to 5000 mg/l that was recommended for the anaerobic digestion of wastewater (Saw 1988).

Figs. 7.27 and 7.28 illustrate the alkalinity values at pH end points of 5.75 and 4.3, respectively. The ratio of intermediate alkalinity (from 5.75 to 4.3 pH end point) to partial alkalinity (5.75 pH end point) was below 0.3 throughout the course of this study. Therefore, the ratio obtained in this study indicated that there was sufficient buffering capacity in the system to handle high feed TVFA concentrations (Ripley et al., 1986). The highest intermediate to partial alkalinity ratio of up to 0.295 was found during the LR3 run, whereas the lowest ratio of 0.21 was observed in the LR4 run. These results might reflect the high and low refuse TVFA concentrations that were used in the LR3 and LR4 runs, respectively, rather than the impact of the variable parameter (recycled leachate) on the anaerobic

Fig. 7.23 Leachate COD during the Second Phase of the VSR Semi-Continuous Experiments

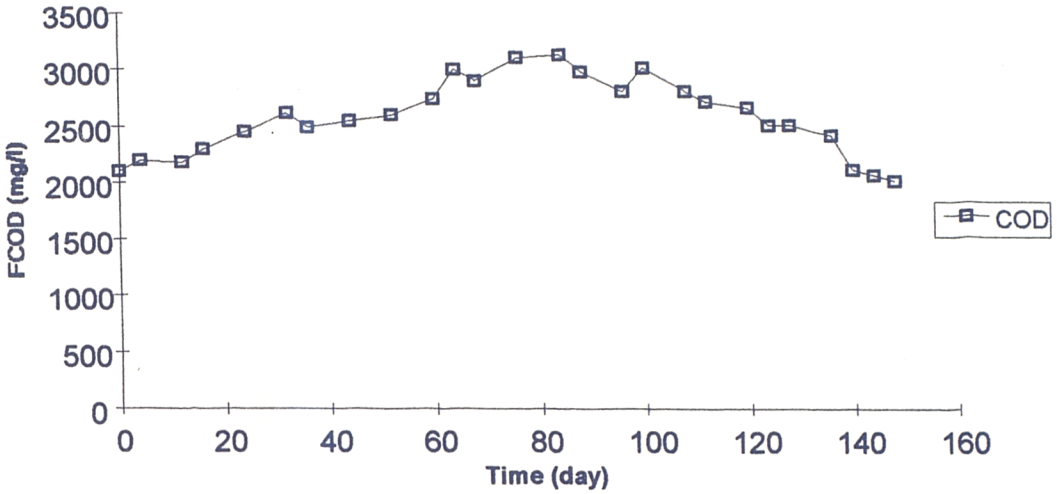


Fig. 7.24 Leachate VFA Concentrations during Leachate Recycle (LR) Phase

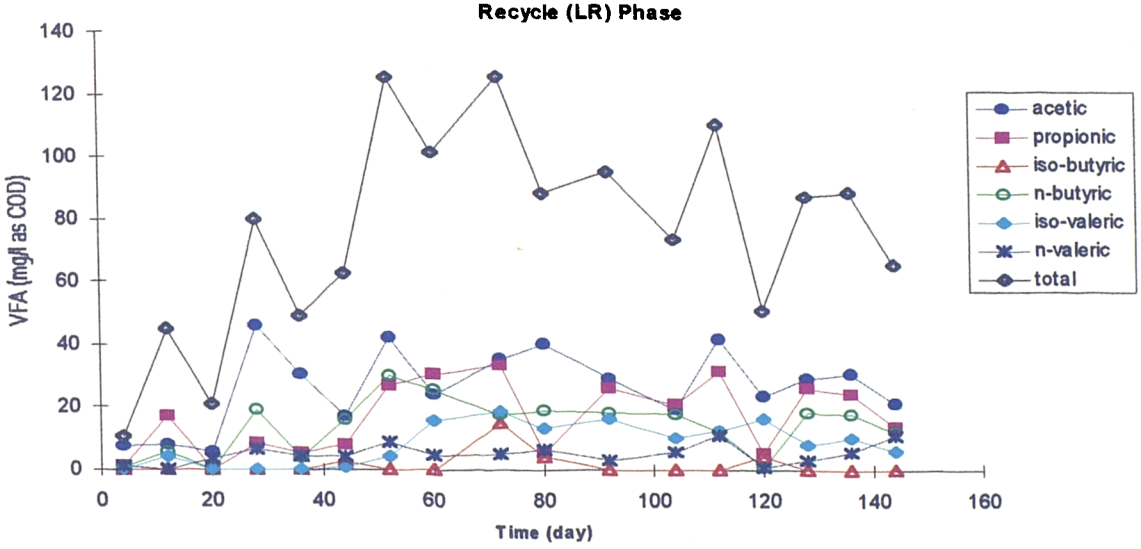


Fig. 7.25 Leachate pH during the Second Phase of the VSR Semi-Continuous Experiments

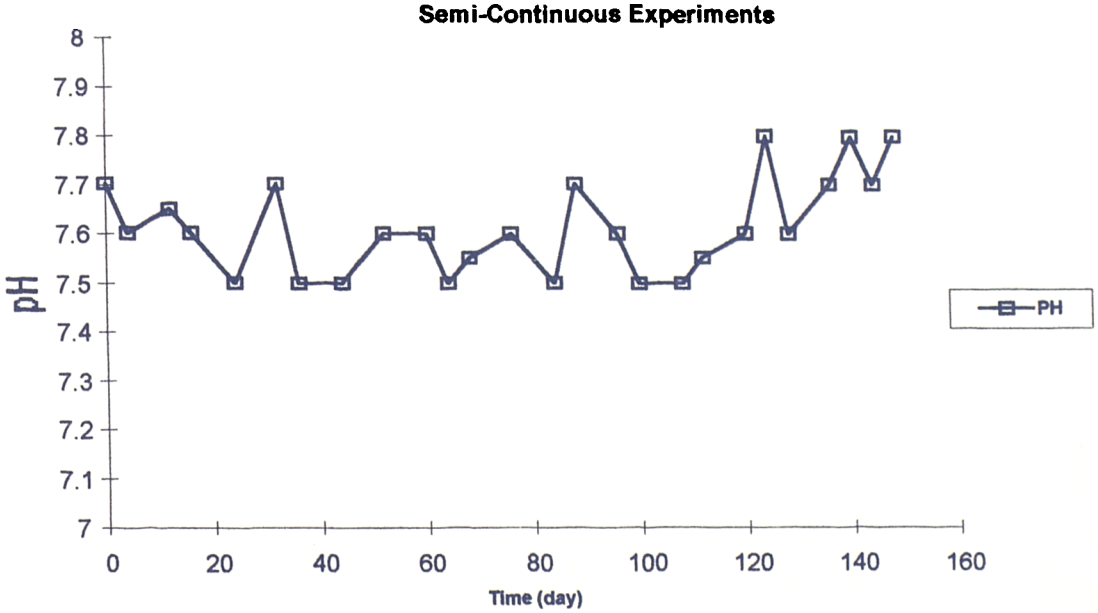


Fig. 7.26 Leachate Total Alkalinity (4.5 End Point)

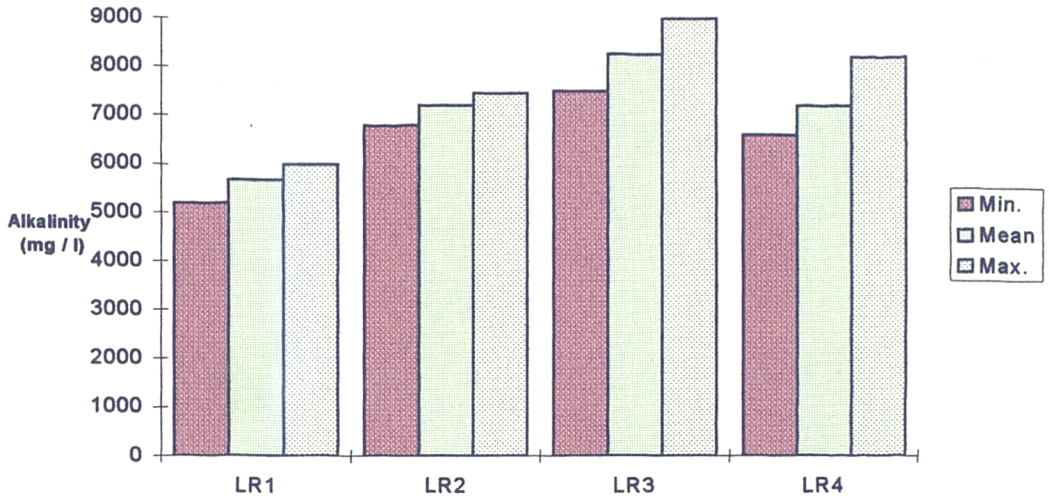


Fig. 7.27 Leachate Partial Alkalinity (5.7 End Point)

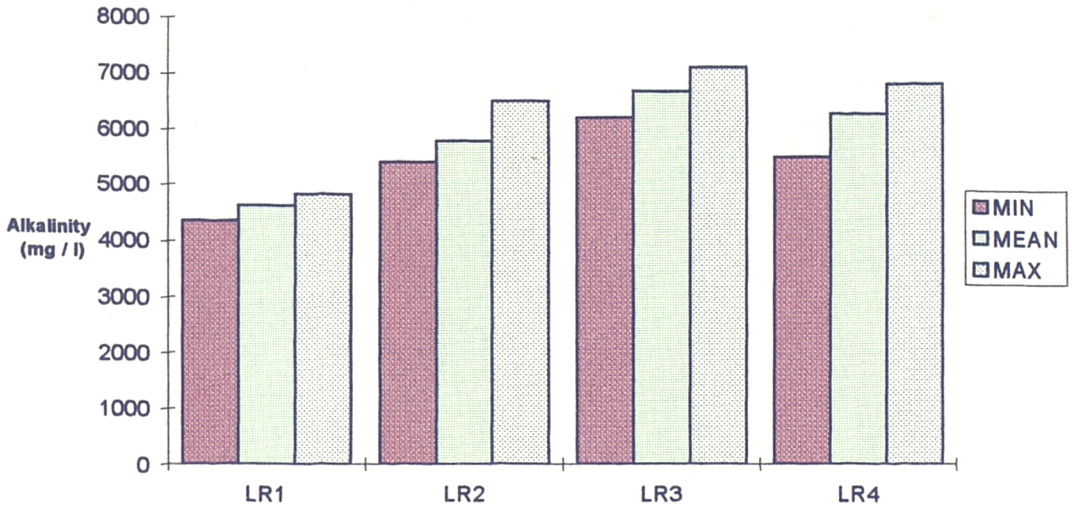
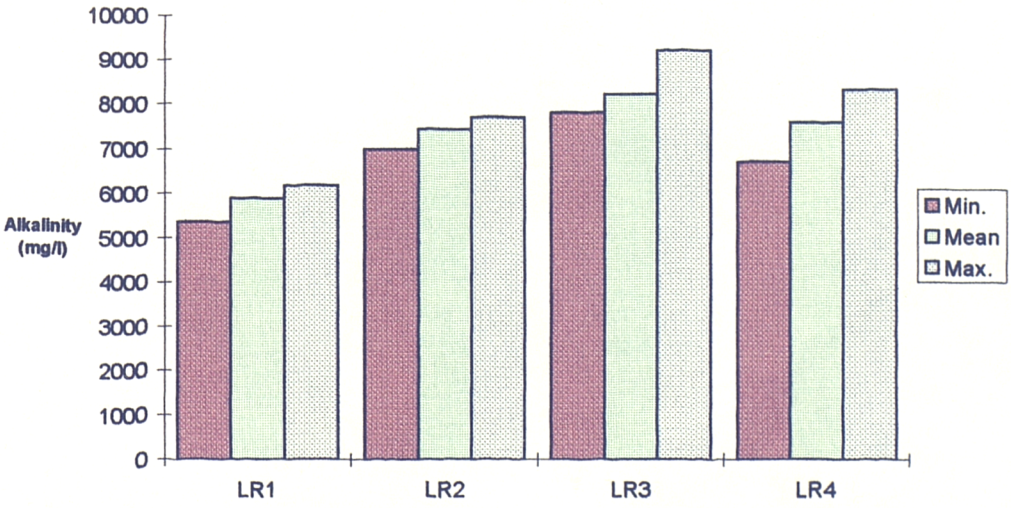


Fig. 7.28 Leachate Alkalinity (4.3 End Point)



digestion process.

iv) TKN and NH_3-N.

Fig. 7.29 indicates the concentrations of total nitrogen (TKN) and ammonia-nitrogen in the leachate during the LR experiments. Total nitrogen had mean values of 787, 1470, 1680 and 1385 mg/l for LR1 to LR4, respectively. It consisted of approximately 90% of ammonia-nitrogen which, therefore, was considered as the main nutrient source during the course of the VSR semi-continuous experiments.

Leachate ammonia-nitrogen concentrations for the LR1 run, obtained during the DRR study, had a mean value of 723 mg/l, which compared with LR2 to LR4 mean values of 1300, 1510 and 1253 mg/l, respectively. These values showed an increasing trend of 44, 52 and 42 % for LR2, LR3 and LR4, respectively, compared to LR1 run. Ammonia nitrogen concentrations were lower than expected in the LR4 run, since it was reported to increase with decreasing moisture content in the digestion process. This trend of increasing ammonia-nitrogen with decreasing moisture content was observed up to the end of the LR3 run. The reason for these low ammonia nitrogen values in the LR4 run might be due to there being less protein in the Salford urban waste than in the rural/agricultural Anglesey solid wastes. The maximum ammonia-nitrogen concentration of 1600 mg/l that was observed during LR3 run of this phase was lower than the reported inhibitory ammonia-nitrogen level.

v) Heavy metals.

Table 7.22 shows the heavy metals concentrations for the VSR semi-continuous experiments. The performances at all operational conditions

Fig. 7.29 Leachate Total and Ammonia- Nitrogen Concentrations during Phase 2 Study

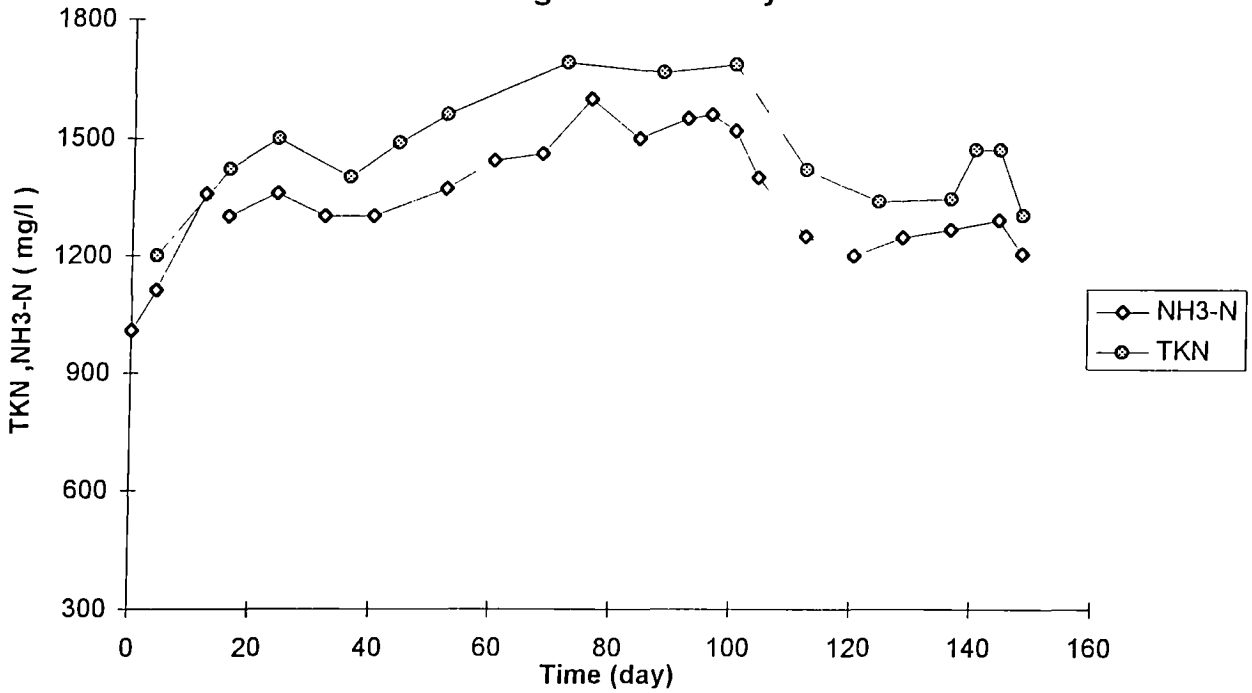


Table 7.22 Metals Concentrations (mg/l) in the Leachate Samples at the End of both Phases of the VSR Semi-Continuous Experiments.

Metals	End-Phase 1	End-Phase 2
Zinc	0.3	0.2
Cadmium	0.1	0
Iron	1.5	0.74
Copper	0.2	0.1
Nickel	0.5	0.2
Lead	1.1	0.3
Sodium	1108	1455
Potassium	1029	1760
Calcium	75	89
Magnesium	154	148

were normal, which indicates that heavy metal concentrations did not exceed the prohibitive levels of toxicity. In addition, the heavy metals present in the leachate samples, such as copper, had low concentrations that were much below the inhibitory levels for the digestion process (Hobson and Shaw, 1976; Su, 1990). Actually, these trace element levels were stimulants for the anaerobic digestion process carried out in this work. This corresponds with the findings of Speece and Parkin (1983) who suggested that these were an essential nutrient source for the micro-organisms involved in the anaerobic digestion process.

Sodium concentrations in the leachate were in the range of 1108 to 1455 mg/l and potassium concentrations were between 1029 and 1760 mg/l. Both the sodium and potassium concentration levels, for both phases, were acceptable and well below the values reported by McCarty (1964b) to cause moderate inhibition (3500-5500 and 2500-4500 for sodium and potassium, respectively). Calcium and magnesium concentrations were in the range of 75-89 and 148-154, respectively. Both calcium and magnesium concentrations were within the stimulatory levels reported by McCarty (1964b).

7.11 Aerobic Post-Treatment.

7.11.1 Introduction and Experimental Procedure.

The digested residues TVFA, VS and FCOD reductions indicated that stability was achieved in the DRR1, DRR2 (LR1) and LR2 runs. However, if the suggested C/N ratio (ranging between 5 and 20) of sufficiently well-composted materials is taken as the sole indicator of the stability of the digested residues (Hirai et al. 1983; Finstein et al., 1986),

further treatment is required to obtain a stable compost material. This post-treatment aerobic step was carried out, despite the fact that the digested residues of these three runs were within the range of the final C/N ratio of the final compost, which was reported to be usually between 15 and 25 (Pescod, 1991).

The composting post-treatment experiments were conducted using the forced air composting reactor (Section 4.5). The final digested residues used in these experiments were collected during the DRR1, DRR2 (LR1), LR2 and LR4 runs. Approximately 2 kg of digested residues were collected, every four days, and stored in a 4°C cold room until between 8 and 10 kg of the digested residues were accumulated. After this, the digested residues were placed in the reactor and allowed to drain for two to four days before the start of the experiment. The materials moisture content of 65% (35 %TS) was reached after dewatering. This moisture content was within the suggested value for composting. Stentiford and Dodds (1992) recommended that the composting moisture content should be in the range of 40 to 65% in order not to affect the biological activity of the process below this level or the material structure therefore reducing the interstitial oxygen (porosity), when water fills the interstices between particles at higher moisture levels than 65%. Almost all of the biological activity was reported to cease when moisture content was lower than 12% (Diaz et al., 1994). Therefore, addition of water might be required, during operating the aerobic composting process, in order to avoid total process inhibition.

In aerobic composting, the main parameters which have to be controlled, in addition to moisture content, are carbon to nitrogen ratio (C/N), aeration and temperature. Initial refuse C/N ratio should be less than 35 and the temperature should be maintained below 60°C, whereas the highest microbial activities during composting were reported to occur between 30 and 55°C (Pescod, 1991). Therefore, in this work, the post treatment aerobic step was carried out under mesophilic conditions, at 35°C, the same as the anaerobic one. An air flow rate of approximately 1.4 m^3/day and a retention time of 10 days were applied during the aerobic composting step.

A sample of approximately 3 kg of the final composted material was used for VS (% of TS) determination, whereas only 0.5 kg were used for the final anaerobically digested residue. Therefore, more accurate results were obtained for the final compost VS determination.

7.11.2 Results and Discussion.

The original C/N ratio of the putrescible fraction of MSW was 31.4 with 384 mgC/g and 12.6 mgN/g dry matter for Anglesey refuse and 23.4 with 320 mgC/g and 13.6 mgN/g dry matter for the Salford refuse (LR4 run). After the completion of the post-treatment step, the C/N ratio was reduced to a range of approximately 19 to 21, for the first three runs (DRR1, DRR2 and LR2), with 244 mgC/g and 11.8 mgN/g dry matter. For the last run, LR4, the C/N ratio decreased to 15.5 with 203.4 mgC/g and 13.1 mgN/g dry matter.

Factors influencing these obtained C/N values, with the lowest at LR4 final compost residues, include low original C/N ratio and high marginal error in the method used to determine the elemental analysis (Appendix A). This method used only 1 mg of dry matter for the determination of C:N:H ratio.

Temperature variation between the top and the bottom of the composting vessel was approximately 2 to 5°C during the post-treatment experiments. This might indicate that the organic matter, for all four experiments, was stable enough to stop aeration before the selected retention time of 10 days.

Other stability parameters, such as TVFA, VS and FCOD reduction, showed a significant reduction after the post-treatment step compared to the corresponding original refuse values. However, these reductions were marginal when compared with the final anaerobically digested residue values before the start-up of this step. The final compost VS (% of TS) values were 44.4, 43 and 38 for DRR1, both LR1 and LR2, and LR4, respectively, which was equivalent to a reduction of between 6 and 9% from the final digested residue values prior to the start of the post treatment step. VS reductions in the range of 54 to 56% were obtained for the final compost materials of the DRR1, DRR2 and LR2 runs, which used the putrescible fraction of Anglesey refuse, and 37% for LR4 which used the Salford putrescible fraction. The final compost FCOD was in the range of 12 to 15 mg/g for all runs; whereas TVFA concentrations showed little or no change at all from final digested residue values.

Stentiford et al. (1985) suggested VS reduction of 40% and FCOD (extracted) percentage reduction of 50%, among many control, physical and chemical stability factors, for the determination of the degree of stability in the composting process in order to stop the aeration step. Actually, according to the two parameters, VS and FCOD percentage reductions of approximately 70%, respectively, in addition to TVFA concentrations of less than 1 mg/g as COD, which were obtained in the DRR1, DRR2 (LR1) and LR2 runs, the final digested residues were fairly stable even before the aerobic post-treatment step was applied.

The finished compost was dark brown, with an earthy odour and humus-like consistency with a pH of between 8 and 8.3. This end product can be used as a soil conditioner, landscaping or landfill cover. However, such compost must be matured for several months if it is to be used for domestic purposes (Coombs and Coombs, 1989).

7.12 Conclusions.

The following conclusions can be drawn from this semi-continuous VSR study:

i) The overall performance of the Vertical Sequential Reactor (VSR) proved that the design was effective for the high solids anaerobic digestion of the organic fraction of MSW but was also a good laboratory tool for the investigation of the internal activities of the digestion process.

ii) During the digested recycle ratio (DRR) phase of this experiment, maximum biogas and methane yields of 0.406 and 0.213 m^3/kg VS added, respectively, and approximately 49% VS reduction were obtained at 0.76

digested residue recycle ratio (DRR1). At this ratio, volumetric methane production was 0.508 m^3 per m^3 reactor per day at an organic loading rate of 2.4 kg VS per m^3 reactor per day.

iii) The optimum digested recycle ratio was found to be 0.5 (DRR2), at which maximum volumetric biogas production of 1.62 and methane production of 0.832 m^3 per m^3 reactor per day were achieved at an OLR of 4.1 kg VS per m^3 reactor per day. Under these conditions, there was a negligible difference between the performance and the maximum VS reduction and methane yield that were obtained at the digested solids recycled ratio of 0.76. At the optimum digested recycled ratio indicated, approximately 80 and 84% of the potential methane yield and VS reduction, respectively, were achieved, compared with the long term batch experiment using the HRR.

iv) The maximum OLR of 5.1 kg VS per m^3 reactor per day was achieved at a digested recycle ratio of 0.33. The low performance efficiencies obtained at this ratio might be attributed to the high OLR of 20.8 kg VS per m^3 reactor within every loading interval of 4 days.

v) During the second phase of this experiment, process efficiencies at a leachate recycling rate of 3.5 l in LR2 were similar to LR1 (optimum DRR2) with less leachate. In this run, volumetric methane production decreased by approximately 9% to reach 0.763 m^3 per m^3 reactor per day. A specific methane yield reduction of only 5% was obtained in LR2, compared with the LR1 run, to reach a mean of 0.192 m^3/kg VS added. At the same time, biogas yield according to VS removal showed a reduction

of less than 3% compared with the same run to reach a mean value of 0.765 m^3/kg VS removed. The effect of lowering leachate recycling between these two runs had a marginal decrease in terms of VS removal of only 3% reduction in the second run. Also, the same TCOD and FCOD reductions of 30 and 69%, respectively, were obtained in these two runs.

vi) The operational conditions of LR2 run might be more desirable economically than the previous one in relation to reducing the operational cost and the reactor volume if leachate treatment was not the main objective.

vii) Overall process efficiencies seemed to decrease significantly with reduction in the moisture content of the reactor below the LR2 level of 69%. With final digested residues moisture contents of 67% and 64% (LR3 and LR4), the volumetric methane production dropped by approximately 30 and 54%, and specific methane yield declined by approximately 25% and 48% compared with the maximum values that were obtained in the LR1 run (61% moisture content). The highest decline in terms of VS, TCOD and FCOD reductions of approximately 28, 39 and 29%, respectively, occurred at the 36% TS (64% MC) experiment compared with LR1 values.

viii) Observation of the internal activities of the process, as indicated by the progress of acidification, was fully successful with the VSR experiments.

ix) The required retention time for treatment of any waste stream can be determined using the observation of internal process activities. For example, the retention time for the LR1 run to almost complete the stabilisation of the organic matter, considering the acidification and TVFA concentration date could be as low as 12 days instead of 24 days.

x) An important engineering consideration is to operate high organic strength waste in the LR1 mode, simulating an internal two-phase system. On the other hand, for economical purposes (low operational cost for leachate recycling), low strength waste should be operated in the LR3 mode, which simulates more a single phase operation. The system in the first case (LR1) can be used as acidogenic reactor for VFA production.

xi) The VSR process, designed with internal liquid recirculation, provided successful leachate treatment for all operational modes examined in this study.

xii) According to the stability criteria adopted in this work, digested recycled ratios of 0.76 and 0.5 and leachate recycle of 6 and 3.5 l only achieved stability in terms of TVFA of less than 1 mg/g as COD. Therefore, aerobic post treatment was considered to be required to obtain a well-established compost material.

xiii) Post aerobic treatment of 10 days was successful in providing a well stabilised composted material with a VS reduction of up to 56% and a C/N ratio of approximately 15 to 21.

CHAPTER 8

HORIZONTAL ROTARY REACTOR SEMI-CONTINUOUS STUDIES

8.1 Introduction and Objectives.

This semi-continuous operation was carried out in order to study the impact of mixing on the high solids anaerobic digestion of the putrescible fraction of MSW, at a total solids of 35% and a mixing speed of 3 rpm. The main objective was to determine the effect of mixing on the overall process performance efficiency but, in addition, a tracer-study was conducted to monitor the movement of the solids inside the reactor.

It was originally intended to evaluate the following variables in these HRR semi-continuous experiments:

i) mixing speed (rpm 1 to the highest possible speed).

ii) mixing duration (ranging from 1 to 24 hours per day).

iii)organic loading rate (OLR).

8.2 Equipment.

A detailed description of the Horizontal Rotary Reactor (HRR), designed for semi-continuous operation, is given in Chapter 4 (Section 4.2).

8.3 Experimental Procedure.

Approximately 20 kg of final digested residue, obtained from the DRR2 run (Table 7.6), were used to initiate this experiment which ran parallel to the VSR semi-continuous experiments. The feed refuse, therefore, was the same as that reported in Table 7.1.

The first study (trial 1) of the HRR semi-continuous experiments was to increase OLR by daily feeding of the reactor. This was done in order to minimise the impact of high initial organic loading (as in the VSR experiments in Chapter 7) on the anaerobic process. In this first run, daily feeding of 1 kg (820 g of refuse and 140 ml of tap water) replaced an equal amount of digested residue with RT of 21 days. Tap water was added in order to keep the feed TS in the range of 34 to 36%. The second trial was carried out using the final digested residue, obtained during LR2, as presented in Chapter 7.

8.4 Results and Discussion.

8.4.1 Operational Problems.

Even though a variable speed shaft was installed, the available motor was only capable of rotating the horizontal reactor at a maximum speed of 3 rpm. Therefore, mixing was fixed at this level throughout the HRR semi-continuous experiments. Unfortunately, this meant that there was no scope for experimenting with mixing speed.

Only around 30 l of the reactor volume could be utilised in order not to cover the shaft, thus blocking the biogas extraction point. A modification was necessary, in order to utilise the full reactor volume and to reduce the void space level. One alternative was to connect tubes between the side-wall of the reactor and the outside part of the shaft. However, this was impossible because of the weak structure of the shaft materials, which could not stand the large holes required for such a connection. More advanced biogas extracting systems were considered, however, lack of time and financial support did not allow the implementation of these ideas.

Other operational problems included a surge of biogas released from the reactor directly after the start of mixing (rotating the reactor). This caused blockages of the gas-meter by pushing the water inside the meter towards the gas exit opening. A less sensitive (dry) gas-meter had to be installed to replace the wet gas meter.

Nevertheless, the semi-continuous experiments were carried out, despite these setbacks, in order to have at least some indication of the suitability of such a system.

8.4.2 Trial 1.

Figs. 8.1 and 8.2 illustrate the biogas production and composition during this first trial. The nitrogen content of the biogas was too high, due to the large void space, which was approximately 60% of the reactor volume. During the first 22 days of this experiment (which lasted for approximately 60 days altogether) with an organic loading rate of 7 to 10 kg VS per m^3 active reactor volume per day, the nitrogen content of the biogas was up to 41% with a mean value of 34.4%. Mean methane and carbon dioxide values, on the other hand, were 30.6% and 34.9%, respectively.

Biogas production had a mean value of 30.5 l/day (ranging between 22 and 36 mg/l), while mean methane production of 9.1 l/day (ranging between 7.2 and 13.6) was obtained during these 22 days.

From day 22 onwards, the daily feeding mode was changed to once every three days, which reduced the OLR by 66%. These changes resulted in an

Fig. 8.1 Biogas and Methane Production during Trial 1 of the HRR Semi-Continuous Experiment.

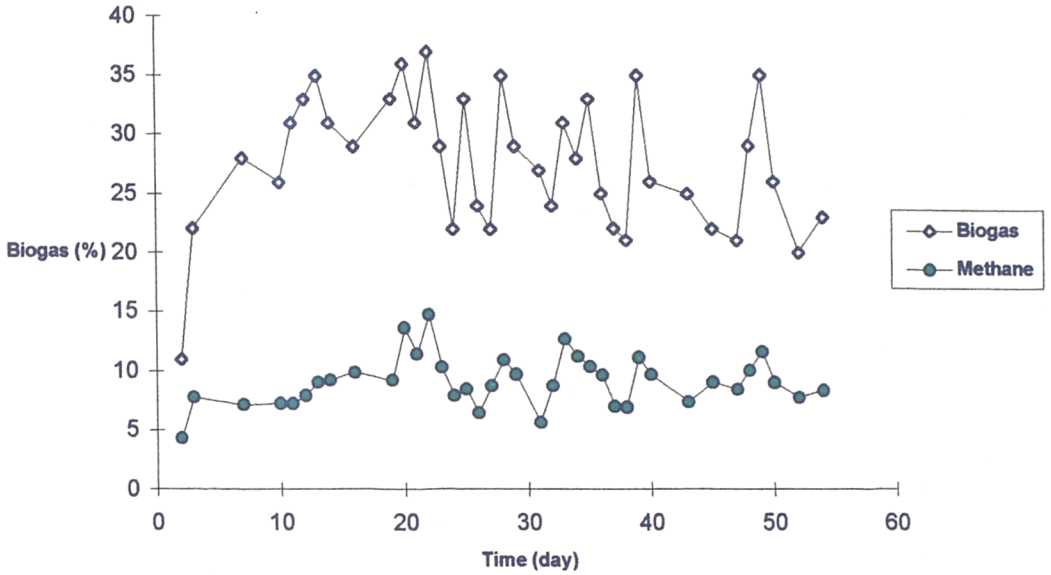
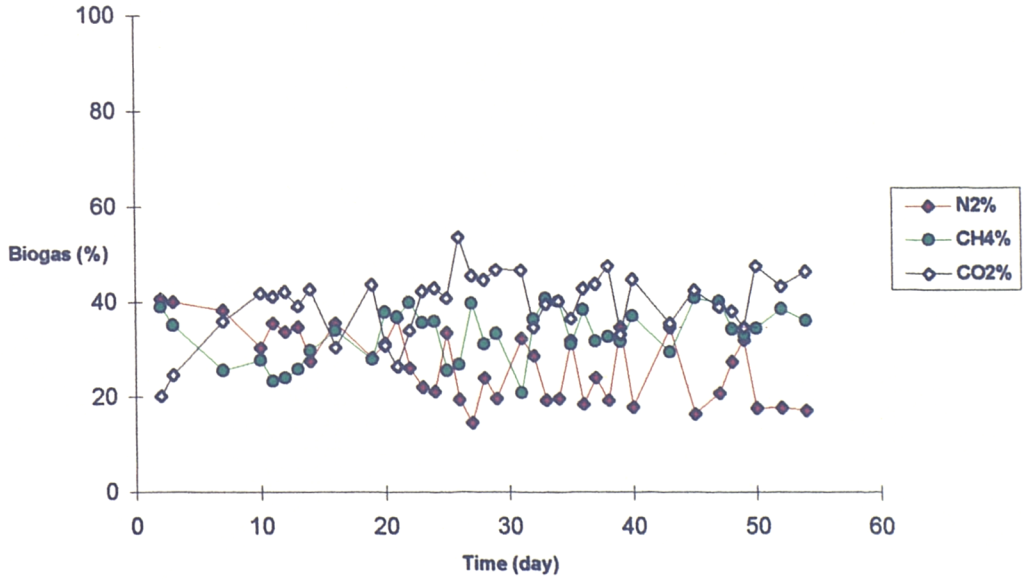


Fig. 8.2 Biogas Composition during Trial 1 of the HRR Semi-Continouos Experiment



increase in the methane content of the biogas to a mean of 35.8% (30 to 41%). Biogas composition showed high carbon dioxide and nitrogen values. Carbon dioxide of up to 48% and a mean value of 40.7% was observed. Nitrogen percentage in the biogas was recorded at its highest level at day 1 after feeding the reactor. However, it decreased 16 to 20% after day 3 from the start of feeding the reactor.

A methane yield of 0.091 m^3/kg VS added was obtained at the end of this trial. This low methane yield and a VS reduction of only 28% indicated the low performance efficiency of the system during this experiment. This might be attributed to both high OLR and the daily exposure of the reactor contents to air during and after feeding the reactor (due to the large void-space).

A sharp increase in TVFA concentration was observed, from 0.7 mg/g (1.2 mg/g as COD) at the beginning of this experiment to a maximum value of 15.2 mg/g (22.8 mg/g as COD) at the end of the experiment. Propionic acid was more than 80% of the TVFA concentration, reaching 19 mg/g at day 60. It seemed to increase in response to daily air exposure, which filled the void-space of the reactor, as accumulation of this acid is reported to be very sensitive to changing environmental conditions.

The ratio of intermediate alkalinity to partial alkalinity was 0.36, which indicated that there was insufficient buffering capacity in the system (Ripley et al., 1986). However, pH remained relatively stable with a mean of 7.1 (ranging from 6.9 to 7.3).

8.4.3 Tracer study.

The tracer study was conducted on the HRR when operating at 21 days RT. This tracer study was carried out during the daily feeding experiment, where 1 kg (wet weight) of digested residue was withdrawn and replaced by refuse. Twenty-four balls (each weighted approximately 6 g, with 1.7 cm diameter) were placed inside the reactor with the first feeding of this experiment. A spirit-level was used to measure the HRR level which was found to decline towards the input aperture by 0.05°. Therefore, the HRR can be considered as a plug-flow reactor.

Approximately 42% and 67% of the tracer had left the reactor by the end of days 18 and 21, respectively. The fact that only 33% of the trace-balls remained in the reactor at the 21 days RT, indicated adequate mixing of the reactor contents. A mean RT of 16.9 days was obtained using the following Eq.:

$$\bar{t} = \frac{\int_0^\infty t\,C\,dt}{\int_0^\infty C\,dt} \qquad (8.1)$$

8.4.4 Trial 2.

In this trial, the reactor was fed with 310 g VS every six days with an OLR of 2.7 kg per m^3 active reactor volume per day. This was equivalent to an OLR of approximately 16 kg VS per m^3 active reactor volume every six days (similar to the optimum DRR2 value in VSR experiments) at RT of 36 days. Increasing the period between loading to 6 days, was at the expense of increasing the impact of high initial OLR. The digested residue that was

used to initiate this experiment was obtained from the VSR during the LR2 run (Table 7.15).

Figs. 8.3 and 8.4 show biogas production and composition during this trial. Steady-state conditions were considered to have been attained from day 31 of this experiment, which lasted for 60 days. A mean methane percentage of 46.4% (up to 56% after 6 days of feeding the reactor) in the biogas produced was achieved during this steady-state period. Despite the fact that there was a high nitrogen content in the biogas on the first day after feeding the reactor (which was similar to the previous trial), the nitrogen content then declined over the remaining five days. Mean biogas and methane production values of 28.4 l/day (17 to 44 l/day) and 12.5 l/day (9.5 to 16.2 l/day), respectively, were obtained.

Biogas and methane production results were evaluated according to the corresponding day after feeding the reactor. A methane yield of approximately 240 m^3/kg VS added per day was achieved in this trial. In fact, this was the highest yield obtained in all the experimental conditions tested throughout this work, apart from in the long batch HRR experiment.

Fig. 8.5 shows the final digested residue that was obtained at the end of trial 2. The TS contents of the residue had a mean value of 30.5 (ranging between 29.2 and 32.4), while VS values between 43 and 48%, with a mean of 46.3 (% TS), were obtained during this trial. A volatile solids reduction of more than 50% was observed in the final stages of this experiment, with a mean reduction of 47%.

Fig. 8.3 Biogas and Methane Production during Trial 2 of the HRR Semi-Continuous Experiment.

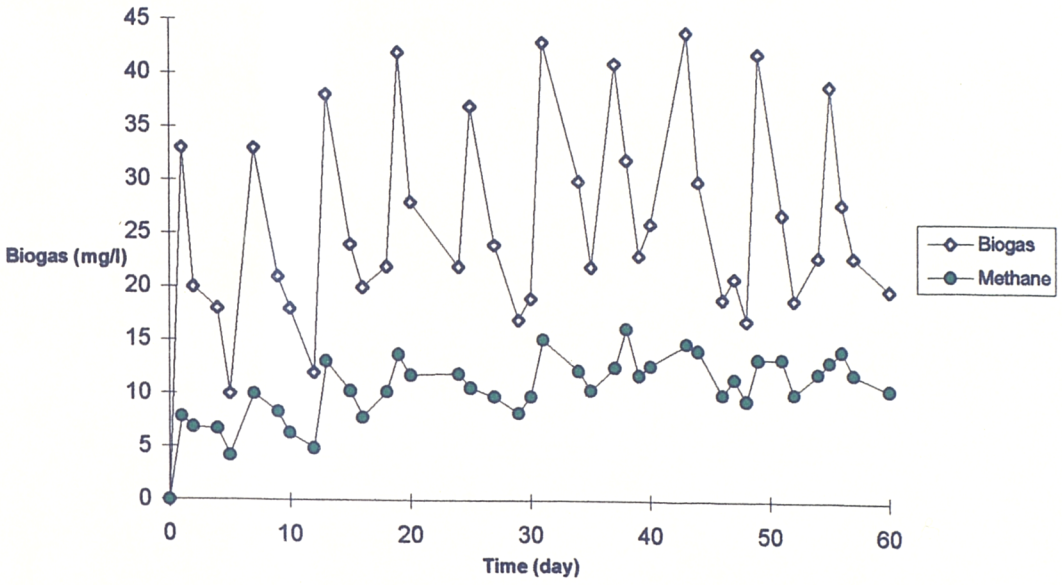
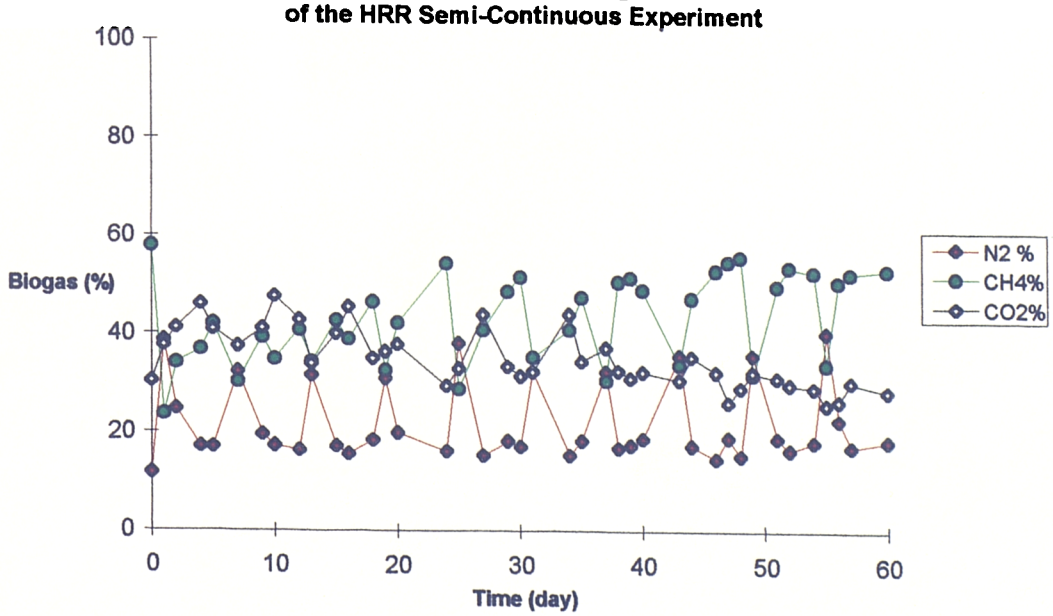


Fig. 8.4 Biogas Composition during the Second Trial of the HRR Semi-Continuous Experiment



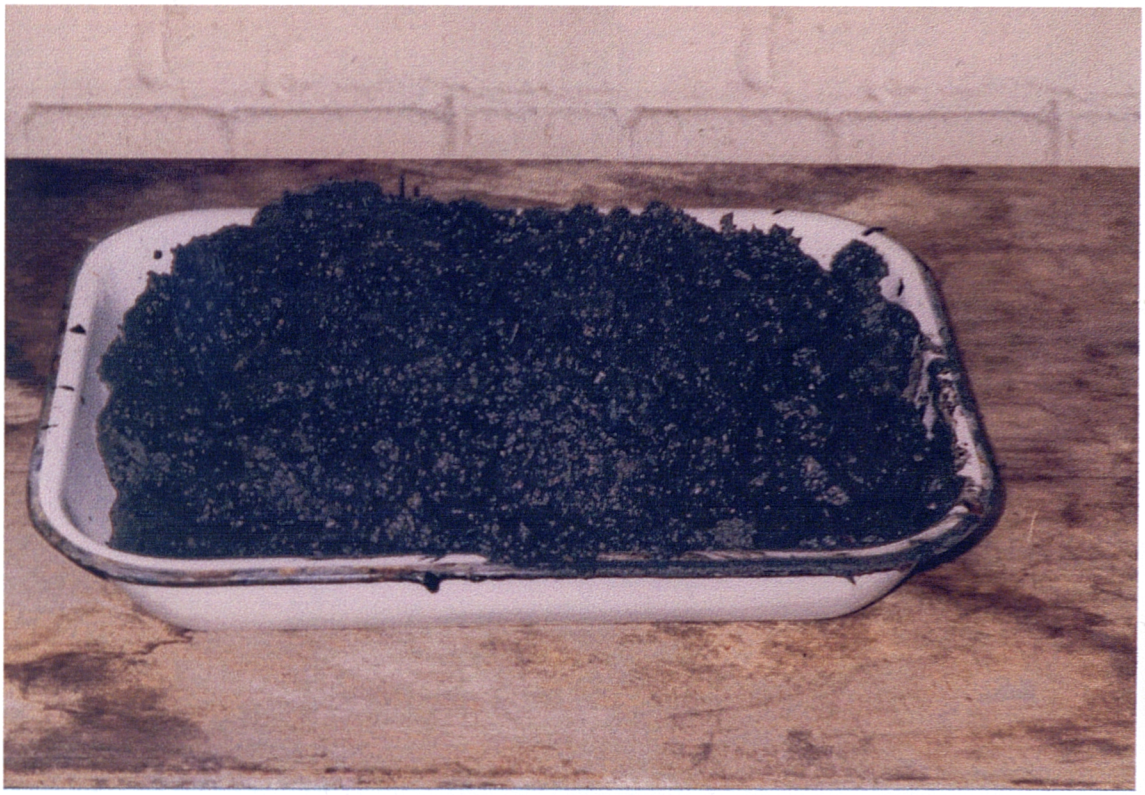


Fig. 8.5 Final Digested Materials (HRR, Semi-Continuous)

The final digested residue had a mean TVFA concentration of 0.34 mg/g (ranging between 0.12 and 0.56 mg/g). This was equivalent to 0.52 mg/g as COD (0.23 and 0.82 mg/g as COD). Also, the ratio of intermediate alkalinity (6000 mg/l) to partial alkalinity (1700 mg/l) of 0.28 and a mean pH value of 7.6 (7.3 to 7.8) were observed.

8.5 Conclusions.

i) Due to operational obstacles, the system did not provide all the data that had been hoped for. However, from the few indicatory measures which were observed (methane yield and VFA concentrations in the second trial), a good potential for this reactor could be perceived.

ii) Encouraging results were obtained in the second trial with the application of an OLR of 2.7 kg VS per m^3 active reactor volume per day.

iii) A methane yield of 0.240 m^3 per kg VS added, a VS reduction of approximately 50% and low TVFA concentrations of less than 1 mg/g as COD, were achieved in the second trial at 36 days RT, which indicated a good performance efficiency for this reactor.

iv) A proposed modification for the design is needed, incorporating a properly constructed reactor. If this were possible, and there was sufficient financial support, it would be possible to realise the experimental objectives which were initially envisaged for this reactor.

CHAPTER 9

MATHEMATICAL MODELLING OF THE SEMI-CONTINUOUS VERTICAL SEQUENTIAL REACTOR

9.1 Introduction.

Mathematical models of anaerobic digestion can be used to guide the design of reactors and to examine their operational performance and characteristics. Originally, most models were developed to describe the digestion of wastewaters and sludges in continuously-stirred tank reactors (CSTR). However, modifications of these models have been applied to the treatment of municipal solid waste. In this chapter, three major kinetic models, namely the Monod, first-order kinetics and Chen-Hashimoto models are reviewed and their applicability considered.

9.1.1 Monod Kinetics.

The Monod kinetics model is based on the following equation describing the substrate depletion rate:

$$\frac{dS}{dt} = -\frac{K.S.M}{K_S + S} \qquad (9.1)$$

Where, M is the microbial biomass concentration,

S the substrate concentration, and

K, Ks are kinetic constant parameters associated with a specific biomass/substrate system, with units (1/day) and (mg/ℓ), respectively.

The application of the Monod kinetics model for solid waste treatment is limited, for the following reasons:

- It was originally developed for reaction systems involving a single group of bacteria (monocultures) (Dunn et al., 1994).
- Its applicability is limited to soluble substrates, hence it can hardly model the biodegradation of complex solid substrates (Mata-Alvarez, 1992).

Other simpler models, such as the first-order reaction model, were reported to be more suitable for predicting design and operational criteria than the Monod equation. Moreover, this Monod equation cannot predict the dependence of the effluent substrate concentration on the influent substrate concentration (Chen and Hashimoto, 1980).

9.1.2 First-Order Reaction Model.

The application of this model for the prediction of digester performance was originally proposed by Pfeffer (1974) as an alternative to Monod kinetics following the difficulty he experienced in modelling the digestion of municipal wastes. The model assumes that the substrate depletion rate is proportional to its concentration, according to the following equation:

$$\frac{dS}{dt} = -KS \qquad (9.2)$$

Where, K is the rate constant in units of (1/day).

The first order model is an empirical expression, yet it is considered favourable since it involves a single constant kinetic parameter, while providing an adequate fitting of experimental data regarding solid waste treatment in completely mixed continuous reactors. Cecchi et al. (1990b), using the first-order model, obtained a fitting of semi-dry solids digestion data similar to that of the Monod model although, compared to the Chen-

Hashimoto model the fitting was rather poor. However, the first order model is still adopted because of its inherent simplicity. It remains to be determined whether it is possible to successfully utilise it in a complex reactor system such as the one examined in this work.

9.1.3 Chen-Hashimoto Model.

The Chen-Hashimoto model (1980) was developed as an extension of the Monod model, in an attempt to overcome the inability of the latter to take into account the effect of influent substrate concentration on the specific biomass growth rate. The model is based on the expression for the bacterial specific growth rate, μ, as suggested by Contois (1959):

$$\mu = \frac{\mu_m . S}{B.M + S} \qquad (9.3)$$

Where, μ_m is the maximum specific growth rate (1/day),

M is the biomass concentration, and

B is a dimensionless kinetic parameter.

Using the Contois expression, Chen and Hashimoto developed a model applicable to CSTR reactors, as follows:

$$\frac{S}{S_0} = \frac{K}{\mu_m . \theta - 1 + K} \qquad (9.4)$$

Where, S_o is the influent substrate concentration,

θ is the retention time, and

K a dimensionless kinetic parameter equal to Y*B, Y being the growth yield coefficient (mass cell / mass substrate).

The parameters μ_m and K are generally constant for a specific waste type. However, they are both functions of the digester temperature, with μ_m increasing and K decreasing with rising temperature. The above equation

shows that the Contois kinetic model predicts that the effluent substrate concentration is directly proportional to the influent substrate concentration. Chen and Hashimoto have suggested that the best results will be obtained when the biodegradable fractions of the substrate concentrations S and So are used.

The model was tested originally by Chen and Hashimoto using municipal refuse and animal waste data and achieved good predictions. Subsequently, Hill (1983) successfully used the model to determine the optimum operational parameters for the continuous digestion of dairy and animal wastes.

9.1.4 Testing the Models.

The results of the semi-continuous vertical sequential reactor were used to evaluate the suitability of the first-order kinetics model and a proposed modification of the Chen-Hashimoto model that caters for the special modelling requirements involved. These requirements are due to the use of a Plug Flow Reactor (PFR) with solids and leachate recycling.

9.2 Objectives.

The main objectives of the mathematical modelling of the semi-continuous vertical sequential reactor were:

i). To develop a steady-state kinetic model that is suitable for a plug flow reactor with solids and leachate recycling.

ii). To determine the values of the kinetic parameters by fitting the developed model to the obtained experimental results for both digested recycle ratio (DRR) and leachate studies.

iii). To determine the values of the controlled variables (DRR and leachate recycle) that will optimise the reactor efficiency.

iv). To optimise the overall system efficiency.

9.3 Model Development.

Two different kinetic models were considered for their applicability for the modelling of the semi-continuous vertical sequential reactor, namely the first-order model and the Chen-Hashimoto model (based on Contois kinetics). The Monod model was not considered on the grounds that its fitting capabilities are reported to be comparable to those of the first-order model, whilst it is more complicated compared to the simple first-order kinetic model.

Appendix C1 contains the detailed derivation of the mathematical model applicable for a PFR with recycle, when biomass growth is assumed to follow first-order reaction kinetics. The final expression that relates to the influent/ effluent substrate concentrations is :

$$\frac{S}{S_F} = 1 - \frac{M_0 * \left\{\exp.\left(K_1 * \theta\right) - 1\right\}}{Y * \left(1 - DRR\right) * S_F} \qquad (9.5)$$

From a modelling point of view, Eq. 9.5 is mathematically simple. However, when fitting is to be considered, it has the disadvantage that the terms Mo (inlet biomass concentration) and S_F (refuse substrate concentration) appear on the right hand side (RHS) of the expression. The presence of Mo requires special attention, since direct measurement of this variable was not made, and only estimated values can be calculated implicitly using other data. Similarly, according to the assumption that led to Eq. 9.5, the concentration S_F should correspond to the biodegradable

substrate (e.g. BVS) portion of the organic load and, again, this fraction can only be indirectly estimated. The combined effect is that a high degree of uncertainty will be added to the fitting procedure, leading to poor and unreliable estimates of the single kinetic parameter K_1.

Another disadvantage of first-order kinetics is that there is no simple way to model the effect of the water content in the reactor (as will be shown for the Contois-based model in the sequel). Any attempt to insert the water content in the picture (e.g. in a manner similar to the extension of Contois kinetics that were performed) will sacrifice the simplicity of the model, which is its main advantage. Finally, the first-order model is reported to exhibit good fitting performance for simple reactor layouts and it is uncertain if it will be appropriate for the complex vertical sequential reactor examined. Therefore, it was decided that the issue of first-order reaction kinetics was not going to be pursued any further, and effort was to be applied in favour of the more complicated and potentially superior Chen and Hashimoto model. The latter will be shown to be more elegant from a modelling and fitting point of view, as none of the drawbacks mentioned in the first-order kinetics related equation (Eq. 9.5) are present in the Contois based expression. Finally, the Chen and Hashimoto model has been frequently applied for the fitting of data from complex reactor/substrate systems, exhibiting good performance (Cecchi et al., 1990b).

The semi-continuous vertical sequential reactor was modelled on the assumption that it could be approximated by a continuous plug flow reactor. The physical layout of the reactor, consisting of 6 vertically stacked chamber units undergoing a complete cycle every 24 days,

resembles that of an idealised PFR, where no axial mixing is involved. Moreover, the approximation of a semi-continuous process, where a chamber unit was loaded every 4 days, with a continuous one can be justified when the long times required for completion of the anaerobic digestion of municipal solid wastes are considered.

The recycle of digested materials and leachate in the reactor results in a departure from the normal PFR operation, posing special modelling requirements. The recycle of the digested materials provides a healthy and stable bacterial population, that assists in the initiation of the biodegradation of the refuse organic solids. In a similar fashion, the recycled leachate provides methanogenic bacteria to the system and, additionally, an adequate supply of moisture content. The latter is necessary for the hydrolysis of the insoluble organic matter and general enhancement of the anaerobic process (improved mixing and diffusion of substrate and bacteria).

Other factors that contribute to the moisture content within the reactor are the natural moisture content of the refuse and the solids recycle. By modifying the digested solids recycle (DRR), the moisture content of the reactor will be affected. In the following sections, the modelling of the DRR effects will be considered first, followed by the development of the full model, involving both solids and leachate recycle. Fig. 9.1 illustrates a diagram of the plug flow reactor (PFR) with digested solids and leachate recycling.

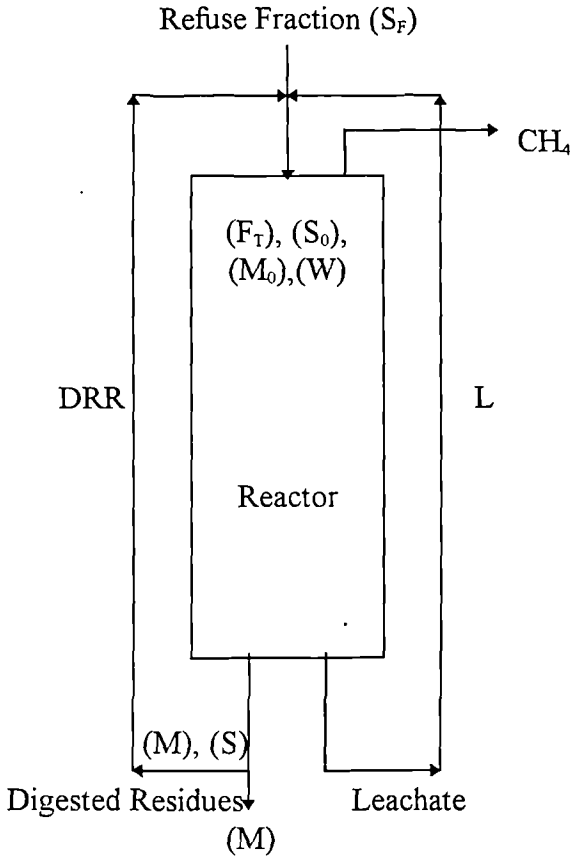


Fig. 9.1 Diagram of the Plug Flow Reactor (PFR) with solids and leachate recycling.

9.3.1 Modelling the Digested Solids Recycle Effects (DRR).

The mathematical modelling of the PFR begins by considering a differential control volume dV at an arbitrary height in the reactor where the reaction mixture has already travelled a volume V of the reactor. Assuming steady-state, then the following mass balance applies for any compound:

$$[\text{influent}] - [\text{effluent}] + [\text{generation}] = 0 \qquad (9.6)$$

According to Eq. 9.6, the mass balances for the biomass and the substrate in the differential control volume are:

Biomass: $$F_T dM = \mu M dV \tag{9.7}$$

Substrate: $$F_T dS = -\frac{\mu M}{Y} dV \tag{9.8}$$

Where, the variables involved are:

F_T Total wet solids feed to the reactor (refuse plus digested recycle), (m^3/d)

M Bacterial concentration (kg/m^3)

μ Bacterial specific growth rate (1/day)

V Volume (m^3)

S Substrate concentration (kg/m^3)

Y Biomass growth yield coefficient (mass cell / mass substrate)

The bacterial specific growth rate is given by the Contois Eq. 9.3. Solution of the above system of differential equations (9.7, 9.8) and subsequent integration for the whole reactor volume provides the following expression for the ratio of effluent to influent biomass concentration (details of the solution steps are found in Appendix C2):

$$\ln\left[\left(\frac{S}{S_0}\right)^{-K} \frac{M}{M_0}\right] = \mu_m . \theta \tag{9.9}$$

Where, the subscript (o) refers to reactor influent conditions,

K is the kinetic parameter of the Chen-Hashimoto model, equal to B * Y, and

θ is the retention time and equal to V/FT.

Equation (9.9), therefore, contains as variables the biomass concentrations M and M_0. The values of these were not obtained experimentally so they must be replaced. The biomass concentration at the reactor inlet M_0 is due only to the digested recycle; a simple mass balance at the reactor inlet provides the value of the M/M_0 ratio as:

$$\frac{M}{M_0} = \frac{1}{DRR} \tag{9.10}$$

Another variable in Eq. 9.9 that should be removed is So, that is the substrate concentration at the reactor inlet that results from the mixing of the refuse and the digested solids recycle. In all experiments, the variable that was controlled was the substrate (i.e. volatile solids) of the refuse. S_o can be substituted by S_F, the substrate concentration of the refuse. By means of a mass balance of the substrate in the reactor inlet:

$$\frac{S_F}{S}(1 - DRR) + DRR = \frac{S_0}{S} \tag{9.11}$$

By substituting Eq. 9.10 and 9.11 in Eq. 9.9, the ratio of effluent to influent substrate concentrations can be obtained:

$$\frac{S}{S_F} = \frac{1 - DRR}{\exp.\left(\frac{\mu_m \theta}{K}\right).\sqrt[K]{DRR} - DRR} \tag{9.12}$$

Equation 9.12 provides the means for calculating the values of the kinetic parameters μ_m and K, as it can be fitted with experimental data of biodegradations performed at various DRR, S and S_F values. It must be pointed out that Eq. 9.12 is very general and could be used in theory for any variables describing the concentration of the limiting substrate S, such as VS, COD, etc. However, the best results, as was suggested by Chen-Hashimoto, were obtained with the use of concentrations of the

biodegradable fractions for S (e.g. BVS). As a concluding remark it must be stated that the mathematical model developed here is just an application of Contois kinetics to a different reactor system, namely the PFR with recycle. This may be contrasted with the Chen-Hashimoto model which is basically an application of Contois kinetics for a simpler system of a CSTR without recycle.

9.3.2 Modelling the Moisture Content of the Reactor.

The presence of increased moisture content in the reactor results in increased efficiency of the conversion process, a fact that has been observed during the conduct of these experiments. In terms of mathematical modelling, the values of the bacterial specific growth rate, μ, given by Contois' equation (9.3) will be affected during variations of moisture content in the reactor, increasing moisture content increasing the observed μ value. A higher μ value results in faster bacterial growth and consequently, faster conversion of substrate. The Contois equation in its normal form does not take into account the effects of varying moisture content in the reactor.

The proposed method to overcome the deficiency indicated is to modify the Contois equation to include the water mass fraction in the reactor, W, as an additional variable. This modified basic kinetic expression will be used subsequently to develop the PFR model. The two key constraints that have to be observed are:

- the modified expression should be formulated in a consistent manner in terms of dimensionality, so as to preserve the original units of μ (1/day); and

- increased values of W should result in increased μ values, when the remaining variables (M, S) remain constant, as observed in the experimental stage.

The proposed modification of the Contois equation that satisfies both constraints mentioned above is the following:

$$\mu = \mu_{contois} \frac{W - K_W}{W} = \frac{\mu_m . S}{B.M + S} * \frac{W - K_W}{W} \qquad (9.13)$$

Where, W is the water mass fraction in the reactor (mass water / total contained mass), and

Kw is a proposed new kinetic parameter that embodies the effects of moisture content and is dimensionless as is the mass fraction W.

Inspection of the units in Eq. 9.13 reveals that the original units of μ are indeed preserved. Moreover, for positive values of the Kw parameter, the fraction (W-Kw)/W is always less than 1, increasing slowly towards 1 as W increases. In other words, the latter fraction correctly conveys the expected effect of moisture content, as originally specified.

It must be stated that this proposed modification is not the only conceivable way to model the effects of moisture content and certainly no claims are made that it is the best method possible. However, it is a rational extension of the original Contois equation, incorporating a practical variable (W) that can be easily calculated and a kinetic parameter (Kw) that can be fitted (estimated) in a similar fashion to that used for the previous kinetic parameters, μ_m and K.

The water mass fraction, W, is indirectly controlled by the leachate recycle and the DRR, since the input refuse fraction and the final digested

materials usually have different moisture contents. In fact, it had been observed that the moisture content of the refuse was consistently lower than that of the final digested materials. Subsequently, for different DRR values (i.e. different relative quantities of refuse/digested residue) the moisture level of the mixture will be affected. However, for constant values of the DRR and leachate recycle, the water mass fraction W, if considered within the PFR framework described earlier, may be assumed to be relatively constant throughout the reactor height. This means that W may be regarded as a constant within the integration of the differential mass balances of the PFR, Therefore, the development of the mathematical model based on the proposed modified Contois equation (9.13) follows steps that are almost identical to the model based on the DRR presented in the previous section. The final equation that incorporates both moisture content and DRR effects is:

$$\frac{S}{S_F} = \frac{1 - DRR}{\exp.\left(\frac{\mu_m . \theta . A}{K}\right) * \sqrt[K]{DRR} - DRR} \qquad (9.14)$$

Where, $A = \frac{W - K_W}{W}$

Since W is not directly controlled, a method for its calculation was developed, based on the variables that directly control its magnitude, namely the digested residue recycle ratio and the leachate recycle. The former variable is directly associated with DRR, whilst the latter needs to be represented by a suitably selected variable. This is defined as follows:

$$L = \frac{\text{kg Leachate Recycled}}{\text{kg Wet Refuse + kg Wet Digested Residue Recycle}} \quad (9.15)$$

It is to be noted that the definition of L in Eq. 9.15 allows values that are greater than 1, since it is not the mass fraction of the leachate recycled. Values of L can be readily obtained for given leachate recycle values.

The desired relationship between W and the directly controlled variables DRR and L can easily be obtained by considering the total liquid and total mass quantities that are inserted into a chamber unit, as follows:

$$W = \frac{\text{Total Liquid}}{\text{Total Mass}} = \frac{\text{Liquid in Refuse + Liquid in Digested Residue Recycle +Leachate}}{\text{Wet Refuse + Wet Digested Residue Recycle + Leachate}} \quad (9.16)$$

For given moisture contents of the refuse and digested recycle, W_F and W_R, respectively, the dependence of W on DRR and L can be obtained by substituting the terms in Eq. 9.16 as:

$$W = \frac{DRR(W_R - W_F) + L + W_F}{1 + L} \quad (9.17)$$

9.4 Fitting Procedure.

The actual experiments were performed for 3 different DRR values and 4 values of the leachate recycle, one point being overlapped between the two phases of the experiment. Data from the first phase (variable DRR, 3 points) were used for the fitting of the simple kinetic model describing the effects of digested residue recycle alone (Eq. 9.12), whilst data from the second phase (variable L, 4 points) were used for the fitting of the full kinetic model describing the effects of both DRR and moisture content in

the reactor (Eq. 9.14). Finally, the combined effects of concurrent DRR and L variations were fitted to the full kinetic model (employing modified Contois kinetics) using experimental data for all 6 individual cases examined. The mean values for the required parameters were used for fitting, as obtained during steady-state operation.

For each fitting, two alternative approaches were considered, utilising two distinct methods for estimating the biodegradable fraction of the volatile solids. In the first approach, biogas yield data were used according to the following equation:

$$\frac{B_0 - B}{B_0} \cong \frac{S}{S_F} \qquad (9.18)$$

Where, B stands for the observed methane yield (m^3 CH_4 per kg VS added), and Bo is the ultimate methane yield, corresponding to the maximum methane yield that could be observed if the digestion was allowed to proceed for a very long period. This value was obtained from the HRR batch experiment and may be safely considered independent of both DRR and L.

In the second approach, data for the percent volatile solids reduction were used, according to the following equation:

$$\frac{VSR_0 - VSR}{VSR_0} \cong \frac{S}{S_F} \qquad (9.19)$$

Where, VSR is the observed % VS reduction (based on the refuse VS), and VSRo the ultimate VS reduction, obtained from the batch experiments in a similar fashion to that used for the Bo value.

Both approaches lead to equations that are non-linear and cannot be fitted using conventional linear regression techniques. A non-linear least squares fit of the experimental data had to be utilised within an optimisation algorithm. The objective of the optimisation was to select the values of the kinetic parameters μ_m, K and K_W so as to minimise the squared sum of the errors (SSE) between the observed and calculated values, defined as follows:

$$SSE = \sum_{i=1} \left[\left(\phi_{obs,i} - \phi_{pred,i} \right)^2 \right] \qquad (9.20)$$

Where, ϕ is the chosen indicator.

The solution of the non-linear optimisations was performed by writing a GAMS program, used as an interface for communication with the actual optimisation solver. GAMS is a modelling environment widely used for the solution of optimisations and a brief summary of the GAMS programming language is contained in Appendix D1, with samples listing for the actual problems solved in Appendix D2.

For each different value of the operational parameters examined (DRR and L) a relatively constant OLR was maintained. In order to ensure that steady-state conditions were achieved, the mean values from the last cycle of each phase were used. This steady-state assumption is reinforced by the small variation observed in the methane production (Tables 7.3 and 7.13, Chapter 7).

Table 9.1 gives a summary of the values used in the various fitted equations. The observed experimental data that were used for the fittings can be found in Chapter 7, Sections 7.9 & 10.

Table 9.1. Fixed Values Used for all Fittings.

RT (day)	24
Reactor Volume (L)	38
W_F (Average Refuse Moisture, %)	0.58
W_R (Average Digested Solids Moisture, %)	0.67
Ultimate CH_4 Yield (L CH_4/kg VS added)	255
Ultimate VS Reduction (%)	55.8

9.5 Optimisation Procedure.

The objective of the optimisation was to use the various versions of the mathematical model developed to select the values of the controlled variables examined (DRR and L) so as to optimise the efficiency of the reactor, while ensuring stable operation. The values of the kinetic parameters chosen were the same as those estimated by fitting the kinetic models. For optimisation purposes, an "average" refuse (feed mixture) was considered with a fixed % TS, % VS, W_F and W_R.

As in the fitting procedure, two approaches were used for optimisation. The first considered the reactor efficiency to be the highest possible

methane production per m^3 of reactor, given by the product of B*OLR, OLR being the organic loading rate (kg VS per m^3 per day). In the second approach, the efficiency measure considered was the maximisation of the VS reduction per m^3 of reactor, given by the product VSR*OLR.

The organic loading rate OLR for a fixed average refuse, given that the retention time is fixed, is a function of both DRR and L. Qualitatively speaking, as far as DRR is concerned, the less its value (i.e. less digested residue recycled) the more refuse can be processed in the reactor, thereby increasing the effective OLR. In a similar fashion, the less leachate added (L decreasing), again the more refuse can be processed in the reactor, thereby increasing the effective OLR. For the average refuse considered in the optimisation, an estimation of the effective loading rate is given by:

$$LR = \frac{\rho . TS . VS}{24} * \frac{1 - DRR}{1 + L} \tag{9.21}$$

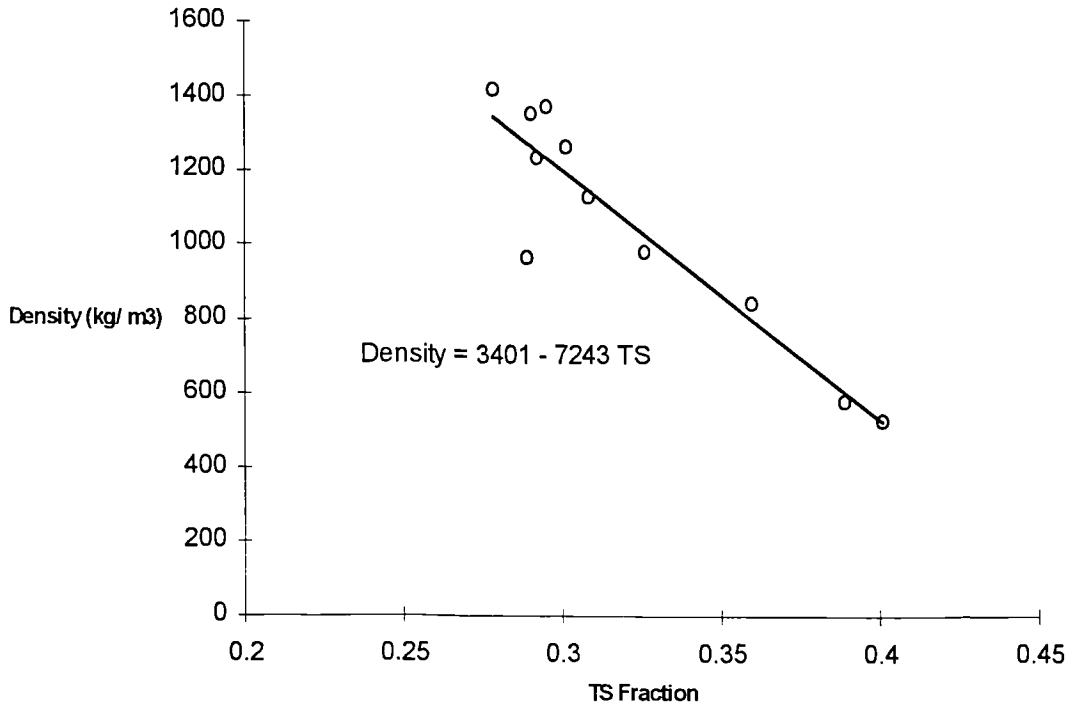
In order to obtain realistic estimates of the density, ρ, of the mixture (wet refuse and digested residue weight plus leachate) that was loaded into the chamber unit, experimental observations of the dependence of wet density on the TS ratio were used. The experimental density data were subsequently fitted using simple linear regression, as displayed in Fig. 9.2. The following linear equation was obtained :

$$\rho = 3401 - 7243 * TS = 3401 - 7243\left(1 - W\right) \tag{9.22}$$

Where, $W \leq 0.45$

In this way, the densities used for the calculation of the loading rate (Eq. 9.21) were slightly elevated. However, this elevation can be justified if the fact that the leachate added is partially filling the gaps (void space) between the solid waste is considered. This somehow compensates for the

Fig. 9.2 Effect of Input Total Solids Content on Density



model's limitation to describe the leachate drainage that is experimentally observed.

The optimisation was first performed individually for each one of the controlled variables DRR and L. In order to calculate the value of the controlled variable that optimised the selected efficiency measure, the first partial derivative had to be set equal to zero and the resulting equation solved for the desired control variable value. For instance, in the case that DRR is controlled to optimise methane production, the following partial differential equation has to be solved:

$$\frac{\partial(B.LR)}{\partial(DRR)} = 0 \qquad (9.23)$$

Finally, a combined optimisation for determining simultaneously the best operational values of both controls DRR and L was conducted, by writing another GAMS program.

9.6 Results and Discussion.

9.6.1 Kinetics Study.

Table 9.2 contains the values for the kinetic parameters as estimated by the non-linear least-squares fitting procedure. These estimated values agree with values reported elsewhere for similar waste types and reactor temperature, as shown in Table 9.3. The wide range of reported kinetic constant values reflects the variation in reactor types and treated waste materials.

Table 9.2 Summary of the Kinetic Parameters Estimated Values Using Different Experimental Data for Various Phases of the Experiment.

Controlled Variables	SSE	$\mu_{max.}$	K	K_W	Comment
3- DRR	0.008	0.077	1.316	------	Ultimate CH_4
	0.003	0.114	1.857	------	Ultimate VS Reduction
4- L	0.002	0.125	0.692	0.45	Ultimate CH_4
	0.0004	0.100	0.467	0.383	Ultimate VS Reduction
Full 6 Points	0.011	0.171	1.137	0.48	Ultimate CH_4
	0.005	0.196	1.251	0.45	Ultimate VS Reduction

Table 9.3. Comparison of Reported Kinetic Constant Values for the Chen-Hashimoto Model with those Obtained in this Study.

Waste Type	μ_m	K	Experimental Conditions	Reference
Beef-Cattle Manure	0.326	1.086		Chen-Hashimoto (1980)
MSW	0.33	0.3	Batch fed	Pfeffer (1974)
Source Separated OF- MSW	0.03	1.7	RT = 25 days OLR = 2.1	Cecchi et al. (1990b)
Pulverised Refuse	0.077	1.316	DRR model (CH_4)	This work
Pulverised Refuse	0.114	1.857	DRR model (VS)	This work

The use of mean values for the fitting was considered necessary to ensure that steady-state conditions were modelled. However, this usage leads to a small number of experimental points being used for the fitting and thus

explaining the small squared sum of the errors (SSE) values contained in Table 9.2. The full 6-points fitting exhibits relatively higher SSE. In general, when non-linear least squares fitting is applied, the resulting curve is closer to the actual observed values by contrast to linear regression, where a straight line cannot possibly fit all points. Therefore, in linear regression higher SSE values are usually expected.

Figs. 9.3 and 9.4 contain the predicted and observed values for the effect of DRR on ultimate methane yield and VS reduction (Eq. 9.12) and good data fit can be seen. At a DRR value of around 0.2 the plotted curves approach 1.0, which means that the process has reached its failure point where there is no substrate conversion and, therefore, no methane yield. Hence, the model predicts that the process has to be operated at DRR values higher than 0.2.

Figs. 9.5 and 9.6 illustrate the fitting for the leachate experiment based on ultimate methane yield and VS reduction, depending on the moisture content W of the reactor (Eq. 9.14). The values of W were obtained by using Eq. 9.17, which gives the relationship between L and W and, again, a good fit was obtained. The limiting value for W was approximately 0.55, at which point the plotted curve was approaching one, due to very much reduced moisture content in the reactor. It must be stated that even with no leachate recycle, the moisture content of the reactor (due to the refuse and the digested residue moisture) was above the predicted limiting value of

Fig. 9.3 Predicted and Observed Values with the Variation of DRR Based on Ultimate Methane Yield.

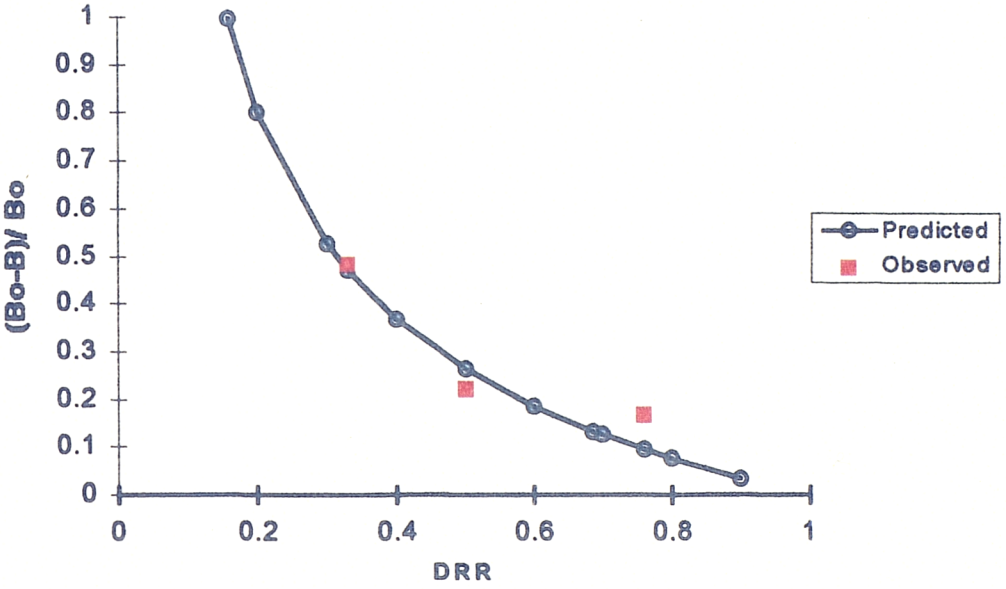


Fig. 9.4 Predicted and Observed Values with the Variation of DRR Based on Ultimate Volatile Solids Reduction

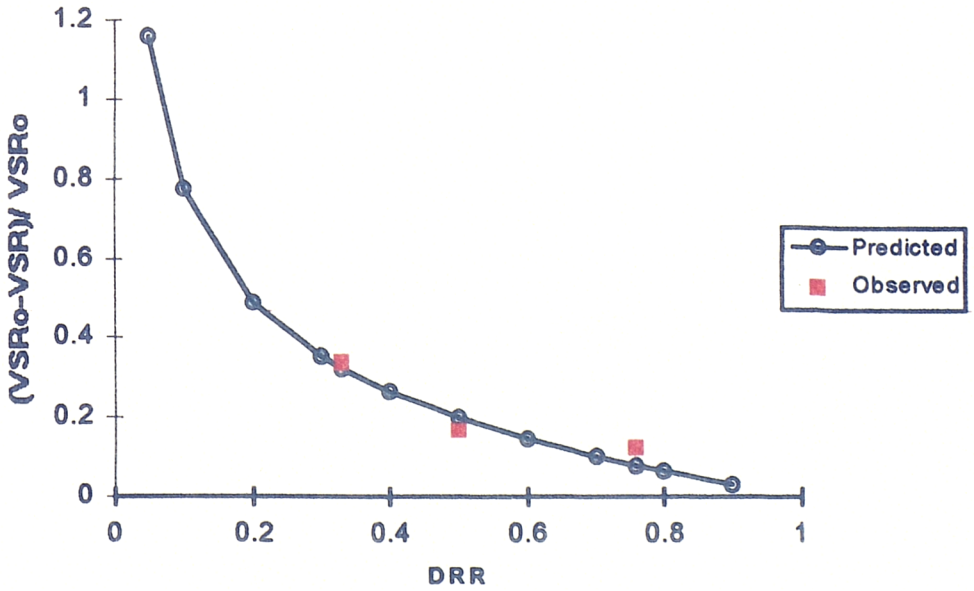


Fig. 9.5 Predicted and Observed Values with the Variation of Leachate Mass Fraction Based on Ultimate Methane Yield

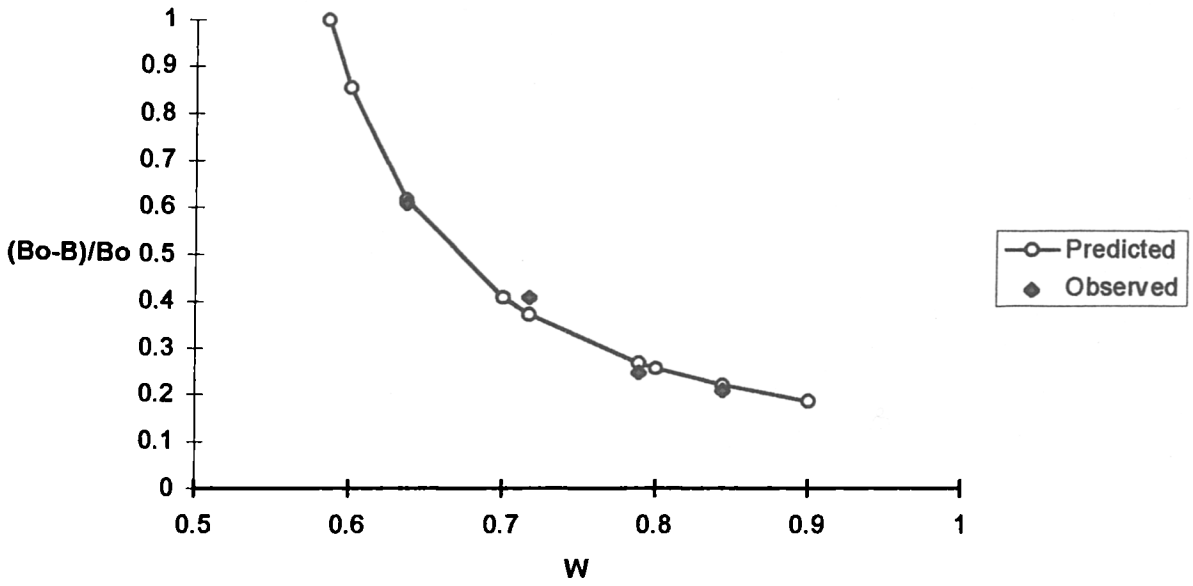
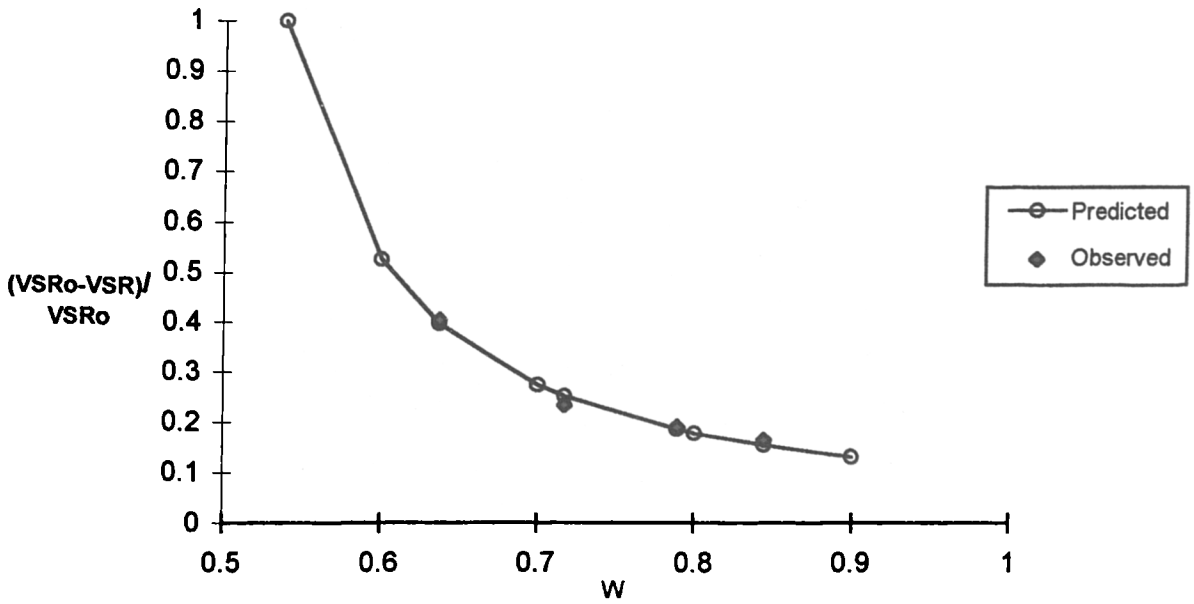


Fig. 9.6 Predicted and Observed Values with the Variation of Leachate Mass Fraction (W) Based on Volatile Solids Reduction



0.55. Nevertheless, the maximum TS in the reactor should not exceed 45%, and in order to maintain stable operation the total solids should be around 30%. Fig. 9.7 contains the same information as Fig. 9.4, in terms of the leachate parameter L.

The combined DRR-leachate Eq. 9.14 was subsequently fitted using data points from both experimental phases 1 and 2. The corresponding kinetic parameter values are shown in Table 9.2. Fig. 9.8 and 9.9 compare the combined and individual phase-related models. The full model, describing the methane yield dependency on both DRR and L, predicts almost identical behaviour compared to the phase-related curves. This is achieved by fixing, on the one hand, the leachate recycle parameter L=1.2 (equal to the leachate recycle in phase 1) for the DRR effects comparison (Fig. 9.8), and on the other hand, the DRR = 0.5 (phase 2 value) for the comparison of L effects (Fig. 9.9). It can be concluded, therefore, that the combined model is adequate to be used for overall optimisation with respect to the operational parameters DRR and L.

Finally, it can be seen that the values of the kinetic constants of the combined model, which has demonstrated a good fit in the previous Fig. 9.8 and 9.9, lie close to those calculated by the DRR experiment (Table 9.2). However, a comparison between the combined and leachate models shows that the K value of the latter is slightly reduced. Despite this fact, the fittings provided were practically identical, thus rendering the observed difference insignificant.

Fig. 9.7 Predicted and Observed Values with the Variation of Leachate Recycle Ratio (L) Based on Ultimate Methane Yield

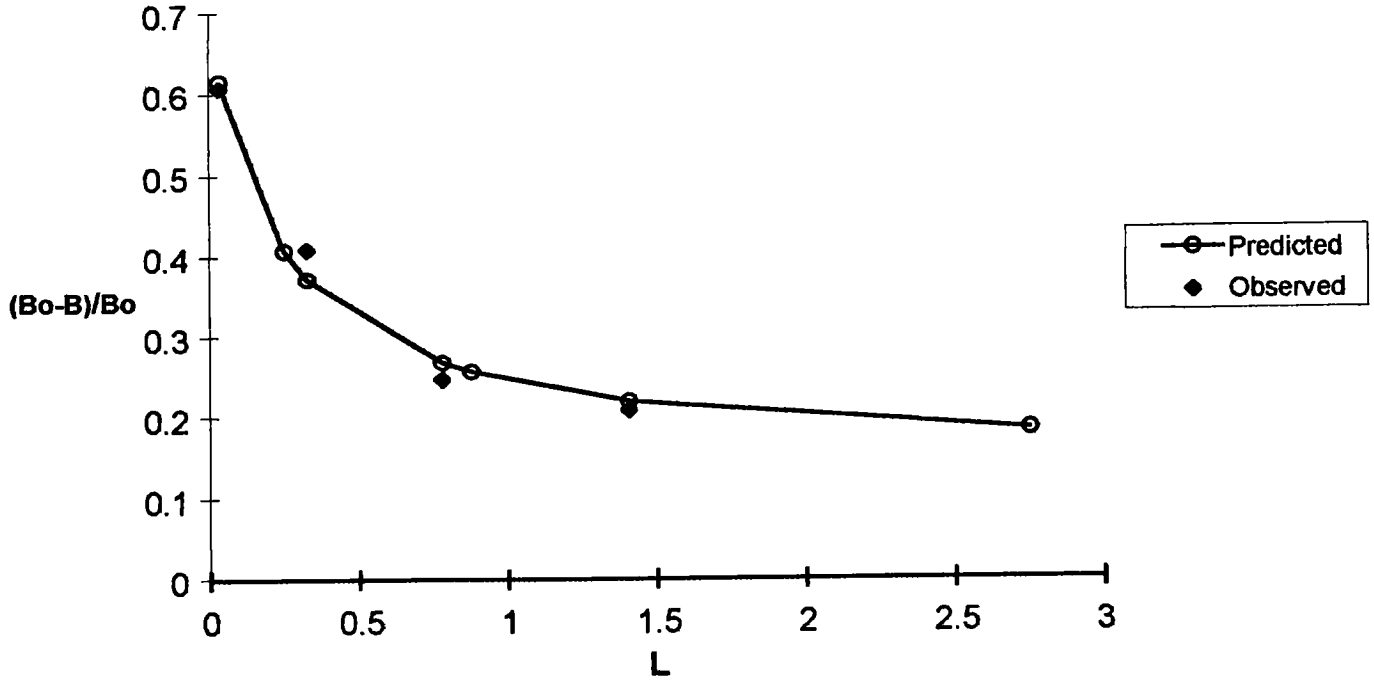


Fig. 9.8 Effect of DRR on the Methane Yield Fraction with a Fixed Leachate of 6 l (L = 1.25) : Comparison between the Combined and Phase 1 models.

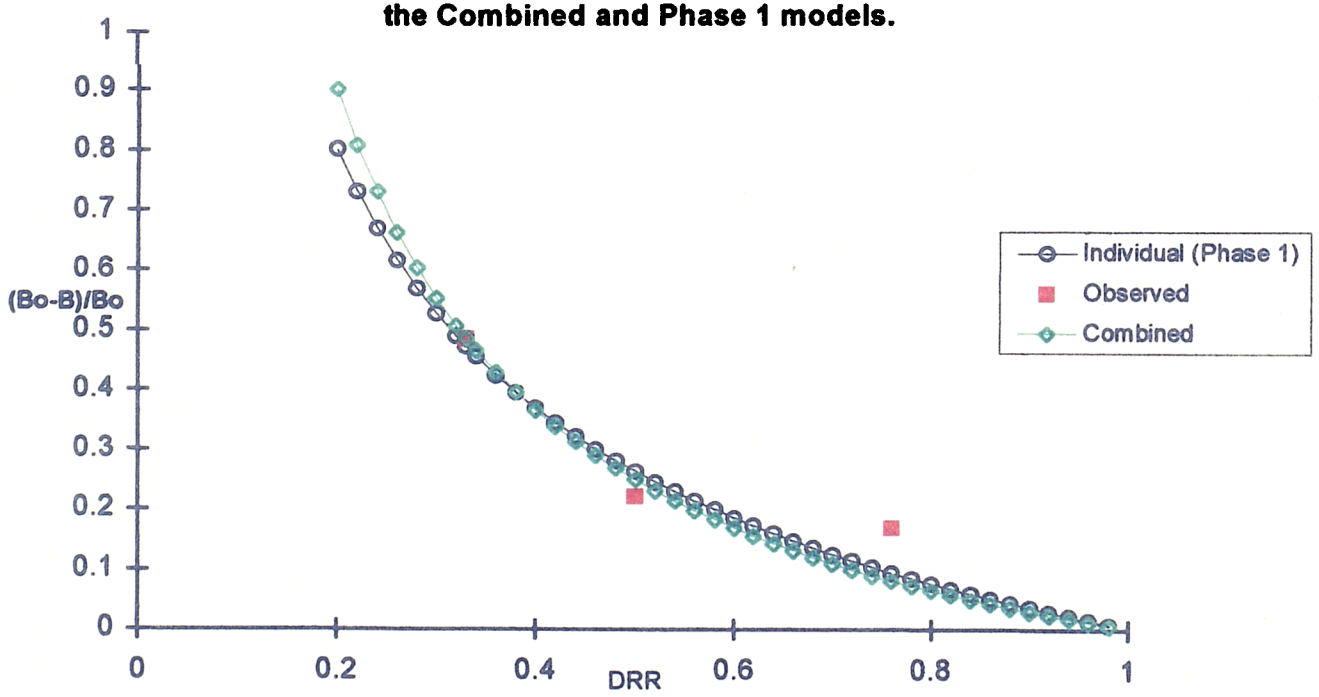
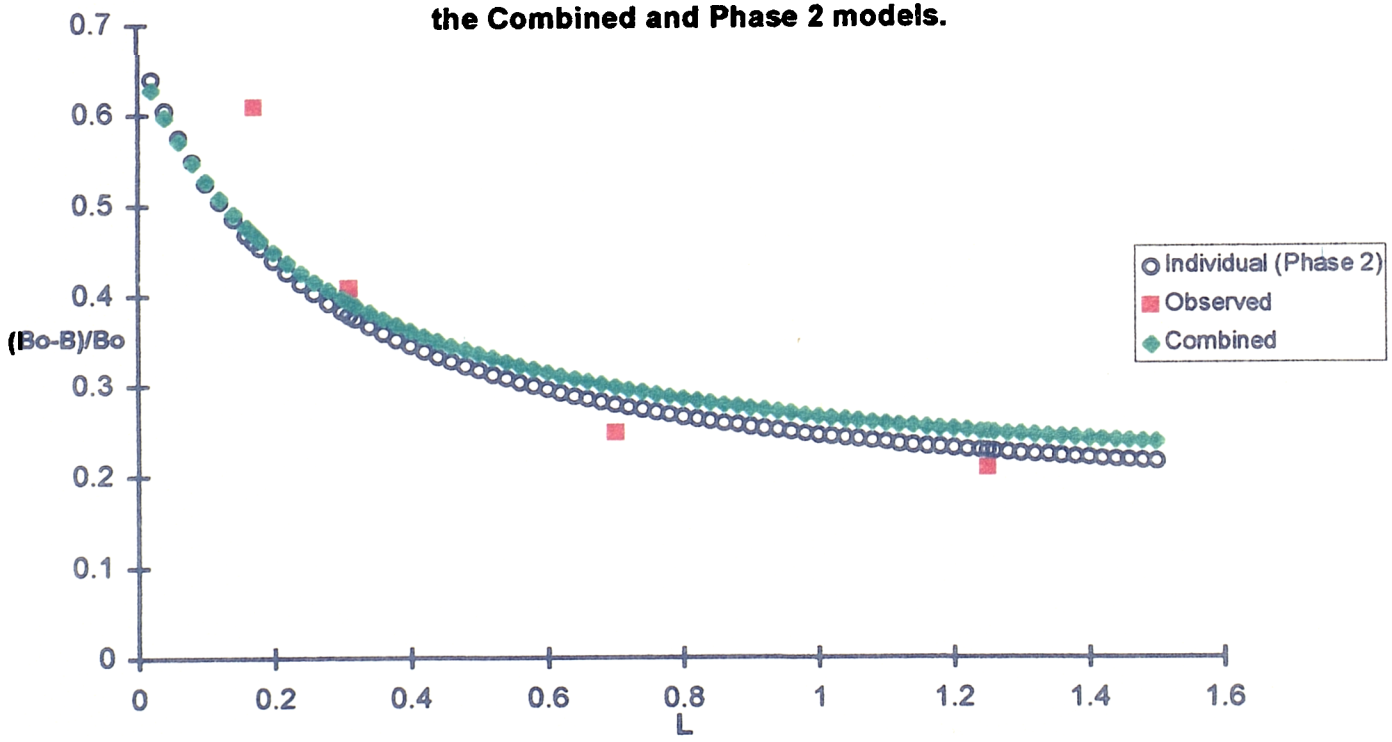


Fig. 9.9 Effect of Leachate Recycle Ratio on the Methane Yield Fraction with a Fixed DRR of 0.5 : Comparison between the Combined and Phase 2 models.



9.6.2 Optimisation Study.

Table 9.4 contains the parameter values of the average waste that was used for all optimisations. The use of a single waste simplifies the comparisons between alternative operational optimisation cases.

Table 9.4 Average Waste Characteristics Used in Optimisation

W_F (Average Refuse Moisture, %)	0.58
W_R (Average Digested residue Moisture, %)	0.67
Average refuse VS content	0.64

Single variable optimisations for the phase-related models were carried out graphically, whereas the combined DRR-L optimisation was performed using a GAMS program (Appendix D3). Fig. 9.10 illustrates the efficiency of volumetric methane production as a function of DRR for the first phase of the experiment (L fixed at 1.25). The optimal DRR value under this condition was 0.44, corresponding to a methane efficiency of 1.058 m^3 CH_4 per m^3 reactor per day. A similar optimisation with respect to DRR, using volatile solids reduction data, is presented in Fig. 9.11. The optimal DRR value is reduced to 0.33, and the respective VS removal efficiency is 2.72 kg VS (raw refuse feed-related) per day per m^3 reactor.

The results of the optimisations, in terms of the L parameter which

Fig. 9.10 Effect of DRR on Methane Production Efficiency: Optimal DRR Values

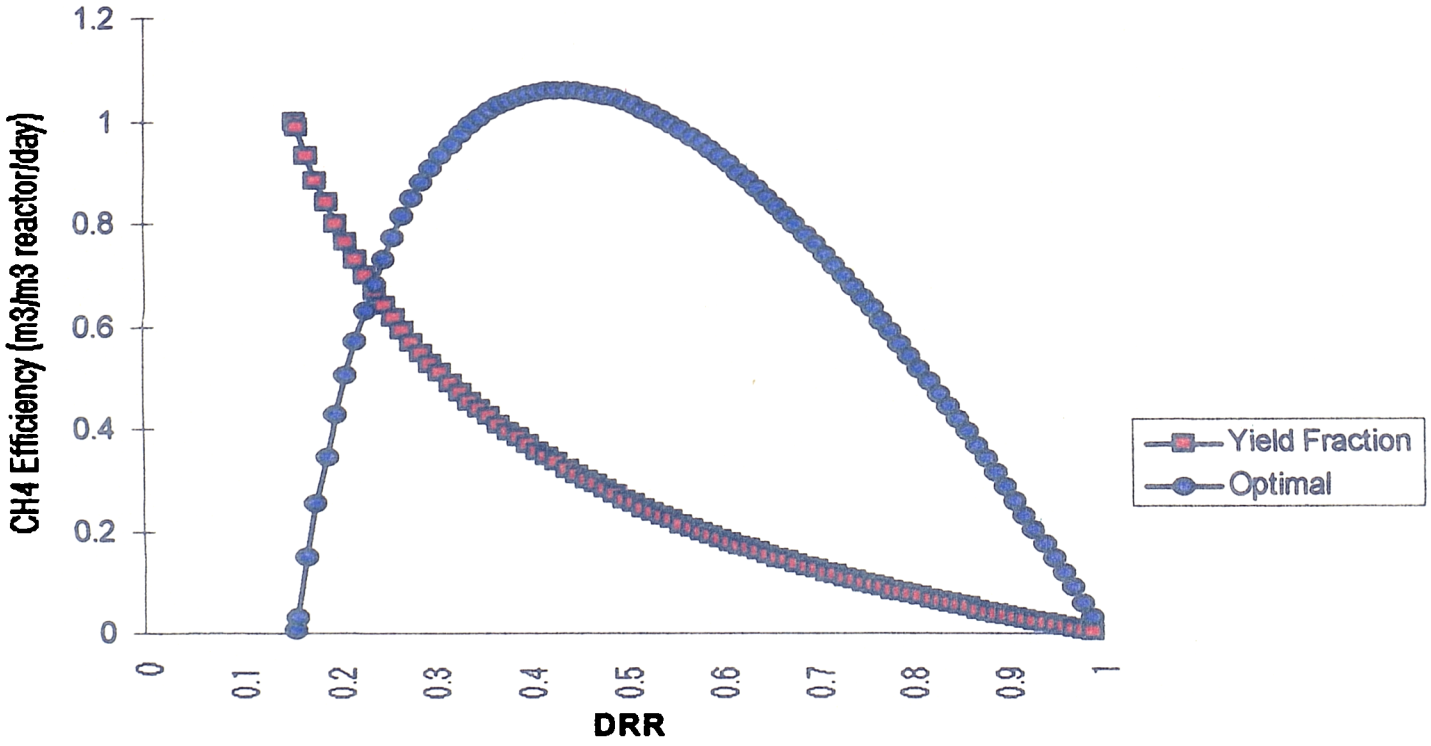
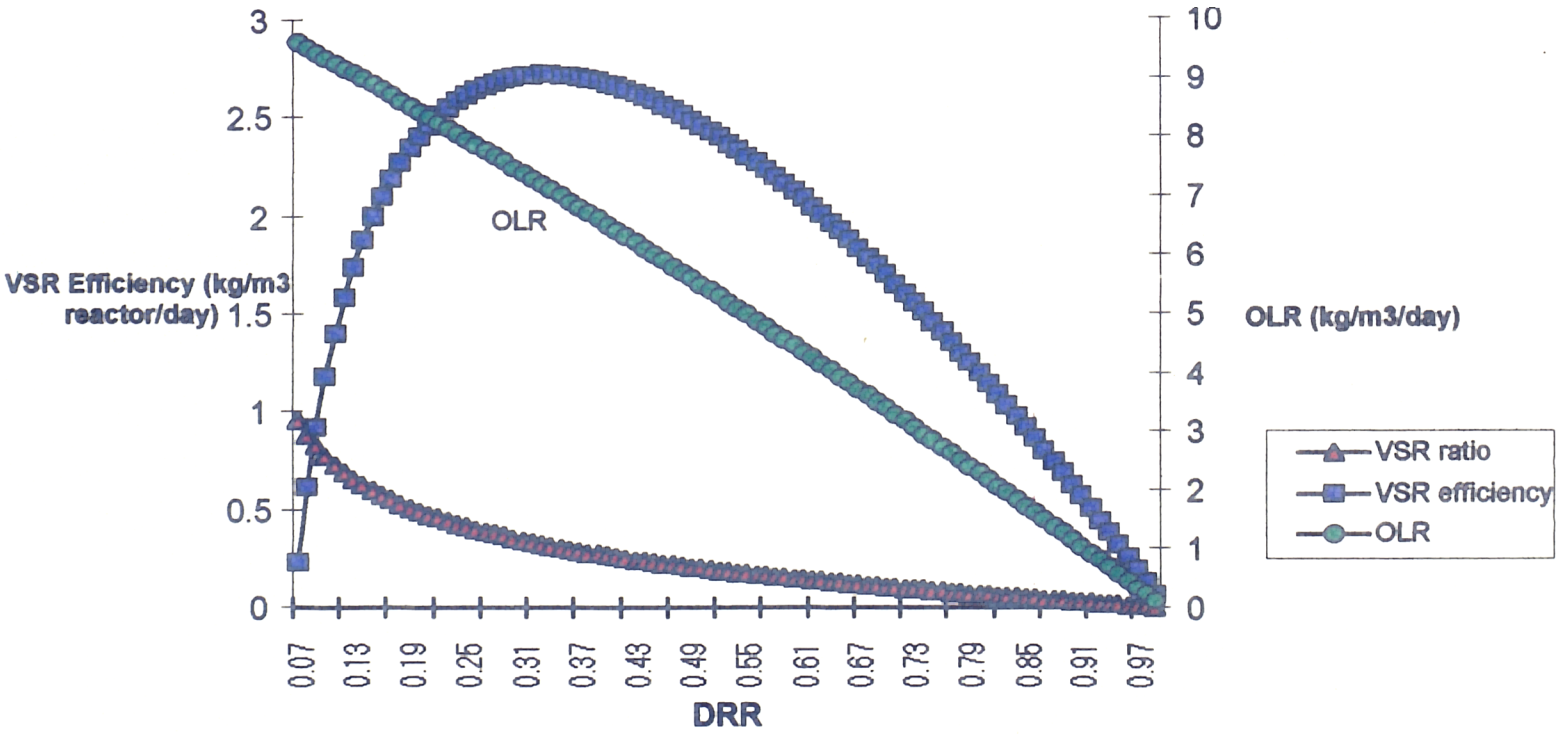


Fig. 9.11 Effect of DRR on Volatile Solids Reduction Efficiency: Optimal DRR



corresponds to leachate recycle, for the second phase of the experiment are shown in Fig. 9.12 and 9.13, using CH_4 production and VS removal efficiencies, respectively. The obtained results followed the same trend that was observed during DRR optimisation. The optimal L value drops from 0.88 (equivalent to around 4.4 litres leachate recycled), using CH_4 production data, to 0.78 when VS removal data are used. However, the values of the respective efficiency measures were largely unaffected.

The lower optimal operational parameter values obtained using VS reduction data indicate that it would be more reliable to use CH_4 yield data for both optimisation and kinetic modelling steps, on the grounds of better correspondence with the observed behaviour. The reason for this superiority is rather circumstantial though, since in theory similar results were expected from both approaches.

The reported optimal operational parameter values correspond to the absolute optimum efficiency. However, a study of Fig. 9.10 and 9.12 reveals a broad range around the precisely optimal DRR and L points where similar CH_4 production efficiencies are exhibited. For instance, Fig. 9.10 indicates that all DRR values in the range [0.38-0.48] result in practically indistinguishable efficiencies. Therefore, from an operational stability point of view, it would be better (i.e. safer) to select the upper limit of the optimal range rather than using the absolute optimal value, so as to avoid operating at values close to the reactor failure threshold (as obtained from the kinetic studies).

Fig. 9.12 Effect of Leachate Recycle Parameter (L) on Mehane Production Efficiency: Optimal L

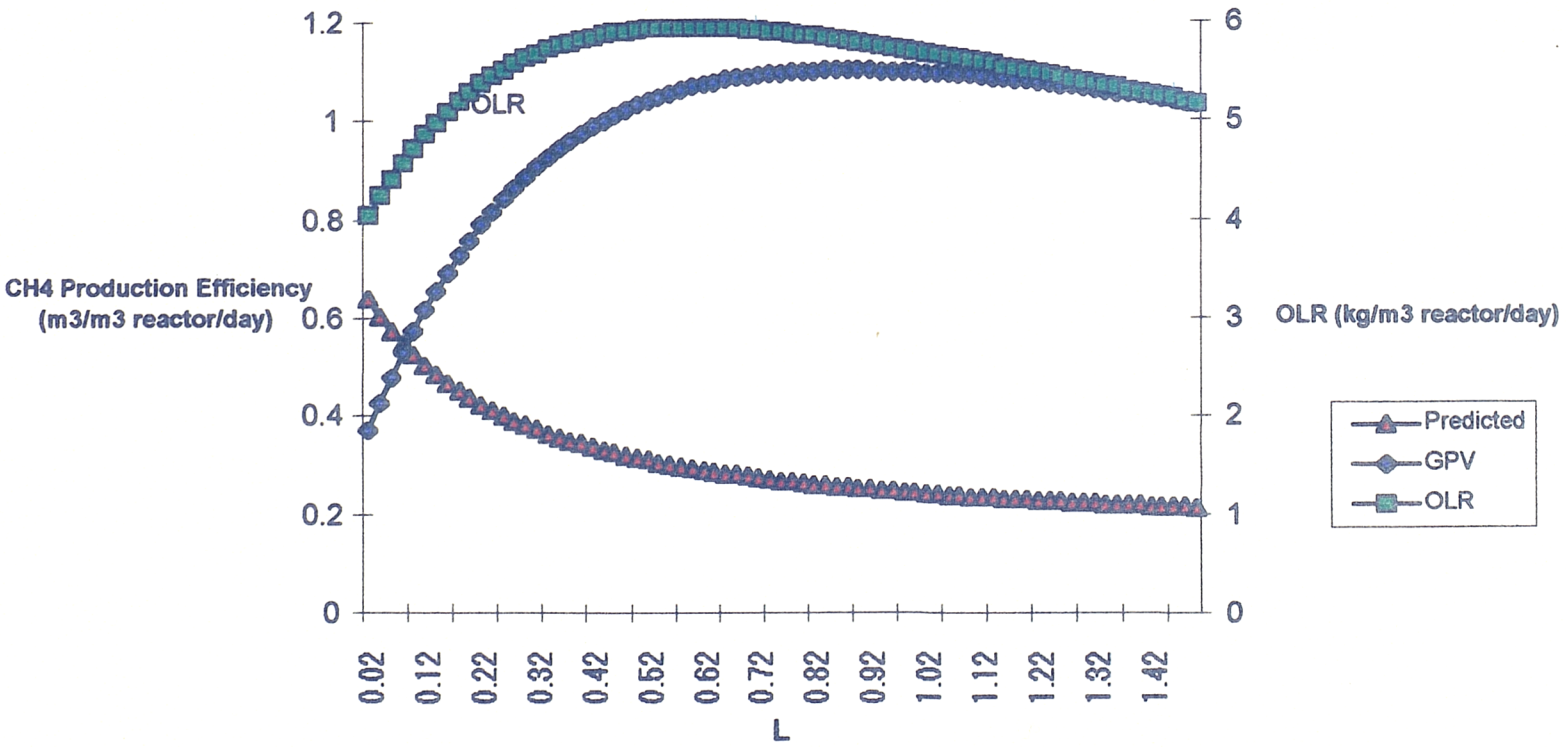
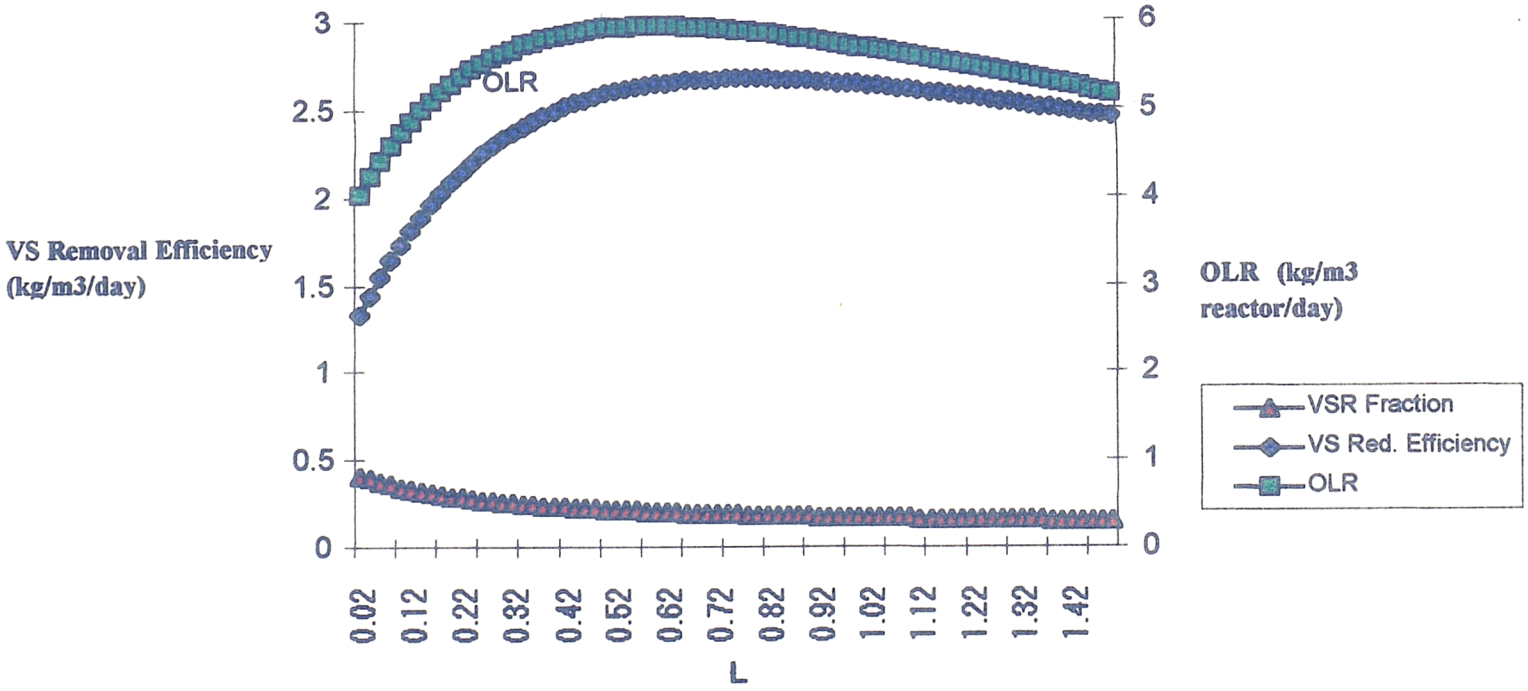


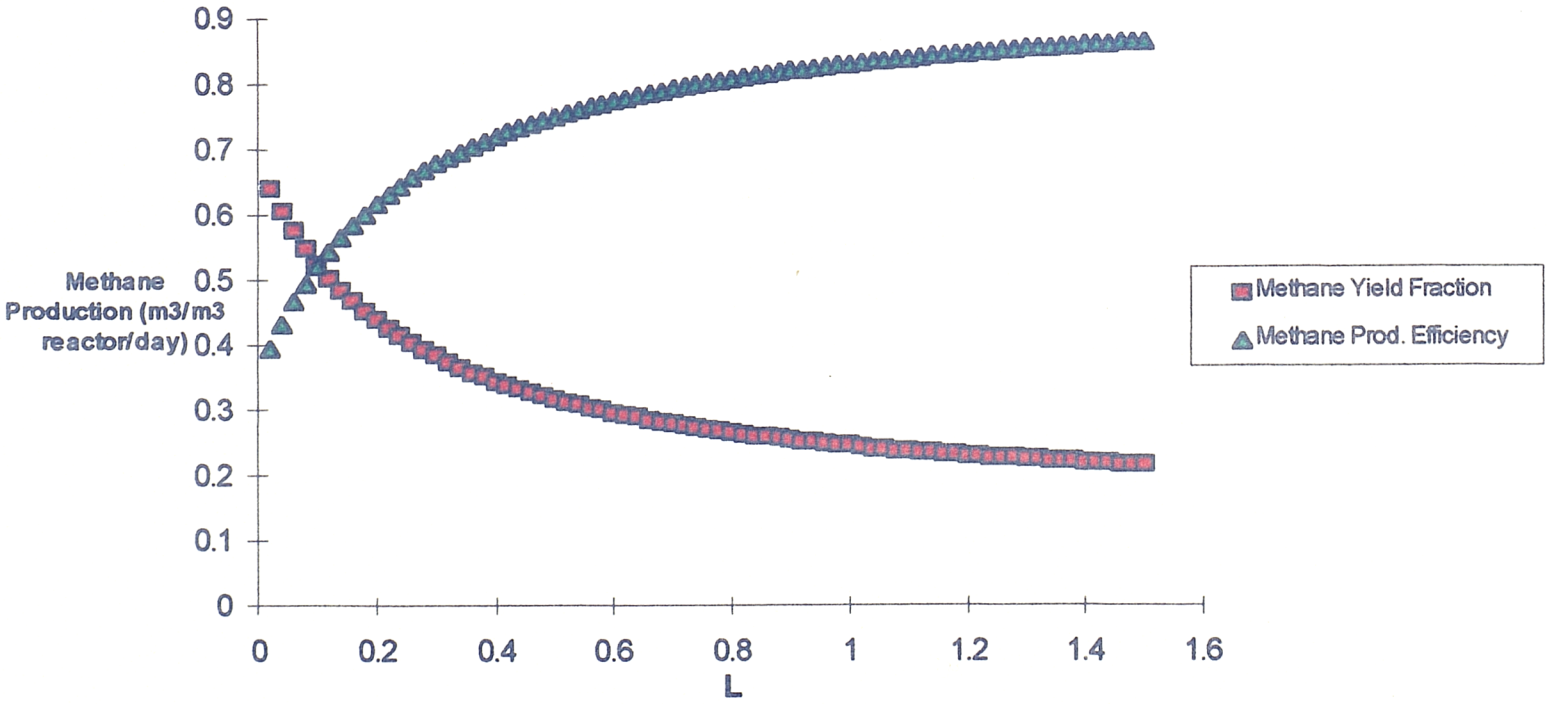
Fig 9.13 Effect of Leachate Recycle Parameter (L) on Volatile Solids Efficiency : Optimal L Values



In the case of leachate optimisation it was assumed that more refuse can be placed in the chamber units as L is reduced. Although, theoretically, this is correct, in the actual experiment the OLR was almost unaffected by the leachate recycle, which had mainly drained from rather than remaining in the chamber. An attempt to determine the optimal L value under the constant OLR assumption is shown in Fig. 9.14. The trend observed indicates that it is not possible to select an optimal L in this case. When the effect of L variation on the OLR is discarded, the increase in the moisture content of the system, by increasing the amount of recycled leachate , is translated by the model as benefit for the process efficiency (faster bacterial growth and substrate degradation rates). Although the marginal increase in efficiency rapidly deteriorates as L increases, increased methane production will occur until the point is reached where the maximum methane yield is obtained. When water management and cost-benefits are taken into consideration, the value of L must be kept as low as possible.

Table 9.5 contains the optimal values of the controlled variables, using the models of the various experimental phases. The combined optimisation for L and DRR (using the combined kinetics model) gives the best balance between these two controlled variables. The optimal values obtained (DRR = 0.46 and L=0.94) are in good agreement with the operational conditions examined in the actual experiments. It must be stated that the efficiency improvement is rather small, and all optimisations predict almost the same CH_4 production efficiencies despite the different operational parameter values. This behaviour is attributed to the relatively broad optimal ranges exhibited in terms of both parameters (Fig. 9.9-9.12). Thus, it is predicted theoretically that there exists a significant amount of

Fig. 9.14 Effect of Leachate Recycle Ratio (L) on Volumetrec Methane Production Efficiency with a Fixed Loading Rate (4.3 kg VS /m3 reactor/day)



tolerance allowed in the selection of the best operational conditions. This has to be considered as an advantage of the sequential semi-continuous reactor from an operational point of view, especially when the large degree of uncertainty involved in biological reactor systems is considered.

Table 9.5 Summary of the Optimal Values of the Controlled Variables with the Corresponding Values of the Optimal Efficiency Measures (per m^3 reactor per day).

Experimental Set-up	DRR	L	CH_4 Efficiency	VS reduction Efficiency
Phase 1	0.44 0.33	fixed = 1.25	1.058 ------	------ 2.72
Phase 2	fixed = 0.5	0.88 0.78	1.103 ------	----- 2.67
Combined model	0.46	0.94	1.150	-----

9.7 Overall Modelling Conclusions.

9.7.1 Kinetic Model Development.

A steady-state mathematical model was developed, based on the Contois bacterial growth kinetics applied for a PFR with recycle. Generally speaking, the physical layout is adequately conveyed to the model, except for the leachate recycle where the water in reality does not remain in the chamber unit but drains out. This behaviour is very difficult to model, especially due to the lack of detailed leachate flow measurements within the reactor. A novel approach was proposed to take into consideration the

effect of varying liquid content within the reactor, expressed as an extension of the basic Contois model.

The whole modelling issue is centred around the solids residue recycle DRR and leachate recycle L, both useful and easily manipulated (i.e. practical) variables. It must be stated that although the retention time θ appears in the kinetic expression, the effect of variation in RT can only be roughly estimated. Further experiments will be required with various θ values in order to assess its effect on reaction rates.

The proposed model involves three kinetic parameters that are associated in a non-linear manner with the intended control variables DRR and L.

9.7.2 Evaluation of the Kinetic Parameters.

Non-linear least-squares fitting was implemented to calibrate the kinetics model for the experimental data and to obtain the best kinetic parameter estimations. Adopting the reported recommendations of Chen-Hashimoto for using the biodegradable portions of the digested substrate, two different sets of experimental data were used for the various fittings, namely methane yield and VS reduction data. The two data sets were fitted to both phase-specific models, involving the effect of a single parameter (DRR or L), and a combined model. Close fits were observed with all different approaches, yet optimisation data suggested that methane yield fit was more appropriate, compared with VS reduction fittings, to describe the observed experimental data. The combined model, using all 6 experimental points, conveys all the information of the phase-specific

models. It is considered, therefore, to be completely adequate, making use of the partial models obsolete.

The fitted model predicted limiting values of DRR and L, beyond which the reactor fails (i.e. no substrate conversion). The threshold DRR value is 0.16 where lower digested residue recycle ratios result in insufficient initial biomass concentrations and, consequently, reactor operation is inhibited. In similar fashion, liquid contents, W, in the reactor below 0.59 lead to reactor failure. However, leachate recycle on its own cannot cause reactor failure if the moisture provided by the refuse and the recycled solid residue is adequate to ensure reactor water content above the limit.

9.7.3 Optimisation of the Controlled Variables.

Using the kinetic parameter values obtained by the various fitting methods, the optimal values for the DRR and L controlled variables were established by maximising two measures of volumetric reactor efficiency for a given average refuse, namely the methane production and VS removal per m^3 reactor. Reasonable optimal values for DRR and L were obtained, corresponding to efficiency measures close to those experimentally observed. The optimal values of the DRR and L derived using the VS reduction data were lower than the respective ones obtained using methane yield data, a factor that leads to recognition of the appropriateness of the latter fitting alternative.

9.7.4 Overall Optimisation.

The overall reactor optimisation performed using the combined kinetics model and the kinetic parameters obtained from the methane yield data

fitting, resulted in the following best values for the controlled parameters: DRR = 0.46 and L = 0.94, corresponding to a maximum methane production of 1.15 m^3 CH_4 per m^3 reactor per day. However, optimisation data indicated that a broader range of operating values around the absolute optimal ones could be selected in practice without significant reduction in the CH_4 production rates.

CHAPTER 10

CONCLUSIONS AND RECOMMENDATIONS

10.1 Conclusions.

Detailed conclusions have been given at the end of each results chapter. A summary of the conclusions of these studies is given below:

10.1.1 Batch Experiments.

i) The start-up of the batch Horizontal Rotary Reactor (HRR) experiment of the high solids anaerobic process was successful using a seed sludge to fresh refuse ratio of 0.26 and 53 g of sodium bicarbonate per kg of refuse. However, the time required to complete the process was around 6 months, despite continuous mixing of the reactor at 3 rpm. The methane yield was around 0.255 m^3/kg VS added, while VS reduction was approximately 56%. These values were used as ultimate methane and VS reductions for the rest of the study.

ii) The Vertical Conical Reactor (VCR) was found to be unsuitable for high solids anaerobic digestion. The first start-up of this reactor, with a seed sludge to fresh refuse ratio of 0.49, appeared to reduce the process completion time to five months. After this time, a digested residue of adequate stability was obtained, which was comparable with the final residue from the batch HRR experiment. The VS reduction was approximately 53% and VFA of less than 1 g/l as COD was achieved. The methane yield could not be measured due to a crack in the inner wall of the reactor.

iii) Rapid start-up of a batch Vertical Sequential Reactor (VSR) experiment and short completion time were achieved when digested solids materials were used as an innoculum, at a digested solids to total weight ratio of 0.33. Methane yield of up to 0.183 m3/kg VS added and 45% VS reduction were obtained at RT of 25 days. This methane yield was approximately 72% of the ultimate methane yield.

10.1.2 Semi-Continuous Experiments.

i) The overall performance of the VSR proved that the design was suitable for the high solids anaerobic digestion of the organic fraction of MSW.

ii) Maximum biogas and methane yields of 0.406 and 0.213 m^3/kg VS added, respectively, and approximately 49% VS reduction were obtained at 0.76 digested recycle ratio (DRR1).

iii) The optimum digested recycle ratio was found to be 0.5 (DRR2), at which maximum volumetric biogas production of 1.62 and methane production of 0.832 m^3 per m^3 reactor per day were achieved at an OLR of 4.1 kg VS per m^3 reactor per day. In addition, there was a negligible difference compared with the maximum VS reduction and methane yield that were obtained with a digested solids recycled ratio of 0.76. At this optimum digested recycled ratio, approximately 80 and 84% of the potential methane yield and VS reduction, respectively, were achieved, compared with the long term batch experiment using the HRR.

iv) The maximum OLR of 5.1 kg VS per m^3 reactor per day was achieved at a digested recycle ratio of 0.33.

v) During the second phase of this experiment, process efficiencies at a leachate recycling rate of 3.5 l in LR2 were close to LR1 (optimum DRR2) with less leachate. This means that the operational conditions in the LR2 run might be more desirable economically than in the previous run in relation to reducing operational cost and reactor volume.

vi) Overall process efficiencies seemed to decrease significantly with reduction of the moisture content in the reactor below the LR2 level of 69%.

vii) Observation of the internal activities of the process was fully successful in the VSR experiments. Determination of the required retention time can be achieved using the observation of the internal activities of the process.

viii) The VSR process designed with internal liquid recirculation provided successful leachate treatment, based on VFA and COD removal, for all operational modes examined in this study.

ix) Aerobic post treatment of the residue after anaerobic treatment was considered to be required to obtain a well-established compost material.

x) The HRR was not able to be studied for the expected set of objectives, due to operational difficulties. Nevertheless, the results that were obtained

showed the high potential of this reactor for high solids digestion. A mean methane yield of 0.240 m^3 per kg VS added and VS reduction of up to 50% were obtained at a feed TS of approximately 35%, a RT of 36 days and OLR of 2.7 kg VS per m^3 active reactor volume per day.

xi) Finally, a mathematical model describing continuous operation of the VSR was developed utilising data produced and a novel kinetic approach. Using this model, optimisation of the VSR operation was evaluated under various OLR.

10.2 Recommendations for Further Work.

There is scope for future work in the following areas:

i) To improve the design and construction of the horizontal rotary reactor (HRR) which is indicated by the present study to have a high treatment potential.

ii) To evaluate the operational conditions that were used for the vertical sequential reactor (VSR) on a pilot-scale and eventually on a commercial-scale for the anaerobic digestion of the putrescible fraction of MSW.

iii) To modify the lab-scale VSR compartmental design which, for practical purposes, should:

a- use industrial clips for easier and faster access to the reactor compartments instead of the laborious manual access method used in this project;

b- use hydraulic lifting gear;

c- make the loading compartments equal to the days of RT required in order to optimise the daily OLR and to minimise the initial impact of high OLR.

iv) To further develop the proposed model with more experiments on various RT (θ) values in order to assess its effect on digestion rate.

v) To optimise the high-rate hydrolysis-acidification phase which is the rate-limiting stage in the digestion of MSW.

vi) To study the groups of bacteria involved under the examined operational conditions that were examined here and the effects of these conditions on their total numbers and growth rates.

vii) To experiment with using the proposed design for other types of wastes, such as agro-industrial wastes.

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APPENDIX A

ANALYTICAL EQUIPMENT

Analytical Equipment:

i) Analyse: Volatile Fatty Acids (VFA).

Apparatus: Gas-Liquid Chromatography (GLC).

Model: PYE UNICAM 304 Chromatograph, with flame ionisation detector (FID), equipped with a PU4700 auto-injector and CDP4 Phillips computing integrator.

Column: Column packed with 10% AT-1000 on 80/100 mesh chromosorb W-AW, 2 meter length, 2 mm bore.

Temperature: Column 165°C.; Injector 180°C; Detector 180°C.

Carrier gas: Nitrogen at 25 ml/min.

Fuel: Air and hydrogen.

Sample size: 1 µl.

The apparatuses were daily calibrated using standard solution of 1,000 mg/l for acetic acid and only 500 mg/l for the other volatile fatty acids. In addition, 5 ml of concentrate formic acid was mixed with 5 ml of filtered sample before injecting into the gas/liquid chromatography.

ii) Analyse: Gas Chromatography.

Apparatus: BECKER MODEL 403 gas chromatography with thermal conductivity (TC) detector.

Column: 1.5 m length x 4 mm packed with Poropak Q.

Temperature: Column 55°C.

Carrier gas: Helium at 50 ml/min.

Sample size: 1 ml.

Gas peaks were recorded and calculated manually from the surface areas of each one of the three determined gas peaks. Each gas surface was multiplied for the calculation of percentage composition with the following constants: Carbon dioxide: 1.76; Methane: 2.36; Nitrogen: 2.06. The methane and carbon dioxide contents in the biogas were calculated using the following equation:

$$\%CH_4 = \frac{2.36\ A_{CH_4}}{2.06\ A_{N_2} + 2.36\ A_{CH_4} + 1.76\ A_{CO_2}} 100\% \qquad A.1$$

$$\%CO_2 = \frac{1.76\ A_{CO_2}}{2.06\ A_{N_2} + 2.36\ A_{CH_4} + 1.76\ A_{CO_2}} 100\% \qquad A.2$$

iii) Analyse: Metals.

Apparatus: Atomic Absorption Spectrophotometer (AAS).

Model: PYE UNICAM series equipped with SP9 computer.

Fuel: Air-acetylene, fuel lean flame.

Nebulizer: Spray chamber, burner type.

Sample size: 6 ml/min at 0.5 second interval.

iv) Analyse: Elemental Analyser (C:N:H)

Model: CARLO ERBA 1106

The Carlo Erba 1106 (Fig. A.1) is a combustion analyser primarily intended for the determination of the % carbon, % hydrogen and the % nitrogen in pure compounds. Around 1 mg of sample is accurately weighed, (to 3 places of a mg), into a pure tin crucible and introduced into

the reaction furnace at the same time as a 10 ml plug of oxygen. Flash combustion occurs first with the tin, raising the local temperature around the sample to approximately 1600°C ensuring complete vaporisation of the compound. This then reacts with the excess of oxygen and also the oxidising packing, forming the molecules of interest shown in the right-hand part of the diagram.

The mixture is swept by the He carrier gas into the reduction furnace where the mixed oxides of nitrogen are reduced to nitrogen gas, the carbon dioxide and water vapor are not effected by this stage. The final stage is the separation and detection of the individual gases using a GC column kept at 103°C, the gases eluting in the order N_2, CO_2 and finally H_2O. Standards are ran among the samples to calibrate the machine and also to keep a running check on the analyser's performance.

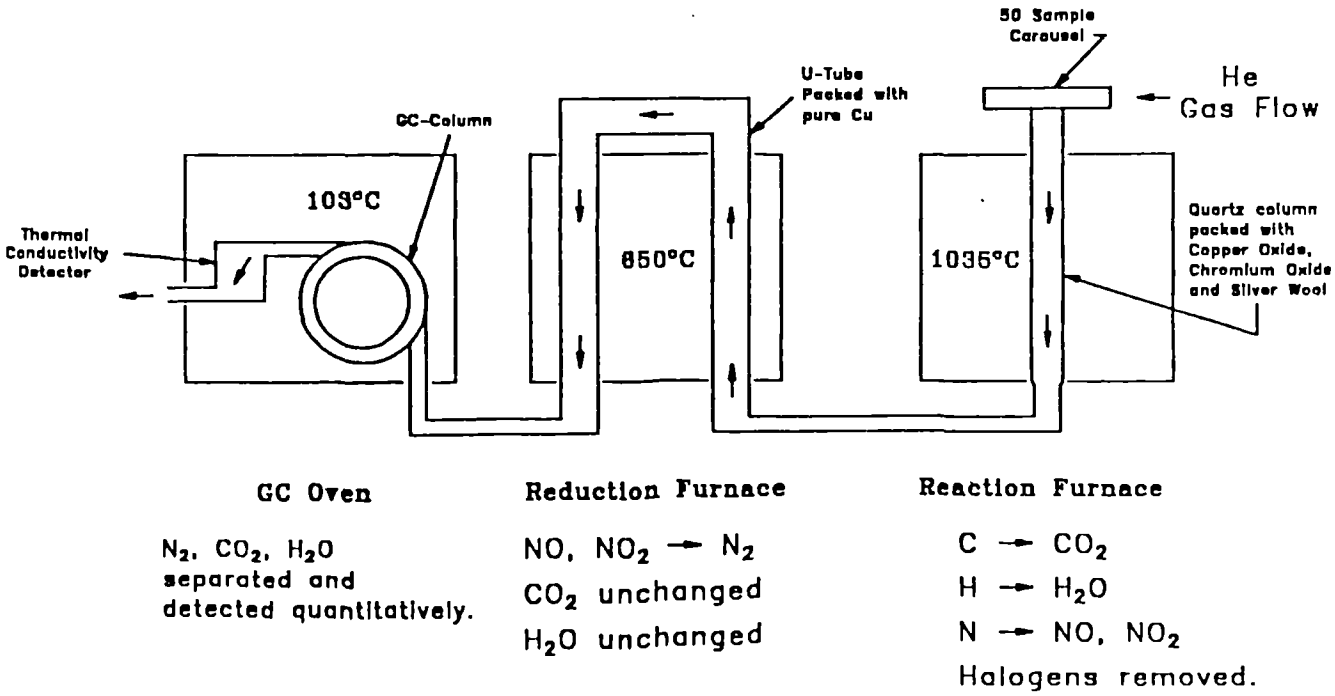


Fig. A.1 Carlo Erba 1108 Elemental analyser.

APPENDIX B

B1: Mass Balance Calculation for VS Reduction.

B2: Calculation to Obtain Volatile Fatty Acid Concentrations as COD Equivalent Values.

B3: Conversion of VFA Concentrations from mg/l to mg/g.

B4: Conversion of Results from mg/l to mg/g for the Water Extract from Dry Solids Samples Method.

APPENDIX B1:

Mass Balance Calculation for VS Reduction:

The calculation of the organic matter reduction (%) was based on a method recommended for solids samples that was reported in the Manuals of British Practice in Water Pollution Control (1979). The calculation procedure is described below:

i) The calculation of the organic matter (% weight) as,

$$d = \frac{a * b}{100} \qquad \text{B.1}$$

Where,

a = refuse total solids (TS%),

b = final digested materials VS (%weight).

ii) Calculate the TS of the dry digested materials (x) as,

$$\frac{d - x}{a - x} = \frac{c}{100} \qquad \text{B.2}$$

Where, c = VS (% weight) of the digested materials.

iii) Calculate the VS reduction (%) as,

$$\text{VS reduction (\%)} = \frac{x}{d} * 100 \qquad \text{B.3}$$

and the total solids (TS) reduction (%) as,

$$\text{TS reduction (\%)} = \frac{x}{a} * 100 \qquad \text{B.4}$$

Appendix B2: Calculation to Obtain Volatile Fatty Acid Concentrations as COD Equivalent Values.

To obtain the COD equivalent, each individual acid concentration was multiplied by a conversion factor, calculated as follows:

$$\text{Conversion Factor} = \frac{\text{Oxygen Molecular Weight}}{\text{Acid Molecular Weight}} \qquad \text{B.5}$$

Table B.1 lists the conversion factors for each acid examined.

Table B-1 COD Equivalents

Acid	COD equivalent
Acetic	1.067
Propionic	1.514
Butyric	1.816
Valeric	2.039
Caproic	2.204

APPENDIX B3: Conversion of VFA Concentrations from mg/l to mg/g.

Fig. B.1 shows the conversion of TVFA concentration values from mg/l to mg/g for thr HRR batch run where the wet solids water extract method was used.

APPENDIX B4: Conversion of Results from mg/l to mg/g.

B4: Fig. B.2 shows the conversion of results from mg/l to mg/g for the water extract from dry solids samples method.

Fig. B.1 Conversion of VFA Concentrations from mg/ l to mg/ g for HRR Batch Run.

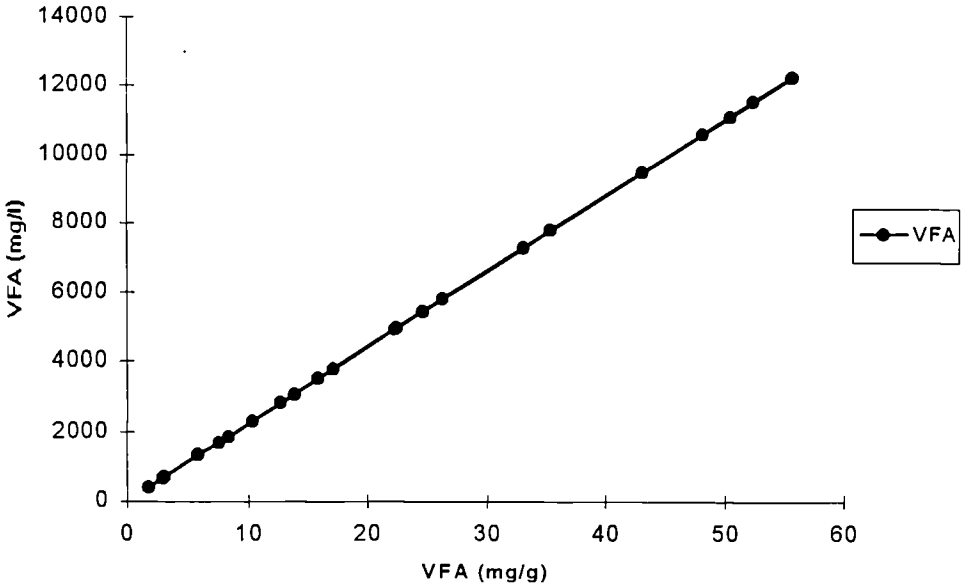
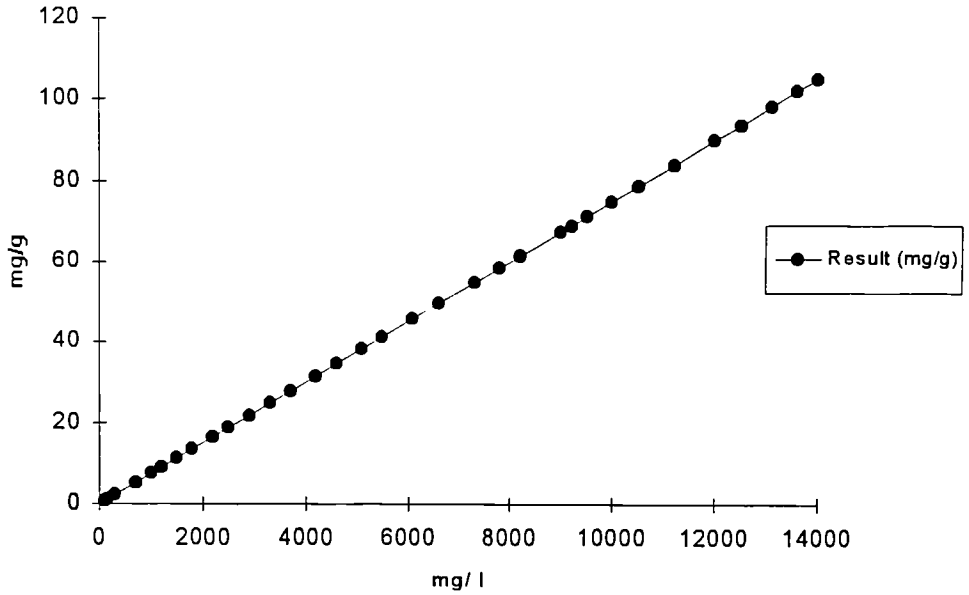


Fig. B.2 Conversion from (mg/ l) to (mg/ g) for the Water Extract from Dry Solids Samples Method.



APPENDIX C

APPENDIX C 1: First-Order Reaction Model Calculation.

APPENDIX C 2: Kinetic Model Differential Equation.

APPENDIX C1 : First-Order Reaction Kinetics Model for Vertical PFR with Recycle

The elementary mass balance equation for biomass and substrate at a differential volume dV in the PFR are:

Biomass: $$F_T dM = \mu M dV \quad \textbf{(C1)}$$

Substrate: $$F_T dS = -\frac{\mu M}{Y} dV \quad \textbf{(C2)}$$

Where, μ in the above equations is the specific biomass growth rate. According to the first order model, μ is constant (i.e. independent of substrate and biomass concentrations). In order to avoid confusion with the derivation of the Contois-based PFR model, the following substitution is made: $\mu = k_1$ (first order constant)

The differential equation in Eq. C1 can be solved separately. In order to provide the biomass concentration at various reactor heights (i.e. volumes), the biomass balance is integrated as follows:

$$\int_{M_o}^{M} \frac{dM}{M} = \frac{k_1}{F_T} \int_0^V dV$$

Therefore,

$$M = M_o \exp\left(\frac{k_1}{F_T} V\right) \quad \textbf{(C3)}$$

Substituting Eq. C3 into the differential mass balance for the substrate Eq. C1:

$$F_T\, dS = -\frac{k_1}{Y} M_o \exp\left(\frac{k_1}{F_T}.V\right) dV$$

Integrating throughout the reactor:

$$\int_{S_0}^{S} \frac{F_T.Y}{M_o.k_1}\, dS = -\int_0^V \exp\left(\frac{k_1}{F_T}V\right) dV \qquad \text{(C4)}$$

In order to evaluate the RHS integral, there is a need to substitute the differential dV, as follows:

$$dV = \frac{F_T}{k_1} d\left(\frac{k_1}{F_T}V\right)$$

Changing the differential and solving Eq. C4:

$$\frac{Y}{M_o}(S - S_o) = -\left[\exp\left(\frac{k_1}{F_T}V\right) - 1\right] \qquad \text{(C5)}$$

Where, S_0 is the substrate concentration in the reactor inlet.

It is favourable for modelling to substitute it for the substrate concentration of the refuse S_F, with a simple mass balance at the reactor inlet:

$$\frac{S_o}{S} = \frac{S_F}{S}(1 - DRR) + DRR \quad \Rightarrow$$

$$S_o = S_F(1 - DRR) + S.DRR \qquad \text{(C6)}$$

Substituting Eq. C6 into Eq. C5:

$$S - S_F = \frac{M_o.\left[1 - \exp(k_1.\theta)\right]}{Y.(1 - DRR)} \qquad \text{where } \theta = \frac{V}{F_T} \qquad \text{(C7)}$$

However, the ratio $\frac{S}{S_F}$,which can be substituted for ultimate biogas, etc., is much more appropriate for modelling, instead of the difference (S-S_F). Therefore, dividing by S_F:

$$\frac{S}{S_F} = 1 - \frac{M_o.\left[\exp(k_1.\theta) - 1\right]}{Y.(1 - DRR).S_F} \qquad \text{(C8)}$$

APPENDIX C2: Kinetic Model Differential Equation

According to Eq. 9.6, the mass balances for the biomass and the substrate in the differential control volume are:

Biomass: $$F_T dM = \mu M dV \quad \textbf{(C9)}$$

Substrate: $$F_T dS = -\frac{\mu M}{Y} dV \quad \textbf{(C10)}$$

Dividing Eq. C9 by Eq. C10 to get a relationship between differentials dS and dM:

$$\frac{F_T\ dM}{F_T\ dS} = \frac{\mu\ M\ dV}{-\frac{\mu\ M}{Y} dV} \Rightarrow \frac{dM}{dS} = -Y \Rightarrow dM = -Y\ dS \quad \textbf{(C11)}$$

The biomass specific growth rate is given by the Contois kinetic expression:

$$\mu = \frac{\mu_m . S}{B.M + S} \quad \textbf{(C12)}$$

Substituting Eq.C12 into Eq. C9 :

$$F_T\ dM = \frac{\mu_m S}{BM + S} M dV \quad \textbf{(C13)}$$

Rearranging Eq. C13:

$$B\frac{dM}{S} + \frac{dM}{M} = \frac{\mu_m}{F_T} dV \quad \textbf{(C14)}$$

Utilising Eq. C11 to substitute the dM with dS:

$$-B.Y\frac{dS}{S}+\frac{dM}{M}=\frac{\mu_m}{F_T}dV \qquad \textbf{(C15)}$$

By integrating (subscript 0) from reactor inlet to reactor outlet:

$$-K\int_{S_0}^{S}\frac{dS}{S}+\int_{M_0}^{M}\frac{dM}{M}=\frac{\mu_m}{F_T}\int_{0}^{V}dV \qquad \textbf{(C16)}$$

Where, K = B.Y (Chen and Hashimoto Kinetic parameter)

Evaluating the integrals:

$$\ln\left[\left(\frac{S}{S_0}\right)^{-K}\frac{M}{M_0}\right]=\frac{\mu_m}{F_T}\ V \qquad \textbf{(C17)}$$

Taking exponentials and substituting V/FT by θ (retention time),

$$\left(\frac{S}{S_0}\right)^{-K\cdot}\frac{M}{M_0}=\exp.\left(\mu_m\theta\right) \qquad \textbf{(C18)}$$

APPENDIX D

APPENDIX D1: Optimisation and GAMS Modelling Environment.

APPENDIX D2: GAMS Source Files for Kinetic Fitting.

APPENDIX D3: GAMS Source File for Combined Model Optimisation.

APPENDIX D4: Sample GAMS Output Files for Kinetic Fitting and Optimisation Solutions.

APPENDIX D1: Optimisation and GAMS Modelling Environment.

i) Optimisation-General.

The term "optimisation" refers to the selection of the exact value of some process parameter(s) so as to optimise some selected measure of efficiency. This measure can be either economically or operationally related. For instance, minimising the operational costs or maximising biogas production are all examples of process optimisation.

Mathematically speaking, optimisation involves the determination of an extreme point of a function (maximum or minimum). In the simple case of one-variable functions, the minimum or maximum can be obtained by taking the first derivative of the function and determining the variable value that makes the first derivative equal to zero. For multi-variable functions, the procedure of extreme point determination is somehow similar, since at an extreme point all partial first derivatives are zero.

During the optimisation of chemical processes some cases arise where the function to be optimised (objective function) appears to be coupled with equalities (e.g. mass and energy balances) and inequalities (e.g. physical constraints). This is the most complicated instance of optimisation and has the following form:

$$\begin{aligned} &\text{Minimise: } f(x) && \text{(objective function, e.g. operational cost)} \\ &\text{Subject to: } h(x) = 0 && \text{(process equation)} \\ &\qquad\qquad g(x) \geq 0 && \text{(process constraints)} \end{aligned} \qquad \text{(D.1)}$$

where x is the vector of all process variables (flow rate, temperatures, etc.) that are to be selected from the constrained optimisation. It is to be noted that the notion of optimisation extends much further than the optimisation of a physical process, as mentioned above. The same mathematical techniques can be applied wherever a minimisation or maximisation of a function is involved. For example, non-linear least squares fitting falls under the same category of problems as in Eq. D1, although it conceptually corresponds to a different situation.

The aim is to estimate the values of the parameters of a fitted equation that will minimise the squared difference between the observed and estimated (through the fitted equation) values of a physical quantity. The formulation in this case is:

Minimise: $$SSE = \sum_{i=1} \left[\left(\phi_{i,obs} - \phi_{i,estimated} \right)^2 \right] \qquad \text{(D.2)}$$

$$\phi_{i,estimated} = f(X) \rightarrow \text{fitted equation}$$

Where,

SSE is the squared sum of the errors,

$\Phi_{i,obs.}$ is the experimentally observed values, and

X is the process control variables.

It is also to be noted that in the minimisation in Eq. D2, the variables optimised for are the parameters of the fitted equation f(x) and not the process related

control variables X (e. g. DRR and L). For example, if a 2nd order polynomial is to be fitted :

$$f(x) = aX^2 + bX + C \qquad \text{D.3}$$

Then the parameters a, b and c are the variables of the optimisation in Eq. D2.

ii) The GAMS Modelling Environment.

The mathematical problem in Eq.D1 requires numerical solution algorithms since, in the general case, a large number of equations and variables is involved. The GAMS language offers a systematic way to enter the data for the optimisation in the form of a symbolic language. An input text file contains all the necessary information (GMS file), which resembles similar source code files of, for example, FORTRAN language. This file is processed by the GAMS interpreter which creates the actual mathematical problem to be solved, invokes the numerical algorithms (solvers) and finally produces an output file (LST file) that contains the solution.

The main advantage of GAMS is that optimisation problems can be represented in a very compact and intuitive form. The main features of the modelling environment are:

PARAMETERS - constants of the optimisation, entered once

VARIABLES - the actual variables on which the optimisation is based. Usually initial values of these variables have to be provided in order to assist the numerical solution (especially when highly non-linear equations are involved)

EQUATIONS - The objective function (f) plus any equality (h) and inequality (g) constraints.

APPENDIX D2: GAMS Source Files for Kinetic Fitting.

D2 Source File 1:

```
$TITLE Least Squares non-Linear Parameter Fitting (DRR, Phase 1)
* ***********************************************
* VSR system parameter estimation
* Approach #1: using methane yields data
* DRR on a WET basis
* ***********************************************
SETS
 N Experimental data sets /1*3/
;
PARAMETERS
 DRR(N) Digested recycle ratio
  /1 0.76
   2 0.5
   3 0.33/
 MYO(N) Observed methane yield (l per kg VS)
  /1 213
   2 202
   3 124/
;
SCALARS
 RT  Retention time (days) /24.0/
 UMY Ultimate methane yield (l per kg VS) /255/
;
POSITIVE VARIABLES
 MMAX  Maximum bacteria growth rate
 K     Chen Hashimoto parameter
 MYR(N) Calculated methane yield ratio
;
FREE VARIABLE SSE Square sum of errors (observed-calculated);
EQUATIONS
 OBJECTIVE  Calculation of SSE
 PREDICT(N) Predictor equation to be fitted
;
* Definition of equations follows
OBJECTIVE.. SSE =E= SUM(N,(MYR(N)-(UMY-MYO(N))/UMY)**2);
PREDICT(N).. MYR(N) =E= (1.0-DRR(N))/(exp(MMAX*RT/K)*(DRR(N)**(1/K))-DRR(N));
* This is a highly non-linear optimisation problem.
* Good initial guesses of the fitted parameters are required.
* Initial predicted ratio equal to observed values
MYR.L(N)=(UMY-MYO(N))/UMY;

* Approximate guesses for MMAX & K (taken from reported values)
* Chen & Hashimoto (1980)
MMAX.L=0.467;
K.L=1.06;
* Some rational upper bounds now
MYR.UP(N)=1.0;
MMAX.UP=10;
K.UP=5;
* Model solution directives
MODEL FIT /ALL/;
SOLVE FIT USING NLP MINIMIZING SSE;
```

APPENDIX D2: GAMS Source Files for Kinetic Fitting.

D2 Source File 2:

```
$TITLE Least Squares non-Linear Parameter Fitting (DRR, Phase 1)
* ***********************************************
* Approach #2: using VS reduction data
* DRR on a WET basis
* ***********************************************
SETS
 N Experimental data sets /1*3/
;
PARAMETERS
 DRR(N) Digested recycle ratio
  /1 0.76
   2 0.5
   3 0.33/
 VSRO(N) Observed VS reduction (%)
  /1 49
   2 46.6
   3 37.1/
;
SCALARS
 RT  Retention time (days) /24.0/
 UVSR Ultimate VS reduction (%) /55.8/
;
POSITIVE VARIABLES
 MMAX  Maximum bacteria growth rate
 K     Chen Hashimoto parameter
 VSRR(N) Calculated VS reduction ratio
;
FREE VARIABLE SSE Square sum of errors (observed-calculated);
EQUATIONS
 OBJECTIVE  Calculation of SSE
 PREDICT(N) Predictor equation to be fitted
;
* Definition of equations follows
OBJECTIVE.. SSE =E= SUM(N,(VSRR(N)-(UVSR-VSRO(N))/UVSR)**2);
PREDICT(N).. VSRR(N) =E= (1.0-DRR(N))/(exp(MMAX*RT/K)*(DRR(N)**(1/K))-DRR(N));
* Initial predicted ratio equal to observed values
VSRR.L(N)=(UVSR-VSRO(N))/UVSR;
* Approximate guesses for MMAX & K (taken from reported values)
* Chen & Hasimoto (1980)
MMAX.L=0.467;
K.L=1.06;
* rational upper boundre
VSRR.UP(N)=1.0;
MMAX.UP=10;
K.UP=3;
* Model solution directives
MODEL FIT /ALL/;
SOLVE FIT USING NLP MINIMIZING SSE;
```

APPENDIX D2: GAMS Source Files for Kinetic Fitting.

D2 Source File 3:

```
$TITLE Least Squares non-Linear Parameter Fitting (Leachate, Phase 2)
* ***********************************************
* VSR system parameter estimation
* 2nd phase with variable leachate recycle
* Approach #1: Using methane yield data
* DRR on a WET basis
* ***********************************************

SETS
 N Experimental data sets /1*4/
;

* The only control variable here is the leachate recycle
PARAMETERS
 L(N) Leachate water percent of the total wet mass of waste
  /1 1.25
   2 0.70
   3 0.31
   4 0.17/
 MYO(N) Observed methane yield (l per kg VS)
  /1 202
   2 192
   3 151
   4 105/
 WR(N) Water content (mass fraction) of the digested recycled material
  /1 0.703
   2 0.692
   3 0.674
   4 0.64/
 WF(N) Water content (mass fraction) of the raw feed refuse
  /1 0.596
   2 0.59
   3 0.585
   4 0.51/
 W(N) Total water mass fraction in the first basket
;

* NOTE that the DRR here is constant
SCALARS
 DRR Digested recycle ratio /0.5/
 RT  Retention time (days) /24.0/
 UMY Ultimate methane yield (l per kg VS) /255.0/
;

* Calculate the W fraction based on DRR, L and WR-WF data
W(N)=(DRR*(WR(N)-WF(N))+L(N)+WF(N))/(1+L(N));

POSITIVE VARIABLES
```

```
 MMAX  Maximum bacteria growth rate
 K     Chen Hashimoto parameter
 MYR(N) Calculated methane yield ratio
;

FREE VARIABLES
 KW  Water kinetic parameter
 SSE Square sum of errors (observed-calculated)
;

EQUATIONS
 OBJECTIVE  Calculation of SSE
 PREDICT(N) Predictor equation to be fitted
;

* Definition of equations follows
OBJECTIVE.. SSE =E= SUM(N,(MYR(N)-(UMY-MYO(N))/UMY)**2);
PREDICT(N).. MYR(N) =E= (1.0-DRR)/
              (exp(MMAX*RT*(W(N)-KW)/(K*W(N)))*(DRR**(1/K))-DRR);

* This is a highly non-linear optimisation problem.

* Initial predicted ratio equal to observed values
MYR.L(N)=(UMY-MYO(N))/UMY;

* Approximate guesses for MMAX & K (taken from DRR fitting values)
MMAX.L=0.081;
K.L=1.477;
* no reported guesses for Kw
KW.L=0.4;

* Some rational upper bounds now
MYR.UP(N)=1.0;
MMAX.UP=10;
K.UP=10;

* Model solution directives
MODEL FIT /ALL/;
SOLVE FIT USING NLP MINIMIZING SSE;
```

APPENDIX D 2: GAMS Source Files for Kinetic Fitting.

D2 Source File 4:

```
$TITLE Least Squares non-Linear Parameter Fitting (Leachate, Phase 2)
* ********************************************
* VSR system parameter estimation
* 2nd phase with variable leachate recycle
* Approach #2: Using VS reduction data
* DRR on a WET basis
* ********************************************

SETS
 N Experimental data sets /1*4/
;

* The only control variable here is the leachate recycle
PARAMETERS
 L(N) Leachate water percent of the total wet mass of waste
  /1 1.25
   2 0.70
   3 0.31
   4 0.17/
 VSRO(N) Observed VS reduction (%)
  /1 46.6
   2 45.2
   3 42.7
   4 33.3/
 WR(N) Water content (mass fraction) of the digested recycled material
  /1 0.703
   2 0.692
   3 0.674
   4 0.64/
 WF(N) Water content (mass fraction) of the raw feed refuse
  /1 0.596
   2 0.59
   3 0.585
   4 0.51/
 W(N) Total water mass fraction in the first basket
;

* NOTE that the DRR here is constant
SCALARS
 DRR Digested recycle ratio /0.5/
 RT  Retention time (days) /24.0/
 UVSR Ultimate VS reduction (%) /55.8/
;

* Calculate the W fraction based on DRR, L and WR-WF data
W(N)=(DRR*(WR(N)-WF(N))+L(N)+WF(N))/(1+L(N));
```

D2 Source File 4:

```
POSITIVE VARIABLES
 MMAX  Maximum bacteria growth rate
 K     Chen Hashimoto parameter
 VSRR(N) Calculated VS reduction ratio
;

FREE VARIABLES
 KW  Water kinetic parameter
 SSE Square sum of errors (observed-calculated)
;

EQUATIONS
 OBJECTIVE  Calculation of SSE
 PREDICT(N) Predictor equation to be fitted
;

* Definition of equations follows
OBJECTIVE.. SSE =E= SUM(N,(VSRR(N)-(UVSR-VSRO(N))/UVSR)**2);
PREDICT(N).. VSRR(N)=E= (1.0-DRR)/
              (exp(MMAX*RT*(W(N)-KW)/(K*W(N)))*(DRR**(1/K))-DRR);

* This is a highly non-linear optimisation problem.

* Initial predicted ratio equal to observed values
VSRR.L(N)=(UVSR-VSRO(N))/UVSR;

* Approximate guesses for MMAX & K (taken from DRR fitting values)
MMAX.L=0.081;
K.L=1.477;
* no reported values for Kw
KW.L=0.4;

* Some rational upper boundry
VSRR.UP(N)=1.0;
MMAX.UP=10;
K.UP=3;

* Model solution directives
MODEL FIT /ALL/;
SOLVE FIT USING NLP MINIMIZING SSE;
```

APPENDIX D2: GAMS Source Files for Kinetic Fitting.

D2 Source File 5:

```
$TITLE Least Squares non-Linear Parameter Fitting (Combined Phases)
* ***********************************************
* VSR system parameter estimation
* Both DRR and leachate variations considered
* Approach #1: using methane yields data
* DRR on a WET basis
* ***********************************************
SETS
 N Experimental data sets /1*6/
;
* Both leachate recycle and DRR are control variables here
* There are data for: 4 leachate (L) values
*                     3 DRR values (one overlapping)
PARAMETERS
 L(N) Leachate water percent of the total wet mass of waste
  /1 1.25
   2 0.70
   3 0.31
   4 0.17
   5 1.25
   6 1.25/
 DRR(N) Digested recycle ratio on WET basis
  /1 0.5
   2 0.5
   3 0.5
   4 0.5
   5 0.76
   6 0.33/
 MYO(N) Observed methane yield (l per kg VS)
  /1 202
   2 192
   3 151
   4 105
   5 213
   6 124/
 WR(N) Water content (mass fraction) of the digested recycled material
  /1 0.703
   2 0.692
   3 0.674
   4 0.64
   5 0.705
   6 0.711/
 WF(N) Water content (mass fraction) of the raw feed refuse
  /1 0.596
   2 0.59
   3 0.585
   4 0.51
   5 0.57
   6 0.60/
```

```
 W(N) Total water mass fraction in the first basket
;
* NOTE that the DRR here is constant
SCALARS
 RT  Retention time (days) /24.0/
 UMY Ultimate methane yield (l per kg VS) /255.0/
;
* Calculate the W fraction based on DRR, L and WR-WF data
W(N)=(DRR(N)*(WR(N)-WF(N))+L(N)+WF(N))/(1+L(N));
POSITIVE VARIABLES
 MMAX  Maximum bacteria growth rate
 K     Chen Hashimoto parameter
 MYR(N) Calculated methane yield ratio
;
FREE VARIABLES
 KW  Water kinetic parameter
 SSE Square sum of errors (observed-calculated)
;
EQUATIONS
 OBJECTIVE  Calculation of SSE
 PREDICT(N) Predictor equation to be fitted
;
* Definition of equations follows
OBJECTIVE.. SSE =E= SUM(N,(MYR(N)-(UMY-MYO(N))/UMY)**2);
PREDICT(N).. MYR(N) =E= (1.0-DRR(N))/
                (exp(MMAX*RT*(W(N)-KW)/(K*W(N)))*
                (DRR(N)**(1/K))-DRR(N));
* This is a highly non-linear optimisation problem.
* Initial predicted ratio equal to observed values
MYR.L(N)=(UMY-MYO(N))/UMY;
* Approximate guesses for MMAX, K and Kw
* (taken from lechate fitting values)
MMAX.L=0.125;
K.L=0.692;
KW.L=0.45;
* Some rational upper boundrirs
MYR.UP(N)=1.0;
MMAX.UP=10;
K.UP=10;
* Model solution directives
MODEL FIT /ALL/;
SOLVE FIT USING NLP MINIMIZING SSE;
```

APPENDIX D2: GAMS Source Files for Kinetic Fitting.

D2 Source File 6:

```
$TITLE Least Squares non-Linear Parameter Fitting (Combined Phases)
* ***********************************************
* VSR system parameter estimation
* Both DRR and leachate variations considered
* Approach #2: using VS reducrion data
* DRR on a WET basis
* ***********************************************
SETS
 N Experimental data sets /1*6/
;
* Both leachate recycle and DRR are control variables here
* There are data for: 4 leachate (L) values
*                     3 DRR values (one overlapping)
PARAMETERS
 L(N) Leachate water percent of the total wet mass of waste
  /1 1.25
   2 0.70
   3 0.31
   4 0.17
   5 1.25
   6 1.25/
 DRR(N) Digested recycle ratio on WET basis
  /1 0.5
   2 0.5
   3 0.5
   4 0.5
   5 0.76
   6 0.33/
 VSRO(N) Observed VS reduction (%)
  /1 46.6
   2 45.2
   3 42.7
   4 33.3
   5 49.0
   6 37.1/
 WR(N) Water content (mass fraction) of the digested recycled material
  /1 0.703
   2 0.692
   3 0.674
   4 0.64
   5 0.705
   6 0.711/
 WF(N) Water content (mass fraction) of the raw feed refuse
  /1 0.596
   2 0.59
   3 0.585
   4 0.51
   5 0.57
   6 0.60/
```

```
 W(N) Total water mass fraction in the first basket
;
* NOTE that the DRR here is constant
SCALARS
 RT  Retention time (days) /24.0/
 UVSR Ultimate VS reduction (%) /55.8/
;
* Calculate the W fraction based on DRR, L and WR-WF data
W(N)=(DRR(N)*(WR(N)-WF(N))+L(N)+WF(N))/(1+L(N));
POSITIVE VARIABLES
 MMAX   Maximum bacteria growth rate
 K      Chen Hashimoto parameter
 VSRR(N) Calculated VS reduction ratio
;
FREE VARIABLES
 KW  Water kinetic parameter
 SSE Square sum of errors (observed-calculated)
;
EQUATIONS
 OBJECTIVE  Calculation of SSE
 PREDICT(N) Predictor equation to be fitted
;
* Definition of equations follows
OBJECTIVE..  SSE =E= SUM(N,(VSRR(N)-(UVSR-VSRO(N))/UVSR)**2);
PREDICT(N).. VSRR(N)=E= (1.0-DRR(N))/
                (exp(MMAX*RT*(W(N)-KW)/(K*W(N)))*
                (DRR(N)**(1/K))-DRR(N));
* This is a highly non-linear optimisation problem.
* Initial predicted ratio equal to observed values
VSRR.L(N)=(UVSR-VSRO(N))/UVSR;
* Approximate guesses for MMAX, K and Kw
* (taken from lechate fitting values)
MMAX.L=0.1;
K.L=0.467;
KW.L=0.383;
* Some rational upper bounds now
VSRR.UP(N)=1.0;
MMAX.UP=10;
K.UP=10;
* Model solution directives
MODEL FIT /ALL/;
SOLVE FIT USING NLP MINIMIZING SSE;
```

APPENDIX D3: GAMS Source File for Combined Model Optimisation.

D3 Source File for Combined Optimisation:

```
$TITLE Combined Optimisation for DRR and Leachate (CH4 Yield Basis)
* ***********************************************
* VSR system parameter estimation
* Both DRR and leachate variations considered
* Approach #1: Maximisation of CH4 per m3 reactor
* An average waste (refuse) is assumed
* ***********************************************

* No SETS required

* Both leachate recycle and DRR are control variables

SCALARS
 RT  Retention time (days) /24.0/
 UMY  Ultimate methane yield (m3 per kg VS) /0.255/
* Kinetic parameters taken at values as fitted
 MMAX Maximum bacteria growth rate /0.171/
 K   Chen Hashimoto parameter /1.137/
 KW  Water kinetic parameter /0.480/
* Next are parameters of an "average" waste
 WR  Water mass fraction of the digested recycled material /0.67/
 WF  Water mass fraction of the raw feed refuse /0.58/
 AVTS Total solids of raw feed refuse /0.42/
 AVVS Volatile solids fraction of the above refuse AVTS content /0.639/
;

POSITIVE VARIABLES
 L  Leachate water percent of the total wet mass of waste
 DRR Digested recycle ratio on WET basis
 W  Total water mass fraction in the first basket
 MY  Calculated methane yield (m3 per kg VS)
 LR  Loading rate (kg VS per day per m3 reactor)
 DEN Wet density of the mixture in basket (kg per m3)
;

FREE VARIABLES
 CH4VOL CH4 volumetric production (m3 CH4 per m3 reactor)
;

EQUATIONS
 OBJECTIVE  Calculation of CH4 production per m3 reactor
 PREDICT   Predictor equation of CH4 yield (m3 CH4 per kg VS added)
 WATERMF   Water mass fraction at first basket calculation
 DENSITY   Basket mixture density (regressed experimental data)
 LOADRATE  LR calculation
;
```

D3 Source File for Combined Optimisation:

```
* Definition of equations follows

* Calculate the W fraction based on DRR, L and WR-WF data
WATERMF..  W =E=(DRR*(WR-WF)+L+WF)/(1.0+L);
DENSITY..  DEN =E= 3401.0-7243.0*(1.0-W);
LOADRATE.. LR =E= DEN*AVTS*AVVS*(1.0-DRR)/(24.0*(1.0+L));
PREDICT..  MY =E= UMY*(1-
           (1-DRR)/(exp(MMAX*RT*(W-KW)/(K*W))*(DRR**(1/K))-DRR));
OBJECTIVE.. CH4VOL =E= MY*LR;

* This is a highly non-linear optimisation problem.

L.L=0.2;
DRR.L=0.6;
* Calculate all remaining initial values
W.L=(DRR.L*(WR-WF)+L.L+WF)/(1+L.L);
DEN.L=3401.0-7243.0*(1.0-W.L);
LR.L=DEN.L*AVTS*AVVS*(1-DRR.L)/(24.0+(1+L.L));
MY.L=UMY*(1-(1-DRR.L)/(exp(MMAX*RT*(W.L-KW)/(K*W.L))*(DRR.L**(1/K))-
DRR.L));
CH4VOL.L=MY.L*LR.L;

* Some rational upper bounders
L.UP=5;
DRR.UP=1;
W.UP=1;
LR.UP=20;
MY.UP=UMY;
* CH4VOL must be unbounded, since it's the optimised variable

* Model solution directives
MODEL OPTIMAL /ALL/;
SOLVE OPTIMAL USING NLP MAXIMIZING CH4VOL;
```

APPENDIX D4: Sample GAMS Output Files for Kinetic Fitting and Optimisation Solutions.

D4 Output File 1 (Fitting):

Least squares non-linear parameter fitting (Combined phases) APP#1

```
* ********************************************
* VSR system parameter estimation
* Both DRR and leachate variations considered
* Approach #1: Using methane yield data
* DRR on a WET basis
* ********************************************

Model Statistics    SOLVE FIT USING NLP FROM LINE 113

MODEL STATISTICS

BLOCKS OF EQUATIONS     2   SINGLE EQUATIONS          7
BLOCKS OF VARIABLES     5   SINGLE VARIABLES         10
NON ZERO ELEMENTS      31    NON LINEAR N-Z          24
DERIVATIVE POOL         9   CONSTANT POOL            26
CODE LENGTH           765

GENERATION TIME     =      1.820 SECONDS

EXECUTION TIME      =      2.040 SECONDS      VERID TP5-00-038
GAMS 2.25  PC AT/XT                    10
Least squares non-linear parameter fitting (Combined phases) APP#1
Solution Report     SOLVE FIT USING NLP FROM LINE 113

          S O L V E    S U M M A R Y

   MODEL  FIT            OBJECTIVE  SSE
   TYPE   NLP           DIRECTION  MINIMIZE
   SOLVER MINOS5           FROM LINE  113

**** SOLVER STATUS     1 NORMAL COMPLETION
**** MODEL STATUS      2 LOCALLY OPTIMAL
**** OBJECTIVE VALUE              0.0109

 RESOURCE USAGE, LIMIT      20.930   1000.000
 ITERATION COUNT, LIMIT     43       1000
 EVALUATION ERRORS          0        0

 Estimate work space needed  --   39 Kb
 Work space allocated        --  180 Kb

 EXIT -- OPTIMAL SOLUTION FOUND
 MAJOR ITNS, LIMIT          9   200
 FUNOBJ, FUNCON CALLS       77   77
 SUPERBASICS                3
 INTERPRETER USAGE          9.91
 NORM RG / NORM PI     2.721E-07

            LOWER    LEVEL    UPPER   MARGINAL

---- EQU OBJECTIVE     .          .        1.000
```

OBJECTIVE Calculation of SSE

--- EQU PREDICT Predictor equation to be fitted

	LOWER	LEVEL	UPPER	MARGINAL
1	.	.	.	0.066
2	.	.	.	0.084
3	.	.	.	-0.041
4	.	.	.	0.005
5	.	.	.	-0.172
6	.	.	.	-0.030

GAMS 2.25 PC AT/XT 23:55:21 PAGE 11
Least squares non-linear parameter fitting (Combined phases) APP#1
Solution Report SOLVE FIT USING NLP FROM LINE 113

	LOWER	LEVEL	UPPER	MARGINAL
--- VAR MMAX	.	0.171	10.000	EPS
--- VAR K	.	1.137	10.000	.

MMAX Maximum bacteria growth rate
K Chen Hashimoto parameter

--- VAR MYR Calculated methane yield ratio (fraction)

	LOWER	LEVEL	UPPER	MARGINAL
1	.	0.241	1.000	EPS
2	.	0.289	1.000	.
3	.	0.387	1.000	.
4	.	0.610	1.000	.
5	.	0.079	1.000	EPS
6	.	0.468	1.000	.

	LOWER	LEVEL	UPPER	MARGINAL
--- VAR KW	-INF	0.480	+INF	.
--- VAR SSE	-INF	0.011	+INF	.

KW Water kinetic parameter
SSE Square sum of errors (observed-calculated)

**** REPORT SUMMARY : 0 NONOPT
0 INFEASIBLE
0 UNBOUNDED
0 ERRORS
GAMS 2.25 PC AT/XT 23:55:21 PAGE 12
Least squares non-linear parameter fitting (Combined phases) APP#1
E x e c u t i o n

---- 115 VARIABLE SSE.L = 0.011 Square sum of errors
(observed-calculated)

---- 116 VARIABLE MMAX.L = 0.171 Maximum bacteria growth rate

---- 117 VARIABLE K.L = 1.137 Chen Hashimoto parameter

---- 118 VARIABLE KW.L = 0.480 Water kinetic parameter

---- 119 VARIABLE MYR.L Calculated methane yield ratio

1 0.241, 2 0.289, 3 0.387, 4 0.610, 5 0.079, 6 0.468

---- 121 PARAMETER W Total water mass fraction in the first basket

1 0.844, 2 0.789, 3 0.717, 4 0.637, 5 0.854, 6 0.839

---- 124 PARAMETER TEST Temporary parameter for the observed data points

1 0.208, 2 0.247, 3 0.408, 4 0.608, 5 0.165, 6 0.482

EXECUTION TIME = 0.880 SECONDS VERID TP5-00-038

APPENDIX D 4: Sample GAMS Output Files for Kinetic Fitting and Optimisation Solutions.

D4 Output File 2 (Optimisation):

Least squares non-linear parameter fitting (Combined phases) APP#1

```
   * ********************************************
   * VSR system parameter estimation
   * Both DRR and leachate variations considered
   * Approach #1: Using methane yield data
   * DRR on a WET basis
   * ********************************************
```

Combined optimisation for DRR and Leachate (CH4 yield basis)

MODEL STATISTICS

```
BLOCKS OF EQUATIONS     5   SINGLE EQUATIONS      5
BLOCKS OF VARIABLES     7   SINGLE VARIABLES      7
NON ZERO ELEMENTS      15   NON LINEAR N-Z        9
DERIVATIVE POOL         6   CONSTANT POOL        11
CODE LENGTH           177

GENERATION TIME     =      1.430 SECONDS

EXECUTION TIME      =      1.760 SECONDS      VERID TP5-00-038
GAMS 2.25  PC AT/XT              13:42:19 PAGE    9
Combined optimisation for DRR and Leachate (CH4 yield basis)
Solution Report     SOLVE OPTIMAL USING NLP FROM LINE 84

        S O L V E    S U M M A R Y

   MODEL  OPTIMAL          OBJECTIVE  CH4VOL
   TYPE   NLP            DIRECTION  MAXIMIZE
   SOLVER MINOS5           FROM LINE  84

**** SOLVER STATUS     1 NORMAL COMPLETION
**** MODEL STATUS      2 LOCALLY OPTIMAL
**** OBJECTIVE VALUE              1.0792

 RESOURCE USAGE, LIMIT        10.316   1000.000
 ITERATION COUNT, LIMIT       36       1000
 EVALUATION ERRORS            0        0

   M I N O S   5.3   (Nov 1990)       Ver: 225-DOS-02

 EXIT -- OPTIMAL SOLUTION FOUND
 MAJOR ITNS, LIMIT          7   200
 FUNOBJ, FUNCON CALLS      72    72
 SUPERBASICS                2
 INTERPRETER USAGE          2.00
 NORM RG / NORM PI     4.556E-08

            LOWER    LEVEL    UPPER   MARGINAL
```

```
--- EQU OBJECTIVE     .       .       .     -1.000
--- EQU PREDICT     0.255   0.255   0.255   6.111
--- EQU WATERMF       .       .       .     5.548
--- EQU DENSITY  -3842.000 -3842.000 -3842.000 5.4176E-4
--- EQU LOADRATE      .       .       .     0.177

 OBJECTIVE  Calculation of CH4 production per m3 reactor
 PREDICT    Predictor equation of CH4 yield (m3 CH4 per kg VS added)
 WATERMF    Water mass fraction at first basket calculation
 DENSITY    Basket mixture density (regressed experimental data)
 LOADRATE   LR calculation

            LOWER   LEVEL   UPPER  MARGINAL

--- VAR L          .     0.943   5.000     .
--- VAR DRR        .     0.467   1.000     .
--- VAR W          .     0.805   1.000     .
--- VAR MY         .     0.177   0.255    EPS
GAMS 2.25  PC AT/XT                    13:42:19  PAGE   10
Combined optimisation for DRR and Leachate (CH4 yield basis)
Solution Report    SOLVE OPTIMAL USING NLP FROM LINE 84

            LOWER   LEVEL   UPPER  MARGINAL

--- VAR LR         .     6.111  20.000     .
--- VAR DEN        .  1992.041   +INF      EPS
--- VAR CH4VOL    -INF   1.1507   +INF      .

 L        Leachate water percent of the total wet mass of waste
 DRR      Digested recycle ratio on WET basis
 W        Total water mass fraction in the first basket
 MY       Calculated methane yield (m3 per kg VS)
 LR       Loading rate (kg VS per day per m3 reactor)
 DEN      Wet density of the mixture in basket (kg per m3)
 CH4VOL   CH4 volumetric production (m3 CH4 per m3 reactor)

**** REPORT SUMMARY :      0     NONOPT
                           0 INFEASIBLE
                           0 UNBOUNDED
                           0   ERRORS

EXECUTION TIME     =        0.600 SECONDS      VERID TP5-00-038

USER: CACHE DESIGN CASE STUDIES SERIES          G911007-1447AX-TP5
   GAMS DEMONSTRATION VERSION
**** FILE SUMMARY
INPUT    C:\GAMS\WORK\FULLOPTN.GMS
OUTPUT   C:\GAMS\WORK\FULLOPTN.LST
```