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OPERATIONAL MODES FOR EFFECTIVE RECOVERY OF ENERGY FROM RYEGRASS USING ANAEROBIC DIGESTION

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ABSTRACT

FACULTY OF ENGINEERING AND APPLIED SCIENCE

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OPERATIONAL MODES FOR EFFECTIVE RECOVERY OF ENERGY FROM RYEGRASS USING ANAEROBIC DIGESTION

DAVID NEYLAN

In the United Kingdom a large proportion of agricultural land is laid to grass which is used for grazing and also harvested for animal feed. Grass is also potentially the crop most suited to energy production in the UK because of its high yield, low maintenance and suitability for growing under the climatic conditions. Anaerobic digestion is a potential technology for conversion of grass to energy and the current work looks at the design and operation of digester types that could be used to maximise the energy yield per hectare of crop and take advantage of the requirement to store harvested material over the winter period.

Initial experiments established the methane potential of ryegrass (*Lolium perenne*) to be 0.245 m^3 kg^{-1} VS added. This was determined in a series of conventional batch digestion studies at different inoculum to substrate ratios using an anaerobic sludge taken from a municipal wastewater digester. The research then went on to examine potential energy losses through the use of conventional continuous stirred tank reactor (CSTR) digester design and from this began to focus on plug flow designs that could be simulated through a batch digestion model. Experimental work used a batch feed cycle to simulate a continuous fed plug flow reactor, although the results are equally applicable to a cyclic batch feeding regime. The minimum feed cycle length to gain 70% of the methane potential was found to be six days at an initial substrate loading rate (ISLR) of 10 g VS L^{-1} and twelve days at an ISLR of 20 g VS L^{-1}; in both cases this was equivalent to an Organic Loading Rate (OLR) of 1.7 g VS L^{-1} day^{-1}. In a batch or plug flow system it is necessary to add an inoculum, and experiments were designed to show the advantages and disadvantages associated with using the liquid or solid fractions derived from separated digestate material for this purpose. Both proved to be suitable as an inoculum at a 10 g VS L^{-1} batch loading, but a higher gas yield was achieved from the separated solids inoculum due to the capturing of residual VS by increasing the solids retention time of the system.

Results from a number of experiments indicated that in a ryegrass digestion system mechanical stirring could be problematic, and there were indications that this type of mixing might not be necessary for optimal performance. At an ISLR of 20 g VS L^{-1} some small advantages were found as a result of stirring during acclimation of the inoculum to the feedstock but this could be compensated for by the adoption of once per day liquid recirculation around the digester. This mixing strategy was therefore adopted in subsequent experiments.

30L digesters were used to test a digester operating mode in which solids were allowed to accumulate over a number of feed cycles, achieved by removing only the liquor which passed a 1 mm mesh at the end of each cycle. The solids accumulation rate for ISLR of 10 g VS L^{-1} loading on a seven-day cycle would allow the digester to operate for 30 weeks if no solids were broken down. In practice the rate of VS destruction measured extended this by between ~24-67% depending on the initial solids make up of the digester. In a subsequent smaller-scale solids accumulation experiment a specific methane yield of 0.415 L CH_4 gVS^{-1} was achieved over 10 feed cycles (weeks) and showed this reached an optimum at an I:S ratio of 3 – 3.5 on a VS basis.

Declaration of Authorship

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declare that the thesis entitled

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and the work presented in the thesis are both my own, and have been generated by me as the result of my own original research. I confirm that:

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- none of this work has been published before submission.

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List of Abbreviations

AD	Anaerobic Digestion
ABR	Anaerobic Baffled Reactor
BMP	Biochemical Methane Potential
COD	Chemical Oxygen Demand
CSTR	Continually Stirrer Tank Reactor
DTI	Department for Trade and Industry
FVW	Fruit and Vegetable Waste
MSW	Municipal Solid Waste
HRT	Hydraulic Retention Time
IA:PA	Intermediate Alkalinity : Partial Alkalinity (Ripley ratio)
IBLR	Initial Batch Loading Rate
I:S	Inoculum to Substrate ratio (VS basis)
ISLR	Initial Substrate Loading Rate
LCA	Lifecycle Cost Analysis
NFABR	Normal Feed Anaerobic Baffled Reactor
OFMSW	Organic Fraction Municipal Solid Waste
OLR	Organic Loading Rate
OPL	Organic Power Ltd.
SFABR	Split Feed Anaerobic Baffled Reactor
TS	Total Solids
VS	Total Volatile Solids
VFA	Volatile Fatty Acids
WAS	Waste Activated Sludge
WGC	Whole Grain Crop

Chapter 1.0

Introduction

1.1 Anaerobic Digestion

The term anaerobic digestion refers to the process of microbial breakdown of organic material in the absence of oxygen. Anaerobic digestion is a naturally occurring process that has been harnessed to reduce the strength of wastes and convert biomass to biogas, a methane-rich energy source. There have been many decades of research into various aspects of anaerobic digestion and the level of activity has increased with the advent of global warming and growing interest in renewable energy sources, in which biomass is a key component.

In the UK anaerobic digestion has mainly been used for sewage treatment to stabilise the wastewater to form biosolids, the final solid product of the process. This is necessary in order to comply with Sludge Use in Agriculture Regulations (1989), relating to the use of the stabilised material on land. Anaerobic digestion has been employed mainly to reduce the amount of biosolids and it currently treats 66% of this country's sewage sludge (DETRA 2009). The production of biogas, although a valuable product, has been of secondary importance

With the renewed focus on the sustainability of energy supplies, biomass is now seen as a potential major contributor to meeting future power and fuel needs (DEFRA 2007). Anaerobic digestion is therefore emerging as a competitive technology for energy production from both organic wastes and crops grown specifically for this purpose. This shifts the criteria upon which the success of the process is judged. One of the determining factors is that energy crops have an economic value to the agricultural producer, and production of these crops also has a lifecycle cost and potential environmental impacts that need to be considered. It may be necessary to review the fundamental nature and operation of the digestion process in order to ensure the best use is made of both the substrates and the digestion plant. There are also wider issues to consider, such as what are the best crops to cultivate for energy production to avoid

competition with food production; how to optimise use of the land base to satisfy both needs; and which is the best AD technology to adopt?

1.2. Scope of the project

The framework for the research described in this document was provided in part by the EU CROPGEN Project (www.cropgen.soton.ac.uk), the main objective of which was to consider anaerobic digestion for energy production as part of an integrated farming system using energy crops and agricultural residues. The work presented in this thesis was carried out partly in cooperation with Organic Power Ltd (OPL), a partner in the CROPGEN project with the role of investigating innovative modes of digester design and operation. The OPL-Maltin system approximates a plug flow hydraulic regime, fully described in section 2.4.7.

1.3 Critical issues

It is a critical aspect of the energy production process that the energy output should be substantially greater than the energy input needed to run and service the process itself. Inputs include provision of feedstock, transport, and pre-treatment. In the digestion process itself two of the major inputs are maintaining the digester at a suitable operating temperature, and mixing the contents.

Mixing is generally considered necessary to obtain good digestion, by ensuring good contact between the inoculum and the substrate. Heating is also a basic requirement to achieve good digestion, with mesophilic (35 - 40 ^{o}C) and thermophilic (50-55 ^{o}C) being the most common temperature ranges in commercial processes. It is possible to operate outside these ranges but at a reduced rate of methane formation leading to a requirement for larger plant. In digesters that process energy crops or high solids municipal wastes, heat generated within the process can raise the digester temperature, and harnessing this could be a useful way to reduce the required energy input.

Growing of crops for energy production can offer an alternative use for the land or make use of under utilised land. The past decade has seen an unprecedented growth in the number of digesters being built for energy crop digestion in Germany and Austria. This has been stimulated by subsidies for renewable energy through the so-called 'Feed-in-Tarrif' laws (German Biogas Association, 2008). What is unique about the concept is the requirement to maximise the energy return from the substrate leaving a highly energy-depleted but nutrient-rich fertiliser product for return to the land.

This approach has led to the development of new designs for digestion plant including two-stage digesters and the coupling of long-term digestate storage tanks into the gas recovery system. There is still further scope for innovation in digester design and operating protocols to further maximise the recovery of the energy potential from crops.

Anaerobic digestion has other direct effects on the sustainability of farming; the new market in energy production could lead to the reduction of livestock as it is now becoming economic to produce electricity rather than meat and milk. Metener in Finland (www.metener.fi) operates a dairy farm with anaerobic digestion facilities and is switching from cattle to grass digestion for just these reasons. The price for organic certified produce also has a premium in the UK, and anaerobic digestion could allow farmers to become organic while maintaining yields by the substitution of digestate for fertiliser. The precise economic case for on-farm anaerobic digestion varies according to electricity and milk prices but the point is anaerobic digestion can give dairy farmers a choice of markets and brings the goal of energy-neutral farming closer.

1.4 Aim and objectives of the research

The overall aim of the research was to seek ways in which the maximum energy potential of energy crops could be recovered through anaerobic digestion by improvements in system design and process operation.

The specific objectives of the research were:

- To select an energy crop for study that could be widely grown in the northern European temperate climatic zone
- To determine the maximum potential methane yield from the selected crop and whether this is a reliable indicator of the feedstock's performance under test conditions
- To critically review reactor designs and operating protocols used for digestion of energy crops
- Optimise the digestion of ryegrass for specific methane yield
- To develop through experimentation the concept of a plug flow system for digestion of high solids energy crop materials
- Highlight the issues involved with reactor optimisation and control.

The work envisaged at the start of this project was a mixture of practical laboratory investigations and desk studies relating to process hydraulics to consider plant design

and operational strategies that would allow balancing of the process to meet seasonal fluctuations in biomass availability and the changing needs of the agricultural sector. Experimental work was used to develop theoretical principles, improve process management and influence future digester design to increase the overall efficiency of on-farm energy crop digestion.

1.5. Statement of hypothesis

Anaerobic digestion of ryegrass is a renewable energy technology for the conversion of biomass to clean and versatile fuel. Energy crop digestion requires the re-evaluation of process parameters from the best throughput or gas production per unit volume of reactor to the highest energy yield per unit area of farmland. The dominant anaerobic digestion system is not best suited to maximising the energy ratio from whole crop digestion. How can ideal plug flow translate theoretical process advantages to the anaerobic digestion of energy crops, into system design?

Chapter 2

Literature review

The literature review considers the following topics:

- Anaerobic digestion of crops as a bio-fuel technology
- Environmental benefits of on-farm anaerobic digestion
- Energy crops for anaerobic digestion
- Anaerobic digester types and operation for farm scale digestion
- Anaerobic digestion of ryegrass
- Anaerobic digester electricity and heat requirements
- Basis for further research

2.1 Anaerobic digestion of crops as a bio-fuel technology

Anaerobic digestion produces biogas which contains the fuel gas methane and can be used directly in combustion to produce heat; in a boiler to raise steam; as a fuel for combined heat and power production (CHP); and as a vehicle fuel. The EU Renewable Energy Roadmap (COM(2006)848) set out the framework to meet a 20% renewable energy in the EU by 2020, target. Of all the technologies predicted to make a contribution, biogas from biomass and biowaste combined are a significant part of the electricity generation. The EU Biomass Action Plan (COM(2005)628) estimates the full potential of biomass around 185 Mtoe of renewable energy of which 100 Mtoe is available as organic wastes including forestry and agricultural residues. The EU Directive on Biofuels (2003/30/EC), classifies upgraded biogas as a liquid bio-fuel alongside bio-ethanol and bio-diesel which are predominantly produced from higher-value extracts of plants and are therefore referred to as first generation biofuels. Bio-methane as a liquid biofuel fuel when generated from anaerobic digestion clearly falls in the second generation category. Anaerobic digestion is therefore recognised as having a major role in meeting these renewable energy targets.

2.1.1 Energy from biomass

Elsayed (2003) used Lifecycle Cost Analysis (LCA) to compare a range of bio-fuel technologies including bio-diesel from oilseed rape, ethanol from fermentation and pyrolysis and the thermal processing of woody materials and straw. Table 2.1 compares the energy ratios of some of these biofuels. The LCA of anaerobic digestion

considered by Salter (2004) was based upon the conversion of biogas to heat and power, and therefore only CHP technologies have been included for comparison.

The anaerobic digestion of crops lies between the CHP combustion technologies which can achieve energy ratios of *c.*7–10 and the liquid fuels at energy ratios of *c.*1.5 - 2.5. When deciding how to make use of a crop, anaerobic digestion offers greater energy yields than bio-diesel and bio-ethanol which are seen as the only viable road fuels in the short term, Hamelinck et al (2005), while still being able to produce a fuel in the form of gas, although the market for gaseous vehicle fuels is not yet fully developed.

Table 2.1 Comparison of energy ratios for bio-fuel technologies

Bio-fuel technology	Energy ratio output/input
CHP of wood chip from short rotation coppice (gasification)	9.80 – 10.87
CHP large scale, wood chip from forestry (combustion)	7.19
*Anaerobic digestion of sugar beet	5.80
*Anaerobic digestion of wheat whole crop	5.43
*Anaerobic digestion of ryegrass	4.70
Bio-diesel from oilseed rape	2.29

(Elsayed 2003, *Salter 2004, $^{+}$Tillman 2006)

The combustion technologies generally make use of woody biomass and therefore do not compete directly with the common feedstocks for anaerobic digestion. Grasses however are a crop type where both routes are viable. The calorific value of hay was taken as 16.5MJ kg^{-1} close to the value of wood while the biogas potential for grass was taken as 585m^3 t^{-1}DM (319m^3 CH4 t^{-1}DM) which equates to 10.4MJ kg^{-1} DM, Hoffmann et al (2010). This shows that there is less energy available to anaerobic digestion but there are a number of other issues to consider.

Hoffmann et al (2010) compared the combustion of grass hay and Whole Grain Crop, WGC, with the anaerobic digestion of grass silage and WGC; burning the biogas in a CHP unit. Heat and electricity only and CHP were compared at four scales to asses the potential CO^2 reduction per hectare. The CO^2 emission savings were calculated against the provision of heat and electricity under German conditions with the relevant assumptions and data. As digestion was considered solely for CHP that is the only comparison made here. The LCA for the crop production did cover all the production

and processing energy costs but the key omission from the balance was the recycling of nutrients either as ash or digestate.

Table 2.2. Comparison of land take for biomass, AD and combustion.
Adapted from Hoffmann et al (2010)

	Combustion		Digestion	
Plant size MWe	Grass hay area ha (ha MW^{-1}) [*]	WGC area ha (ha MW^{-1}) [*]	Grass silage area ha (ha MW^{-1}) [*]	Rye-silage area ha (ha MW^{-1}) [*]
0.1	88 (880) [14]	90 (900) [14]	79 (790) [10]	101(1010) [9]
1.0	1055 (1055) [14]	1085 (1085) [14]	692 (692) [12]	888 (888) [10]
5.0	5273(1055) [16]	5423 (1085) [16]	3376 (675) [12]	4332 (866) [10]
10.0	10,547(1055) [16]	10,847(1085) [16]	6752 (675) [12]	8663 (866) [10]

[*] potential CO2 saving, Mg CO2 per year

One of the interesting comparisons was the land take for the energy delivered by each power plant, Table 2.2. Both rye-silage and grass silage used for digestion require less area than hay or WGC for combustion for the same power output. Grass silage needs only 65% of the land if used for digestion compared with combustion of hay. This was due to the different operating efficiencies between the various power generators and scenarios explored. Combustion for CHP showed a greater CO^2 saving than for biogas CHP but if digestate replaced nitrogen fertiliser the energy balance would be improved.

Prochnow et al (2009) carried out a detailed two part study into Bioenergy from grassland. The first part was a review of the use of grass for biogas production while the second part was a review of grass for combustion. This study compared animal husbandry with energy production and estimated CO_2 savings on that basis. For grass to be used for combustion the species favoured are those with the higher carbon content of lignin and cut later when the plant is more mature, resulting in a lower content of nitrogen, amongst other elements, that decrease as the plant ages. When grass is used for digestion the new growth with more leaf, where the nutrients are more concentrated, and less stem is more suitable as the lignin does not digest.

Table 2.3. GHG emissions from grassland based on animal husbandry and biogas production. Prochnow et al (2009)

	GHG emissions kg CO_2eq ha^{-1} a^{-1}	Reference
Irish dairy farming	12,068	Styles and Jones
Irish cattle husbandry	5,237	2007
Irish sheep husbandry	3,751	
Irish suckling beef - conventional	3,468 – 7,067	Casey and Holden
Irish suckling beef – agri environmental	2,674 – 5,647	2006
Irish suckling beef - Organic	1,208 – 3,514	
German intensive grassland farming	9,400	Haas et al
German extensive grassland farming	7,000	2001
German Organic grassland farming	6,300	
NZ dairy farming	5000	Lieffering et al 2008
German Biogas to electricity	-4,125	Rosch et al 2009
German Biogas electricity + 50% heat	-5,562	

Table 2.3 shows the CO_2 eq costs of a variety of animal husbandry practices under various conditions. The carbon intensity ranges from conventional dairy farming through beef, through to the substantial carbon savings of anaerobic digestion of biomass. There are a number of competing uses for agricultural land and the issues have to be decided between to arrive at a desired outcome but anaerobic digestion offers a variety of environmental benefits. All of the conversion technologies mentioned have a place, but none are as versatile as anaerobic digestion.

2.2 Environmental benefits of on-farm anaerobic digestion

Agriculture is responsible for about 10% of the total CO_2 equivalent of greenhouse gas (GHG) emissions in the EU and notably contributes 58.1% of methane (CH_4) and 64.5% of nitrous oxide (N_2O) emissions. These gases have a greater GHG potential than CO_2 and arise as a result of manure and soil management practice (CH_4 and N_2O) and enteric fermentations (CH_4) Marmo (2007).

DEFRA (2009) reported that agriculture is the second largest source of UK greenhouse gas emissions. One of the major benefits which could arise from AD in farming is in the improved management of agricultural organic wastes, and there are good reasons to consider these for digestion from an environmental point of view. Methane emissions

from livestock come mainly from two sources, enteric fermentation and manure. For the UK as a whole in 2003 they were reported by Baggot et al, (2005) as:

Enteric methane emission = 764.9 kt (86%)
Livestock manure management = 124.8 kt (14%)

Most of the contribution from livestock manure management is from slurry-based systems which contribute approximately 74% of the methane emission (Table 2.4).

Table 2.4. Annual UK methane emissions by manure management practice

Type	Amount	Proportion
Slurry based systems	96.7kt CH_4 $year^{-1}$	74%
Solid manure systems	14.5 kt CH_4 $year^{-1}$	11%
Daily spread and pasture	19.1kt CH_4 $year^{-1}$	15%
Total	130.3 kt CH_4 $year^{-1}$	100%

based on Mistry and Misselbrook (2005)

Amon et al (2006) compared five manure treatment systems to assess methane, NH_3 and N_2O emissions. The methane mostly comes off in the storage stage while the ammonia emissions result mainly from field application.

Table 2.5. GHG emissions by manure treatment system, Amon et al (2009).

Manure treatment	Greenhouse gas emissions		
method	g NH^3 m^{-3} [% *]	g CH_4 m^{-3} [% *]	kg CO_2 eq m^{-3}
No treatment	226.8 [18/82]	4047.0 [100/0]	92.4
Slurry separation	402.9 [81/19]	2363.3 [99/1]	58.8
Anaerobic digestion	226.8 [4/96]	1344.6 [100/0]	37.9
Straw cover	320.4 [16/84]	4926.3 [100/0]	119.7
Slurry aeration	422.6 [49/51]	1739.3 [100/0]	53.3

*[S/F] emissions from storage, S and field application, F.

No treatment meant storage at ambient temperature, 17C, where all the GHG is vented to atmosphere. The CH_4 emissions come from the storage, less from separated liquid and more when straw is added as a cover. The composting process and slurry aeration effectively take up the feedstock that would form methane under anaerobic conditions. There was still an appreciable amount of CH_4 released in the post digestion

storage tank, Table 2.5. shows that only 67% of the methane was captured from the digestion. With separated slurry the liquid went to storage and the solids were composted. When the slurries are applied to the land both digestate and untreated slurry have similar NH^3 emissions while separated liquid was lower as the composted solids release c.70% NH^3 emissions.

As the majority of the GHG load originates from the methane and anaerobic digestion can capture it, NH_3 has to be mitigated by better spreading practice or lowering the solids in the digestate.

The digestion of livestock slurry alone is hampered by the low energy yield, energy crops however, can be used as a means of boosting the volumetric biogas production of AD plants while the trace elements and buffering in slurries contribute to process stability, Braun et al (2003); Amon et al (2007). This concept of co-digestion has been widely adopted in Austria and Germany and offers immediate abatement for the methane from slurry, which then contributes to offsetting fossil fuel use rather than being vented to the atmosphere. The use of digestate to replace nitrogen fertiliser could significantly reduce inorganic fertiliser inputs onto the farm and reduce environmental impacts as a result of energy and transport savings associated with their manufacture and distribution.

Centralised biogas plants were implemented in Denmark in response to the 1987 Fresh Water Act that restricted the amount and the period of nitrogen application on the land. This meant that farmers had to spread their animal slurries over a wider area than was previously the case, increasing transport costs and the need for storage facilities: 6-9 months was typically needed. Along with Denmark's CO_2, waste reduction and energy targets, centralised plants offered a number of solutions. The shared facilities of treatment and storage improved the logistics of manure handling and met the legislative needs. As well as the cost savings the farmer achieved better sanitation and nutrient utilisation in the digestate, giving an economic benefit, Hjort-Gregerson (1999).
The CAD approach for the UK was examined in detail by Mistry and Misselbrook (2005) and they concluded that returns for on farm AD were poor but CAD facilities could be feasible if gate fees, electricity generation and some government support could be combined.

Their report concluded that three areas of research should be considered;

1. A more intensive process to increase throughput
2. Increase of biogas production with feedstock addition
3. Optimise the digestion parameters to approach theoretical values

These aims fall within the scope of the current project as the use of energy crops is a way in which process intensification can be achieved, although co-digestion itself is not a significant part of the research. The farm environment is the natural place for anaerobic digestion to be implemented as biomass is the business of agriculture.

2.3 Energy crops for anaerobic digestion

2.3.1 Status of on-farm renewable energy production from energy crops

Germany is leading the rapid expansion of on-farm biogas production due to the long-term government subsidy of the energy price, Wieland (2003), and energy crops are the principle means of boosting gas yields in comparison with digestion of animal manures and slurries. In 1999 there were ~850 biogas plants in Germany with <100 MWe power output, and 50% of these used energy crops for co-digestion with animal slurries, with only 7% operating solely on manures.

Table 2.6. Number of biogas plants in Europe producing electricity.

Country	**Agricultural AD plants**	**Installed capacity MWe**
Austria	159 +150 to end 2007	29 +40 to end 2007
Belgium	6	12.3
Denmark	58 on farm 20 CAD	40
France	3	n/a
Germany	>3000 *3700 in 2008	550 *1300 in 2008
Great Britain	<20	<2
Ireland	5	0.2
Italy	80	62
Netherlands	12	3.8
Switzerland	71	n/a

M. Kottner (2005), *German Biogas association (2008).

The German Biogas Association (2008) reported more than 3700 plants in 2007, while electrical generation output has grown 3 times faster, approaching 9% of all renewable electricity at 1300 MWe. This demonstrates the key role of energy crops in renewable energy capacity already installed in Germany. Table 2.6. shows the installed European anaerobic digestion capacity in 2005 with some updates from 2007 and 2008. At present the UK has very little installed capacity with many older plants installed on dairy farms, primarily for slurry management, and little CHP generation.

2.3.2 Choice of energy crop

Wieland (2003) compares various crops for their methane yield, both per tonne of Organic Dry Matter (ODM, or volatile solids, VS) and per hectare, and also gives typical plant operating data for a variety of anaerobic digestion processes. The Cropgen project gathered a more up to date and extensive list. Figure 2.1 shows the range of crops tested but more interesting is the large range of methane potentials associated with many of the crops. There are several reasons for this but it highlights the difficulty of comparison across Europe as well as between authors. The crops that stand out are fodder and sugar beet, maize, barley and triticale, but there is a wide choice and in practice individual conditions on a particular farm will determine the energy crop utilised.Salter (2007).

Table 2.7. Methane yield from energy crops. After Weiland (2003).

Crop	Methane m^3 $tODM^{-1}$	m^3 CH4 ha^{-1} $year^{-1}$
Forage beet and leaf	456	5800
Potato	276	2280
Maize	410	5780
Wheat	390	2960
Barley	360	2030
Rape	340	1190
Ryegrass	410	4060
Alfalfa	410	3965
Clover	350	2530

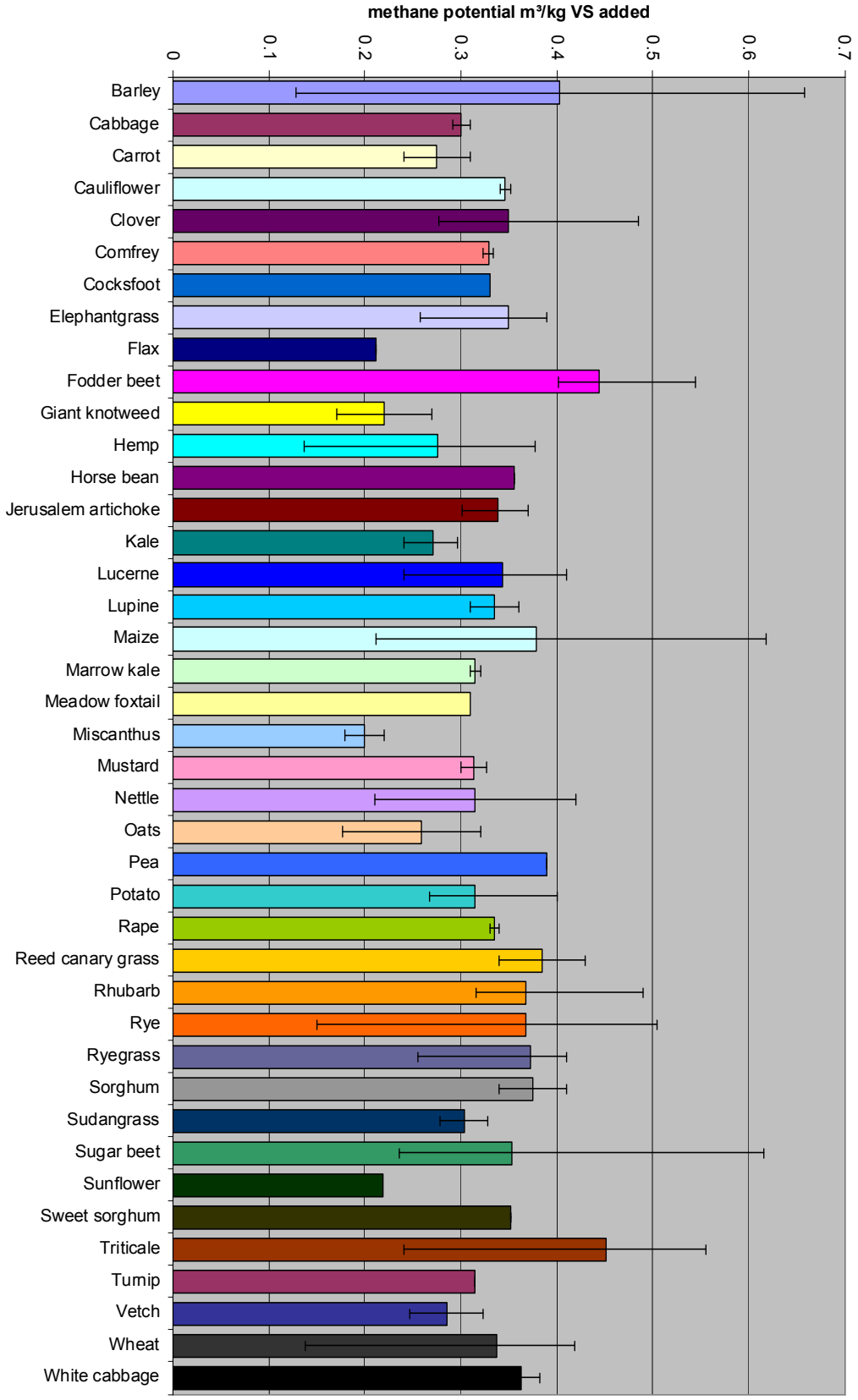

Figure 2.1 Methane potential of energy crops, Cropgen database. Salter (2007)

Of the crops listed in Table 2.7, fodder beet and maize appear to be the natural choices in terms of methane production per hectare-year. These two crops have a restricted growth area in the UK, however, and where maize, for example, can be cultivated with high yields it would have to compete with other more profitable cereal crops. Until very recently there have been restrictions on the use of sugar beet in energy production and any surplus is more likely to be taken up by the rapidly expanding bio-ethanol market. Sugar beet also has high economic and life cycle costs in cultivation and its growth is in direct competition with food production.

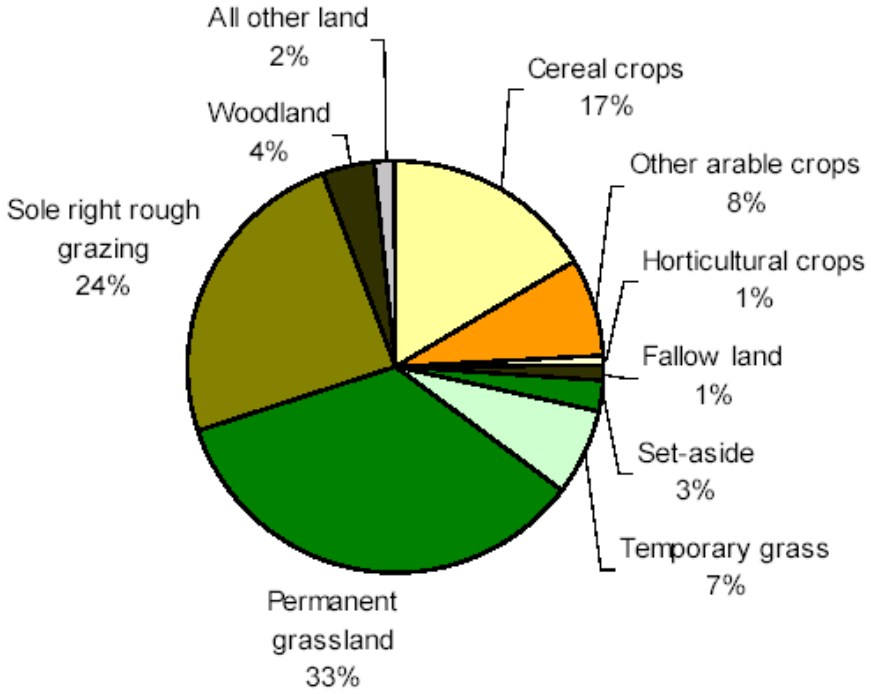

Figure 2.2. DEFRA 2007, 2008 and 2009 census of agricultural land in the UK

Traditional agricultural land use practices also have implications for the choice of energy crop. The results of the annual Defra census for agricultural land in the UK for the years 2007, 2008 and 2009 (figure 2.2) vary slightly year to year but the land usage is broadly the same. It showed that 37% was arable while 57% was permanent grassland and rough grazing. Of the arable land 70% was under crop cultivation, with ~11% set aside or fallow, and ~19% temporary grassland. This means that a total of 64% of all agricultural land is under grass of some sort. Unless the landscape is to be changed drastically in order to produce energy crops, the most probable choices for the UK are therefore; grass, of which ryegrass is a major species, and wheat which is the major arable crop - maize accounts for ~1%. From Table 2.7. it can be seen that

ryegrass is a very good gas producer, third overall and ahead of wheat, indicating the large resource that is available.

2.4 Anaerobic digester types and operation for farm scale digestion.

As part of this research, three types of digester are considered each of which has in one form or another been applied to the digestion of energy crops or solid waste residues. The following section reviews these types of digester in this context. Further details of the hydraulic regimes employed and the theoretical basis for these, both of which are important in understanding of the operation control and effectiveness of the process, are given in Appendix B.

2.4.1 Farm digester types

There has been considerable development in anaerobic digestion technology over the past 20 years, particularly in the development of high solids and two phase systems these are both suited to centralised anaerobic digestion installations, but their high investment costs and use of sophisticated technology makes them less suited for on-farm application. The most common digestion systems currently available and in use on farms are completely mixed Continuously Stirred Tank Reactors (CSTR) which operate at a low solids concentration and are sometimes referred to as 'wet' digesters. Where digesters operate at a high solids concentration they are referred to as 'dry' digesters, but their application on farms is currently limited to a few demonstration or pilot plants. There is, however, an increasing interest in small-scale and low-cost dry fermentation systems particularly in Germany for the mono-fermentation of energy crops and also for the treatment of yard manure and bedding from cows, pigs and poultry.

2.4.2 Batch digesters

Several batch-processes without mechanical mixing have been developed for farm use, but until recently only a few have been operated at a farm-scale. Most batch process designs can be described as leach beds which use recycling of leachate to inoculate, wet, and provide nutrients for rapid start-up and subsequent bio-conversion of the substrate to methane. The basic operation of leach bed anaerobic digesters is described by authors such as Ghosh (1985); O'Keefe et al (2000). Leach beds tend to operate at high solids (>35%) in simple non mixed reactors; their major disadvantage is

the lack of a mechanism for continuous feed of the substrate to the digester. Although apparently simple, three basic leach bed configurations are recognised, which differ in the respective locations of the acidification and methanogenic phases. In the single-stage batch design, the leachate is re-circulated to the top of the same reactor in which it was produced. In the sequential batch design, the leachate of a freshly-filled leach bed, containing high levels of organic acids, is pumped to another more mature leach bed where methanogenesis takes place. The leachate from this is then pumped back to the freshly filled reactor, providing alkalinity and promoting stable pH. This configuration also ensures cross inoculation between new and mature reactors which eliminates the need to mix the fresh wastes with seed material. The third design uses a hybrid batch-leach bed coupled to a high rate methanogenic digester such as an upflow anaerobic sludge blanket (UASB) reactor where the bulk of the methanogenesis takes place Anderson et al (1994), Saw (1992), Chen (1995).

2.4.3 Examples of batch digesters in use on farms

Two different low-cost batch fed leach bed designs are currently becoming established and are examples of dry fermentation with and without percolation.

The Bekon process

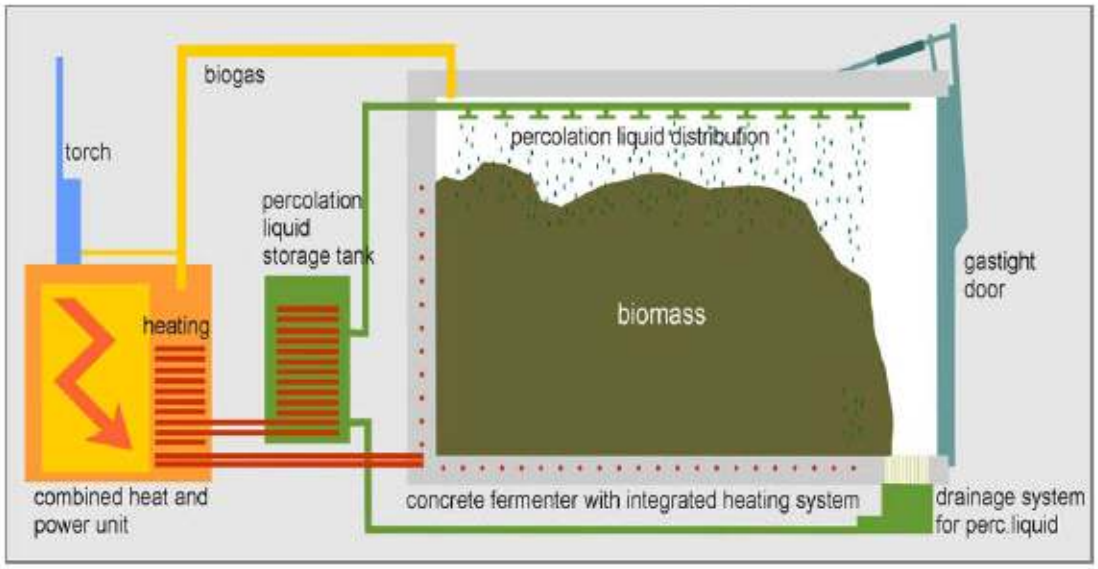

Figure 2.3. Diagram of the Bekon high solids batch system.

The percolation process uses a gas-tight fermenter chamber with a typical volume of about 150 m^3, coupled to a tank for storage and heating the percolation water. High solids material (typically 50% DM) can be loaded in with standard machinery through the door that is then sealed to allow anaerobic digestion. Liquor is re-circulated to act as mixing, digestion proceeds for four to six weeks when new material is added.
Bekon report biogas yields of 100 m^3 t^{-1} for fresh grass, 180 m^3 t^{-1} for maize silage, and 125m^3 t^{-1} to 145m^3 t^{-1} for organic household wastes.

Silage Bag digestion

AgBag is the UK name for an on-farm bagging system for silage making and has been adapted mainly for composting but some anaerobic digestion work is being carried out. A bagging machine unfolds a very long bag as it is filled, all the pipework is unfurled at the same time allowing the bag to be as long as is needed with some control of the aeration or liquor circulation. The bag can only be used once as it is too difficult to empty without damage. 400 m^3 of shredded material is the maximum capacity of one bag but it is common to lay a series of bags if more volume is needed.

To achieve anaerobic digestion the bag is filled with a mixture of fresh substrate and anaerobically treated matter for inoculation, and placed on a heated base. The ratio of fresh and digested material has to be defined carefully in order to avoid an uncontrolled acidification German Biogas Association (2008).

2.4.4 Continuously Stirred Tank Reactors (CSTRs)

These are sometimes described as 'wet' digesters and are characterised by having a mixing system. They are fed either continuously or semi-continuously, and operated at solids concentrations of <12%; at this concentration the viscosity of the feed does not preclude full mixing within the digester. CSTR designs are the most widely used type of digester currently in operation and represent the more conventional engineering practice, with systems designed for treatment of sewage sludge, animal slurries and industrial sludges. There is considerable design and performance information available for such systems. Most CSTRs are heated and mixed mechanically creating a uniform and stable environment in the digester. In order to operate this type of digester with high solids biomass such as energy crops the physical consistency of the material must be made to resemble that of a slurry via pulping with dilution water or recycled separated liquor. If the substrate is non homogenous there is a tendency, even in well mixed systems, for some separation with the heavier fractions sinking and the lighter

fractions floating to produce a scum layer. There is also a tendency where the material may be fibrous, for example grass, that the fibres knit together and can foul mechanical mixing devises and pumps (EPA 1987). These factors need to be taken into account in the design and a means of removing grit and other heavy particles engineered along with scum control and suitable mixing systems.

A number of propriety mixing devices have been tried and tested for low solids digesters and these include: confined and unconfined gas mixing, and mechanical devices, Christodoulides (2001). One of the disadvantages of a CSTR digester design is that a portion of incompletely digested material will be discharged from the digester (an unavoidable consequence of mixing, see Appendix B). The retention time of the digester is expressed as an average, where in fact material will have theoretical retention times spanning a range from zero (short circuiting) to infinity. This potential for 'short-circuiting' will reduce the biogas yield and increase the need for residual treatment to stabilise un-reacted material. Where this type of reactor is used for the treatment of animal manures it is also likely to impair the proper hygienisation of the wastes, i.e. the kill-off of microbial pathogens which require a minimum retention time for destruction. The hydraulic characteristics of digester systems, an important aspect of the current work.

Other drawbacks in using a CSTR design for energy crop digestion include: the requirement to dilute the feedstock before it enters the digester; the additional energy that is involved in maintaining the solids in suspension once they have been diluted; and the requirement to separate the liquor from the fibre at the end of the process so that the liquor can be re-circulated. In effect the process involves considerable energy costs in pumping, mixing, separation and heating, Salter (2006).

CSTR digester designs do, however, offer some advantage in that biomass that has been reduced to slurry is much easier to handle and the equipment that can be used, e.g. pumps and mixing equipment, is less sophisticated and cheaper. The pipework and plant layout may also be simpler.

2.4.5 Examples of CSTR digesters in use on farms

Biogas Nord

Britain is expanding the on-farm capacity of AD primarily on dairy farms, where there is already a supply of cattle slurry, with a view to produce energy from the addition of

crops. Biogas Nord is a German company that has installed two digesters in the UK and has two under construction at the time of writing. These can be considered typical of the on-farm digesters that are so numerous in Austria and Germany.

Figure 2.4. Biogas Nord, 2800 m^3 digester. Lowbrook, Farm, Dorset, UK.

The feedstocks are cattle slurry piped as liquid into the reactor, with grass silage, whole maize or chicken litter added to increase the biogas yield. The solids are loaded at 2 – 4 kg VS m^{-3} d^{-1}, fed at 30-minute intervals via an auger to maintain an HRT of 70 days. The discharged material is held in a storage lagoon but it is common to separate the fibre and spread it on arable land with the liquids returned to pasture to offset nitrogen fertiliser additions.

The main tank is heated to 37 – 40 ^oC from the waste heat generated by a CHP unit on site. The construction is very simple and consists of a flat bottomed concrete cylinder with a central column that holds up wooden joists that span to the edge. The tank wall contains the heating pipes and is insulated with 100 mm of expanded foam, clad with corrugated steel. The roof is a double skin of gas tight membrane with a pressurised band to hold it to the digester body. The inner membrane contains the biogas above the digestate while the outer membrane holds pressurised air to maintain shape and force the biogas to the CHP unit. The wooden joists keep the membranes out of the reactor during maintenance but also hold a net that is used to capture sulphur compounds from the evolution of H_2S. Air is introduced in small amounts into the gas space to precipitate sulphur onto the net or back into the liquid.

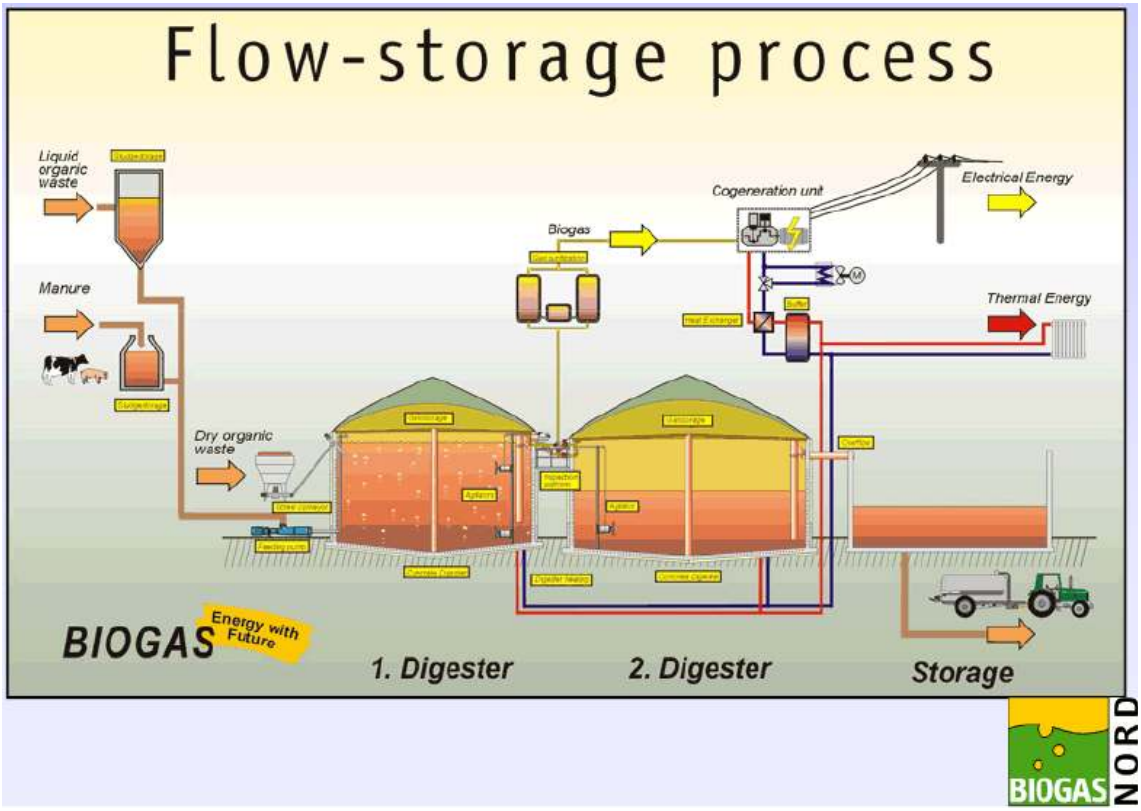

Figure 2.5. Schematic of a typical Biogas Nord system.

Mixing is supplied by impellers suspended in the digestate from overhead cables operable from the outside. The biogas is piped to a 250 kVA piston engine CHP unit where it is burnt continuously. The operator claims 5% of the electricity is used for maintenance of the reactor with the rest exported to the grid. The heat is used for the digester with the excess vented to the atmosphere in this case, but it can be piped locally for district heating. The amount needed for temperature maintenance varies seasonally and is not quantified at the Lowbrook farm installation as it is a waste product. The system diagram from Biogas Nord shows two main digesters and a storage tank, the second digester is an expansion of the system and is used in the same way as the first.

Biogen-Greenfinch and Freenergy

Both companies are British manufacturers of gas-stirred CSTR reactors similar in operation to the Biogas Nord type digester. Freenergy differs in that it exclusively uses a hard top cylindrical digester and has developed a rotating valve to control the supply of biogas to the digest for mixing. The heating is supplied internally via heated draft tubes above gas outlets. Freenergy also uses a modular 250 m^3 glass fibre cuboid tank but otherwise the overall process design is the same, although the reactors are generally in the 100-500 m^3 range or modules of 250 m^3.

Biogen-Greenfinch also uses gas stirring within cylindrical digesters but the company has started to use the rubber-top design more common in Germany on its latest plants. Both companies have a strong on farm business but are expanding into the food-waste market

Figure 2.6. Freenergy modular 250 m^3 reactors with cylindrical gasometers.

Figure 2.7. Biogen-Greenfinch digesters.

2.4.6 Plug Flow digesters

These typically receive feed at one end whilst effluent is removed from the other. True plug flow reactors are not mixed and ideally the feed passes through without forward or backward dispersion. The system differs from the CSTR as the influent and effluent are time separated and cannot mix together, hence undigested material is not lost. The design of plug flow reactors varies considerably, as can be seen in the examples below, but they can be either tubular, compartmented, or consist of CSTRs linked together in series. It is also quite common for a plug flow reactor to act, in effect, as a two-stage process with hydrolysis and acid production occurring at the influent end and methanogenesis at the outflow, Ghosh (1997). This can lead to problems with feedstocks such as energy crops, crop residues and municipal solid waste. In these cases unless microorganisms are continually seeded back into the reactor methanogens may be washed out preferentially, causing decreased stability. Addition of sewage sludge or animal slurry or recycling of the effluent can help overcome such problems. In some horizontal plug flow digester designs it is necessary to mix the contents vertically to prevent stratification which otherwise results in solids settlement and scum formation. This can be done by re-injecting gas along the length of the reactor (OPL) or by installing paddle mixers (Linde). Plug flow can also be achieved

when using high solids input material in vertical tower design digesters (Dranco and Valorga). In these mixed feedstock and inoculum are conveyed to the top of the tower and then pass down the tower as material is removed from the base. More detailed descriptions in the next section 2.4.7.

Plug flow systems potentially have the following advantages:

- simple and robust;
- low energy requirement for mixing;
- suited to high solid wastes so long as suitable designs and management protocols can be developed to prevent solids settling;
- do not suffer from 'short circuiting';
- can be fed and discharged continuously;
- can be designed to bring about recycling of active biomass.

Disadvantages may include:

- tubular shape and greater surface/volume ratio means greater heat loss;
- requirement for continual re-inoculation of the digester.

2.4.7 Examples of plug flow reactors

The Anaerobic Baffled Reactor

The Anaerobic Baffled Reactor (ABR), Bachmann et al. (1983, 1985), as the name suggests is a compartmented digester, in which the rectangular vessel is divided into chambers by vertical plates which force the flow of digestate around them as shown in Figure 2.8

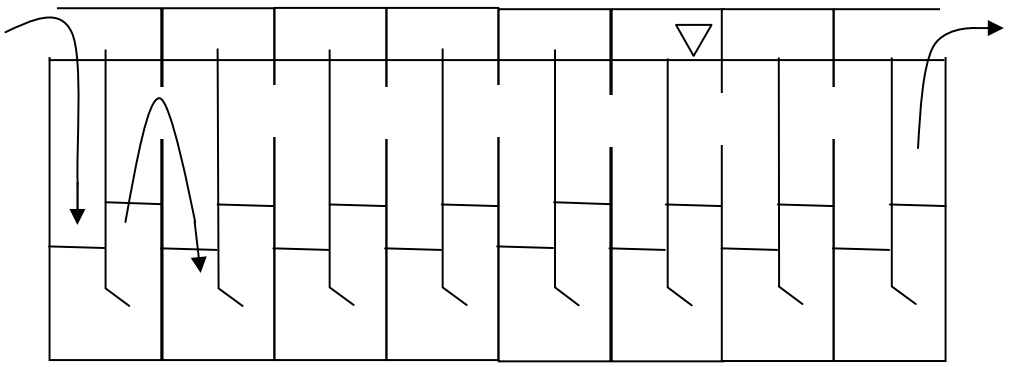

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Figure 2.8. Schematic of the ABR with eight compartments

Stuckey and Nachaiyasit (1997) state that the ABR design allows a high rate of hydraulic throughput without washout of the biomass and therefore achieves a high reaction rate and removal efficiency per unit volume. The design is simple and cheap to construct as there are no moving parts. Mixing is achieved by the evolution of gas within the digester and the hydraulic throughput is governed by the exit weir. Localised conditions exist in each chamber as the biomass is held within these while the liquor flows through. This partial separation of biomass and liquor leads to an uncoupling of the liquid hydraulic retention time (HRT) from the solids retention time (SRT), to give SRTs of ~ 100 days while the HRT is ~ 20 hours

ABR systems are most suited to high strength wastewaters with a low solids content because poorly degradable suspended material would dilute the microbial solids reducing the removal efficiencies, Bachmann (1985). This is a limiting factor in the ABRs practical use and the characteristics of the feedstock, pre-treatment and handling need would need careful consideration in the application of this type of reactor to solid substrate energy crops. ABRs, however, demonstrate features of the plug flow system which may be advantageous or disadvantageous and are therefore discussed here.

Sallis and Uryanic (2003) noted that at high loadings there was VFA accumulation and lowering of pH. This problem was mainly associated with start up and can be avoided by reducing the initial load and introducing a recycle, Bachmann (1985); this helps to stabilise conditions in the initial chambers, but Bachmann (1985) estimated that this strategy decreases the COD removal efficiency compared to no recycle at constant OLR and HRT. This is due to the recycle increasing the mixing in the digester and reducing the HRT, thus removing more biomass and leading to greater by-pass of undigested material. It is likely therefore that recycle acts mainly as a dilution and dispersion mechanism spreading the initial load more evenly across the digesters chambers. To overcome the apparent overloading problem Sallis and Uryanic (2003) introduced a regime of split feeding (SF) to the ABR to mitigate this disadvantage. The SFABR approach improved the performance of the ABR when comparative tests were done using the same substrate. Splitting the feed across a number of the initial chambers changes the hydraulic characteristics of the digester, although the effect of this is not discussed at any length by the authors.

Gorbicki and Stuckey (1991) used mathematical modelling and experimental work to evaluate the hydrodynamics of the ABR. They used Levenspiel's (1974) dispersion model which showed the ABR to have intermediate characteristics between those of a

CSTR and plug flow reactor. The greater the number of compartments the closer the behaviour became to that of a plug flow system. The ABR can also be modelled as a series of CSTRs; using this approach the shorter the HRT the better the correlation, but as the HRT increases the apparent number of CSTR components in series increases above the actual number of chambers, Gorbicki and Stuckey, (1991).

Bachmann (1985) predicted the performance of ABR using various parameters of which the most important were found to be COD removal, specific methane yield, and HRT.

Organic Power Ltd.

www.organic-power.co.uk

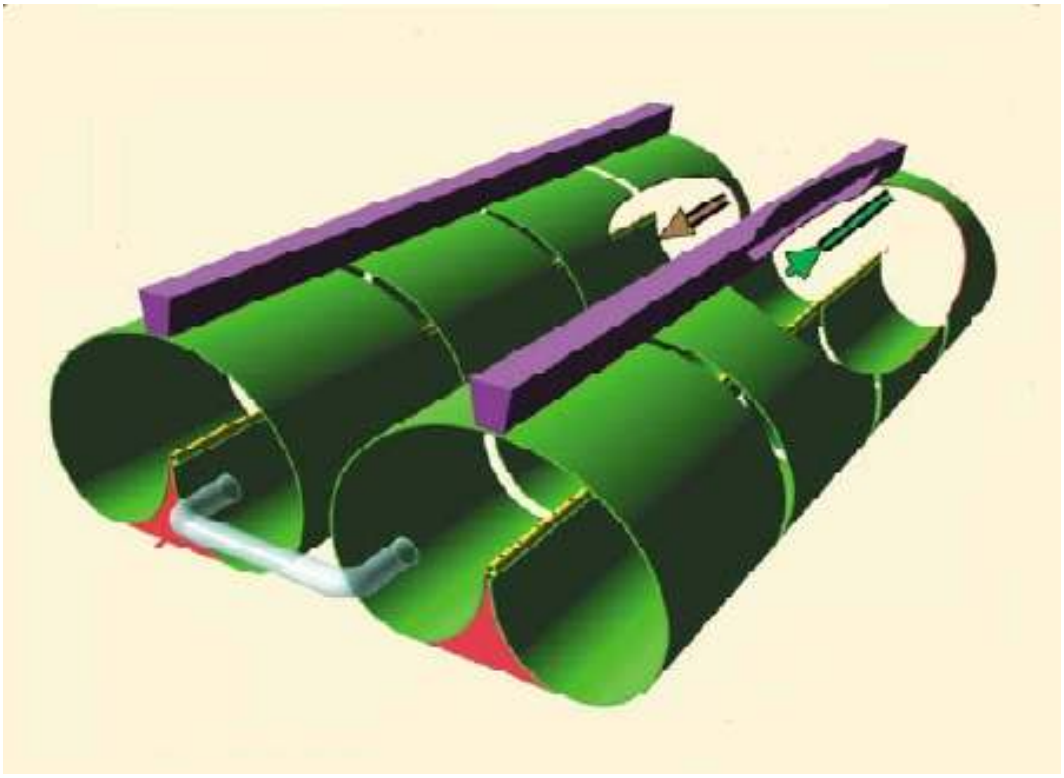


Figure 2.9. Schematic of the OPL pilot scale reactor.

OPL have a 50 m^3 demonstration plant in Horsington, Somerset. The reactor consists of 8 CSTR tanks in series. This is a wet system similar in concept to the ABR but with gas mixing and an inverted cardioid tank shape. The reactor is submerged in a lagoon which is heated to keep the contents at mesophilic temperatures. Tracer studies have confirmed that this configuration approaches plug flow.

The Tubular Reactor

There are a number of different tubular plug flow designs that are commercially available, some using horizontal mounted reactors whilst in others the reactor is mounted vertically. In both cases the principle is the same in that the material moves along the tube as a 'plug' and its passage is not hindered by baffles or constrictions. The selection of horizontal or vertical mounting will depend on the rheology of the substrate, as it would not be practical to design a vertical tower reactor for use with a liquid medium, although a deep shaft would be possible. The advantage of the tubular reactor over a CSTR is that the contents can exist in different biochemical states, so that acidic conditions do not inhibit methanogenesis. Bouallagui et al. (2002) found that at intermediate loadings the pH of 4 at the inlet of the digester increased to pH 7 at the outlet indicating a transition from acidogenesis to methanogenesis along the digester. They also found that as the loading was increased the outlet pH dropped, indicating the spread of acidic conditions throughout the digester. The transitions in state were smooth but the overall effect is not dissimilar to that achieved in two and multiphase digesters. Dinsdale (1999) also used a tubular digester to treat fruit and vegetable waste (FVW) with waste activated sludge (WAS) but here the process was separated with the acetogenesis carried out in a CSTR and methanogenesis in a tubular reactor. This methanogenic digester was inclined at 20 degrees with the inlet at the lower end, in a design attributed to Chapman (1986). It is not clear why a CSTR is used for acetogenesis and a tubular reactor for the methanogenic stage, and no real advantage was proposed for the use of plug flow.

Bouallagui et al (2002) used a tubular design digester for the treatment of fruit FVW. They ran the digester by varying the retention time between 12 - 20 days and altering the concentration of the feed solids to 4%, 6% and 8% TS. A 6% feed solids concentration at a 20-day HRT gave the best specific methane yield of 0.452 $m^3 kg^{-1}$ VS fed, while the best volumetric methane yield was at 8% TS over a 15 day HRT. This shows that the process can be optimised in two ways with the shorter retention time and higher substrate solids concentration (i.e. higher loading) giving a better methane productivity, but in doing so reducing the amount of energy that can be extracted from the substrate. To achieve the latter a longer retention time and lower feedstock solids concentration (lower loading) was required. If the feedstock were a commercial agricultural crop rather than a waste a careful economic consideration would be required to balance the additional methane yield against the cost of the substrate and the cost of the additional digester volume that would be required to achieve this. A second study by Bouallagui et al (2004) used similar conditions of HRT and feedstock

solids concentration but at temperatures of 20, 35 and 55 ^{o}C. Data analysis included an energy balance calculated from the calorific value of the methane minus the energy required for feedstock heating; the study ignored stirring and other mechanical forms of energy as they consumed only ~1% of the total energy production.

The highest conversion of the biomass to methane (specific methane yield) of 0.603 m^3 kg^{-1} VS was achieved at thermophilic temperatures at a low loading whereas the best volumetric methane productivities of 1.84 m^3 m^{-3} day^{-1} was achieved at a thermophilic temperatures at high loadings. The best energy ratio (8.59), however was achieved at a mesophilic temperature using an intermediate loading (8% feedstock TS concentration applied at a 20-day HRT). Again the best performance indicator depends on the outcome required.

Another aspect studied by Lastrella et al (2002), was the use of recycled digestate. With their inclined plug flow reactor fed on FVW the loading and biogas yield was increased by the recycling of digestate. There seems to have been a degree of axial mixing as digestion was possible without recycling the digestate as an inoculum, impossible with true plug flow.

Linde dry digestion.

Linde-KCA Umweltanlagen GmbH now STRABAG Umweltanlagen GmbH.
http://www.strabag-umweltanlagen.com/

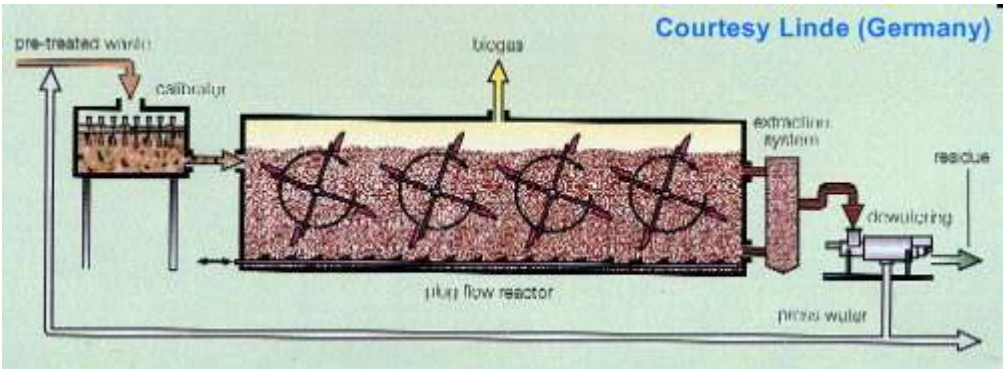


Figure 2.10. Linde dry digestion process.

Linde has a number of plants all over Europe treating MSW at total solids content of between 15% -45%. The reactor is a horizontal rectangular tank with a lot of the equipment mounted on the outside making it simple and robust but there is very little performance data for evaluation of this digester.

Dranco system for energy crops

Organic Waste Systems (OWS) – Dranco. http://www.ows.be

Dranco has developed a vertical, plug flow, high solids reactor that has been used to treat MSW and has been adapted for energy crop use.

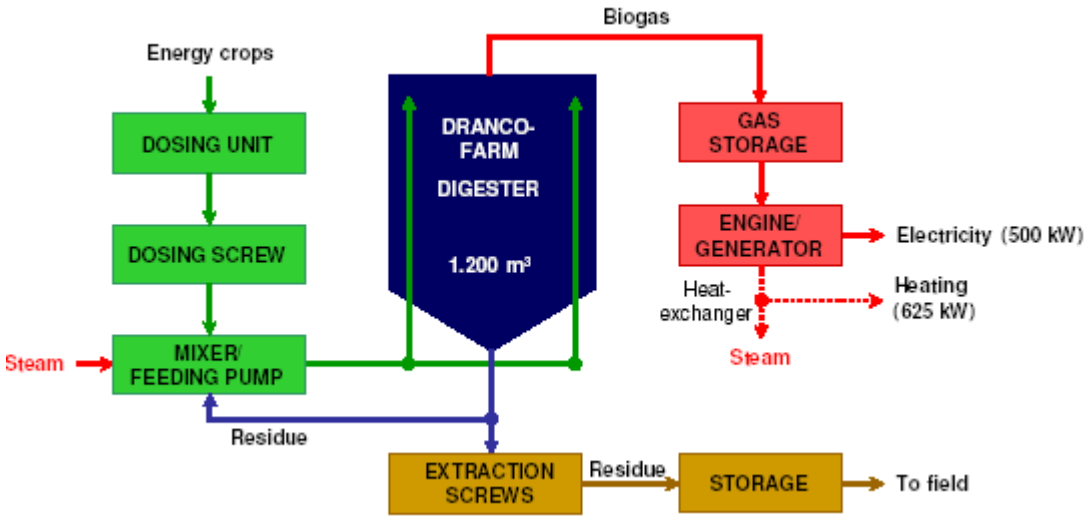


Figure 2.11. Flow scheme of the OWS Dranco energy crop demonstration plant.

The reactor can be fed on chopped Maize, Sunflower, Rye, solid manure and grasses, fresh or ensiled, without water addition. The feedstock is mixed with recycled digestate at a ratio of ~ 5:1 (inoculum to substrate), and fed to the top of the tower where it descends to the extraction point at the base.

A full-scale plant at Nüstedt, Germany is 1200 m^3 and processes 12,500 tonnes of mixed energy crop, with an OLR of ~3 kg m^{-3} d^{-1} producing an average of 82.65 Nm^3 CH_4 t^{-1} of material (~30% DM). This equates to 275 Nm^3 CH_4 t^{-1} DM, enough to power a 750 kW CHP, with the heat used for the thermophilic reactor (50-55 ^oC). The process uses 5% of the total electricity generated to run, with the remainder exported to the grid, De Baere (2006).

2.5 Anaerobic digestion of ryegrass

As grass is mainly cellulose which is a polymer of glucose $C_6H_{12}O_6$, stoichiometrically it would be expected to produce 50% CH4, Buswell (1952). Murphy (2010) presents a more detailed equation;

$C_{28.4}H_{44.5}O_{17.7}N + 8.425H_2O \longrightarrow 15.335\ CH_4 + 13.065\ CO_2$

Showing that the CH_4 content of biogas based on a VS destruction rate of 60% is in the order of 54% and the associated specific yield is 0.305$m^3CH_4\ kg^{-1}$ VS added.

Pouech et al (1998) carried out BMP tests on eleven energy crops including ryegrass, and concluded that all the crops were viable feedstocks for increasing biogas yields when co-digested with animal slurries. The crops were characterised across a number of parameters, and it is interesting to note that the values do not vary greatly, with VS:TS ratio 91% to 98%; methane content ~59% to 66%; and gas yield 340 to 400 m^3 CH_4 tonne VS^{-1}. Wheat, Clover and Ryegrass were further tested at each of three growth stages with the conclusion that the growth stage matters much less than the overall productivity per hectare of the crop.

Table 2.8. Fibre analysis by crop (after Pouech et al, 1998)

Crop	Lignin %DM	H.cellulose %DM	Cellulose %DM	TkN %DM	Methane $m^3\ tVS^{-1}$
Wheat	5.75	29.50	25.10	2.42	384
Barley	8.40	29.20	24.90	2.67	356
Maize	7.12	28.20	21.30	1.92	397
Alfalfa	15.80	14.20	16.70	3.78	340
Clover	14.50	14.90	15.30	3.51	350
Ryegrass	6.93	21.10	21.70	2.01	390
Silage	-	-	-	-	409
Forage sorghum	7.27	31.10	30.60	1.60	295
Grain sorghum	3.15	24.00	16.50	1.71	372
Sweet sorghum	6.83	25.80	30.00	2.01	352

Other data not widely reported for crop material include the chemical composition (Table 2.8), The inclusion of fresh and ensiled ryegrass in the table supports the idea that a higher methane potential was available; but in the text silage was viewed as having the same methane potential as fresh ryegrass, showing that ensiling does not degrade the substrate and therefore is allowable as a method of feedstock storage.

Mähnert et al. (2005) carried out a study using different grass species digested in both batch and semi-continuous mode. The species were perennial ryegrass *(Lollium perenne*), Cocksfoot (*Dactylis glomerata*) and Meadow foxtail (*Alopecurus pratensis*).

The batch digestion was carried out at 2.0-litre scale for 28 days using the grasses as mono-substrates, fresh and ensiled. 1.5 kg of inoculum was fed with 0.05 kg substrate resulting in an inoculum to substrate ratio of ~70 to 1 on a VS basis and a loading average of ~ 4 g VS l^{-1}. It seems that the grass was loaded on a wet weight basis and this results in a slightly varying VS load; the TS and VS content are similar, with the exception of Cocksfoot silage that has a higher TS content. The biogas yields were between 0.65 and 0.86m^3 kg^{-1}VS:

0.83 and 0.86m^3 kg^{-1}VS ryegrass - fresh and ensiled;

0.72 and 0.65m^3 kg^{-1}VS, Cocksfoot - fresh and ensiled;

0.75m^3 kg^{-1}VS for meadow foxtail.

The differences between duplicates were greater than the difference between silage and fresh material. The methane yields were not fully reported but were between 0.31 and 0.36 m^3 CH4 kg^{-1} VS for meadow foxtail and ryegrass respectively.

Table 2.9. Substrate characterisation after Mähnert et al. (2005).

	TS	VS	VFA	pH	C:N	XP	XF	Saccaride	XL
		%TS	g kg^{-1}			%TS	%TS	%TS	%TS
Batch experiments									
Ryegrass	17.6	90.1	0.5	6.5	16.4	14.7	24.8	10.8	2.1
Cocksfoot	18.6	89.1	0.5	6.7	13.7	18.5	24.8	9.8	2.3
Meadow foxtail	15.8	91.1	0.5	6.6	--	--	25.3	3.3	2.2
Ryegrass (silage)	18.7	88.5	6.9	4.6	15.5	17.0	31.3	3.4	4.9
Cocksfoot (silage)	27.3	88.8	14.3	6.1	14.3	18.4	30.1	3.1	4.6
Semi-continuous experiments									
Ryegrass	25.6	90.6	0.7	6.5	19.8	11.8	29.1	19.3	2.4
Cocksfoot	22.9	88.8	0.5	7.1	12.0	21.4	28.0	9.8	2.6
Meadow foxtail	24.2	90.6	0.6	7.1	13.5	18.8	31.5	9.1	2.1
Mixture	24.2	90.0	0.6	6.9	15.1	17.4	29.5	12.7	2.4
Slurry for semi-continuous experiments									
Cattle Slurry	6.5	80.0	7.9	6.8	--	--	--	--	--

The semi-continuous trials by Mähnert et al (2005) were conducted on the same grasses in 9-litre reactors. The OLR was 0.7 and 1.4 kg VS m^{-3} day^{-1} with a mix of the

three grasses, a 33% cattle slurry with 67% grass mix (VS basis), and a cattle slurry control at 2 litres, run alongside. There was a 4-week stabilisation period before the 6-week experimental period at the higher load, then a transition of 3 weeks before a 13-week experimental period at the lower load.

The grass digestion at 0.7 kg VS m^{-3} day^{-1} produced an average of 0.61 m^3 kg^{-1} VS biogas, and 0.56 m^3 kg^{-1} VS for the 1.4 kg VS m^{-3} day^{-1} load, both below the average of 0.76 m^3 kg^{-1} VS from the batch trials. 80% and 74% of the batch gas potential was achieved at the lower and higher load respectively. This was explained as showing that increased OLR reduces the specific biogas yield. The HRT was not explicitly stated, so it is not clear how much washout could be a cause of the reduced biogas yield with respect to the batch trial.

A further part of the study was to compare the specific biogas yields from slurry, grass-slurry mix and grasses only. The biogas yield for the cattle slurry was ~0.35 m^3 kg^{-1} VS and for the grasses ~0.65 m^3 kg^{-1} VS while the yield of the mixture was proportional to that of each component, indicating no synergistic effects.

Holiday (2005) trialled ryegrass digestion for the UK Department of Trade and Industry, looking at its suitability for energy production. The study had a number of objectives and is a useful source of information on various aspects of ryegrass digestion. The trials used two sizes of CSTR and both fresh and ensiled ryegrass. The retention times were 60 days for the 300L digester which was run for 3 months on silage then 5 months on fresh ryegrass. The 1.5 m^3 reactor ran for 5 months on silage at an HRT of 300 days. The smaller digester operated for ~3 retention times but the larger reactor did not complete half a retention time.

These retention times were based on feed volume, and the variability in the specific volume of ryegrass is reported as ranging between 0.8 - 1.2 kg m^{-3}. The OLR is not directly specified but seems to be < 1 kg VS m^{-3} day^{-1}. The mean average of production was 0.342 m^3 CH_4 kg^{-1} DM for ensiled grass and 0.229 m^3 CH_4 kg^{-1} DM for fresh grass, indicating an advantage in using ensiled grass over fresh material

2.5.1 Fresh and ensiled feedstock

Pakarinen et al (2008) investigated methods of ensiling energy crops and what effect this had on biogas yield. The underlying idea was that the methane potential in the fresh crop could only diminish when stored and they looked to minimise this loss in

methane potential. Apart from the handling, storage and spoilage the main issue with silage is the production of liquids with a high organic content (COD 100-200 g l^{-1}). This liquid can be lost to the biogas process due to the way feedstock is handled, and is not picked up by the standard TVS analysis. An average 11% loss of dry matter was reported for maize, with little soluble fraction losses, but were unable to identify the precise insoluble VS fraction that was lost. Ryegrass correctly baled showed little loss, but the fact remains that the silage liquor is a possible loss of methane potential and has to be accounted for when feedstock is assessed.

The experience of Manhert et al (2005) and Holiday (2005) shows aspects of ryegrass digestion that may have a bearing on its use as a feedstock. The apparent volume of the grass can vary, making it difficult to load consistently at a given rate. Ryegrass floats on the digestate making it hard to stir and pump as it wraps and clogs pipes. The separation may also make it difficult not to preferentially remove the solid or liquid proportion and thus affect the retention time.

2.6 Anaerobic digester energy requirements

A number of studies have looked at the energy requirements of the digestion process itself (Salter 2004; 2007). The energy requirement can be broken down into a two primary categories: direct and indirect energy requirement (Salter, 2004). The indirect energy requirements are the embedded energy in the digester itself and is accounted for in the Lifecycle Cost Analysis, LCA. This will depend on the size of the digester, the anticipated life expectancy, the materials of construction, and mechanical complexity.

The direct energy requirements are those needed for pumps, heaters, mixers and other mechanical equipment required for the day-to-day operation of the plant. As the energy derived from the process is used to run the digester the net energy production is a good measure of the efficiency. If the process, or parasitic, energy can be reduced the overall efficiency is increased. The parasitic energy can be further divided into electrical and heat inputs. Salter (2004) details two AD plants one of 480 m^3 and the other 1500 m^3; the measured electrical consumption works out to 74 and 183 W m^{-3} d^{-1}, and the calculated heat requirement 48 and 77 W m^{-3} d^{-1}, respectively. Stirring is by far the biggest percentage of electrical energy and consumes 44% and 65% respectively, but the larger reactor is stirred for 24 hours while the smaller reactor is stirred for 8 hours a day. Heating is required to overcome losses from the reactor to the ground and air as well as the heat needed to take the feedstock from ambient temperature to

the digester operating temperature. The smaller digester was better insulated and 81% of the heat load is for feedstock heating with 10% heat lost to the air and 9% lost to the ground. Contrast this with the less well insulated 1500 m^3 digester where 50% of the heat was used for the feedstock, 41% of the heat is lost to the air, and 9% to the ground.

If the insulation was equal then the energy required to maintain reactor temperature depends on the surface area to volume ratio (SA:Vol), of the digester.

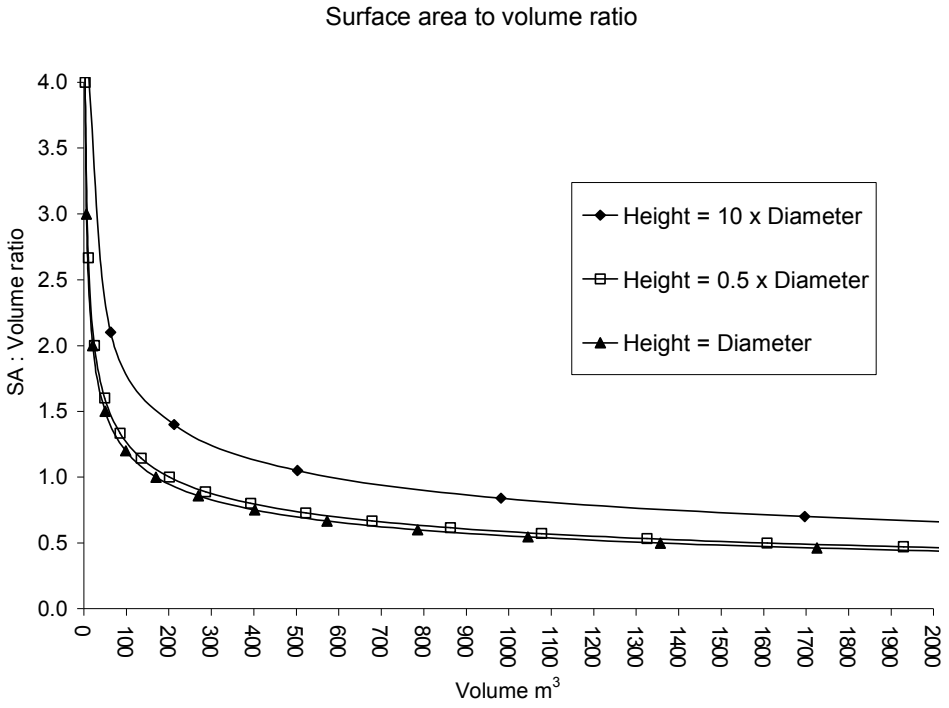


Figure 2.12. Surface area to volume ratio as a function of volume for cylindrical reactors with differing aspect ratios.

Figure 2.12. shows how digesters surface area to volume ratio reduces as volume increases and these are compared, for a cylinder, across three different aspect ratios; height = 10 times diameter for extremely tall or long pipe structures, height = 0.5 times diameter for more common tanks and finally where height is equal to diameter. As the SA:Vol ratio decreases for a given wall construction the heat loss decreases as there is less area for heat to transfer through following the general equation (Salter 2004):

$$q = UAdT$$

where q = heat loss, Watts.

U = overall coefficient of heat transfer, W m^{-2} $^oC^{-1}$.

A = cross sectional area through which the heat is lost, m^2.

dT = temperature difference across the surface in question, ^oC.

The largest direct electrical energy usage is mixing which is seen as an essential feature of any 'wet' CSTR design. Salter (2007) estimated this to be between 1.36 and 5 W m^{-3} of digester volume.

Karim et al (2005) compared the three main mixing modes; mechanical, gas recirculation and liquid recirculation against gas production. The substrate was cattle slurry at concentrations of 50, 100 and 150 g TS L^{-1} (34, 53 and 75g VS L^{-1}), the HRT was 16.2 days and the OLR was 3.1, 6.2 and 9.3 g TS L^{-1} day^{-1} (2.1, 3.3 and 4.6g VS L^{-1} day^{-1}). A power input of 8 Wm^{-3} was used for the three stirring systems in 3.73L working volume reactors. No effect of mixing on digester performance was found for the 50 g TS L^{-1} mix, but at higher loadings both the mixing and the mixing mode became important. Apart from the start-up phase, stirring increased gas yield but there was no real difference between the stirring modes. Gas mixing was abandoned at the highest load due to blockages, and there was no significant difference between the other two modes, so it is clear that secondary considerations are also operating. The power input was kept constant but this may result in different amounts of mixing as they all have different efficiencies.

Vavilin et al (2004) studied mixing intensity of the batch digestion of MSW and slurry and found when the loading was high intensive mixing resulted in acidification and failure of the process while low mixing intensity was found to be crucial for successful digestion. When loading was low mixing had no significant effect on the process. This finding led to the hypothesis that mixing disturbed the establishment of methanogenic zones that are needed to withstand rapid acidification. The amount of methanogenic biomass is crucial to the survival of those centres and vigorous mixing can disperse the biomass within the reactor where it is overwhelmed by the acidic conditions. The conclusion being that if methanogenisis is the rate limiting step then mixing is detrimental but if a hydrolysis is the rate limiting step then stirring will enhance biogas production.

Christodoulides (2001) in a review of a number of industry sources quotes values between 2.5 - 12.9 W m^{-3} of digester as the energy required for gas mixing to deliver a mixing energy of 1.5 – 3.2 W m^{-3}, with the difference due to the efficiency losses associated with compressors. For mechanical mixing systems the same author quotes values in the range 0.3 – 6.1 W m^{-3}. The difference between stirring and mixing is hard to define and the precise effect of mixing is difficult to quantify but can be regarded as

the biggest electrical demand of the plant and therefore must be a prime consideration when looking for savings in energy.

The energy required for heating the feedstock and maintaining the temperature of the digester is also important as this could have a major impact on the overall net energy yield from the process. Where the biogas is used for CHP production this is not such a great concern as there is usually sufficient low grade heat available to meet the heat demands of the plant. Where the methane is used for vehicle fuel the upgrading process does not generate any heat, which would have to be generated by burning a proportion of the biogas itself. This would have a much bigger impact on the net energy yield of the process and the energy ratio.

It has been assumed to be the case that mesophilic anaerobic digesters need to be heated, Bouallagui et al (2004), as digesters have traditionally worked on rather dilute energy-depleted substrates. It was only when digesters started to be fed with energy rich substrates such as energy crops and municipal wastes that Lindorfer et al. (2006) reported 'natural' heating to be significant to the point that in Austria a number of mesophilic digesters heat themselves, and in some cases even had to be cooled. This natural self-heating is microbially evolved and can lead to overheating of the digester and a breakdown of the process. Cooling systems when installed use a large amount of water, and yield only low grade heat. The study by Lindorfer et al. (2006) was carried out on a 2000 m^3 commercial digester fed on pig slurry and energy crops including maize, rye and wheat. An energy balance was conducted around the system with only a small heat deficit of <5%. This deficit is the gap between the calculated energy inputs and outputs compared with real data. The difference was attributed to the changing composition of the feedstock. The significant outcome was the attribution of self heating to the metabolic energy of the micro-organisms becoming greater than the heat loss of the reactor. Self heating is therefore an important phenomenon that could make a significant contribution towards the net energy gain from a digester.

2.7. Real CSTR operation on energy crops

2.7.1 Metener and JyU CROPGEN results.

The BMP value determined for Timothy grass silage mixed with cattle slurry (10.7% VS content, 4.7% w/w) was 0.33 m^3 CH_4 kg^{-1} VS added, after incubation for 224 days at 35C. After 24 days the methane yield was 0.22 m^3 CH_4 kg^{-1} VS added, 69 % of the

BMP. A yield of 0.048 m^3CH_4 kg^{-1} VS was obtained from a post-fermentation experiment when incubated 90 days at 20C, 17.5 % of the BMP.

These results were then compared to those from a farm-scale plant consisting of a feed mixing tank, a main digester and a post digestion storage tank. The main digester was loaded twice daily at OLR 3.1 kg VS $m^{-3}d^{-1}$ giving an average HRT of ~27 days. The silage / slurry mix varied between 9.7-23.3% on a VS basis. The main digester yield was 0.170 m^3 CH_4 kg^{-1} VS, with 0.036 m^3 CH_4 kg^{-1}VS, from the post-digestion tank with a residence time of 90 days, giving a total system yield of 0.205 m^3 CH_4 kg^{-1} VS added, which is ~63% of the BMP value.

The BMP value seems high considering that only 10% of the feed VS is from the energy crop. The results of the first 24 days of the BMP along with the post-digestion tank, digestate experiment show that these two stages yielded 86% of the BMP value, 17% of the BMP from the post-fermentation tank.

As this was a batch test the discrepancy is due to the temperature difference in the post-fermentation tank as well as the residence time difference. The BMP is able to run for 224 days, but the simulation test allows 24 days mesophilic digestion then 90 days psychrophilic digestion, and together only 14% of the yield is lost compared with a 37% loss at full scale against the BMP. A mixture of a high OLR and a short HRT make wash out a distinct possibility for the loss of efficiency; the twice daily feeding bringing the system closer to a continuous regime moving the gas potential to the post-digestion tank.

This example shows how short circuiting reduces the digestion efficiency moving some of the gas potential into a storage tank. Unless covered this leads to GHG emissions calling into question the sustainability of the whole process as the crop has been grown for energy and would not produce methane otherwise. There is also the increased need for land for the same energy output as the specific yield is less than optimal.

2.7.2 Doubling the organic loading rate in the co-digestion of energy crops and manure – A full scale case study

Lindorfer et al (2008) carried out research at a biogas plant located at a farm in Lower Austria. The plant was originally conceived as a two stage CSTR with a main digester volume of 2000 m^3, a second digester step of 1850 m^3 and open digestate storage tanks of 3800 m^3. The substrates were pig manure, energy crops like silages from

maize and rye, ground grains from maize and wheat, and residues from vegetable processing. The plant was originally running at 2.1 kg VS $m^{-3}d^{-1}$ OLR and was increased to 4.17 kg VS m^{-3} d^{-1} OLR in order to supply the gas for increased electricity generation from 500 kW to 1 MW. Three phases were identified;

1. Operation as a 2-step 500 kW agricultural plant with a main and a second digester and a final uncovered digestate storage tank.
2. Transition phase to 1 MW electrical capacity; dosage of substrates into both digester steps; final uncovered digestate storage tank.
3. Final status: two main digesters followed by a first covered and final uncovered digestate storage tanks.

The 3 phases are compared but phase 2 was a transition so it is ignored here.

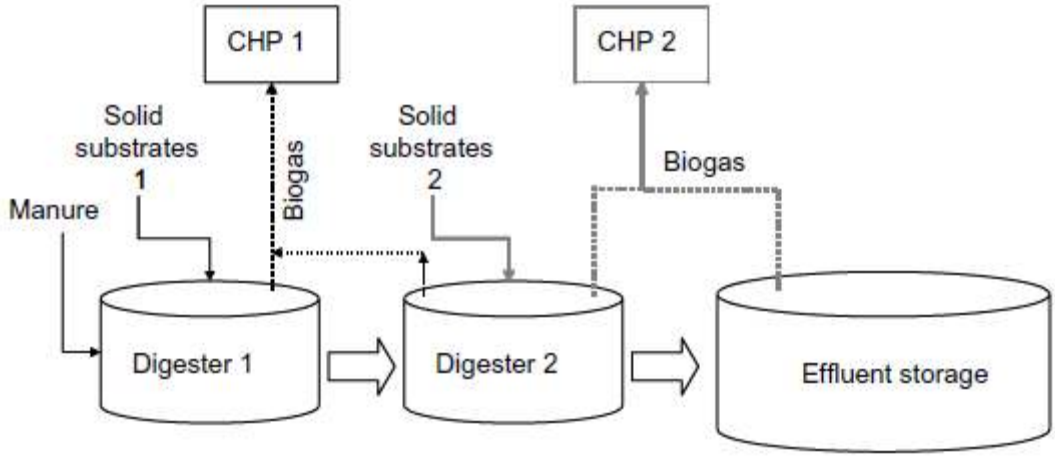


Figure 2.13. Scheme of the studied biogas plant. The original design is illustrated in black, the additional parts which belong to the process enhancement grey.CHP – Combined heat and power plant.

Table 2.10. Summary of digester parameters adapted from H. Lindorfer (2008).

Parameter	**Unit**	**Phase 1**	**Phase 3**	**Difference**
Biogas production	[$Nm^3 \cdot m^{-3} \cdot d^{-1}$]	1.50	2.91	194%
Methane yield Y_{VS}	[$Nm^3 \cdot kg^{-1}$ VS]	0.40	0.36	-10%
HRT	[d]	129.6	74.6	-58%
VS degradation rate	[%]	88.2	83.1	-5.8%
OLR	[kg VS$\cdot(m^3 \cdot d)^{-1}$]	2.11	4.25	201%
Electrical yield	[kWh$\cdot kg^{-1}$ VS]	1.44	1.50	4.2%

The higher loading rate change was chosen as it doubled the electricity obtained from the plant. Table 2.6. shows the effect of this change. The specific yields all suffer but not by very much compared with the increase in output and the reduction in HRT. This is a good example of why a slightly less efficient process was chosen, as it may improve other parameters. In terms of energy production per hectare doubling the loading doubles the land area needed but only 179% of the methane is produced. The difference between phase 1 and phase 3 is that the second stage has moved from digester 2 to a covered storage tank so in reality the system volume has increased from 3850m^3 to 7650m^3. In the light of this the specific methane yield drops from 0.81$Nm^3/(m^3.day)$ - phase 1 to 0.73 $Nm^3/(m^3.day)$ - phase 3. For higher specific methane yield a larger digester is needed and this is where market considerations win out as there is much more land available than digester volume at present. The land area is finite so to increase the amount of bio-fuel available there has to be more digester volume available per unit mass of crop, the reverse of the current situation.
Lindorfer concludes;
However, the most serious development connected to the enhancement is the rising transfer of partly degraded organic material into the effluent storage. This causes a strong increase of the residual methane potential in the effluent and therefore atmospheric emissions of greenhouse gases.

Collecting the gas from the covered storage is the simple solution but then this system should be considered on the whole volume with an HRT of 180 days due to winter spreading regulations.

2.8 Review Summary

The review shows the large range of reactors and systems available for on-farm anaerobic digestion as well as a diversity of feedstock material. AD is a much better energy conversion technology than first generation bio-fuels and can conserve nutrients on the farm unlike biomass combustion. The abetment of GHG emissions from animal slurry is bringing AD to the farm, while energy crops offer a great opportunity to elevate gas yields above the residual from animal slurries. For this reason the use of energy crops is well under way in Austria and Germany and Britain will follow (DEFRA 2009). Ryegrass features as an energy crop but it is not favoured in Germany where maize is the preferred feedstock. The agricultural landscape in the UK is very different, here grass crops dominates and maize is a minor crop. Ryegrass is problematic within the dominant CSTR systems and this brings the question; are other

systems more suited to whole crop digestion? There are a variety of digester systems available that are proven operationally but they have not been specifically designed for crop use. Crop digestion imposes the need to maximise the energy yield per hectare, rather than, per unit volume of digester, which is more commonly the goal. The CSTR reactor systems suffer from the washout of feedstock as reported in section 2.7 and accounts for methane lost in storage tanks reported by Amon (2006),section 2.2. This effect is exacerbated by high loading and short HRT; with respect to the destruction rate to the feedstock. The theoretical considerations of reactor hydraulic design (Appendix B), show that that there is scope for experimental development of the concept of a batch or plug flow system for digestion of high solids, energy crop materials. As the ABR reactor is suited to liquid feedstocks it is therefore not considered appropriate for single phase energy crop digestion. The Dranco, Valorga and Linde plug flow reactors were developed for the dry digestion of MSW and have been switched over to energy crops but the question of whether dry digestion is optimal for specific gas yield is unanswered.

Recent review papers looking at grass digestion, Prochnow et al (2009); Murphy (2010), show that although grass is well established as an energy crop feedstock it is less well investigated in the laboratory. This is surprising considering the variation of species, yield and the importance of the growth states of the grass as well as the various storage options and system configurations. The majority of the work published, with some notable exceptions, is from German and Austrian authors. Of the fifteen or so studies that can be identified since 1997 nearly all are carried out at meseophilic temperatures under batch and semi-continuous feed regimes which is good for comparison but does not always apply to the UK situation.

2.8.1 Basis for research to be performed

Ryegrass was selected for further work not because it is the best crop to digest from a process point of view, but because it is the most abundant and will be important in the take-up of farm scale AD unless there are drastic changes to land use in the UK.

Batch and plug flow operation are to be investigated as they offer theoretical advantages over the more commonplace CSTR in terms of control of the process, handling and guaranteed residence time. A number of plug flow reactor designs available use dry digestion in vertical or horizontal tubes or are liquid only, partitioned or compartmentalised digesters. The extent to which a wet digester is plug flow is subtle and can be misunderstood so the range between liquid only and dry digestion is

in practice inhabited by the CSTR regardless of its shape. Digester performance is driven by economics and practicalities rather than optimised for energy yield per unit area of land. To address this primary issue a number of the important process parameters will be examined to identify how plug flow operation can optimise the digestion of energy crops.

In any system the loading rate is a primary control and this is bound up with the hydraulic retention time, and the actual residence time. With dry plug flow rectors a large portion of digestate is recycled but precisely how this affects the process is not clear. The benefit of the use of recycled digestate in plug flow or batch systems has been touched upon by a few authors, but this aspect which offers an additional opportunity to control the reactor conditions merits more investigation.

Independent of the influent and effluent conditions is stirring and heating. Temperature is the subject of much investigation but is independent of feedstock and reactor configuration. The mesospheric range has been chosen here as it is the most common range making comparison much more possible. Stirring has also had some attention as the link between mixing and gas yield is not simple and there are a number of stirring modes available. The mode and the extent to which stirring is needed, with its impact on the energy output will also be considered.

Chapter 3

Methods and Materials

3.1 General

3.1.1 Reagents

Except where otherwise stated all chemicals used were of laboratory grade.

3.1.2 Water

All reagents used in chemical analysis were prepared with ultra pure water with a conductivity of < 20 MΩ · cm at 25 ºC using a MilliQ electrodeionisation system, (Millipore Corporation, UK).

Feedstocks for digester experiments were prepared using tap water.

3.1.3 Laboratory practice

All laboratory operations were carried out using good laboratory practice in a framework of using risk assessments and, where necessary, COSSH assessments as appropriate. All equipment, laboratory apparatus, and analytical instruments were operated in accordance with the manufacturer's instructions.

All glassware and labware used in the preparation of reagents, dilution media and for storing of samples was washed using laboratory detergent, rinsed in tap water then deionised water.

3.2 Analytical measurements

3.2.1 pH

This was measured using a Fisher plastic gel FB68800 probe linked to a PC with a Logit live data logger which was calibrated on each use by a 2-point calibration with buffers pH 4.0 and pH 7.0 (± 0.01 @ 25^{O}C). The buffers solutions were supplied by Thermo Russell of Auchtermuchty, Fife, and were disposed of after each use.

3.2.2 Alkalinity (full method in appendix A)

Alkalinity was measured according to Standard Method 2320 B (APHA 2005). Sulphuric acid was used as the reagent at concentrations of 0.10N and 0.25N. To estimate the bicarbonate and VFA alkalinity contributions the sample was first titrated to pH 5.75 to calculate the Partial Alkalinity (PA) and then titrated from 5.75 to 4 to calculate the Intermediate Alkalinity (IA). The ratio of the IA and PA was used as an indicator of reactor stability as proposed by Ripley et al (1986).

3.2.3 Gravimetric analysis (full method in appendix A)

Total solids (TS), Total Suspended Solids (TSS), Volatile Solids (VS) and Volatile Suspended Solids were analysed according to Standard Method 2540 G (APHA 2005).

3.2.4 Volatile fermentation products

Volatile Fatty Acids (VFA) were quantified in a Shimazdu 2010 Gas Chromatograph (GC), using a flame ionization detector and a capillary column type SGE BP 21 (30 m long, 0.25 mm i.d., 0.25 µm thickness) with helium as the carrier gas at a flow of 190.8 ml min^{-1}. The GC oven temperature was programmed to increase from 60 to 210 8C in 15 min, with a final hold time of 3 min. The temperatures of injector and detector were 200 and 250 ºC, respectively. The volume injected was 1 µl. Prior to GC analysis, the samples were prepared by acidifying to 10% with formic acid and centrifuging at 10,000 rpm for 10 min.

The samples were measured against a standard containing acetic, propionic, iso-butyric, n-butyric, iso-valeric, valeric, hexanoic and heptanoic acids each at 500 mg l^{-1}. The standard was then diluted to give 3 standards containing the VFAs at 50, 250 plus the original solution at 500 mg l^{-1} which were used for calibration of the GC.

3.2.5 Biogas composition

A biogas sample taken from a displacement gasometer (see section 3.5) was injected into a Tedlar bag (SKC Ltd, UK) for storage and transport. Gas composition was measured using a Varian CP 3800 GC with a gas sampling loop using argon as the carrier gas at a flow of 50 ml min^{-1}. The GC was fitted with a Hayesep C column and a molecular sieve 13 x (80-100 mesh) operated at the temperature of 50 ^{o}C. The GC was calibrated using a standard gas containing 35% of CO_2 and 65% of CH_4.

3.3 Substrate

The substrate used in all the experiments was ryegrass (*Lolium perenne*) collected fresh in the summer of 2006 from one cut. The fresh grass had an initial TS ranging between 160 g kg^{-1} and 320 g kg^{-1} and VS between 120 g kg^{-1} and 280 g kg^{-1} (Figure 3.1a.) and was prone to acidify in parts and dry out in others. Freezing the quantities necessary for the experiments was impracticable and it was therefore decided that the most appropriate preservation method was air drying to produce hay. Hay making is carried out at a large scale on farms and is a traditional practice for the preservation of animal feed; it is equally applicable as a practical method for the preservation of energy grass. Air drying of grass in the laboratory stabilised the moisture content, retained the

colour and improved the handling characteristics of the grass to a point where it did not stick to equipment. The hay produced had a TS of 820 to 900 g kg^{-1} and corresponding VS of 750 to 820 g kg^{-1} (Figure 3.1b.).

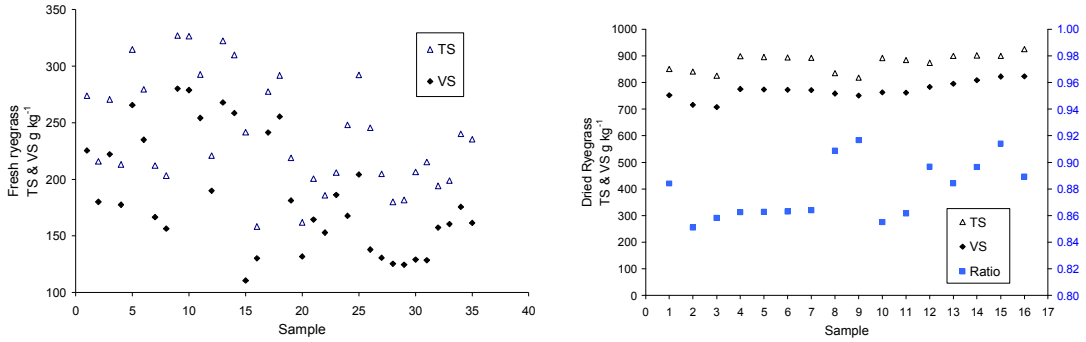


Figure 3.1. a) Fresh Ryegrass solids data b) Dry Ryegrass solids data

In practice the grass actually fed to a grass digester would probably vary seasonally: in the summer months grass is more abundant and water is more scarce than in the winter, so an operator may choose to feed fresh grass in the summer and stored hay, with water addition, in the winter. For practical reasons in the laboratory the use of hay was preferred for accuracy when calculating feed values, but before use water was added to bring the hay back to 80% moisture content on a TVS weight basis: in this way fresh grass feeding was standardised. This approach was considered preferable as ignoring the water content of the fresh grass was not realistic at the farm scale. Unless otherwise stated no water other than that which would be contained in fresh grass was added. The characteristics of the rye grass when fresh and after drying (hay) are given in table 3.1.

Table 3.1. Rye grass hay and sewage sludge characteristics. *(Ryegrass solids.xls)*

No. Samples (x)	Rye grass hay (16)		Rye grass fresh(35)		Sewage sludge	
	Average	STD Dev	Average	STD Dev	Average	Range
Total Solids g kg^{-1}	876.90	32.23	239.07	48.53	33.44 g L^{-1}	3.49 g L^{-1}
Volatile Solids g kg^{-1}	770.95	32.30	186.11	50.35	20.57 g L^{-1}	3.08 g L^{-1}
VS range g kg^{-1}	114.85		155.64			
VS:TS	88%	2%	78%	9%	61.5 %	0.1 %
Inert material w/w	10.6 %	2.0%	5.1%	2.5%	1.8 %	0.01 %
Moisture w/w	12.3 %	3.2 %	76.8%	5.7%	95.2 %	0.01 %

3.4 Inoculum

The initial seed sludge used to inoculate test digesters was anaerobically digested sewage sludge obtained from Millbrook Wastewater Treatment Works, Southampton, UK. Once collected the seed sludge was stored in the laboratory at 37 ^{o}C before use. The characteristics are given in table 3.1.

Except where otherwise stated all batch simulation plug flow experiments were started with this initial seed, then subsequent batches in the same experimental run used digestate from the previous batch as the inoculum for the succeeding batch.

3.5 Digesters

Two sizes of digester were used in the experiments. For all the small-scale trials digesters with a 1.5-litre working volume were used. Each digester was fitted with a mechanical stirrer that continuously mixed the contents when required or could be turned off when a non mixed digester was required. The temperature of the digesters was maintained at 37^{o} C by circulation of water through heating coils surrounding each digester, with the whole digester being placed in an insulated box. Unless otherwise stated digesters were run in duplicate in all trials. Gas production was measured with a bell over water gasometer in which the water was saturated with salt. The gas was introduced above the water surface in the bell and the weight of the bell produced a 0.5 mb pressure on the digester.

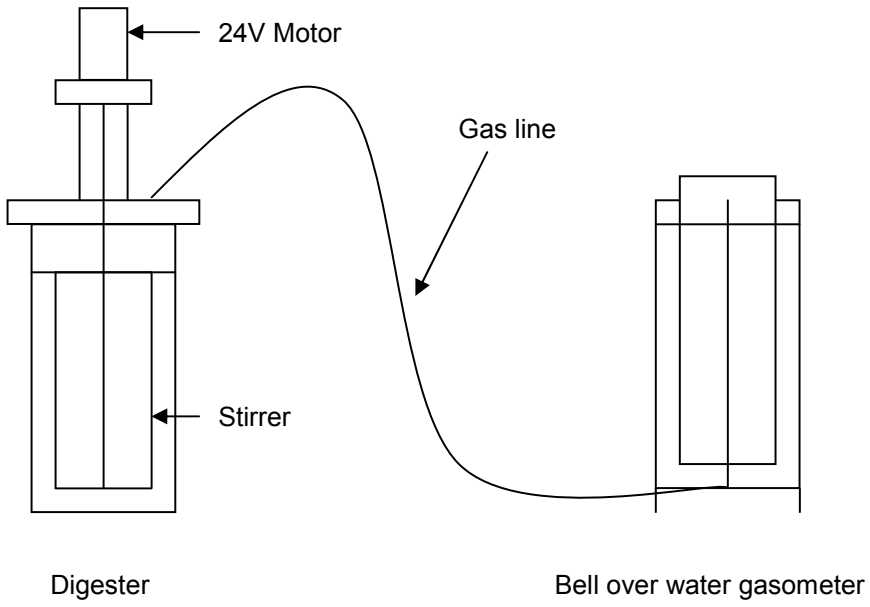


Figure 3.2. Schematic diagram of 1.5 litre digesters.

Two digesters with 30-litre working volumes were also used. These were of a similar design to the 1.5 litre digesters but were individually heated to 37^{o}C within insulated boxes. The larger-scale digesters were used to assess different performance indicators for scaling comparisons with the 1.5 litre digesters.

3.6 Monitoring

3.6.1 Biogas collection and measurement

Gas production was measured once a day from the vertical displacement of the bell of the gasometer. This measurement was then corrected to Standard Temperature and Pressure (STP) taken as 0 ^{o}C and 101.3 kPa. Where appropriate the gas production of any control digesters was subtracted from the gas production of test digesters to remove the contribution from the initial inoculum. The gas composition was taken as an average of daily samples weighted against gas production. A proportion of the gas was taken in a Tedlar gas bag and the composition determined by gas chromatography (section 3.2).

3.6.2 Analytical determinations

Total solids (TS) and volatile solids (VS) were determined at the beginning and end of experimental runs. Alkalinity and pH were used to monitor digester stability and provided values for both total bicarbonate alkalinity as well as a partial alkalinity which indicates the contribution of the various sources of buffering in the digester.

Chapter 4

Methane potential of ryegrass

(Source file *060928 T1 1.5L Baseline 5,10,15,20,25 g VS.xls file*)

4.1 Use of 1.5L digesters to test a range of loading rates with ryegrass as substrate

The aims of the experiment were to find a suitable Organic Loading Rate for subsequent batch trials and to determine the specific methane yield (in m^3 CH4 kg^{-1} VS added) of this particular ryegrass feedstock.

A standard Biochemical Methane Potential (BMP) test was modified by testing at a range of initial loadings higher than those recommended for the BMP test as detailed in Appendix A. The modified test is referred to as the Baseline Methane Potential test. Both the BMP and the Baseline Methane Potential test are batch tests where reactions are allowed to proceed to completion and compared to controls without feedstock addition. The BMP provides a measure of the ultimate methane potential against which the performance of other digestion modes can be compared. In this case the comparison with planned plug flow trials was particularly useful as the test used the same equipment and feedstock.

The use of higher initial loadings was intended to establish whether there was an upper loading rate at which digestion would fail and if so to record the manner of that failure. The experiment was based on the assumption that methane production is a measure of the net outcome of the microbial processes. In addition to cumulative methane production daily production rates were considered in order to give a more sensitive indication of the possible biological state of the process; this approach also highlights the differences between reactors within pairs and across the experiment. The first order kinetic constant was estimated from each loading rate to give an indication of the digestion characteristics of ryegrass.

4.2. Experimental method

Six pairs of 1.5 litre digesters were each inoculated with 1 litre of sewage sludge and fed on ryegrass at initial biomass loading rates (IBLR) of 5, 10, 15, 20, 25 g VS l^{-1} to give a range of VS loadings and of inoculum: substrate ratios calculated on a VS basis, Table 4.1. A control pair with inoculum only was included and treated in the same way as the others to allow determination of the sewage sludge contribution to the methane produced.

The digester volume was in all cases made up to 1.5L with water. For the control pair this required 500 ml and in the experimental digesters the amount of water added decreased with increasing load due to the increasing volume of ryegrass added. The digesters were run until they were producing the same amount of methane per day as the control, which was close to zero.

Table 4.1. Loading rates for 1.5 litre digesters.
('Feed regime'. 060928 T1 1.5L Baseline 5,10,15,20,25 g VS.xls file)

Digester No.	Feed VS load g L^{-1}	VS load grams	Inoculum :Substrate Ratio	Total load g VS L^{-1}
1	0	0	Control	13.71
2	0	0	Control	13.71
3	5	7.5	4.16	18.71
4	5	7.5	4.16	18.71
5	10	15.0	2.08	23.71
6	10	15.0	2.08	23.71
7	15	22.5	1.39	28.71
8	15	22.5	1.39	28.71
9	20	30.0	1.04	33.71

4.3. Experimental results

The volumetric methane production at the different loading rates was proportional to the loading although the agreement between paired digesters was less good at the higher loading rates (Figure 4.1.). At these two loadings, one digester in each pair failed to stir for the first part of the trial due to the large quantity of added material, and this is the most likely explanation for the differences.

The average values for methane production are shown in Figure 4.2. and it can be seen that all digesters followed a rapid, almost linear, initial rate which then decreased

until methane production stopped. At the higher loadings this initial phase lasted longer but all loadings showed a similar methane production rate.

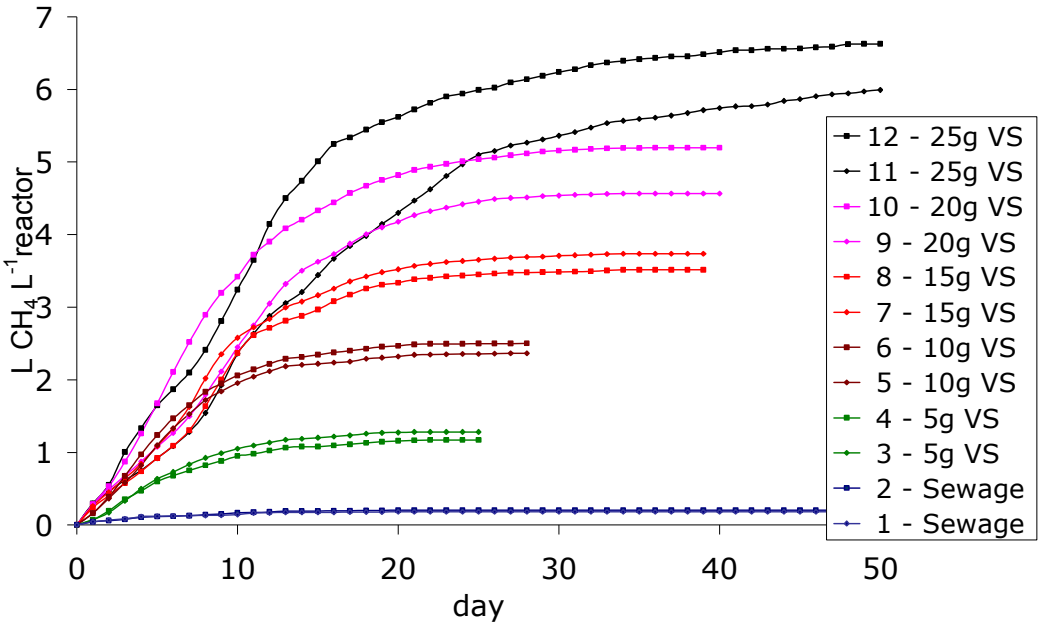


Figure 4.1. CH4 production in all the digesters.

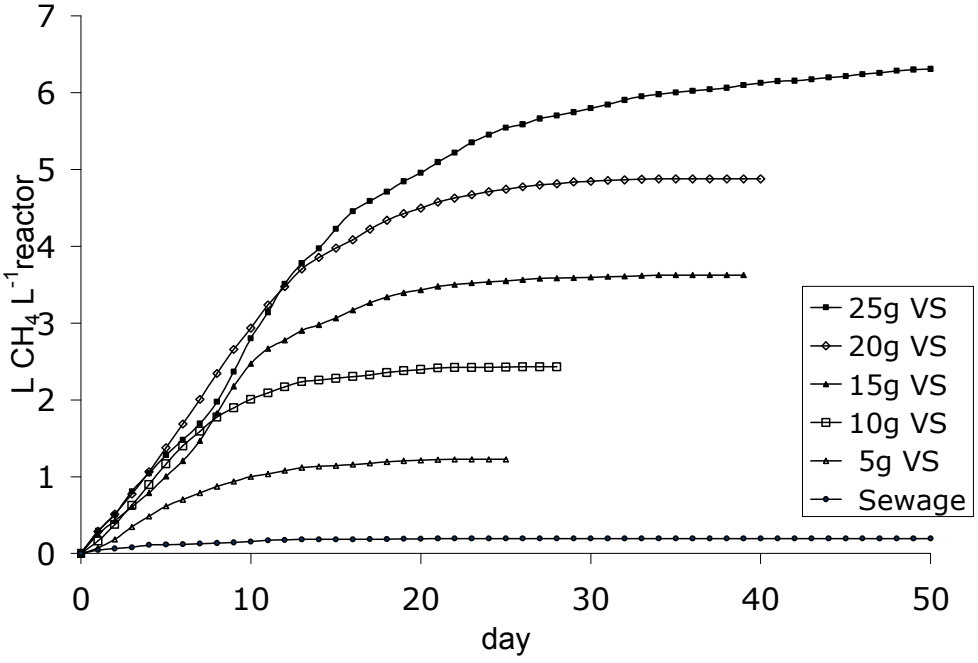


Figure 4.2. Total CH4 production, averages for paired digesters at each IBLR.

The methane volumes were also plotted as the specific methane production (l CH4 g^{-1} VS added, for each of the loadings (Figure 4.1.) with the final values for the specific methane yield within the range 0.234 – 0.265 l CH4 g^{-1} VS and an average value of

0.245 l CH4 g^{-1} VS. Digesters fed at the higher loadings again show the greatest variability, with the highest loaded digester showing the highest specific methane yield of 0.265 l g^{-1} VS, despite it failing to stir except for three days [5 to 8]. Also in the digesters at slightly lower loading the one that stirred continuously showed the lowest specific methane yield. It was clear from both pairs that stirring resulted in lower methane potential.

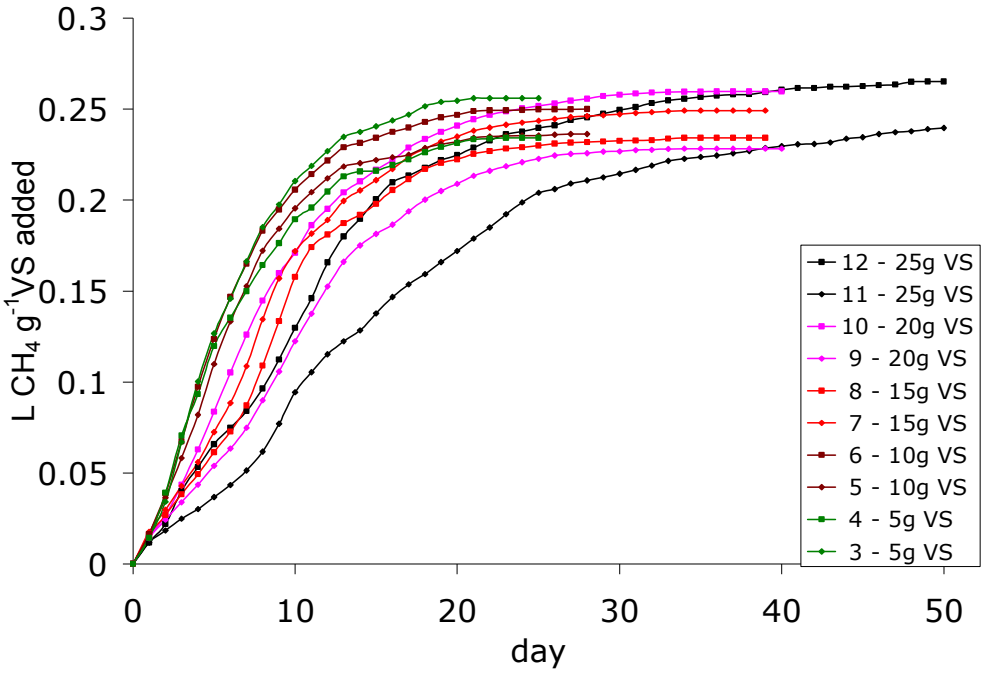


Figure 4.3. Specific methane yield per gram of VS added

If the data are plotted as a daily volumetric methane production (l CH4 l^{-1} day^{-1}) the lower loadings of 5 and 10 g VS l^{-1} showed one main production peak within the first 15 days that reduced to near zero, while the 15 g VS l^{-1} loading had an initial methane production peak, a slowing down, and then a main production peak spanning day 6 to 12 before production reduced to zero (Figure 4.4).

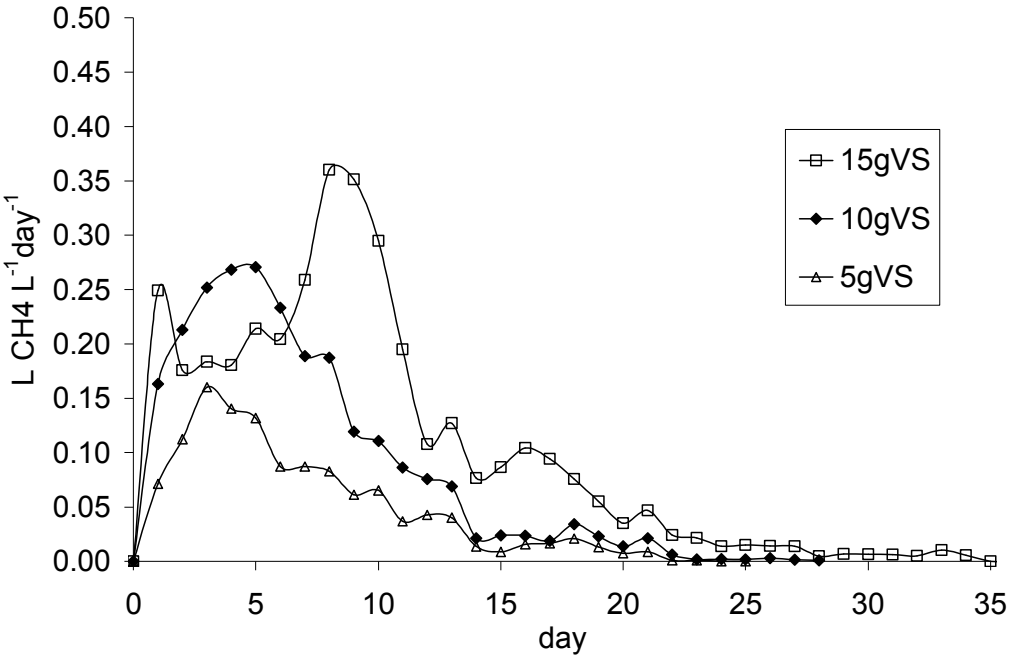


Figure 4.4. Daily methane production lower loads.

Interpretation of the results at the two highest loadings is complicated by the stirrer malfunction in one of each pair of digesters.

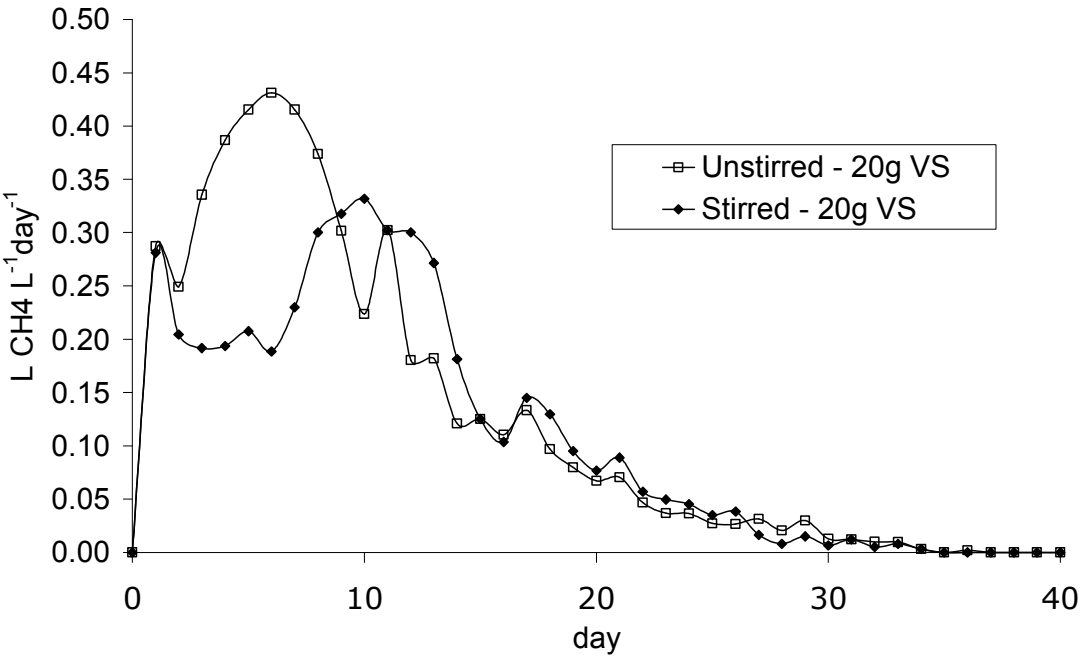


Figure 4.5. Stirred & unstirred 20 g VS l^{-1}

At the 20g VS l^{-1} loading (Figure 4.1.5), both digesters showed a similar initial peak on day one followed by a dip lasting 6 days before production resumed to the first day's level and then to the main production. This contrasted with a one day dip for the unstirred digester followed by the main production peak.

At the 25 g VS l^{-1} loading (Figure 4.6.), the unstirred digester had a larger initial production peak than the unstirred digester, but both showed a second peak. The curves all have a saddle that indicates an interruption of the process but this is less marked in the unstirred digesters.

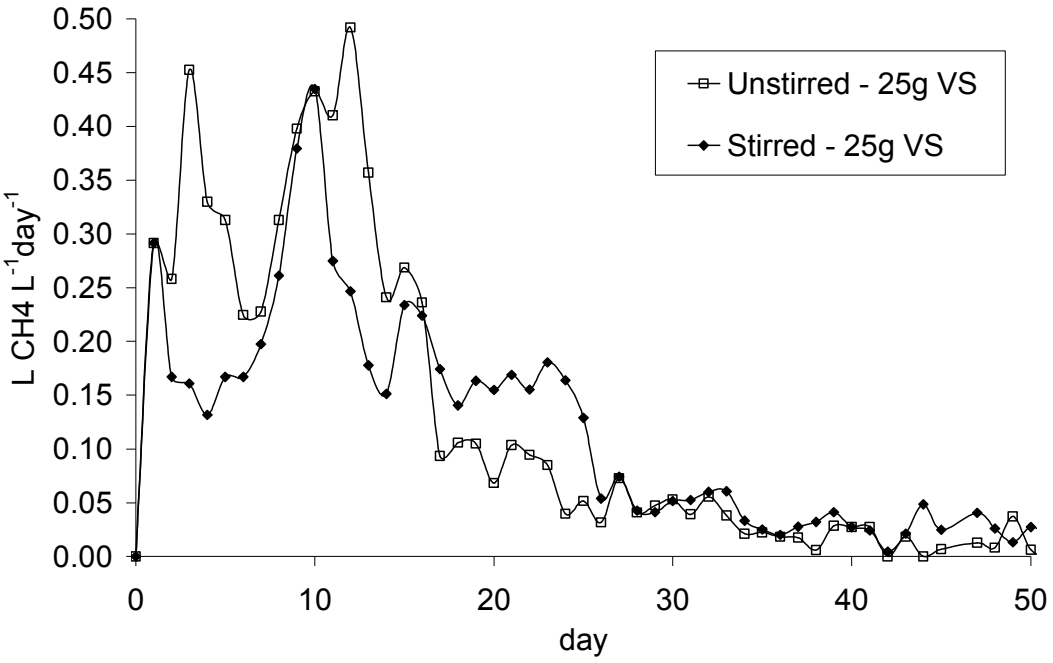


Figure 4.6. Stirred and unstirred 25 g VS l^{-1}.

4.4. Determination of the first order kinetic constant

Figure 4.7. shows the data plotted to give the range of slopes corresponding to the reaction rate constant, **k**. It can be seen that this constant decreases with increasing loading from 0.0662 to 0.0204 day^{-1} for the 10 g VS l^{-1} and 25 g VS l^{-1} loads respectively. The exceptions to this are the two unstirred digesters that out-performed their twins, and one of the digesters at the 10 g VS l^{-1} loading (R5) that had a slightly higher k value than the digesters operating at the lower loading of 5 g VS l^{-1}.

The alkalinity in each digester was measured at the end of the experiment as an indication of its final stability. The control digesters had a final total alkalinity of ~5000

mg L^{-1} of $CaCO_3$ while all test digesters showed higher value which were similar in each pair with R5 & R6 at 10 g VS L^{-1} having the highest value of ~10,000 mg L^{-1} of $CaCO_3$, and the alkalinity decreasing in digesters with higher loadings.

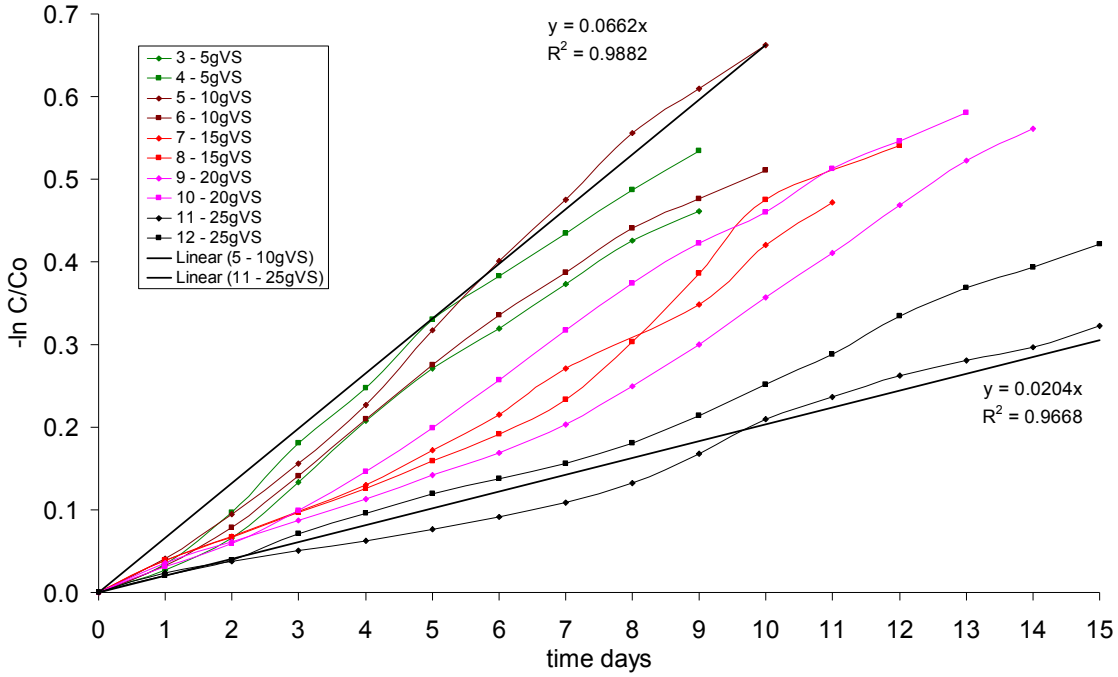


Figure 4.7. Estimation of kinetic constant for the initial phase of digestion.

4.5. Discussion

At all loadings digestion appeared to be complete and the overall process was not inhibited or slowed down by the low inoculum ratios. High initial loadings made mixing more difficult, however. There was reasonably good agreement between paired digesters for volumetric methane production at the lower loadings where stirring was achieved, but agreement was less good where one of the digesters failed to stir. The specific methane yield obtained at the different loadings was very similar in all cases, although stirring again appeared to have an effect, with unstirred digesters showing a slightly higher value. The unstirred digesters also showed slightly better volatile solids destruction, again indicating that at higher loadings stirring may lead to some inhibition. It is quite probable that at the lower inoculum to substrate ratios there is a mismatch between the rates of hydrolysis/acidification and methanogenesis which may lead to some acidification in the digester; this is likely to be aggravated by stirring which prevents the formation of locally favourable zones for methanogenesis ,Vavlin (2004) as discussed in section 2.6 This is supported by the daily volumetric methane productions which show that at loads between 10 g VS l^{-1} and 15 g VS l^{-1} methane is produced without interruption. At higher loads there appears to be some inhibition in

methane production after an initial peak; the effect is more pronounced where the digesters are stirred. Despite some signs of early inhibition none of the digesters failed, and the recovery of the higher loaded digesters may indicate that the inhibition is more a result of the low inoculum to substrate ratio than of the loading on its own. The recovery of the higher loaded digesters is therefore likely to be growth-mediated, with an increasing number of methanogenic bacteria able to match the acidification potential as time progresses within the batch. As the specific methane yield over most of the digester pairs agreed quite well, it would seem that the inoculum to substrate ratio was not of prime importance in achieving the maximum yield provided the reaction was given enough time to reach completion. It would, however, appear better to avoid this potential inhibition and to use a lower loading or higher I:S ratio in further experiments unless acclimatisation occurs or some advantage is seen in using unstirred digesters.

Table 4.2. Summary Results 1.5L Baseline trial.

digester No.	Feed load g VS l^{-1}	Methane Production l l^{-1} digester	VS Destroyed %	Inoculum to Substrate Ratio (VS)	Specific CH4 yield l g VS^{-1} added
R3	5	1.28	52	4.16	0.256
R4	5	1.17	45	4.16	0.234
R5	10	2.36	41	2.08	0.236
R6	10	2.50	51	2.08	0.250
R7	15	3.74	45	1.39	0.249
R8	15	3.51	44	1.39	0.234
R9	20	4.57	44	1.04	0.228
R10	20	5.19	54	1.04	0.260
R11	25	5.99	52	0.83	0.240
R12	25	6.63	55	0.83	0.265
		Average	**48.3**		**0.245**

The average specific methane yield was found to be 0.245 m^3 CH4 kg^{-1} VS added.

The reported methane specific yields from other sources is shown in table 4.3. they were all carried out under batch conditions and at meseophilic temperatures with a mono substrate. Whether these experiments were specifically from biochemical methane potential (BMP) assays is unclear but many other factors are likely to have a more influence on the reported values. What is clear is the wide range of methane

potential ranging between 0.198 and 0.650 m^3 CH_4 kg^{-1} VS. This may be characteristic of the grasses, the cultivar and/or its cutting time. There is variability between feedstocks grown in different parts of Europe and the difference between the work of different research groups will be due to a number of factors including geographic location, variety used and harvesting practice. As stated in Chapter 2.5 the theoretical methane potential, given stoichiometrically, is 0.305 CH_4 kg^{-1} VS added, therefore any value much greater than this should be treated with caution. The reason for this trial was to establish a methane potential for this particular grass for later comparison as the reported range is so great.

Table 4.3. Reported specific methane yield with grass crops

Source	Feedstock	m^3 CH4 kg^{-1} VS added
Neylan 2006 (ave)	Ryegrass hay - Sept	0.23 - 0.27 (0.245)
Mernhert et al 2005	Ryegrass, Cocksfoot, meadow foxtail ensiled.	0.30 - 0.32
Mernhert et al 2002	Ryegrass – fresh / ensiled	0.629 / 0.650
Kaiser and Gronauer 2007	Ryegrass 9 varieties fresh / ensiled	0.198 -0.360
Prochnow et al 2005	Meadow foxtail first cut June	0.298
	September	0.229
	March	0.155
Amon et al 2007	Extensive grass land, silage Aug	0.315
	Silage Nov	0.137
Kaparaja et al 2002	Grass hay, comunition – 5mm	0.270
	10mm	0.350
	20mm	0.320
Weiland (2003)	Ryegrass	0.41
Pouech (1998)	Ryegrass Fresh/ ensiled	0.39 / 0.41
Salter (2004)	Ryegrass Cropgen data	0.25 -0.41

The ryegrass used in these experiments showed a value at the lower end of the range for methane potential bt close to the theoretical value. Apart from the grass itself several other factors could influence this result. These include: sample storage, sample preparation, source of inoculum, temperature, experimental set-up, and errors in the measurement of gas volumes and gas composition. The experiment used dried

grass harvested late in the year which had possibly lost a proportion of its soluble sugars and may have been more fibrous than grass harvested earlier in the season. As mentioned in Chapter 3.0 fresh grass was too variable for laboratory use so hay was used instead. As silage is thought by some to be a better substrate for methane production compared to fresh or dried grass. In practice this is difficult to quantify, as the silage making process not only changes the characteristics of the grass but also causes weight losses that are often not taken into account in the results. It is also the case that ensiling will result in the formation of liquor-bound soluble acids that have a methane potential. These acids being soluble and volatile are not accounted for in the solids determination, as they will boil off during the analysis contributing to the moisture content but not the VS. The VFA will however produce gas giving a higher specific methane yield for a given VS value. It is therefore possible that the BMP can be overestimated for ensiled material if expressed in terms of VS added.

Errors in gas composition could also influence the estimation of specific methane yield. In this experiment all data are expressed as methane volumes rather than biogas volumes. The biogas from the digesters was collected over water in gasometers, and some of the CO_2 would have been lost through dissolution and as a result of diffusion through the water to the atmosphere. This leads to underestimation of biogas production, and therefore biogas volumes have not been given. Methane is much less soluble and therefore the results are more reliable. In later experiments biogas was collected over saline water to minimise losses of CO_2, allowing biogas volumes to be accurately reported. Methane and carbon dioxide concentrations in the biogas were measured using a GC, but possible atmospheric contamination of the biogas sample was also checked for using a gas flow meter with O_2 detection. Where oxygen was found as a contaminant a correction to the gas volume was made. The methane volumes reported were therefore considered to be accurate and not based on the assumption that biogas has a fixed percentage of methane, a mistake that is sometimes made when interpolating BMP data.

With the exception of the two digesters that failed to stir, the initial rate of methane production was very similar at all loadings. The unstirred digesters showed a higher methane production rate, however, indicating that stirring was preventing the digesters giving their best performance. The effect is seen in the difference in the kinetic constant k for the two conditions but there is no reason why the ultimate methane yield should differ. There was some variation between the specific methane yield, and the VS destroyed at the end of the experiment also suggested some difference as this ranged

from 41 - 55% with a mean of 48%. Some of this variability could be accounted for by the partitioning of volatile solids between the solid and liquid phases which resulted in 61% VS in the liquid digestate and 77% VS in the separable fibre. The feedstock itself contained 86% VS.

The inoculum used in the experiment had not been acclimated and it is possible that more methane could be produced by an acclimatised microbial consortium. The results may therefore be conservative when compared to systems that have an adapted inoculum.

It is likely that the specific methane potential found, although at the lower end of the range, is accurate and any differences are a result of the ryegrass itself rather than experimental design. The experiment was regarded as successful as it provided a baseline with which further experimental data using this substrate could be compared. It is unlikely that the ultimate specific methane yield or VS destruction could be improved on without acclimatisation of the population. The baseline values provide a starting point on which to base further experiments as well as highlighting some interesting findings relating to mixing, loading rate and I:S ratio.

Other effects noted as a result of ryegrass digestion were the general improvement in pH at the end of the run, possibly due to the evolution of ammonia. There was also an improvement in alkalinity. This was not clearly linked to the loading rate, but was useful in showing that the digesters were more stable at the end of a run than at the start.

In the experiment the I:S ratio was reduced as the loading increased, but this factor appeared to have no direct effect on the other indicators. The pair of digesters with the lowest loading (R3 & R4) had the highest inoculum substrate ratio and might be expected to have the best performance. In fact the performance is similar to the higher loaded conditions and it would appear that this loading was well below any limiting factors such as the rate of hydrolysis.

4.6 Conclusions

Although this modified BMP test value of 0.245 $m^3 CH_4 kg^{-1}$ VS was low compared with other authors it was successful in providing a baseline to compare the use of this ryegrass this and subsequent experiments. The stepped loading was designed to home in on an optimum specific methane yield and this was found at different initial loadings. This was further complicated by the anomaly produced with the absence of

stirring and deserves further attention as it was replicated at two loadings and produced the best specific yield. The inoculum to substrate ratio resulting from the stepped loading needs further investigation as it may be the control parameter available to plug flow /batch operation that is not available to the CSTR operation. Investigating this will hopefully determine whether I:S ratio increase will increase the breakdown as marked by the kinetic value which seems to be the case here. The first order kinetic constant was estimated for all the loading rates and was between 0.0662 to 0.0204 day^{-1}. The k value was inversely proportional to the loading rate. The broader question of whether acclimation of inoculum to feedstock can out perform the BMP values and hence the value of the BMP assay remains to be answered.

Chapter 5

Comparison of separated solid or liquid as an inoculum in a simulated plug flow regime.

(Source 061027 T2 and T3 1.5L Solid v Liquid & Stirring 10-20 g VS.xls)

5.1 Introduction

It was shown in Chapter 4 that the loading rate/ inoculum substrate ratio influenced the performance of the reactors and for continuous operation a plug flow digester requires that digestate to be recycled as inoculum. It was noted that ryegrass digestate was easy separable and from solids determination the digestate liquor was significantly lower in VS than sewage sludge while the separated solids were higher. At full scale it is common for AD plants to separate the digestate and recycle the liquids to avoid the use of clean water, the solids are usually moved on to composting. This is operationally practical but may not be optimal for the process. The influence of each fraction was of interest as a plug flow reactor can be influenced by the amount and possibly type of inoculum. The basis for this experiment was to compare inoculum containing equal amounts of VS but differing in form, on gas production. One set of reactors was seeded with liquid only inoculum and another set had all the separated solids, made up with liquid inoculum. These reactors were set to run for a number of feed cycles following an ideal plug flow regime, to encourage acclimation of feedstock to inoculum and to improve the time taken to produce 70% of the ultimate gas, found in the previous trial (Chapter 4). This limit was set by inspection of the gas production curves that showed that the majority of the production occurs in the first third of the hydraulic retention time.

5.2 Concept of an ideal plug flow simulation

To model ideal plug flow experimentally a batch digester can be considered as a plug of homogenous material moving through a 'pipe' type system, with no dispersion forward or backward. The duration of the batch represents the time from entry into the 'pipe' to the time that it exits. Figure 5.1. shows a schematic of a linear plug flow digester which has been divided into equal compartments. These compartments are notional and represent the position of the batch digester as if it were moving through this 'pipe' type system. This is necessary to meet the condition of no axial dispersion

while allowing homogeneity within the plug, each position also represents one day's feed with inoculum. On day 1 the digester is charged with substrate and recycled inoculum and allowed to digest, on day 2 it is moved to the second compartment and so on until it exits the reactor. The time allowed for digestion can be varied and in this way optimised. The output digestate may be recycled, whole or separated, to a new batch as inoculum for fresh substrate addition.

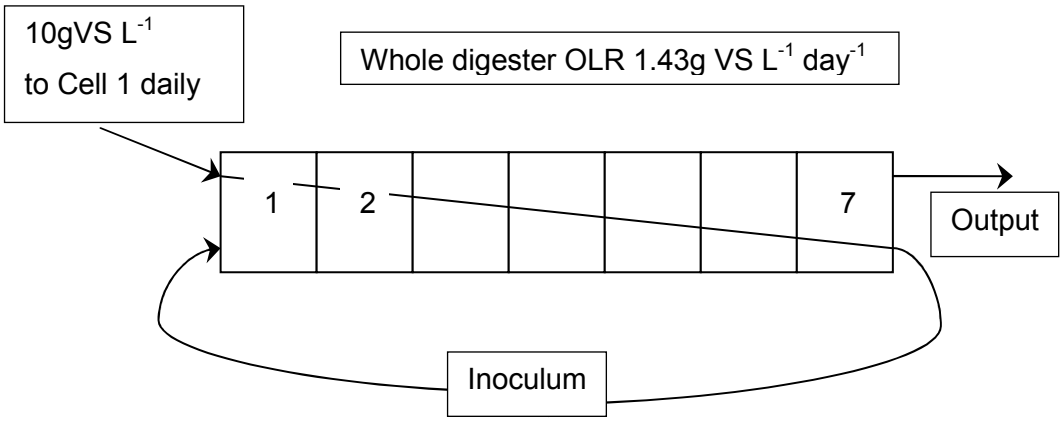


Figure 5.1. Schematic diagram of a plug flow digester modelled using batch digestion.

5.2.1 Parameters for a simulated plug flow

Hydraulic Retention Time (HRT) in the simulated plug flow digester is the flow through the reactor and as material is recycled the HRT is calculated on the volume of output compared with reactor volume in units of days.

The Initial Batch Loading Rate (IBLR) is the amount of feedstock volatile solids added per unit volume to the individual reactor or first compartment at the start of a batch run.

The Organic Loading Rate (OLR), in the simulated plug flow digester is the amount of feedstock volatile solids added per volume of the digester and divided by the length of time it is digested for. For example if the IBLR is 10gVS L^{-1} and this is digested over a seven day period then the OLR is 10÷7 = 1.43gVS L^{-1} day^{-1}.

Biogas production in the simulated plug flow digester is the total biogas production divided by the length of the batch run (days), i.e. the average daily biogas production.

5.3. Experimental method

5.3.1 Reactor setup

A batch experiment was run for 10 days at an IBLR of 10.0 g VS l^{-1} day^{-1} using seed sludge from the previous trial in order to regenerate the inoculum for the experiment (run 1). The digestate from this first run was then separated into its solid and liquid

fraction using a 1 mm stainless steel mesh sieve. Four 1.5 litre digesters were set up to receive an IBLR of 10 g VS L^{-1}. One pair received 1400 ml of liquid-only inoculum which contained 12.14 g VS L^{-1} to give a total volume with feed of 1500 ml. The other pair received all of the separated solids (at 53.18 g VS kg^{-1}) and 870 ml of liquid inoculum and the volume was made up to 1500 ml with water (Table 5.1). All the digesters therefore had the same quantity of inoculum, in terms of volatile solids, but with one pair having all of these solids derived from separated liquor whilst in the other pair the inoculum solids were mainly from the separated fibre fraction. In both pairs of digesters the I:S ratio was equal and the only difference between them was in the form the solids took. The digesters were set up in this way over a number of successive runs (runs 2 - 5) and the cycle time for each of these runs was set by the time required for 70% of the volumetric methane potential (as determined in Chapter 4) to be reached. This was 9 days at an IBLR of 10.0 g VS L^{-1} day^{-1} from the BMP trial. As the digesters may perform in different ways but the feeding regime requires all to be fed on the same day, the cycle length was reduced each cycle with reference to the BMP value.

Table 5.1 Initial loading of digesters.

Digester N^{o}.	Inoculum g VS		Feedstock g VS	Total VS	Water
[1.5 litre]	Liquid	Solid		grams	grams
D3	16.99	0	15.00	31.99	0
D4	16.99	0	15.00	31.99	0
D5	10.56	4.52	15.00	30.08	500
D6	10.56	4.52	15.00	30.08	500

5.3.2 Sampling

Samples were taken for solids analysis at the end of the first run and used to calculate the VS destroyed. Solid and liquid samples were taken from the homogenised material to be added as inoculum in run 2 in order to get an accurate measurement of the solids initially entering the system. At the end of each subsequent run (runs 2, 3 and 4) the solids were removed from the pair of digesters receiving the liquid inoculum, and used to make up the solids lost as a result of taking samples from the pair of digesters receiving the solid fibre inoculum. A record was kept of the amount of solid added back to the system as inoculum to each run to allow determination of the exact retention time and show to what extent the solids accumulated.

5.4. Experimental results

5.4.1 Cumulative volumetric methane production

Figures 5.2. and 5.3 show the cumulative volumetric methane production over successive batch runs in digesters D3 and D4 using the separated liquor from the previous run as the inoculum. Figures 5.4. and 5.5 show the cumulative volumetric methane production over successive batch runs in digesters D5 and D6 using the fibre and a proportion of separated liquor from the previous run as the inoculum. In each case the methane production from the first experiment (Chapter 4) using sewage sludge as an inoculum is included for reference. The results from the first run (run 1) were disregarded when making comparisons as the inoculum was exhausted after the digesters had been allowed to reach zero gas productivity in the first experiment (Chapter 4). In all subsequent runs (2-5) there was an improvement in methane yield with each successive addition of feed and retention of the inoculum. This allowed the run length to be gradually decreased so that run 5 lasted for only 7 days before attaining the target of 70% of the volumetric methane potential. There were, however, differences in the performance of paired digesters. Overall the best performing digester in terms of volumetric methane production was D6 (solid inoculum) but the second digester in this pair, D5, performed very poorly. This was subsequently traced to a cold spot that developed within the heating box in the slot occupied by D5 which meant it was operating at 29 ^{o}C while the others were close to 37 ^{o}C.

Due to the digester management protocol all the digesters had to be fed and sampled on the same day; therefore some of the digesters attained the target of 70% of the BMP yield while others did not. Run 2 was 11 days long, and D5 and D3 did not achieve the target within 11 days while D6 and D4 did, on the 7th and 8th days respectively. Run 3 was 10 days long, D3 and D5 did not make the target but are closer than in the previous run. D4 and D6 again achieve the target on day 8 and day 6 respectively. Run 4 was 9 days and this time all digesters made the 70% target indicating that acclimation was still taking place. The performance of all the digesters was very similar on this run with the exception of D6 which nearly reached the target in 5 days.

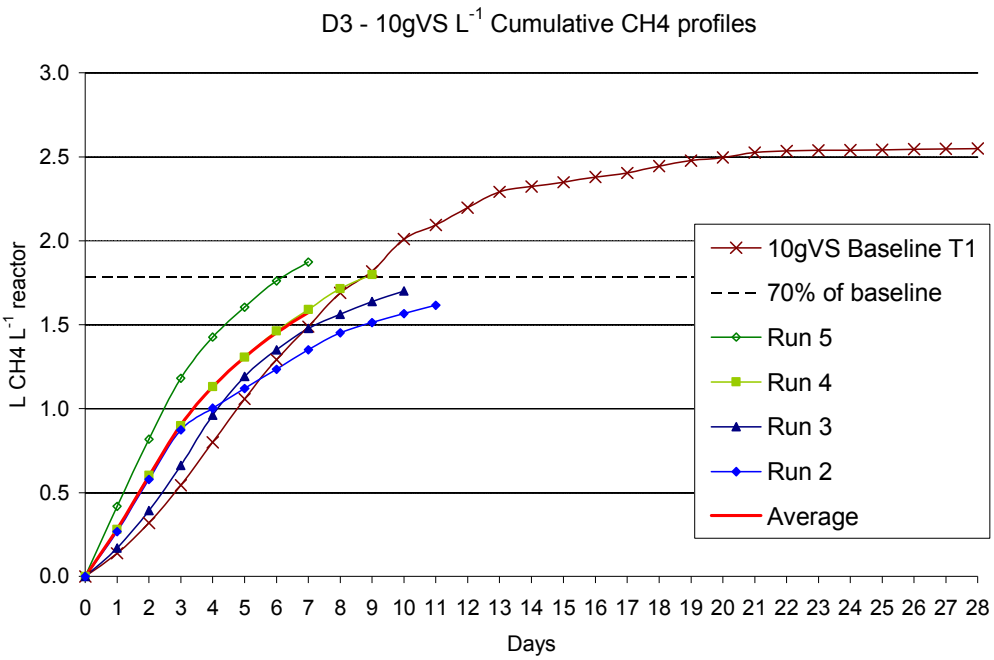


Figure 5.2. D3 Successive trials with liquid inoculum.

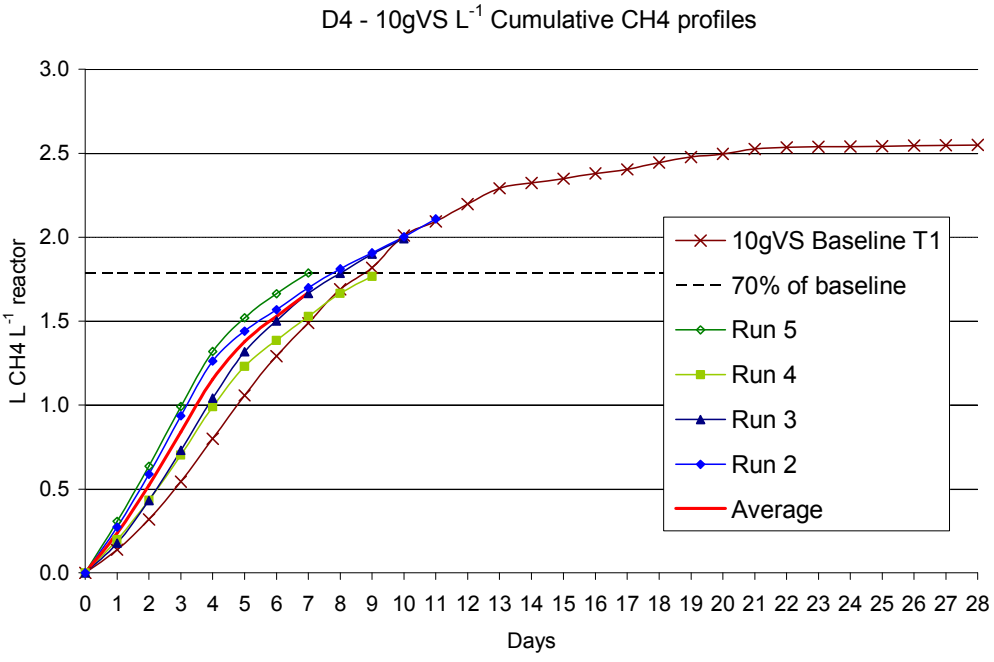


Figure 5.3. D4 Successive trials with liquid inoculum.

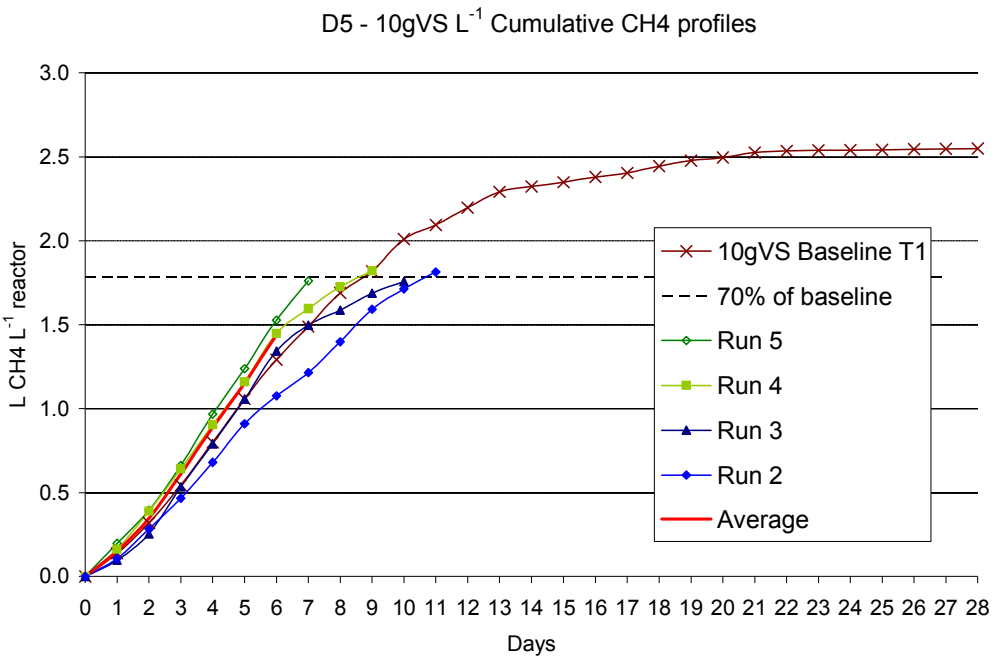


Figure 5.4. D5 Successive trials with solid/liquid inoculum.

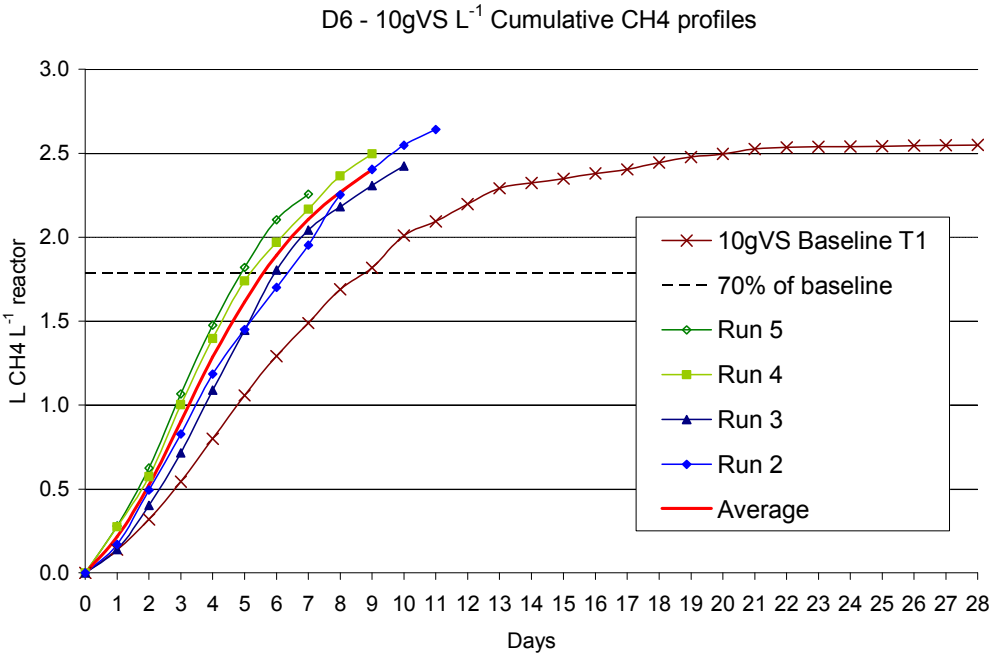


Figure 5.5. D6 Successive trials with solid/liquid inoculum.

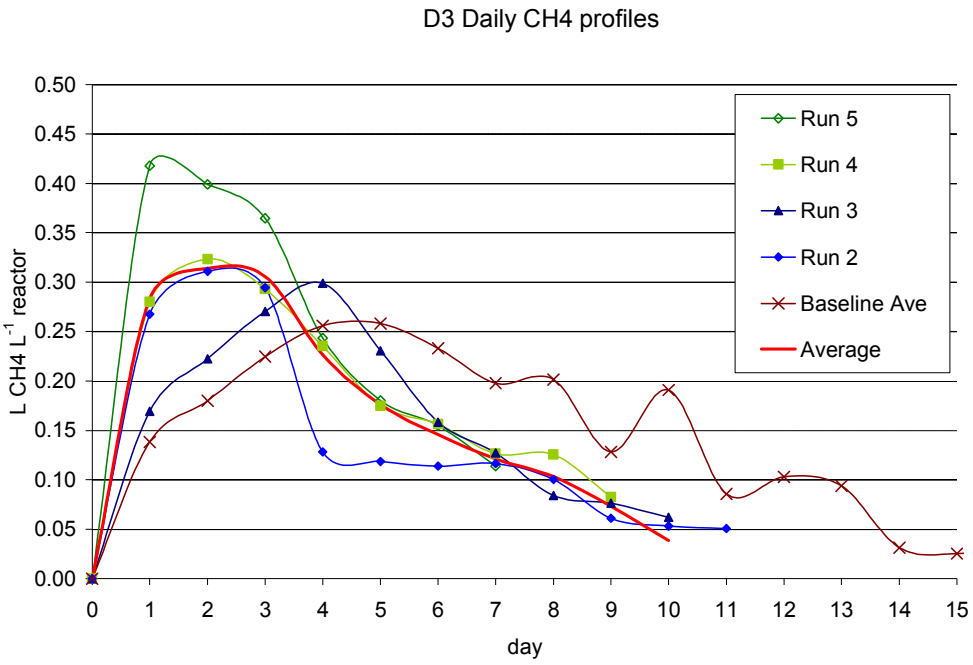


Figure 5.6. D3 Daily gas production with liquid inoculum.

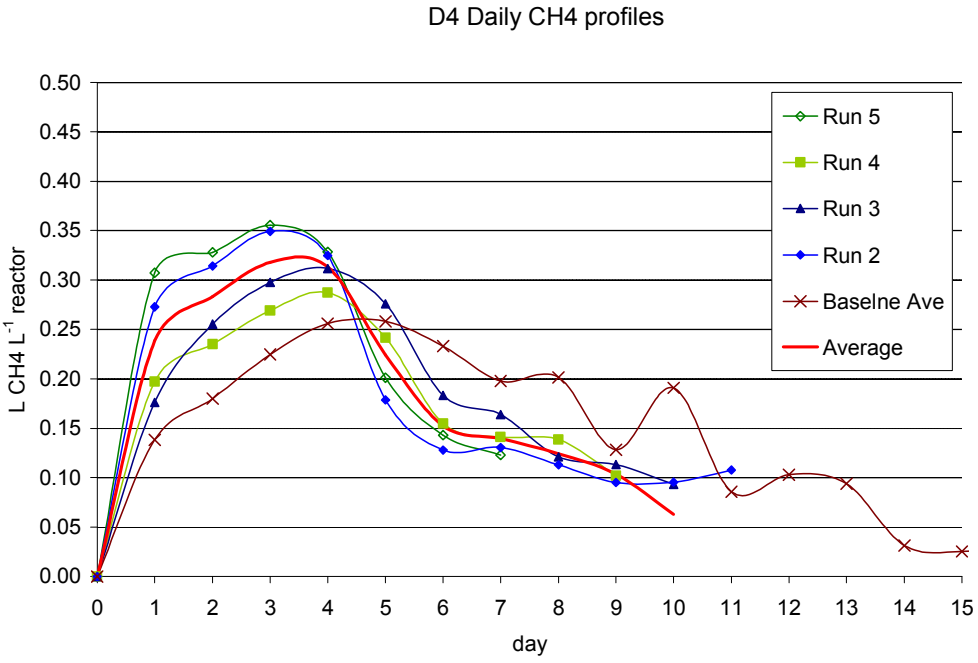


Figure 5.7. D4 Daily gas production with liquid inoculum.

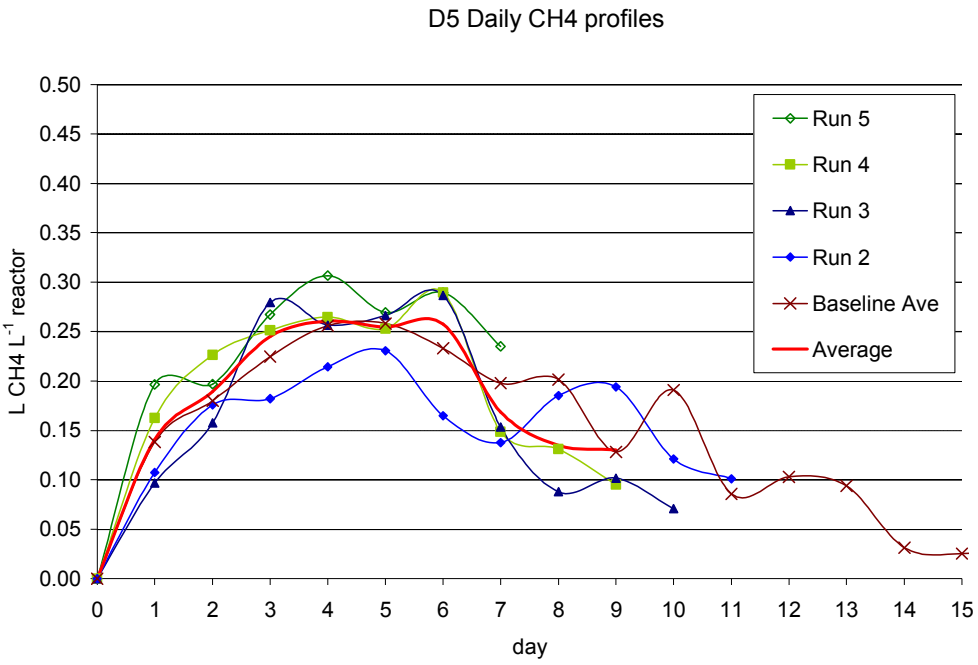


Figure 5.8. D5 Daily gas production with liquid/solid inoculum.

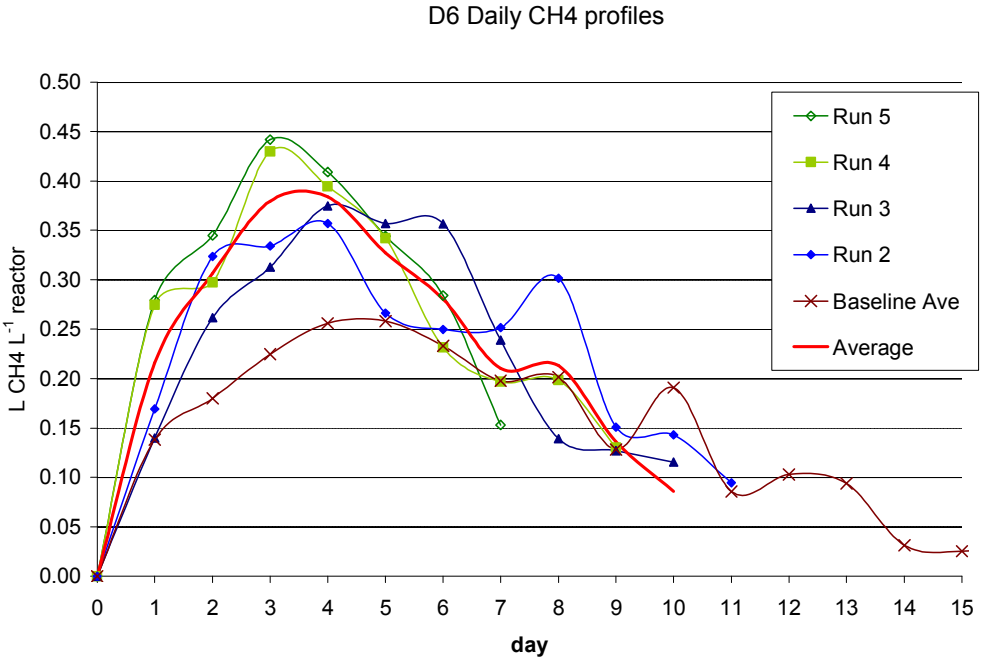


Figure 5.9. D6 Daily gas production with liquid/solid inoculum.

5.4.2 Daily methane production

The daily methane production values for the digesters over the four experimental runs (Run 2 to 5) are shown in Figures 5.6 to 5.9. The shape of the curves show a single gas production peak in nearly all cases with maximum gas production in the first half of the run. The methane production peak, from the digesters with liquid inoculum was not sustained for as long as with the digesters inoculated with the predominantly fibrous material. The underperforming D5 still follows this trend where gas production increases then decreases more gradually than with the liquid inoculum. D6 outperforms the rest, and as stated D5 was operating at a lower temperature than intended, but D6 produced, within 11 days, as much gas as the BMP yield. If the BMP was a good representation of ryegrass at this loading then this raises the question of where the extra gas is produced from?

The increase in volumetric methane production shown in digester D6 could result from substrate carried over in the solid inoculum. After the first run up to 30% of the BMP yield is left in the feedstock; if this is recycled then some of that gas can be produced in the second run. In the first 9 days 70% of the gas is produced, after 18 days 96% of the gas is produced, therefore using separated fibre as inoculum could add to the gas yield. The methane concentration in the biogas progressed from 50% through to 63% as the run progressed and these values were very similar in all four digesters.

5.4.3 Volatile solids addition and destruction

Figure 5.10. shows the inoculum to substrate ratio that was actually achieved over the successive cycles; this varied from 0.99 to 1.87 with a Standard Deviation of 0.26. This shows the difficulty encountered when trying to equalise the I:S ratio. The solids inoculum reactors, D5&D6, varied from 0.99 - 1.44 (SD 0.15) while D3&D4 varied from 1.04 - 1.87 (SD 0.24); showing that overall that D5&D6 had less inoculum and varied less from the intended I:S ratio and that D3&D4 varied more.

The discrepancies can be attributed to minor errors in solids determination for the liquid and solid fractions, which were magnified by the multiplication factor required in estimating the quantity of material to be added. The differences in I:S ratio may account for some of the variation between digester pairs, but in the case of D5&D6 where the greatest variation in gas production was seen, the I:S ratio at the beginning of each run was very similar except in run 4.

Figure 5.11. shows the volatile solids destruction over each of the runs which varied between 17 - 31% with an average of 26%. The large variation again indicates possible problems with solids determination, which was limited by the sample size available for

analysis. At the low loading used the volume of solids remaining at the end of a run was small (~100 ml) and the requirement to use a portion of this for re-inoculation severely limited the ability to measure VS destruction accurately.

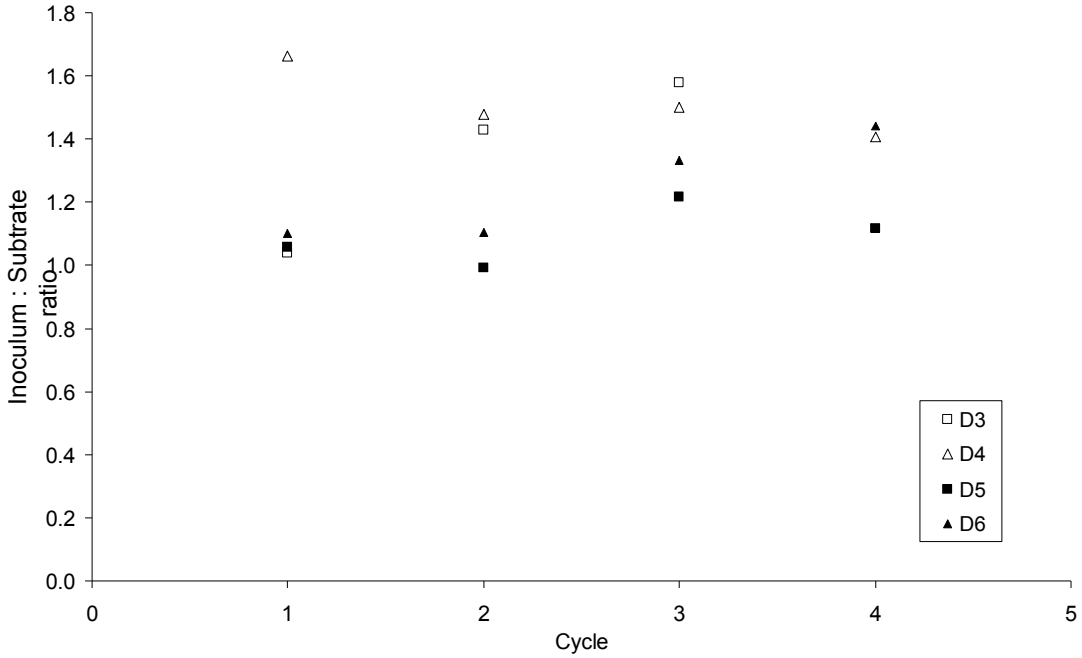


Figure 5.10. D3 & D4 liquid, D5 & D6 solid inoculum, over feed cycles.

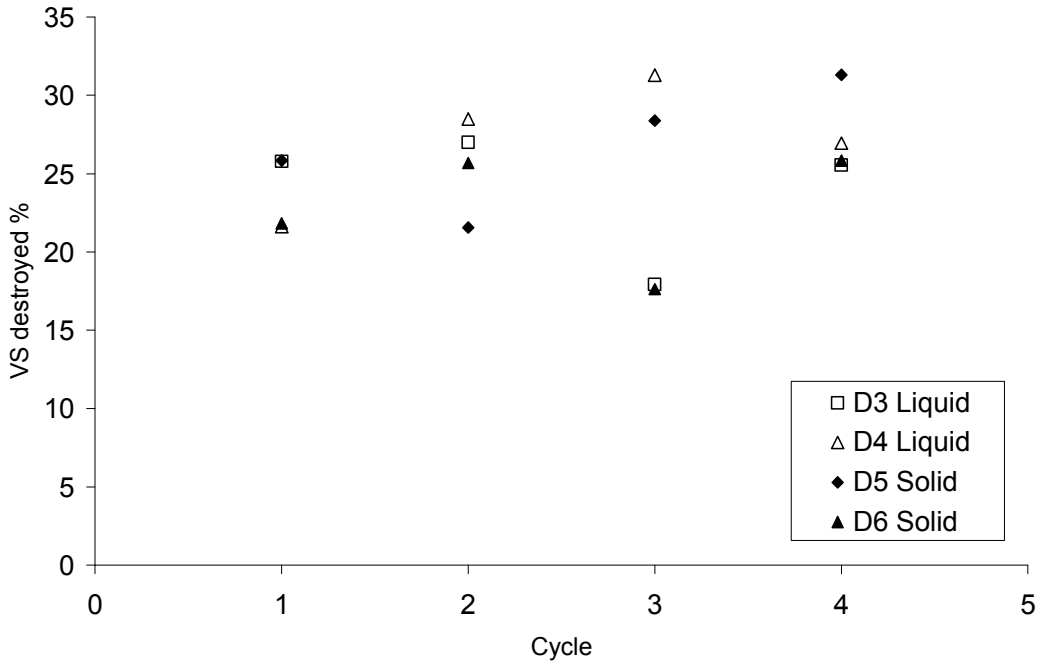


Figure 5.11. All, VS destruction over the feed cycles.

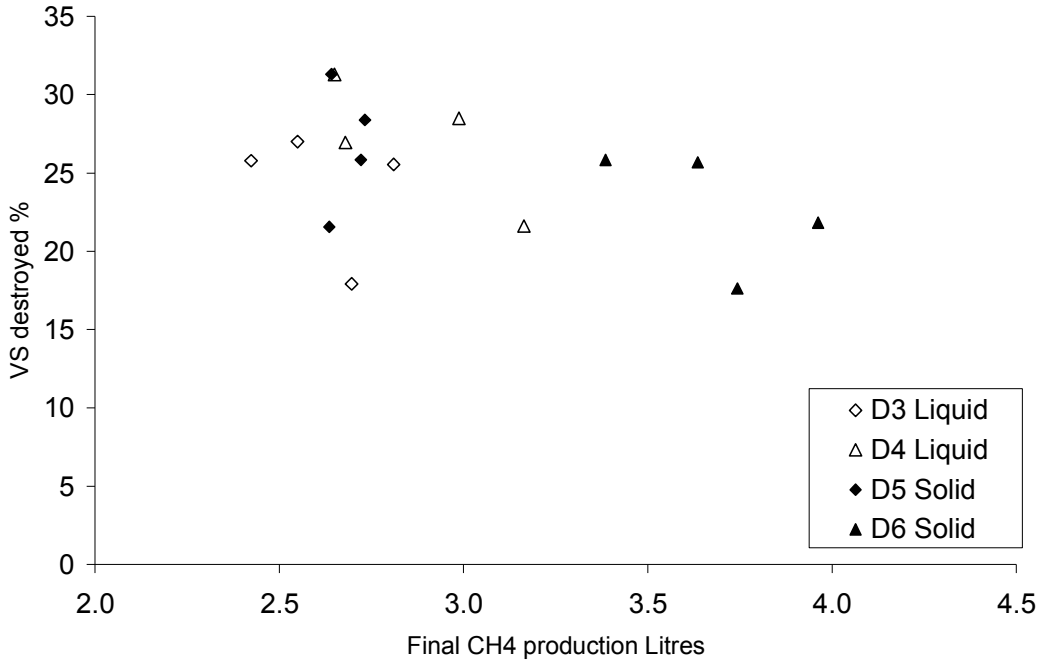


Figure 5.12. VS destruction against total methane production.

When VS destruction was plotted against methane production (Figure 5.12), there was no strong trend although there was a clustering of data points for each reactor, table 5.2. Summarises the averages and associated standard devotion.

The exception was D6 that produces more gas for similar VS destruction to all the others indicating that this correlation cannot be drawn as the VS determination is not sensitive enough to pick up the extra gas production.

Table 5.2. Summary of data; I:S ratios, VS destruction and methane production.

Inoculum type	I:S ratio Average [SD]	% VS destroyed Average [SD]	CH4 L per cycle Average [SD]
D3 liquid only	1.48 [0.35]	25 [5]	2.62 [0.17]
D4 liquid only	1.51 [0.15]	28 [4]	2.87 [0.25]
D5 Solid	1.10 [0.09]	27 [12]	2.68 [0.05]
D6 Solid	1.24 [0.17]	23 [8]	3.68 [0.24]
All reactors	**1.33 [0.26]**	**26 [7]**	**2.96 [0.47]**

Solids measurements did show a marked distinction between liquids and solids in terms of the VS:TS ratio. The liquid inoculum was around 62% VS whereas the solid

inoculum was around 79% VS. There was very little variation in this parameter between the samples taken in each category which strongly indicates the differences in VS concentration in this case were real. It therefore appears that that more highly mineralised depleted substrate with a higher inert content are found more in the separable liquor fraction than in the solid fibre fraction.

5.5 Discussion

Even though there were discrepancies between results from paired digesters, some of which could be attributable to temperature instability, a different pattern of methane production could be seen between digesters with different inoculum types. Despite differences between digesters within each pair, D5 still managed to reach the arbitrary gas production target in the final 2 runs although not operating at optimal temperature. D6 did perform well and shows what is possible when the right conditions are present. The VS data (Figure 5.11) shows that D5 and D6 had the same or slightly lower VS as inoculum as the other pairs, indicating that this was not the determining factor with their performance. It is possible that the overall performance of D3 and D4 may have suffered from temperature problems similar to D5, but as D3 was downstream and D4 was upstream of D6 it seems unlikely that both digesters were affected in the same way, so their performance probably reflects the type of inoculum and not other factors. D4 was the exception to the improvement of performance in each run exhibited by the other digesters, however, with the second and last run being the best; neither of the liquid inoculum digesters managed to increase methane production above the BMP value. Both digesters showed a sharp tailing off of methane production after a short initial production peak, especially when they were performing well.

The higher volatile solids content of the solid fibre inoculum seems to contribute towards greater overall methane productivity, since using this material as the inoculum effectively recycles a higher proportion of VS back to the digester when compared to the liquid inoculum. Alternatively the fibrous material could act as a support medium containing the majority of the organisms within the reactor while relatively small population remain in the free liquid. Solids analysis does not distinguish between lignified carbon and microbial biomass so it is not possible here to say whether extra feedstock or more active biomass is the advantage of recycling the solid portion as inoculum.

There was no problem of build-up of solid material in any of the digesters: this was not surprising, as the overall loading rate (OLR) in most cases was between 0.9 and 1.43 g

VS L^{-1} day^{-1}. At this loading it should be possible to achieve many feed cycles without significant build-up of solids in the liquid-only inoculum digester, although there may be a tendency to accumulate some inert material. In the solids inoculum digester, removing a portion of the liquid in each cycle will remove some of this inert material and give the advantage of retaining substrate for enhanced biogas production. The choice of the inoculum may depend on a number of factors, but it appears likely that the liquid inoculum offers more potential for reducing cycle length, whereas the solid inoculum offers more potential to maximise the methane yield. The choice of inoculum thus potentially allows some flexibility for control over the whole process depending upon the desired outcome.

5.6 Conclusions

Ideal plug flow operation gives the opportunity to manage the inoculum added in with the feedstock. This experiment showed that while liquid only inoculum can be used successfully for ryegrass digestion; there does seem to be an advantage in retaining the solids at the lower loading, both as inoculum and extra feedstock, as this appears to enable the ultimate baseline gas yield to be reached in less than 10 days when originally 40 days were required. This is achieved by obtaining about 70% of the methane yield on the first pass and then retaining the fibre to release more on second pass, and so on. These findings together show a possible operational mode for plug flow where the liquor is preferentially output and the solids are recycled. A potential problem with this mode of operation may be that undigested material within the retained solids will build up, however, and as the older material can not be separated from the younger material, solids will have to be removed from the system at some point. The next issue for consideration in the exploration of operating modes is therefore the question of how fast the material would build up, together with any other consequences of this for the proposed feeding regime.

Chapter 6

Comparison of the effect of stirring and not stirring on biogas production.

(061027 T2 and T3 1.5L Solid v Liquid & Stirring 10-20gVS)

6.1. Introduction

When the methane potential was determined at different loading rates (Chapter 4) a lag phase was noted in all the higher loaded digesters that were stirred, but was missing in the unstirred digesters. This apparent advantage to not stirring was worthy of investigation as it may offer a considerable advantage in terms of energy saving within the digestion process, as well as providing an opportunity to examine the general assumption that stirring improves substrate to inoculum contact and should therefore aid digestion.

6.2 Experimental method

Ideal plug flow conditions were followed in the same fashion as described in Chapter 5, but as the loading was higher the cycle length was longer as it was determined in the same way; the reactors were allowed to digest until 70% of the BMP yield was reached by more than one reactor. Four 1.5 L digesters were used over 3 feed cycles of between 11 and 14 days duration. The digesters operated at an IBLR of 20 g VS L^{-1} and used an inoculum of whole digestate derived from a previous trial, homogenised then divided for the first run and supplemented with water (Table 6.1). This resulted in a low inoculum to substrate ratio. After the first run the inoculum remained with the individual reactor.

Table 6.1. Digester set up for IBLR 20 g VS L^{-1} , for the stirring trial.

Digester N°.	Inoculum g VS		Feedstock g VS	Total VS	I:S
[1.5 litre]	Liquid	Solid	Rye grass	grams	Ratio
D7 Stirred	8.27	11.78	39.90	50.06	0.67
D8 Stirred	8.29	12.90	39.90	51.18	0.71
D9 Not-stirred	9.44	11.89	39.90	51.33	0.71
D10 Not-stirred	5.93	11.62	39.90	47.55	0.59

6.3. Experimental results

Two values of methane potential were obtained as the unstirred digester in the pair performed better; these values are taken separately but the 70% target of total production is an average of the two. The averages for both digesters in each condition are plotted with these curves as reference. They show very close agreement between stirring and not stirring with a slight advantage to stirring, with both sets of digesters taking ~12 days to reach 70% BMP yield, starting off faster than both BMP curves but moving towards the performance of the lower specific yield.

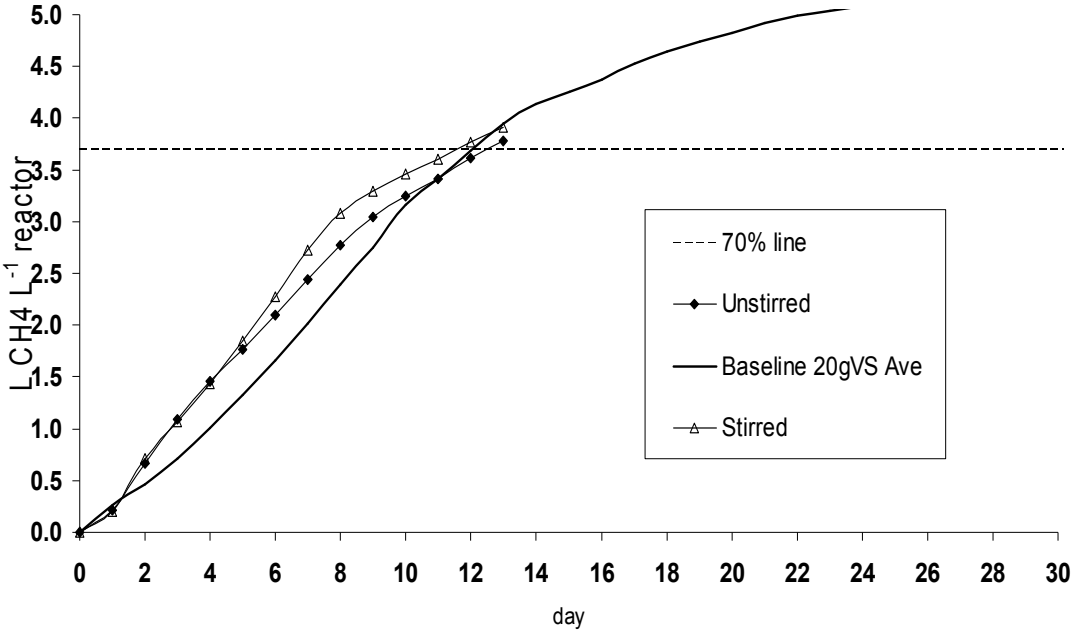


Figure 6.1. Stirred and unstirred averages of 3 cycles with baseline values for comparison.

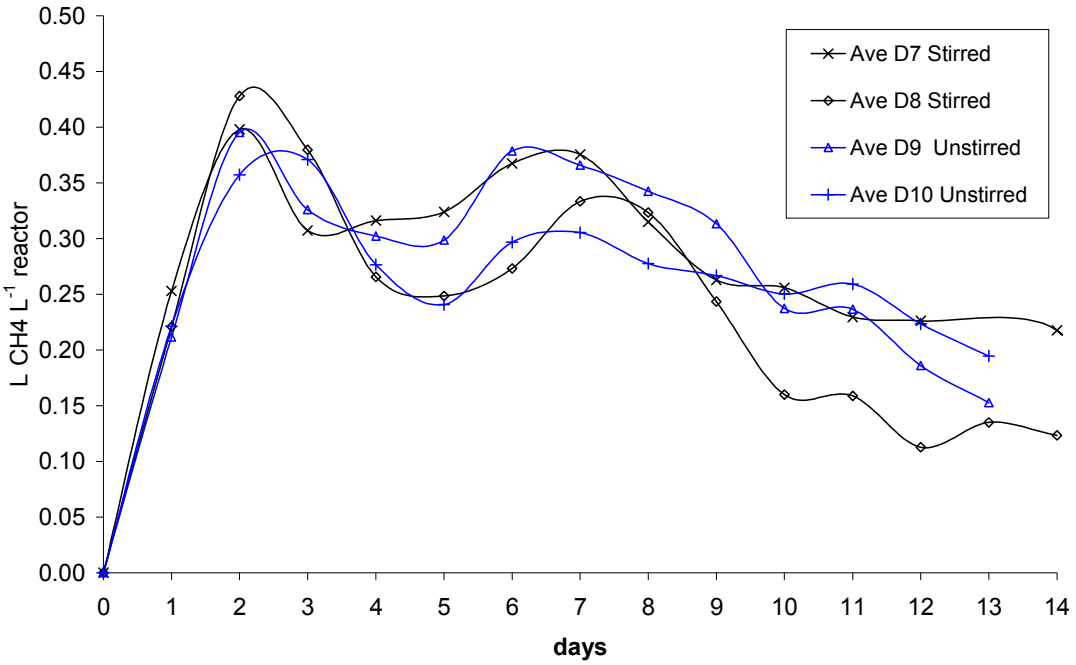


Figure 6.2. Daily gas production for the two stirred and two unstirred digesters averages of 3 cycles.

The daily gas curves show a distinct sag in what would be a sustained single gas production phase except that it is interrupted for 4 days. This uncoupling of reactions that this signals is independent of the stirring. The similarities are surprising since the unstirred digesters had a matt of floating grass only partially submerged as production and entrainment of gas lifts the grass out of the liquor. The interface between the free liquid and the substrate was much reduced.

6.4. Discussion

The improvements from not stirring disappeared over repeated cycles, suggesting that this was linked in some way to digester start-up, possibly caused by bacterial adaptation to the digester conditions.

A study by Karim (2005) found no advantage between stirring and not stirring at low loadings, and an adverse effect on the gas production during the start up phase, though no explanation was put forward. Vavlin (2004) put forward the idea of methanogenic centres that can survive in adverse conditions if they can remain a certain size: mixing can act to break down these centres leading to the overwhelming of the methanogens by acidic conditions. The reason the advantage in not stirring was so pronounced in the baseline trial could therefore be that the biochemical conditions were becoming established and the methanogenic populations were at their most vulnerable due to the higher loading. Each feed cycle showed an improvement for both

stirred and unstirred variants as the bacteria acclimate and the symbiosis was set up. Here stirring had less of a detrimental effect and started to aid the digestion as it should, by increasing the contact. What was surprising was that the grass floats mostly above the digestate when not stirred, there was much less contact between the matted grass and the liquor, but this does not appear to slow the digestion.

Even though the amount of inoculum in the digesters was low on each run, digestion completed and achieved the gas target on average. A digester with a low I:S ratio should be more vulnerable than one with a higher ratio as there are many fewer bacteria in the digester. If the bacteria were in this vulnerable state there should be an advantage to not stirring, but there seems to be enough inoculum to complete digestion and stirring is not more than marginally advantageous. There was no build up of material though some of the material was taken for sampling. As there were no solids accumulated, the full methane potential cannot be expected as any residual gas potential was mostly sampled and only a small amount returned as inoculum.

6.5 Conclusions

The advantage seen in the unstirred baseline experiment was not repeated in subsequent trials and thus appeared to be a feature of start up. The small advantage seen for stirring at these low I:S ratios / high loading rates showed that stirring can be reduced to a minimum to gain the advantage while greatly improving the energy balance. As seen in Chapter 2.6 the difference in energy use is proportional to the amount of stirring provided. Stirring is the principle electrical load so savings here are more beneficial than heat savings as electrical generation can only ever be a minority part of the over all energy yield of a digester.

Chapter 7

The effect of increasing inoculum to substrate ratio by recycling solids and reducing the feed cycle length to increase loading

(Source file 070527 T4 and T5 Solids fill 30L..xls)

7.1 Introduction

In a batch fed or plug flow digester the recycling of solids can provide the inoculum, and also potentially provides the opportunity to gain more methane production from the substrate. The disadvantage of solids retention is that recalcitrant material may build up, reducing the effective digester volume. High solids are also harder to pump and stir within a wet system and are avoided for these reasons. The series of experiments described below was therefore designed to test the effect retaining as much of the material as possible on performance, methane production and specific yield.

7.2. Experimental method

Two 30-litre digesters were used in the experiment. At the start the digesters were full of a ryegrass digestate from previous experiments, where a continuous feed had been used; the digestate was thus acclimated to the feedstock. Before the experiment started the digestate liquor was drawn off from the digesters in order to create spare volume into which fresh feed could be added; the digestate fibre was retained in the digester as the initial inoculum. In the two digesters that were used the solids which were retained at the beginning of the experiment were different, as the two digesters had slightly different histories.

Every seven days fresh ryegrass feed was added to each digester to simulate a plug flow regime with a 7-day feed interval, as shown in Figure 7.1. and described in Chapter 5.2. Before this feed was added to the digester, the liquor was circulated around the digester to provide some mixing, then the free liquor was drawn off but the solids were retained as an inoculum.

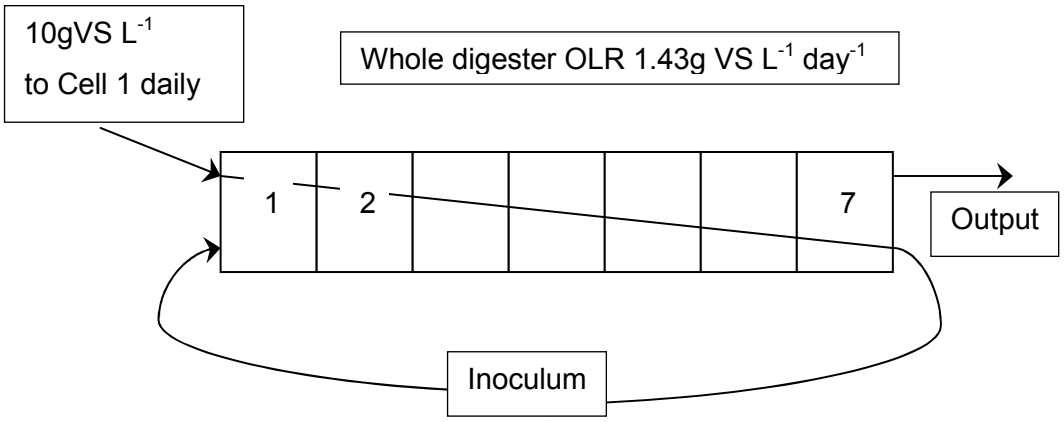


Figure 7.1 Schematic of feed regime.

The initial biomass loading rate (IBLR) at the start of the first cycle was 10 g VS L^{-1} giving an organic loading rate (OLR) equivalent to 1.43 g VS L^{-1} day^{-1} for that cycle. With each successive feeding the free space in the digester decreased as non degradable solid fibrous material accumulated. This build-up was monitored in order to estimate the number of feed cycles that could be achieved before there was insufficient digester volume to accommodate any additional fresh feed. By operating the digester in this manner the I:S ratio also increased with each cycle. The feed cycle was then shortened to a 5 day feed interval to increase the loading rate (Figure 7.2).

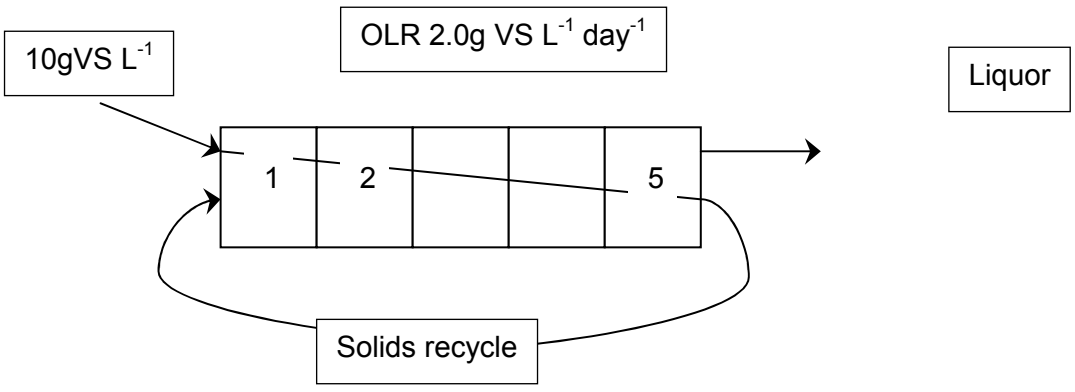


Figure 7.2. Schematic of the shortened feed cycle

7.3. Parameters

The IBLR is the amount of feedstock VS added per feed, expressed in terms of the comartments working volume. The OLR is the feedstock VS loading the digester receives and is dependent upon the length of the cycle. An IBLR of 10 g VS L^{-1} is the

same whether fed daily, weekly or monthly while the corresponding OLR would be 10.00, 1.43 and 0.36 g VS L^{-1} day^{-1} respectively for cycles of these lengths. The HRT is derived from the flow rate through the digester or the amount of volume leaving the system per day divided into the digester working volume. This is a common parameter for the operation of CSTR systems and follows the same principles and only serves to indicate the throughput of the digester and hence the period available for digestion. The inoculum to substrate ratio indicates the proportions of captive biomass to feedstock biomass (VS basis), this is reported here, as one advantage of a CSTR system is the relatively large amount of biomass that is resident within the digester.

The digesters R1 and R2 were run over 15 and 16 feed cycles respectively. Monitoring of the digesters started on feed cycle 5 for R1 and feed cycle 6 for R2. The first 6 monitored feed cycles had a 7-day feed interval and the subsequent 5 cycles had a 5 - day feed interval. This change in feed interval increased the OLR from 1.43 to 2.0 g VS l^{-1} d^{-1}, while the IBLR 10 g VS L^{-1} remained unchanged.

Table 7.1 Experimental set up

Digester N°. [30 litre]	Cycle	Feedstock g VS Rye grass	OLR g VS l^{-1} d^{-1}	I:S ratio range
R1 [7 day]	C5 - C10	308	1.43	3 to 5 : 1
R2 [7 day]	C6 - C11	308	1.43	7 to 9 : 1
R1 [5 day]	C11 - C15	308	2.00	6:1
R2 [5 day]	C12 - C16	308	2.00	7 to 10 : 1

7.4. Experimental results

The cumulative methane production from each of the two digesters is shown in Figures 7.3 and 7.4. These values were taken over a number of successive feed cycles after each digester had been running for 4 feed cycles (R1) and 5 feed cycles (R2), this was to allow an initial period of acclimatisation and stabilisation. Quasi - stable operating conditions were then achieved for 6 cycles at a 7 days feed interval and 5 cycles at a 5 day feeding cycle. During cycle 7 (C7) R2 had a gas leak and the data has been omitted.

The methane production from both digesters showed production slowing as the cycle progressed, this being more acute towards the end (figure 7.3 and 7.4.). The average methane production in R1 was 3.46 L CH_4 L^{-1} $cycle^{-1}$, equivalent to a volumetric

methane production rate of 0.49 L CH_4 L^{-1} day^{-1}. Digester R2 had a slightly higher average of 3.70 L CH_4 L^{-1} $cycle^{-1}$, equivalent to a volumetric methane production rate of 0.53 L CH_4 L^{-1} day^{-1}

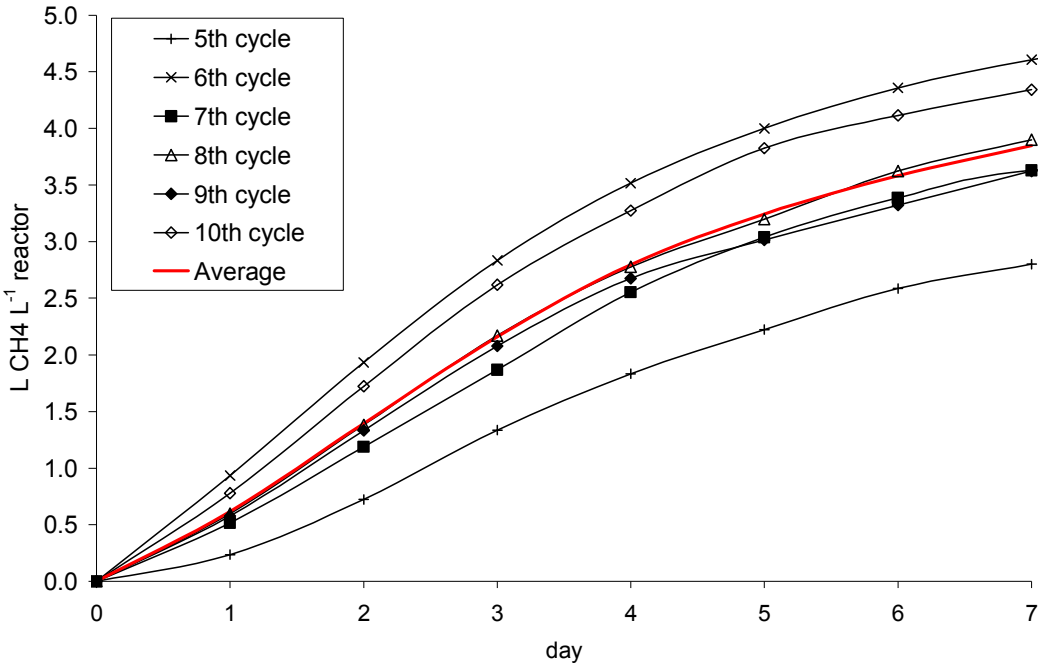


Figure 7.3. Cumulative volumetric CH_4 production in digester R1, 7-day cycles.

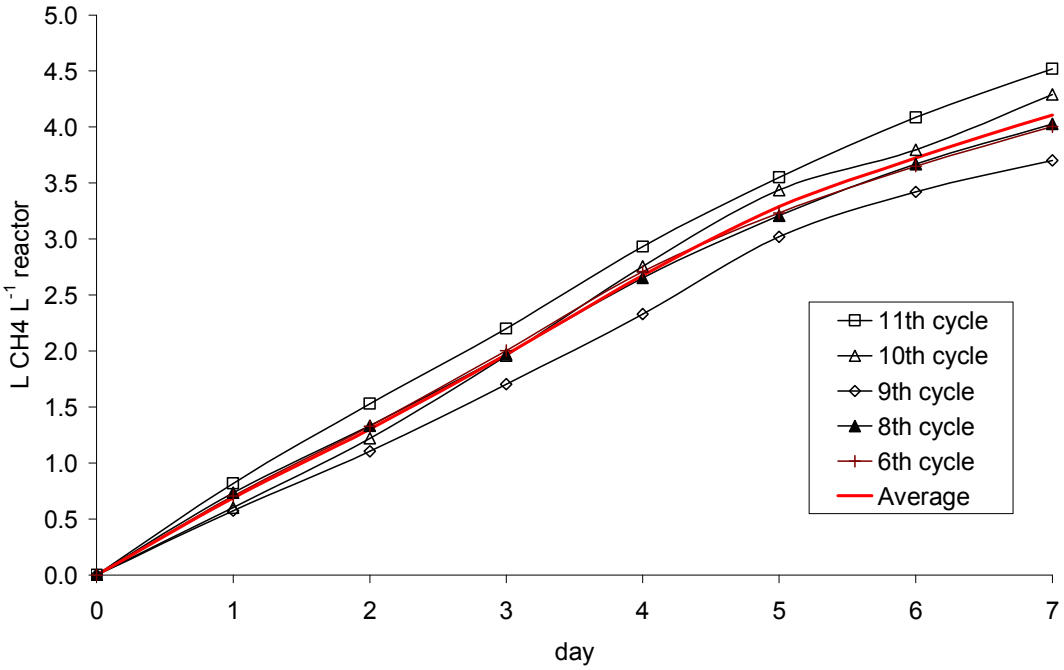


Figure 7.4. Cumulative volumetric CH_4 production in digester R2, 7 day feed cycle (omitting cycle 7).

It can be clearly seen in Figures 7.5 and 7.6 that the daily methane production increased over the first 3 to 4 days after feeding and then declined in digester R1. In digester R2 the early peak lasted for 4 to 5 days with some indication of a slight

reduction after the first day and recovering by the third day. A slight sag in daily methane production appeared from the digester with the higher solids content (figure 7.6.).

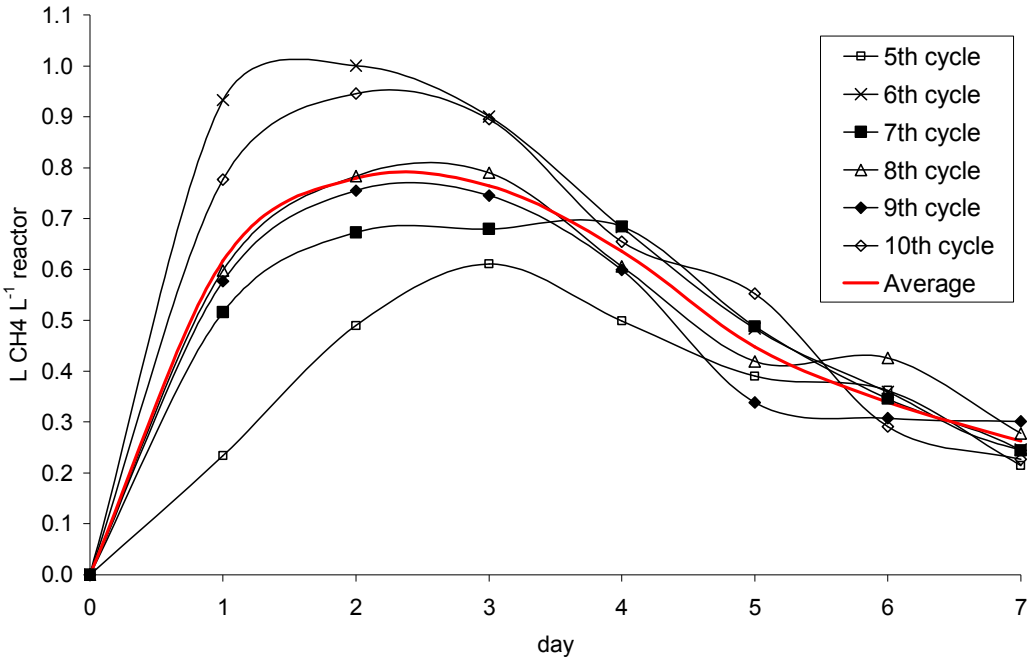


Figure 7.5. Daily CH_4 production in digester R1, 7-day feed cycle.

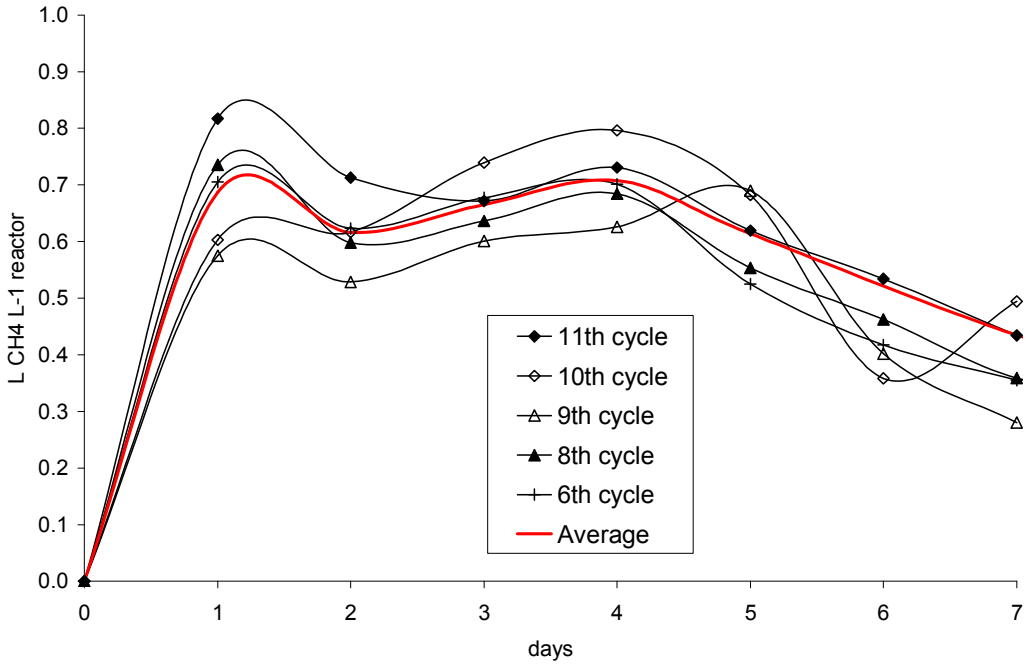


Figure 7.6. Daily CH_4 production in digester R2. 7-day cycle omitting C7.

Figures 7.7 and 7.8. show the cumulative methane production from each of the two digesters when the feed cycle length was reduced to 5 days. These were again taken

over a number of successive feed cycles. The average methane production in R1 was 3.47 L CH_4 L^{-1} $cycle^{-1}$, equivalent to a volumetric methane production rate of 0.69 L CH_4 L^{-1} day^{-1}. Digester R2 had about the same average of 3.37 L CH_4 L^{-1} $cycle^{-1}$, equivalent to a volumetric methane production rate of 0.68 L CH_4 L^{-1} day^{-1}. Again the methane production curves showed a form indicating that the rate of production slowed towards the end of the cycle. This is confirmed when the methane production was plotted on a daily basis as in Figures 7.9 and 7.10. These showed that a peak in methane production occurred one day after feeding, which in some cases extended to the second day. The shapes of the curves for both digesters R1 and R2 were very similar suggesting that the two digesters were acting in very much the same way.

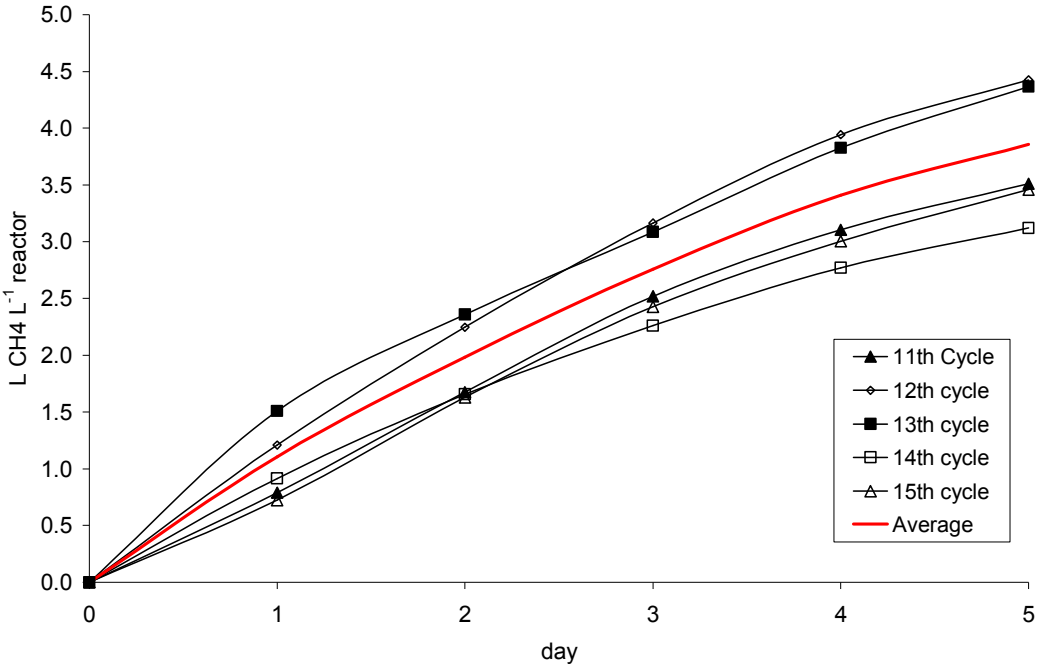


Figure 7.7 Cumulative volumetric CH4 production in digester R1 over 5 successive 5 day feed cycles.

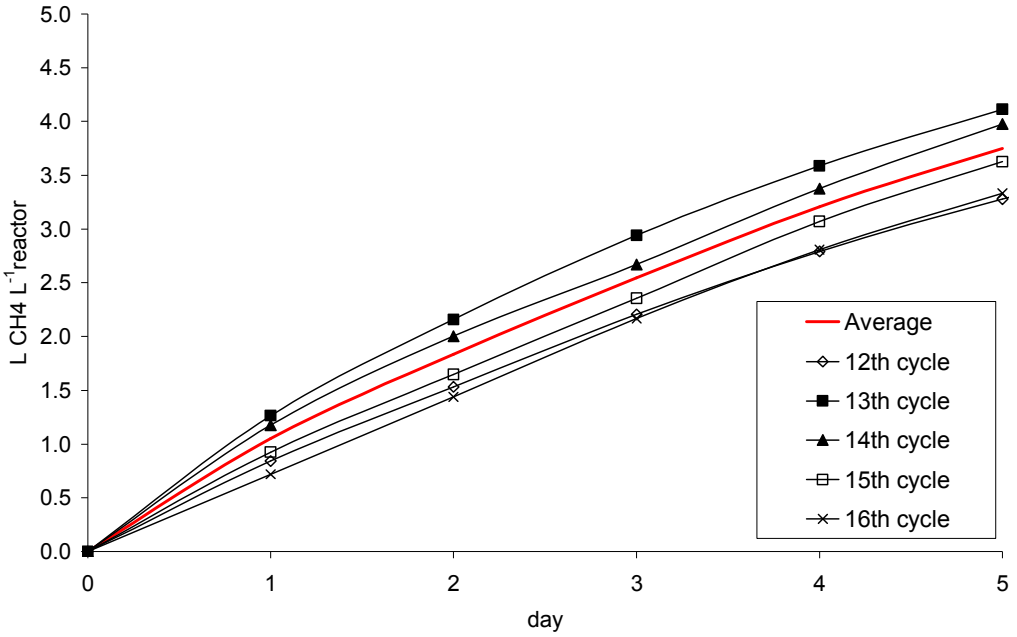


Figure 7.8. Cumulative volumetric CH_4 production in digester R2 over 5 successive 5 day feed cycles.

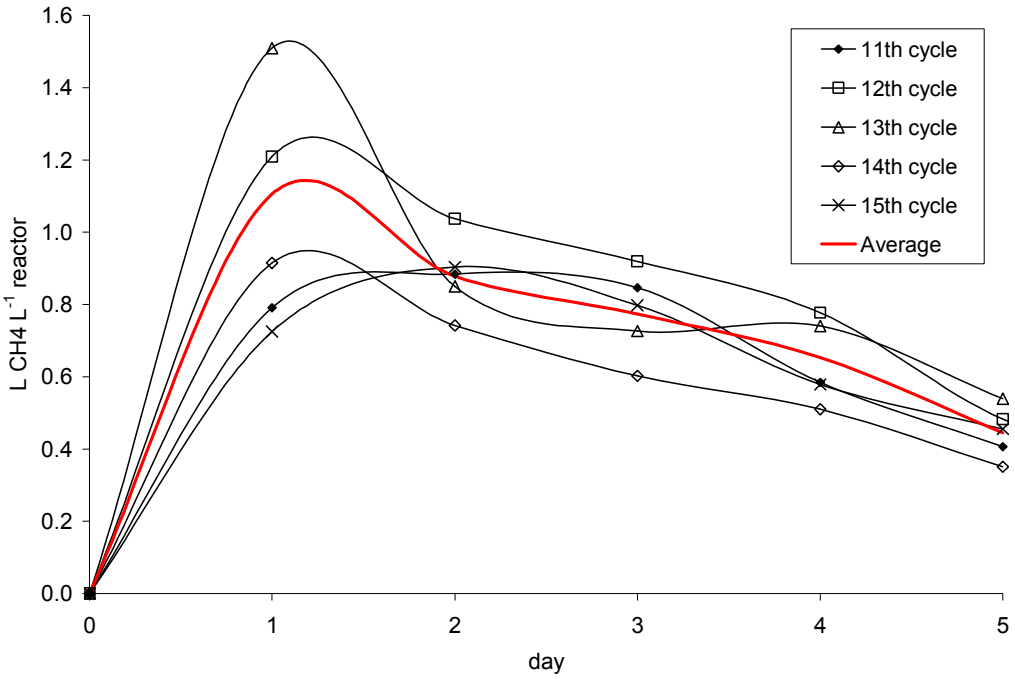


Figure 7.9. Daily CH_4 production in digester R1, 5 cycles of a 5 day feed cycle.

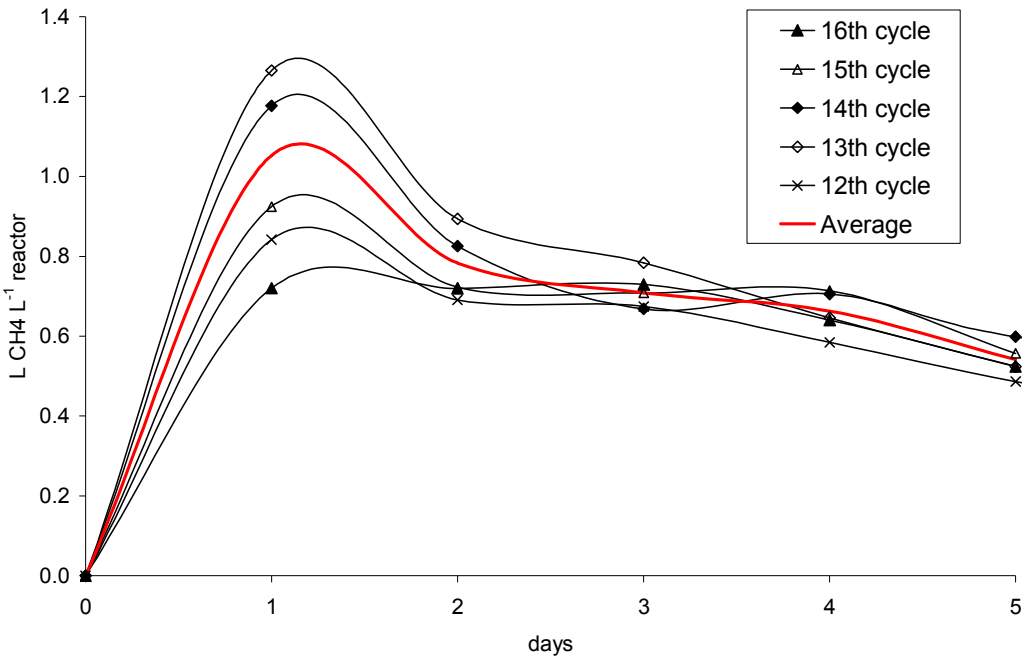


Figure 7.10. Daily CH_4 production in digester R21 on a 5 day feed cycle.

7.5 Discussion

The performance of both the digesters was stable even though they exhibited slightly different methane production characteristics during the 7-day feed cycle period. The major difference between the two digesters at this point was that R2 had commenced operation with a higher solids content than R1. It is therefore likely that there was more residual substrate load in the digester at the start of operation, and this would explain the slightly higher volumetric methane production. The characteristic slight inhibition in methane production after an initial peak (Figure7.6.) is also indicative of an increased load leading to mild acidification and followed by a recovery in methane production. By the time the cycle length was changed to 5 days, these initial differences had become less obvious and the two digesters were behaving in a similar manner and exhibiting more or less the same average volumetric methane production. At the shorter cycle time, however, over successive cycles there was a deterioration in the methane production indicating that the higher loading may not be sustainable. This is not conclusive, as at the time when the shorter cycle was introduced the solids build-up in the system was already high and the relative volume of liquor was decreasing.

The pH and alkalinity in the digesters was also very high: before the experiment R1 had a pH of 8.12 and a Total Alkalinity of <10000mg $CaCO_3$ l^{-1}; R2 was similar with pH 8.22 and a Total Alkalinity of 10833mg $CaCO_3$ l^{-1}. These elevated values are due to

the extended period of ryegrass feeding that moves the pH and TA up at the end of a cycle.

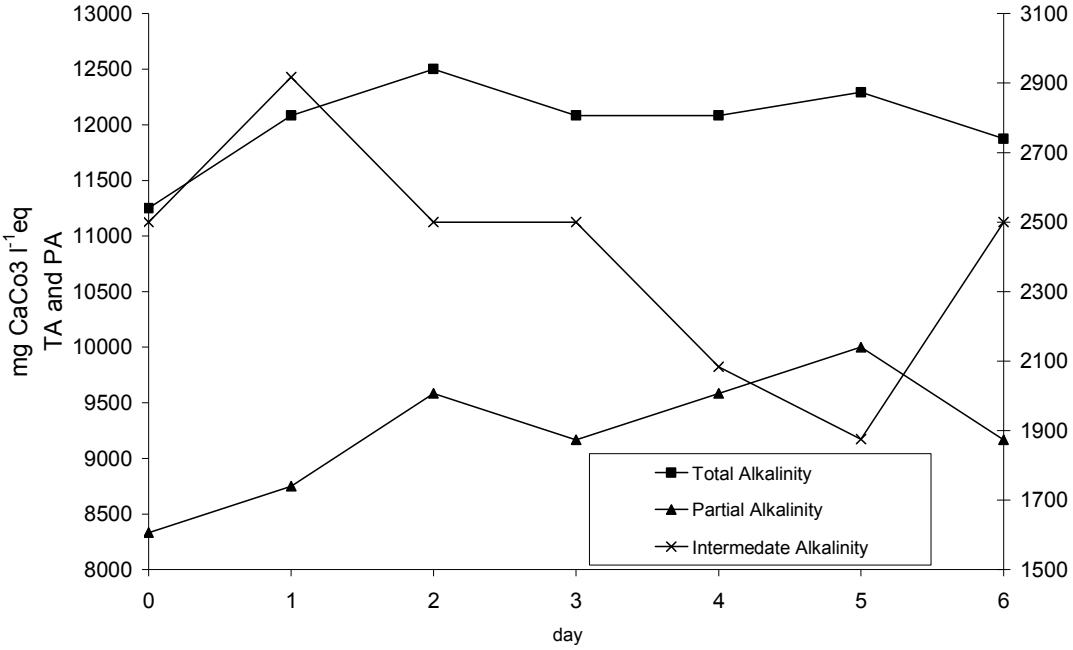


Figure 7.11. Alkalinity from R1 over one cycle. Total and Partial alkalinity shown on the left axis with the Intermediate alkalinity on the right axis.

Figure 7.11. is a snapshot of the change in alkalinity over a 7-day cycle. The total alkalinity is expressed as mg $CaCO_3$ l^{-1} equivalent; the other measures of alkalinity were also used as a guide to VFAs and digester stability following Ripley (1986). The Ripley ratio was very low, reducing from around 0.30 to 0.15 over the experiment indicating stable conditions, with no danger of acidification. The alkalinity did not change very much and it is likely that there is more variation in the measurement of alkalinity than the actual change. The measurement was taken intermittently throughout trial but due to changeable readings, (due to instrument and/or pH probe problems) it was abandoned at the end of cycle 14. The final values were; TA ~12000 and 12500 mg $CaCO_3$ l^{-1} equivalent for R1 and R2 respectively, both with pH values over 8.2.

7.6. Comparison of 7 and 5-day feed cycle length

At the transition point between the 5 and 7-day cycles where the digesters were considered to be performing well, the specific methane yield was 0.39 L g^{-1} VS added, and the volumetric methane production rate was 0.56 L CH_4 L^{-1} day^{-1}. Individual averages for these two key parameters for the two cycle lengths are given in Table 7.2.

Average values for volumetric methane production for the two cycle lengths are shown in Figure 7.12.

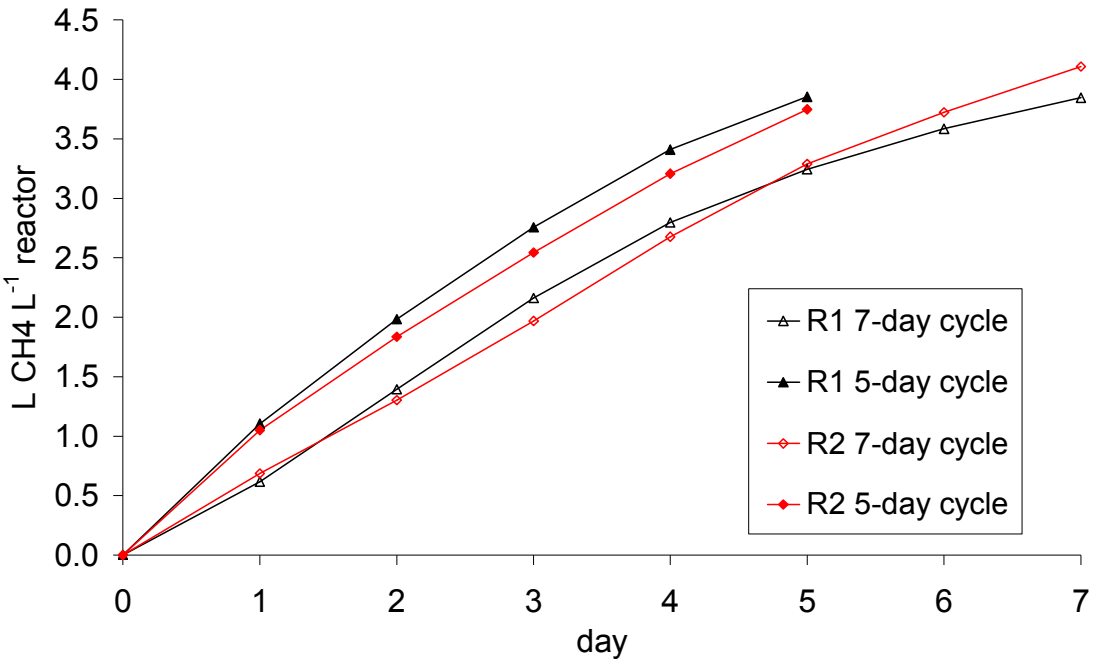


Figure 7.12. Cumulative volumetric CH_4 production averaged over successive cycles at both 5 and 7 days.

When the two cycle lengths are compared it appears that the shorter cycle achieves the same yields but in less time. Although this was the case it was also noted that the yields of the 5-day cycle decreased with each cycle. The digesters were approaching the point where feed could not be added and this obscures the issue as the 5-day cycle may be unsustainable biochemically in the long term, but indefinite accumulation of solids is definitely not sustainable.

Table 7.2. Summary of results for 7 and 5 day feed cycle

Digester (cycle)	L CH4 l^{-1} d^{-1}	L CH4 g^{-1} VS added	HRT days
R1 (7)	0.494	0.346	160
R2 (7)	0.529	0.370	160
R1 (5)	0.694	0.347	100
R2 (5)	0.674	0.337	100

The summary data in Table 7.2 shows that shortening the cycle reduced the HRT from 160 days down to 100 (Section 7.3) and increased the volumetric yield from between 22% and 30% while maintaining a high specific yield. The specific yield increased

above that of the baseline value of 0.25 LCH_4 g^{-1} VS added as the feedstock was accumulating, and the yield was calculated solely on the influent feedstock not the feedstock retained within the digester.

7.7. Solids accumulation in digesters R1 and R2

R1 and R2 contained different amounts of solids at the start of the experiment and therefore the final time required to fill the two digesters was different. Figure 7.13 shows the solids accumulation in R1 and Figure 7.14. in R2. In both cases an estimation of the number of feed cycles it would take to fill the digester has been made, assuming all the solids are retained and that some are broken down. This was projected to be approx 32 cycles for R1 and 25 cycles for R2. A similar projection was made using the assumption that no solids breakdown occurred and the volume occupied in this case was based on the specific volume of the dry matter within the ryegrass. In this latter case R1 would fill in 26 cycles and R2 in 13 cycles. R2 seems to perform better than R1 although it initially had more solids: the period between fill up points is greater at 12 cycles to 8 cycles. This estimate is based on one set of data in which values for the solids build-up show quite large fluctuations in volume (Figure 7.13). The measurement of digestate volume was difficult particularly as the solids in the digester trap gas and this affects the volume. If the material was stirred to release the gas this made it impossible to obtain a depth reading.

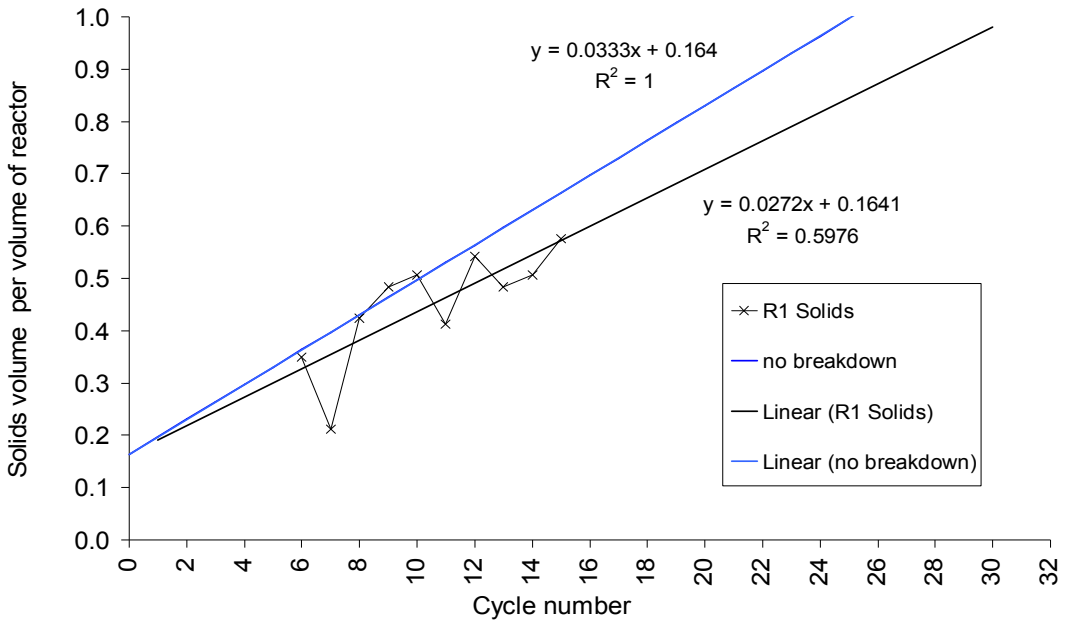


Figure 7.13. Solids accumulation R1.

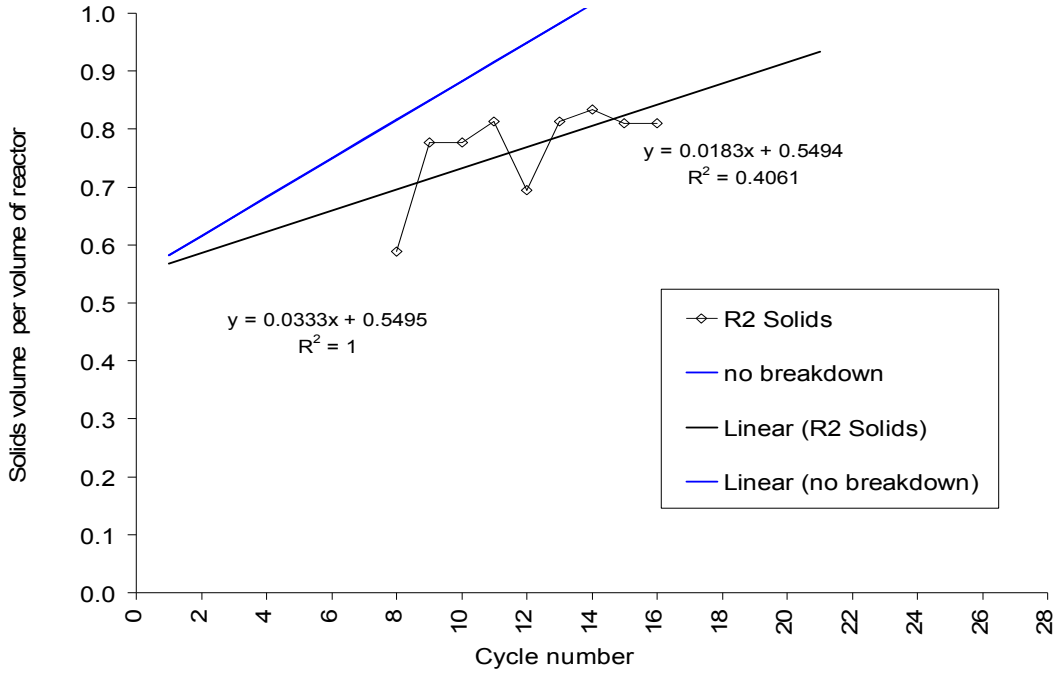


Figure 7.14. Solids accumulation R2.

7.8. Conclusion

This mode of operation of the digesters was found to work well in practice and established that allowing solids a longer period to break down in the digester increased the specific methane yield. It was shown to be possible to operate these digesters without mechanical mixing and a once-daily drain and refill of the liquor was sufficient to maintain activity and prevent acidification by ensuring that the grass fibre was immersed at least once each day. The high buffering capacity of the system increased over the experimental period and consequently this can be viewed as a very stable system. A possible problem of elevated pH is the volatilisation of ammonia into the gas phase.

The shorter operating cycle needs further investigation as the filling of the digesters coincided with a fall off in methane productivity; it is unclear whether this was due to the cycle length or the high solids in the system.

Chapter 8

Assessment of the methane potential and solids destruction by retention of the maximum achievable amount of inoculum

(071114 T6 1.5L D8-D12 grass fill)

8.1 Introduction

In the previous experiment, (Chapter 7) assessment of the build-up of solids in the digester proved to be difficult. The results indicated, however, that the digester could operate successfully in this accumulation mode over a number of successive feed cycles. In this section results are reported from a modified experimental design carried out in 1.5 litre digesters. At this scale all the solids and liquids could be weighed to provide more accurate data for calculation of the mass balance and determination of the inoculum to substrate ratio at the start of each feed cycle. The experiment was run over a longer period of time than the preceding trial to allow assessment of longer-term effects on methane production, as well as of the solids accumulation.

8.2. Experimental method

Three 1.5 L digesters were operated on a 7-day feed cycle with an initial biomass loading rate (IBLR) at the start of each cycle of 10 g VS L^{-1}, giving an organic loading rate (OLR) equivalent to 1.43 g VS L^{-1} day^{-1} based on fresh feed. Each digester was initially filled with an inoculum liquor taken from R2 (30 litre digester) and the digester was filled to a constant volume of 1500 ml at the first feed by adding 15.54 g VS of dried ryegrass and an appropriate volume of water so as to simulate a feed of fresh ryegrass with a 20% dry weight content

Table 8.1. Initial digester set up.

Digester N^{o}.	Inoculum g VS		Feedstock g VS	Total VS	I:S
[1.5 litre]	Liquid	Solid		grams	ratio
D8	22.68	0	15.54	37.16	1.57
D10	23.33	0	15.54	37.81	1.61
D12	22.86	0	15.54	37.34	1.58

The digesters were maintained at 37 ^{o}C and connected to a bell over water gasometer. After 7 days the digester was opened and the entire contents were passed through a 1

mm mesh and the wet weights of the liquor and retained fibre recorded. 15g VS of dried ryegrass was added to each digester along with water to simulate to 20% dry weight content of fresh ryegrass. All the fibre from the previous cycle was then returned together with liquor from the previous cycle to make the volume up to 1500 ml. The liquor not required for this process was analysed for solids content. This feeding procedure was carried out every 7 days on each of the 3 digesters over 21 feed cycles. During the run the digesters were mixed once per day to ensure that any floating grass layer was entrained within the liquid. At the start of each feed cycle an estimate of the inoculum to substrate (I:S) ratio was made by calculating the volatile solids returned to the digester in both the fibre and liquor fractions. The substrate volatile solids content was constant at 15 g VS added (10g VS l^{-1}) at each feed cycle. The digesters were operated at a constant volume but the mass of the constituents were measured to track the changes over the solids/liquid partition throughout the experiment.

8.3. Experimental results

Figure 8.1 shows the volumetric methane production in each of the digesters and the average of all 3 over the 21 feed cycles. There was a general increase in productivity up to cycle 10 followed by a decline after this point. The volumetric production at this peak (10^{th} cycle) was 4.2 L CH4 L^{-1} $cycle^{-1}$, 0.6 L CH4 L^{-1} d^{-1}.

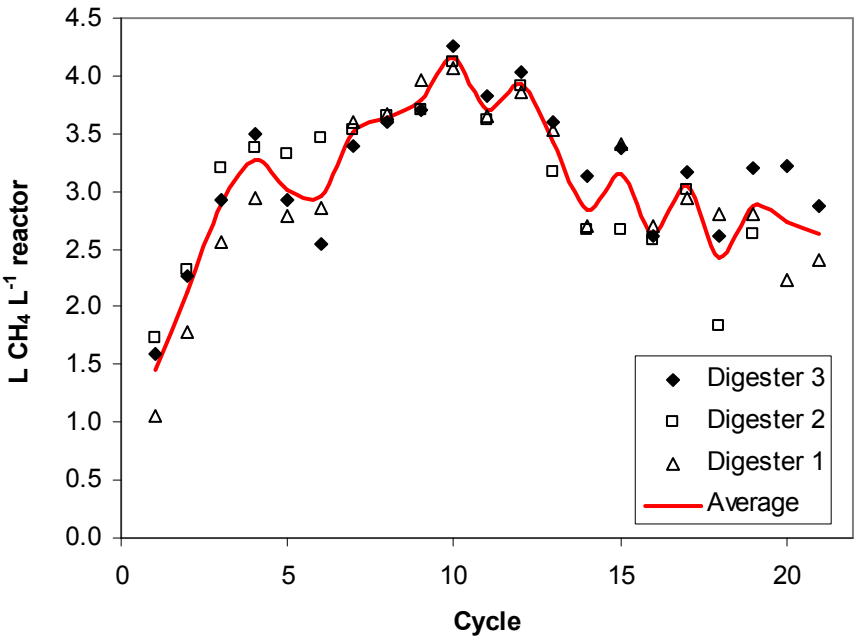


Figure 8.1. Volumetric methane production (L CH_4 L^{-1}) for the 3 digesters and average of all 3 over 21 feed cycles.

The averaged methane production curves for the 3 digesters over the 21 cycles are shown in figure 8.2. These show only a minimal change in gradient towards the end of each cycle, reflecting the loading rate and the cycle length which were chosen to capture the most productive part of the batch methane production curve. As the number of cycles progressed and overall volumetric methane production declined the shape of the individual methane production curves changed and showed a tail-off in methane production at the end of each cycle (Figure 8.2 d).

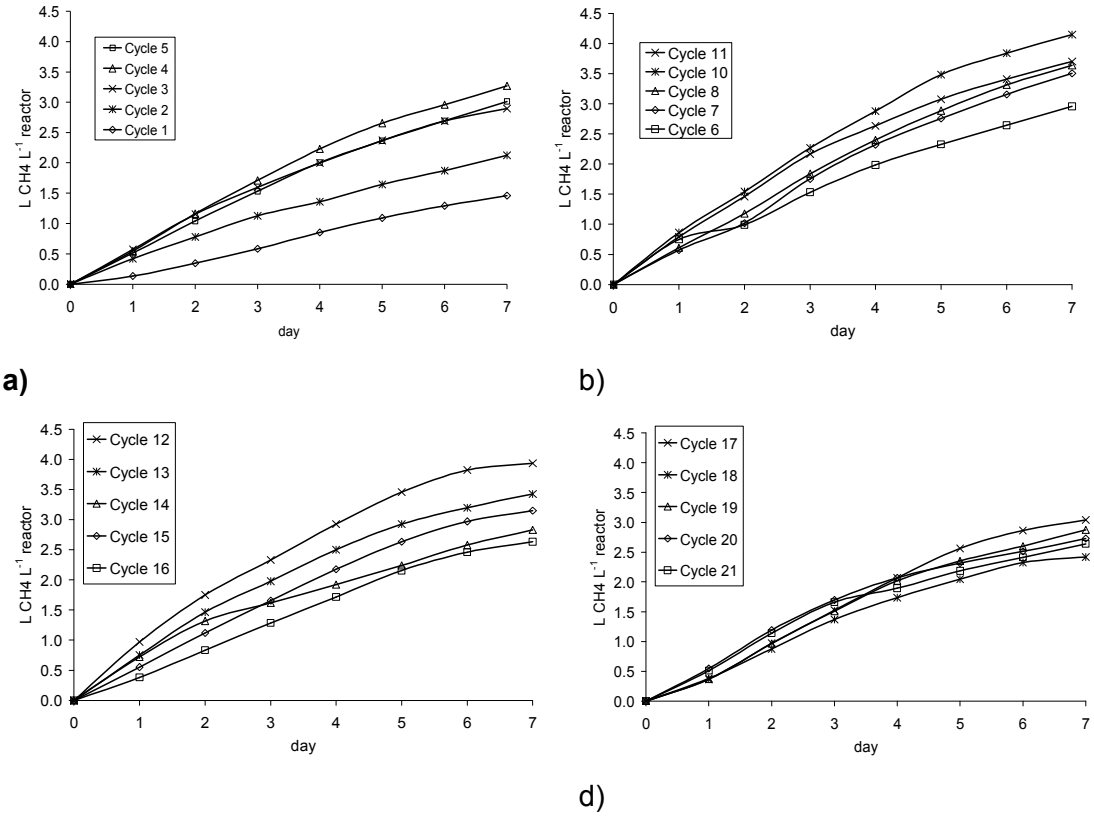
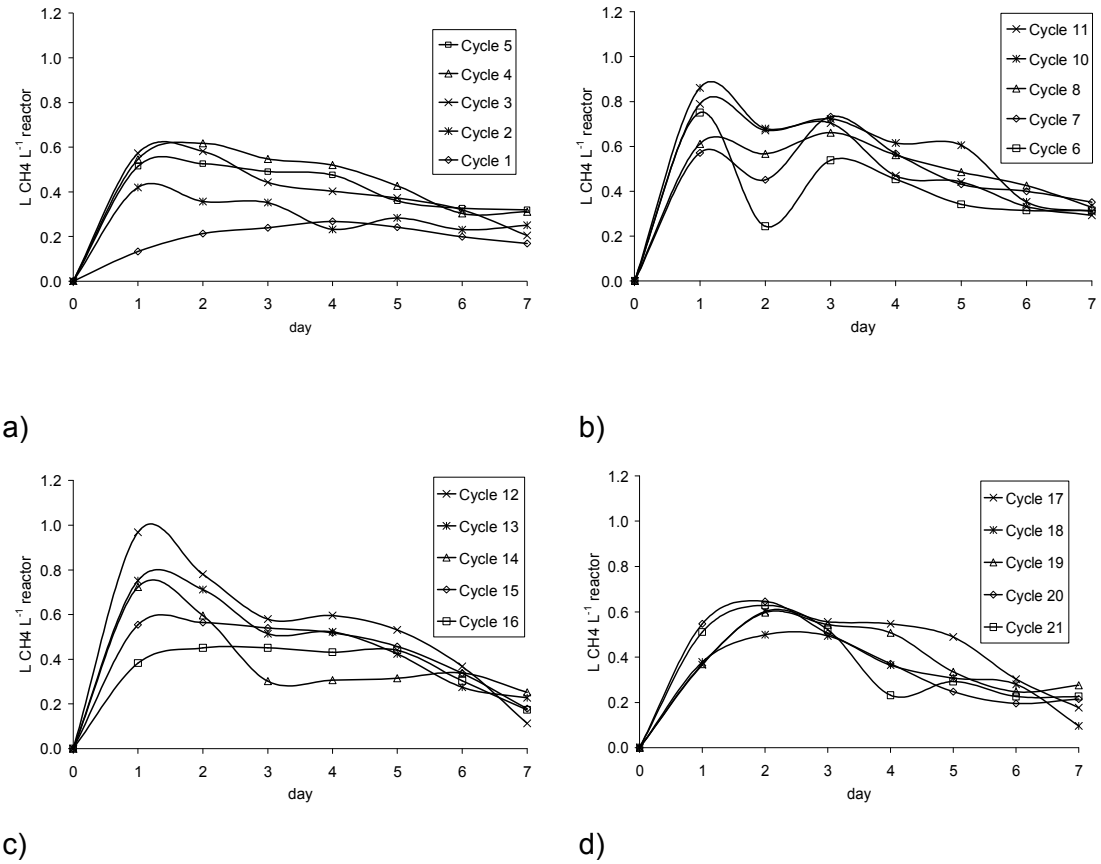


Figure 8.2. Cumulative volumetric CH_4 production over 21 successive feed cycles

The daily methane production curves over the first 5 cycles (Figure 8.3a) show a rapid shift to attaining the maximum methane production on day 2 of the cycle: this had occurred by the second cycle. The maximum methane production at this time was below that achievable and therefore methane production was maintained at quite high levels over the following few days in each cycle. As the number of cycles progressed (Figure 8.3b) the height of the initial peak increased and was followed by reduced production on day 2 of the cycle and then a recovery on day 3. This pattern has been observed previously and is characteristic of this cyclic mode of feeding where the load

and overall productivity is highest. From cycle 12 onwards (Figure 8.3c) the magnitude of the initial peak began to decline and by cycle 15 it was not discernable. This pattern continued over the remaining feed cycles with further reductions in overall productivity (Figure 8.3d)



a) b)

c) d)

Figure 8.3. Daily CH_4 volumetric production over the 21 cycles

All three digesters showed their best volumetric methane production during cycle 10 and the values for each of these digesters at this time along with the average values across the 21 cycles are shown in Table 8.2. The table also shows the calculated specific methane yields as averages and as the maximum achieved.

Table 8.2. Methane data for all digesters over the whole trial.

Digester number	Volumetric Ave. L CH_4 l^{-1} d^{-1}	[Max] (cycle)	Specific yield L CH_4 gVS^{-1}	[max] (cycle) L CH_4 gVS^{-1}
1	0.416	[0.582](C10)	0.291	[0.407] (C10)
2	0.440	[0.588] (C10)	0.308	[0.412] (C10)
3	0.449	[0.607] (C10)	0.314	[0.425] (C10)

8.4. Accumulation of solids in the digesters

The wet weight of the separated fibre and separated liquor at the end of each feed cycle are shown in Figure 8.4. At the start of the experiment the digestate inoculum used contained no fibre; after cycle 1 it contained about 100 g of wet fibre and at the end of cycle 21 this had increased to 800 g. Over this time period 2520 g wet weight of feedstock had been added to each digester. The build-up of the solids was not linear over the time period and the trend line added to Figure 8.4 shows there was a greater degree of solids accumulation over the first 5 cycles than over the subsequent 10 cycles, where the accumulation rate was at a minimum. After cycle 15 there was again an increase in the rate of accumulation. After cycle 20 it became difficult to separate the fibre from the liquor as the fibre had become quite hydroscopic by this time.

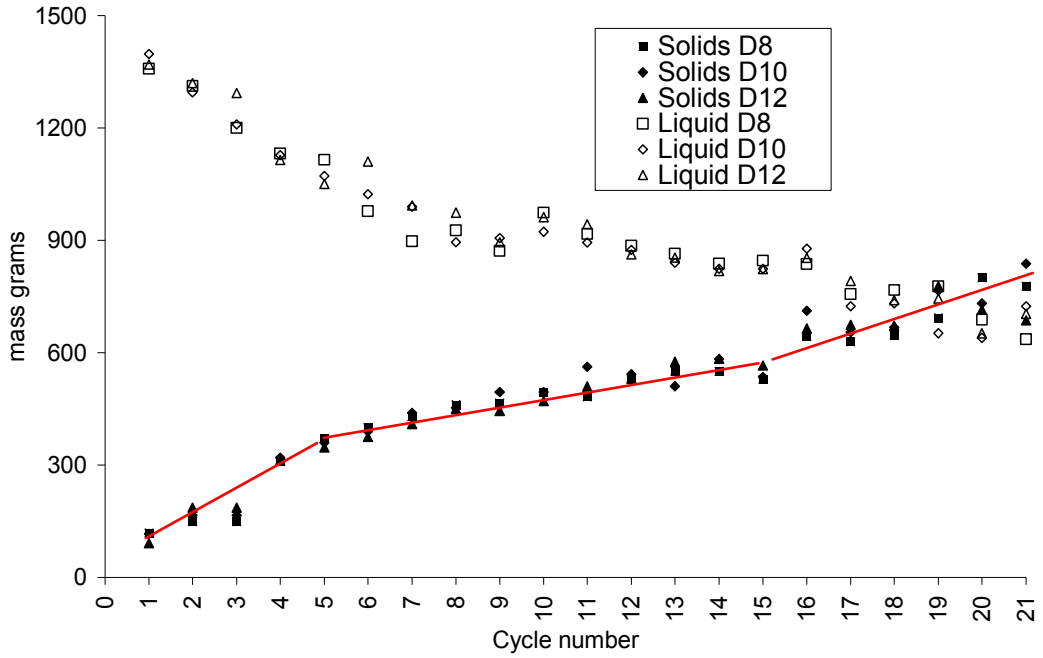


Figure 8.4. Mass change over the solids liquid partition.

The weight of separable liquor decreased with progressive cycles, and because the digesters were maintained at a constant volume the changes mirror those in the solids; however, the proportion of solids within the liquor fraction also changed. In the original digestate inoculum the solids concentration in the liquid fraction was around 10 g VS l^{-1}. This increased to nearly 30 g VS l^{-1} (Figure 8.5), with the largest increases again appearing in the later cycles.

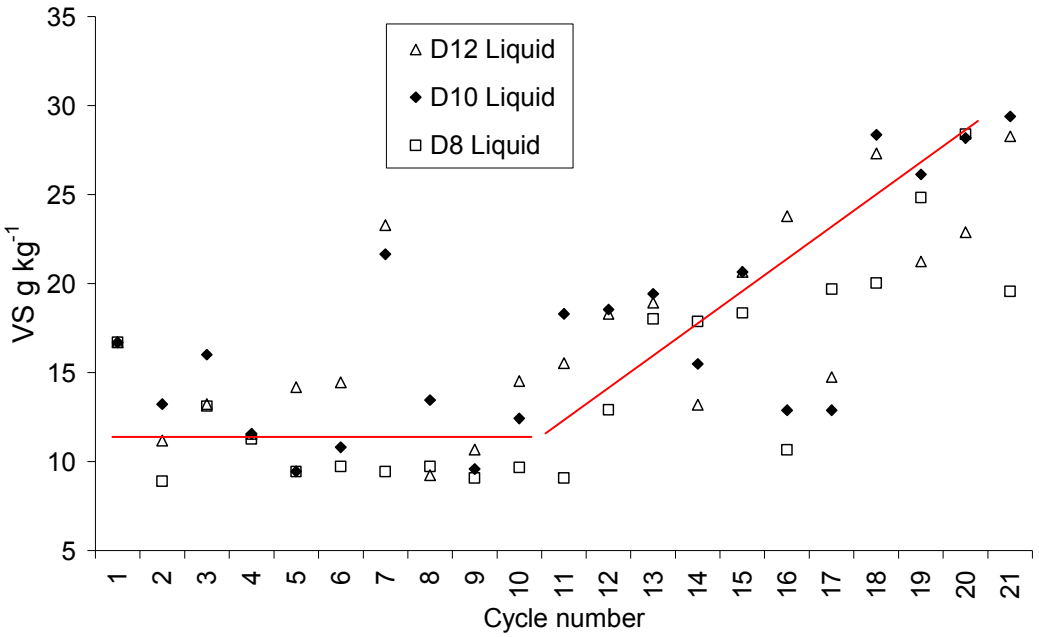


Figure 8.5. VS content of liquor over successive feed cycles.

8.5. Inoculum to substrate ratio

The mass of solids in the digester increases with time, due both to deliberate separation and retention of fibre and to the tendency for the solids in the liquor to increase. At the same time the amount of volatile solids (VS) also increased, although not necessarily in direct proportion to TS. A constant amount of fresh food material was added at the start of each cycle, and it is therefore clear that if the I:S ratio is based on the VS of these components it will increase with progressive cycles, as shown in figure 8.6. The I:S ratio is often used as a simple way of expressing the biomass loading rate, with the VS in the inoculum regarded as mainly bacteria and the VS in the substrate as organic matter that can potentially be degraded. In the case of this digester the interpretation must be different, however, as the VS in the inoculum at the beginning of each cycle will not all be bacteria. In fact as the cycles progress a larger and larger proportion will be non degraded (recalcitrant) organic matter. It is not possible to assess the microbial activity of the inoculum directly unless specific tests are carried out either to enumerate the bacteria within the mixed consortium or by using an activity assay.

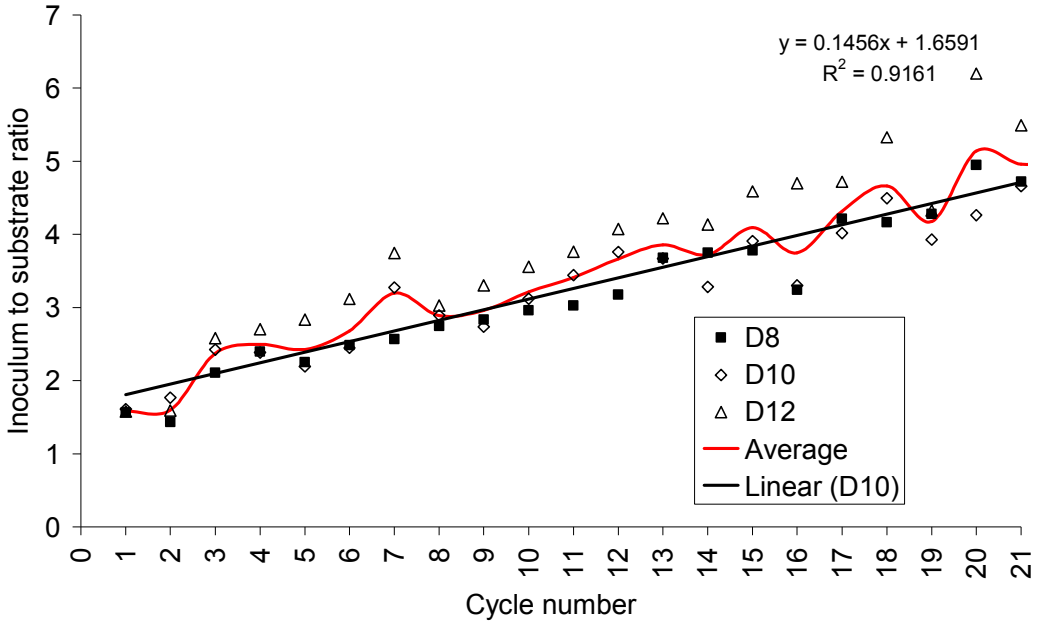


Figure 8.6. Increase of I:S ratio over successive feed cycles

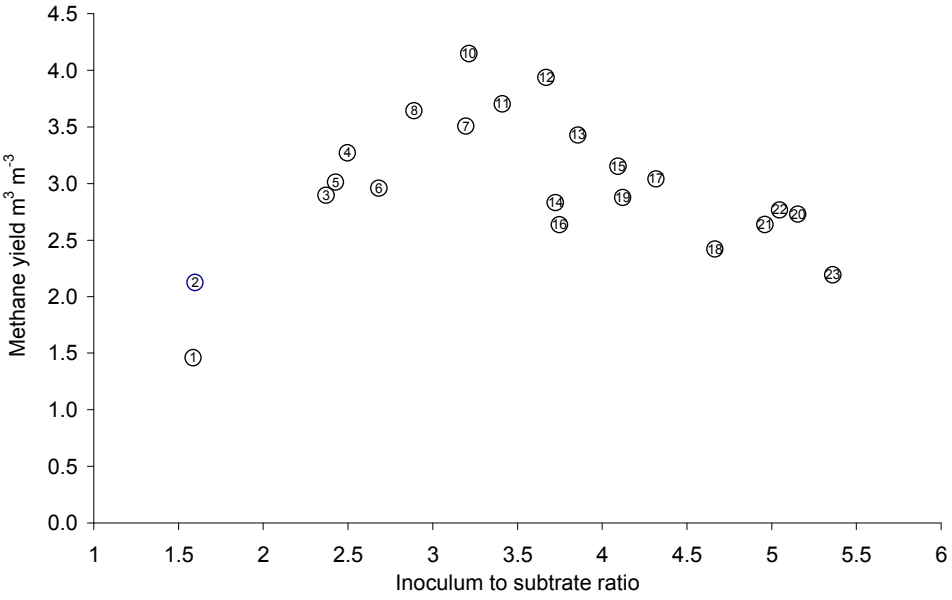


Figure 8.7. I:S ratio compared with methane production over successive feed cycles.

In some respects the digester itself acts as a mechanism for carrying out an activity assay and by plotting the methane yield against the I:S ratio (Figure 8.7) an optimum I:S ratio can be found. By adding the polynomial trendline figure 8.8, the maximum appears to be around 3.2 and was reached around cycle 10.

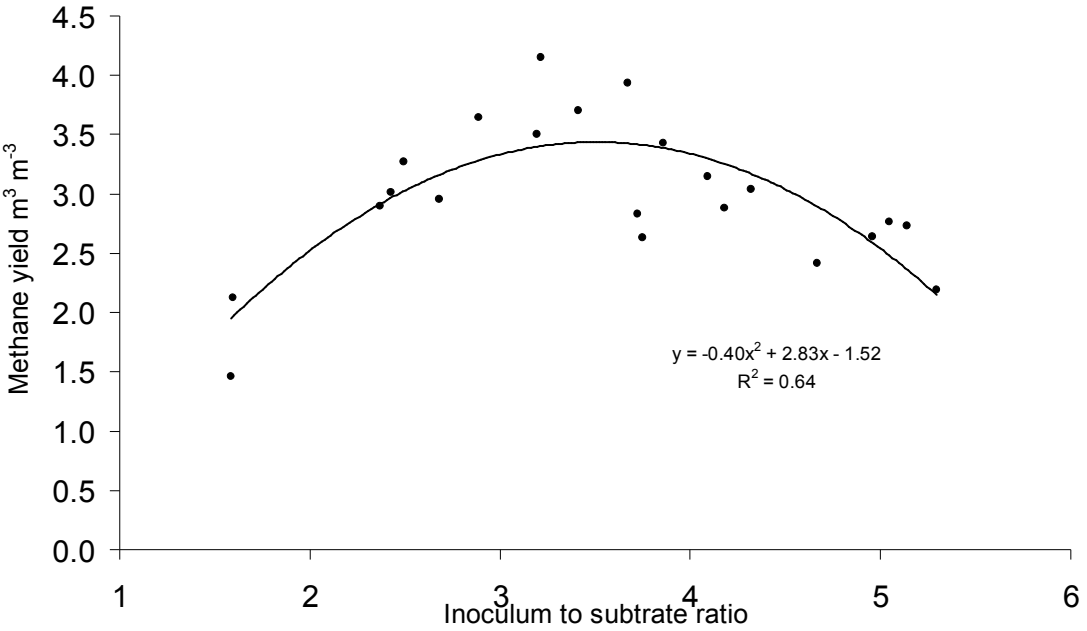


Figure 8.8. . I:S ratio compared with methane production with trendline.

It is likely that up to this time the microbial population has been increasing and has been maintained at a high level of activity. After this point there appears to be some inhibition which causes the volatile solids to accumulate at a faster rate (Figure 8.5), it is probable that after this point not all the VS that is accumulating is in fact recalcitrant. At the moment no hypothesis is proposed to try and explain this change in behaviour other than it appears to be of an inhibitory nature.

8.6 Conclusions

This experiment attempted to correlate the I:S ratio to the gas production as this has been shown to elevate the yield. The yield increased but only up to a point and then other factors worked against the continued rise in specific gas production. Whether the decline was due to the reduction of free liquid or the accumulation of inhibiters was not found here but the result that there seems to be an optimum biomass concentration is worth further investigation. This experiment was never at steady state but the change in I:S ratio was gradual: the effect of holding the I:S ratio at a certain level is a subject for future work. The current experiment aimed to find the level of solids recycle or retention for a plug flow or fed batch system, and concluded that the I:S ratio of around 3.2 was optimum.

Chapter 9

Comparison of the methane yield and production kinetics in a short cycle simulated plug flow digester to the methane potential of the substrate

(070610 T7 1.5L Solids Wasting 10 & 20gVS)

9.1 Introduction

This experiment had the objective of determining the solids destruction and the methane yield in a single pass digester. It was anticipated that attempts to maximise the volumetric methane yield from the digester would compromise the specific methane yield. In a commercial digester this type of compromise is always likely to occur, as operators receive payment for the biogas they produce, and the capital cost of the plant is discounted against the value of these sales. In reality this means that small plants with a short hydraulic retention time (HRT) and high volumetric gas yield tend to be favoured over plants with a longer HRT which have higher specific methane yields but lower volumetric productivity. This experiment provided the opportunity to compare the methane yield and kinetics from a fed batch digester with those of the methane potential test (Chapter 4).

9.2. Experimental method

Four 1.5 litre digesters were operated on a short feed cycle with two receiving an initial batch loading rate (IBLR) at the start of each cycle of 10g VS L^{-1} and two of 20g VS L^{-1}. This gave organic loading rates (OLR) of approximately 1.43 and 2.86 g VS L^{-1} day^{-1} respectively based on fresh feed. Each digester was initially filled with an inoculum digestate taken from R2 (30-litre digester). The digesters were maintained at 37 ^{o}C and connected to a bell over water gasometer. During each cycle the digesters were mixed once per day to ensure that any floating grass layer was entrained within the liquid. At the end of each cycle the digester was opened and the entire contents were passed through a 1 mm mesh. All of the fibre was removed and was not returned to the digester. In the case of the lower loaded digester 120 g of fresh feed was then added and the weight made up to 1500 ml using the separated liquor. Any liquor left over and

all of the separated solids was sampled for TS and VS and a value for the whole digester calculated.

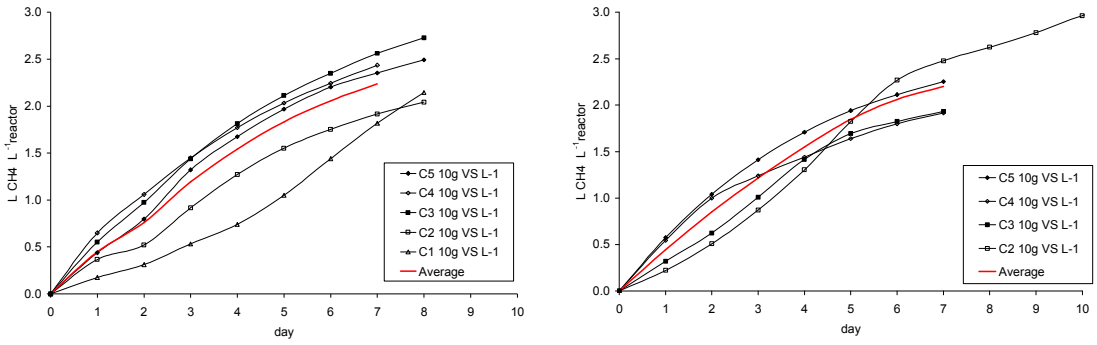
The same procedure was carried out on the higher loaded digesters but in this case 240 g of fresh feed was added to each digester. By operating in this way, all the feed fibre material that had not broken down to a particle size of less than 1 mm was removed from the digester at the end of the cycle. The methane yield within a cycle therefore originates only from the substrate added, with no contribution from any leftover feed solids from the previous cycle. The feed cycle lengths varied from 7 - 10 days but for the final 4 cycles the digesters mainly operated on a 7-day feed cycle.

Table 9.1 Loading conditions for the digester pairs.

Digester N^{o} 1.5 litre	IBLR g VS L^{-1}	OLR VS L^{-1} day^{-1}	Cycle length Days [ave]
D9	10	1.43	7 – 8 [8]
D11	10	1.43	7 - 10 [8]
D10	20	2.86	7 - 8 [9]
D12	20	2.86	7 - 10 [8]

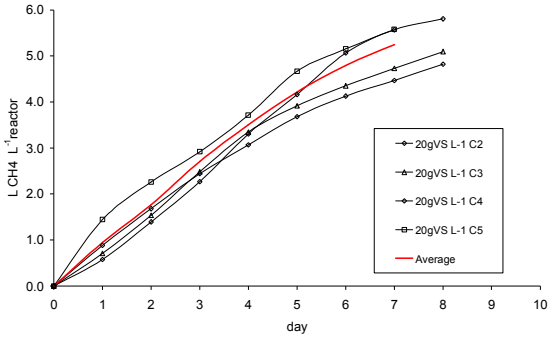
9.3 Experimental results

The cumulative volumetric methane production in the digesters is shown in Figure 9.1. The 10 g VS L^{-1} digesters (a&b), achieved volumetric yields of around 0.30 L CH4 L^{-1} digester d^{-1} and the 20 g VS L^{-1} digesters (figure 9.2. a & b), around 0.70 L CH4 L^{-1} digester d^{-1}.

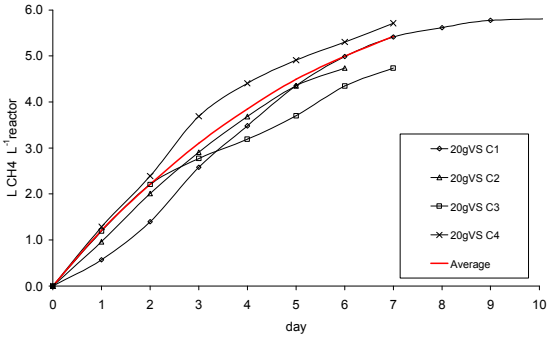


a) D9 – 10 g VS l^{-1} all cycles. b) D11 – 10 g VS l^{-1} all cycles.

Figure 9.1. Cumulative volumetric methane production in digesters D9 and 11 with an IBLR of 10 g VS L^{-1} (a&b).



a) D10 – 20 g VS l^{-1} all cycles.



b) D12 – 20 g VS l^{-1} all cycles.

Figure 9.2. Cumulative volumetric methane production in digesters D10 and 12 with an IBLR of 20 g VS L^{-1} (a & b).

The daily volume of methane produced in each of the digesters as an average over the operational cycles is shown in figure 9.3, and illustrates quite well the relative performance of the two loading rates. The methane production peak in the first few days of the cycle was more pronounced at the higher loading compared to the very constant production at the lower loading. The characteristic fall-off in methane production and then secondary recovery after the initial peak is shown in two of the digesters but is quite small.

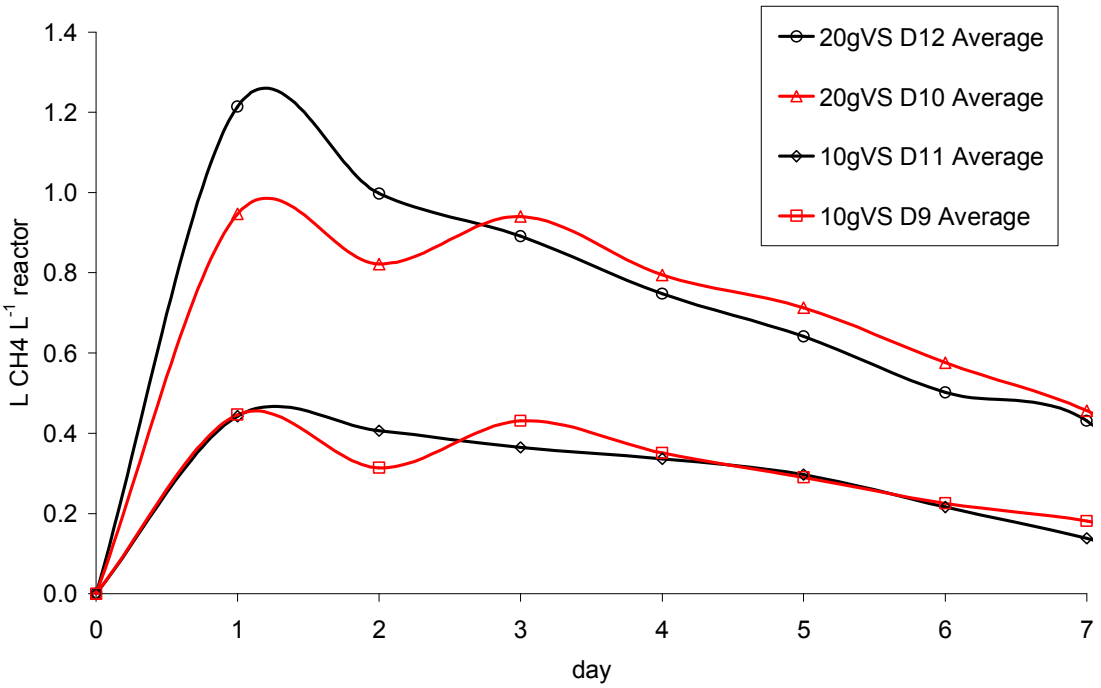


Figure 9.3 Daily volumetric methane production average values from the different cycles carried out at IBLRs of 10 g VS L^{-1} and 20 g VS L^{-1}.

Table 9.2. Performance of all digesters.

Digester number	OLR ave g VS l^{-1} d^{-1}	Specific yield L CH_4 g^{-1}VS	Volumetric ave L CH_4 l^{-1} d^{-1}	I:S ratio
D9 [10g]	1.18	0.252	0.305	1.49
D11 [10g]	1.17	0.241	0.266	1.35
D10 [20g]	2.24	0.295	0.714	0.97
D12 [20g]	2.22	0.293	0.728	0.90

Table 9.2 shows the performance of all the reactors over all the cycles. The variation from the plan was due to changes in cycle length, though small, alter the averages. The changes in VS concentration in the inoculum that were due to the calculation occurring before (based on previous results) the results from the solids determination were available. The inoculum to substrate ratio was lower in the higher loaded reactors but they performed better on both volumetric and specific yield, indicating that I:S ratio was not crucial here. This performance was surprising as the cycle length was shorter than the 12 to 14 days that were needed to gain the majority of the methane potential (Chapter 4). The specific methane yields also are better than the lower load which was operating within the feed cycle defined in Chapter 4. However well the IBLR of 20gVS l^{-1} performed it must be remembered that residual methane content of the effluent solids was still substantial and this need to be dealt with.

9.4. Solids destruction

The VS concentration of the separated digestate removed at the end of each cycle was measured and from this the percentage VS destruction for each cycle was calculated. This value was plotted in figure 9.4 and shows a range between 17% and 40% with the higher loaded digesters giving a higher percentage volatile solids destruction than the lower loaded digesters, except for cycle 4 where the destruction rates were similar. The average volatile solids destruction across the whole set of digesters was 29.9%, but even with this attempt at greater accuracy some samples such as D12 showed considerable variation.

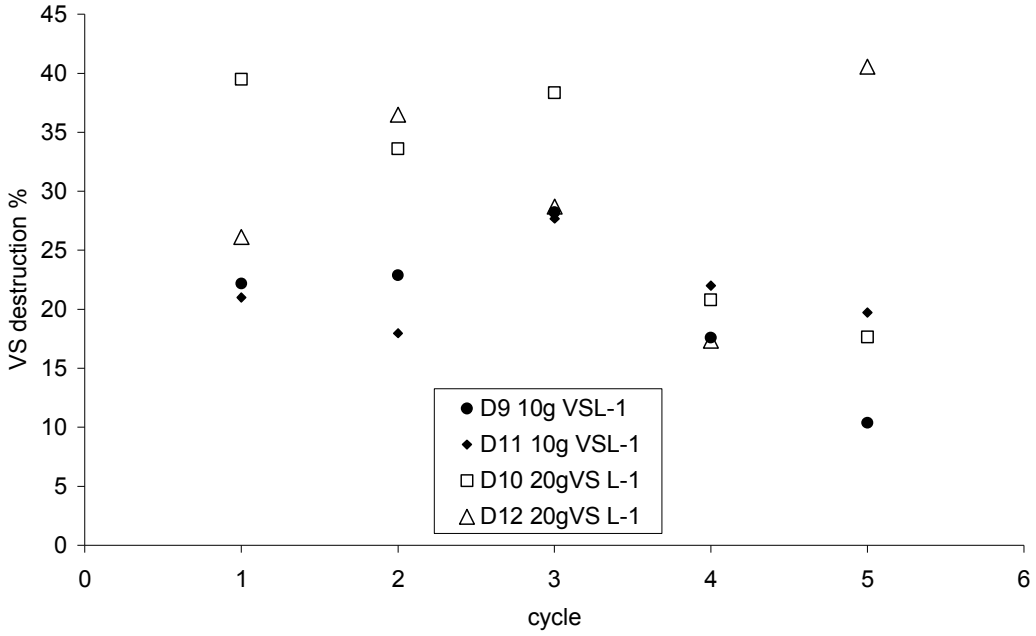


Figure 9.4 VS destruction for each feed cycle in each of the digesters

9.5. Kinetics

The first order reaction constant **k** can be estimated in the same way as for the batch experiment described in Chapter 4. The difference is that in this case all the undigested feedstock solids have been removed at the beginning of each feed cycle. It is also assumed that the inoculum liquor returned to the digester has a negligible methane potential. Although the VFA in the liquid phase are critical for the production of methane, here batch loading was such that there was not significant potential left in the liquor as seen in fig 9.2. Also the VS analysis shows a greater inert component than in the solid material and when separated liquor was digested further (after other similar trials) gas yield was undetectable.

The graphical method containing the results used to determine the constant k for each digester is shown in Figure 9.5.

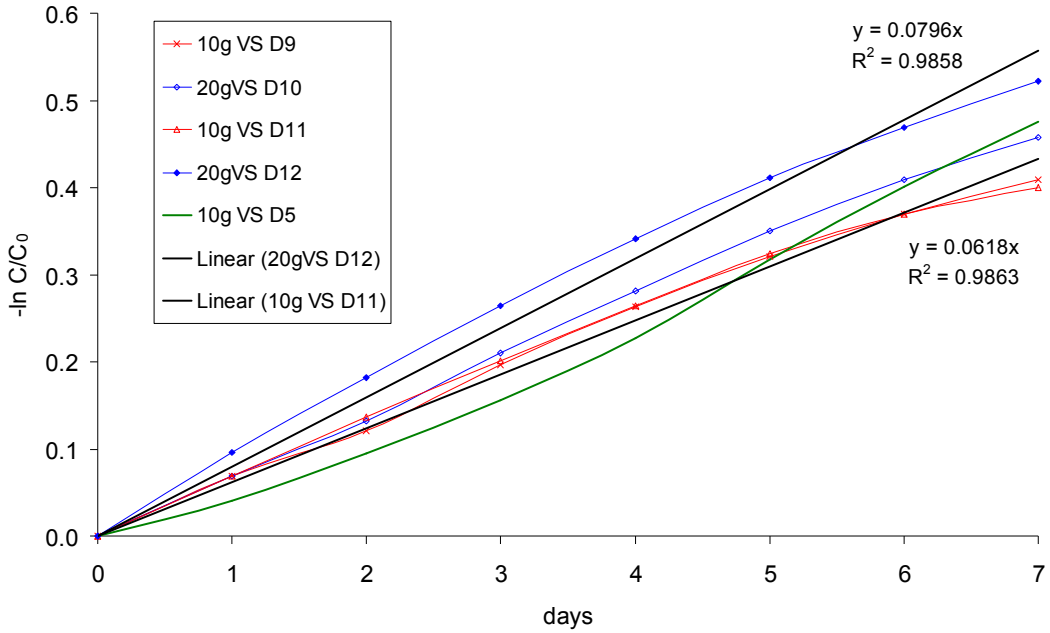


Figure 9.5. Kinetic coefficient for solids wasting experiments compared with best performer from Chapter 4.

When the first order kinetic constant from the first trial was compared, Figure 9.5, D5 (10 g VS l^{-1}) with a k value of 0.0662 d^{-1} was slightly better than the two 10 g VS l^{-1} reactors and p values of 0.372 and 0.339 were obtained for these loadings.
D12 (20g VS l^{-1}) had a k value of 0.0796 d^{-1}, but the paired reactor did not equal this performance and the p values were 0.001 and 0.016 respectively.

9.6. Conclusion

This mode of operation was serviceable and showed that doubling the OLR can double the volumetric gas yield but the residual gas potential from the output effluent has to be captured in a secondary process/ storage, not quantified here. The low I:S ratios seem not to effect the VS destruction or the gas yield.
The k values found were not significantly different from the best baseline value except for the best performing reactor D12 (20g VS l^{-1}) while its pair fell outside the significance range.

Chapter 10

Results summary and discussions

10.1. Introduction

The previous chapters detail individual experiments that proceeded from a general starting point, influenced by findings along the way. As the feedstock and equipment was similar there was an opportunity to compare reactor performance across the different feed regimes. This chapter presents a brief summary of each experiment and a comparison in order to identify operational modes that could be developed into real systems.

10.2. Methane potential of ryegrass

The initial trial seemed to show that a wide range of loadings and possible I:S ratios could achieve good digestion of ryegrass to yield a methane potential between 0.228 and 0.265 m^3 CH_4 kg^{-1} VS added [average 0.245] . At initial loadings above 10 g VS l^{-1} a sag in the gas production rate was identified, indicating an interruption in digestion. When the kinetic constant k value was estimated the range was between 0.0662 and 0.0204 day^{-1} with that the faster reaction at a lower loading rate. Taken together these two findings led to adoption of two loading rates for the subsequent experimental work: one that did not exhibit this interruption and a higher one that did, in case acclimation changed this initial outcome. The usefulness of this batch testing for estimation of the first order reaction constant was undermined by the improvement caused by not stirring, but this did not show an improvement on the ultimate yield. The VS destruction was between 41% - 55% [average 48%], but the analysis also found that the liquid and solid phases had a different VS:TS ratio, pointing to opportunities for control.

Although the bicarbonate alkalinity improved with ryegrass addition and showed no stability problems even at low I:S ratios, performance generally decreased with decreasing I:S ratio, although not completely as the lowest loading was not the best performer.

10.3. Separated solid or liquid inoculum

The inoculum was separated and liquid and solid inoculum was compared on an equal VS content basis showing that liquids are adequate for digestion but the solid inoculum produced some additional gas and this added to the feedstock potential. This led to

further investigation of the potential of returning the solid as both inoculum and residual feedstock. This was conducted under simulated ideal plug flow conditions.

10.4. Stirring and not stirring

The effect of stirring and not stirring were compared to confirm whether earlier indications suggesting that not stirring could offer an advantage, were reproducible and sustainable over a number of cycles. The results indicated that initial improvements in performance disappeared on successive cycles, suggesting that this was a characteristic of start-up, possibly associated with acclimation. The I:S ratio was the lowest for any of the trials and the gas production and specific yield was below that expected for the loading used.

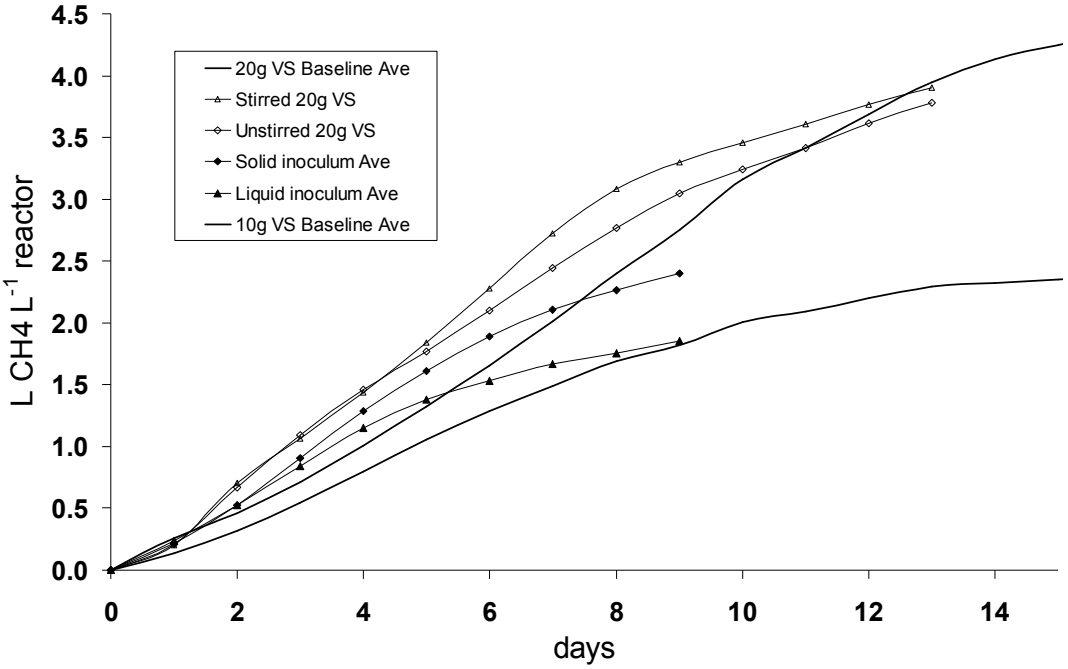


Figure 10.1. Combined volumetric gas production with best performances.

10.4.1 Plug flow compared with batch performance

Figure 10.1 compares the best performance over the first three trials.

In the batch digesters the higher initial batch loading of 20 g VS L^{-1}, R10 gave a better result than the lower IBLR of 10 g VS L^{-1} in R6. This is based on the time taken to reach 70% of the ultimate yield, which in R10 was 11 days; but R10 required only 5.5 days to reach the 70% mark of R6 whereas in R6 itself this took 9 days. Neither of the other 20 g VS L^{-1} regimes (D8 and D10) could improve on the baseline average overall, however, while there is very little difference between the stirred and unstirred variants. It is therefore possible that the difference might be attributable to the initial test being

carried out with a sewage sludge inoculum, which is known to be rich in methanogenic bacteria, and at a slightly higher I:S ratio,

Digesters D4 and D6 which operated at the lower IBLR of 10 g VS L^{-1} showed an improvement over R6, primarily due to the lack of an initial lag phase in gas production. The final volumetric methane yield was similar in the digester with the fibre/liquor inoculum (D6) to R6 both of which achieved ~2.5 L CH4 L^{-1} digester although this was achieved much more quickly in D6. It may be that at the time this particular experiment was carried out the inoculum used had achieved an acclimated population mainly associated with the fibre fraction. Digester D4 showed a lower volumetric productivity with rapid onset of decline: this could indicate that when the liquor fraction only was used as inoculum this carried over less potential substrate.

The maximum gas production rate was very close between all the regimes, with D8 having the most sustained production, closely followed by D6 even with half the loading. The unstirred digester D10 was also a good match for both D8 and D6.

In order to optimise gas production while guaranteeing that the feedstock cannot leave the reactor a target was set of reaching 70% of the potential volumetric methane yield at the relevant IBLR. This equates to methane production of 2.10 and 3.77 L CH4 L^{-1} digester for IBLR of 10 and 20 g VS L^{-1} respectively. The daily production average was 0.30 L CH4 L^{-1} d^{-1} at the lower loading versus 0.21 L CH4 L^{-1} d^{-1} at the higher loading. The best overall performance was from D6 that had the highest daily gas production rate of 0.34 L CH4 L^{-1} d^{-1} averaged over 6 days.

The fact that a lower IBLR on a shorter cycle produced similar volumetric yields to the higher loading on a longer cycle shows the two ways to do the same thing. The lower load has a slight advantage in that the gas production lag at the higher loading was avoided. From this comparison it seems that a lower loading on a ~6 to 7 day feed cycle would maintain a good transformation rate with steady gas production

10.5 Increasing inoculum to substrate ratio

The residual methane yield available from the recycled separated solids was indicated in the previous trial, but more information about this aspect of digestion needed exploring. In this trial no solids were removed from the digester, which had the effect of raising the I:S ratio on each successive cycle. The experiment allowed an estimate to be made of the solids holding capacity of the digester and the number of cycles that

could be operated before the digester would fill up. The experiment was carried out at a 30L scale so that handling losses would be insignificant and in order to give a comparison, in terms of other parameters, with the smaller-scale digesters. As the previous trial had shown stirring to be of little advantage, liquid recirculation was adopted to immerse the grass material in the liquor at least once per day. The retention of the solids even with this minimal mixing improved the methane yield, as the retained solids had a longer retention time and made an increasing contribution to gas production: this effect had been absent in earlier trials.

10.5.1. Reducing the cycle length

To further explore the concept of increasing the loading by reducing the cycle length from 7 to 5 days. By doing this the gas production was increased by 29% for R1 and 22% for R2. The specific methane yield fell in R2 from 0.411 to 0.375 m^3 CH_4 kg^{-1} VS added, but in R1 remained constant at 0.385 m^3 CH_4 kg^{-1} VS added, possibly due to less solids accumulation in that digester. The elevated parameters such as volumetric and specific gas yield included the captive biomass and this was the point. A CSTR operates in this way, all the relevant parameters are worked out on the influent and effluent properties with the pseudo steady state criterion of at least three retention times to ensure stability. This reflects the very slow response of a CSTR to feed regime changes as well as the interference of the reactor contents, whether the gas comes from feedstock or captive biomass in not an issue.

Over successive feed cycles the digesters filled and it was clear that the operational regime was not sustainable over an infinite number of cycles. These trials showed, however, that a digester loaded with fresh grass could be operated for more than 30 cycles, and if these were each of 7 days duration the digester could accumulate feedstock over a six month period such as typically occur in the agricultural cycle during which digestate can not be applied to land. The practicalities of empting a reactor while difficult with a CSTR is not a problem with systems such as Bekon, Dranko and other high solids reactors.

10.6 Retention of the maximum achievable amount of inoculum

1.5l scale digesters were used in the measurement of solids accumulation and to exercise better control over the I:S ratio. The aim was to develop an understanding of how the amount of inoculum effects the methane production. The methane yield increased with increasing I:S ratio reaching a maximum at an I:S ratio equivalent to 3.5, after which point in the solids accumulation process the gas production decreased. This may have been due, at least to some extent, to dispersional mixing becoming

ineffective because of the increased solids content and thickening of the liquor within the digester or a build up of inhibitory factors. More work is needed to find the precise mechanism but this trial provides the starting point. Figure 10.2 shows that at both scales (1.5l and 30l) there is good agreement on the performance indicating where this optimum may be.

10.7. Methane yield and production kinetics in a short cycle simulated plug flow

1.5L digesters were used in an experiment were all the solids were wasted after each cycle. The cycle length was fixed at 7 days and loadings of 10 g VS l^{-1} and 20 g VS l^{-1} were tested. The trial was used to compare directly the reaction kinetics to those in the first trial: the difference between the two trials was the absence of interference from the inoculum. The results showed that the constant determined under each condition was very similar in chapter 4 and chapter 9 at the 10 g VS l^{-1} load at 0.0662 d^{-1} and 0.0618 d^{-1} respectively. Applying a load of 20 g VS l^{-1} gave an increase from 0.0451 d^{-1} to 0.0796 d^{-1} between trials, chapters 4 and 9. The results indicate that the baseline test is a reliable indicator of ultimate yield but the initial gas production rate can be increased. This was the aim of the plug flow trials; to ensure that a good specific yield was maintained while elevating the volumetric yield by reducing the time taken to produce the gas.

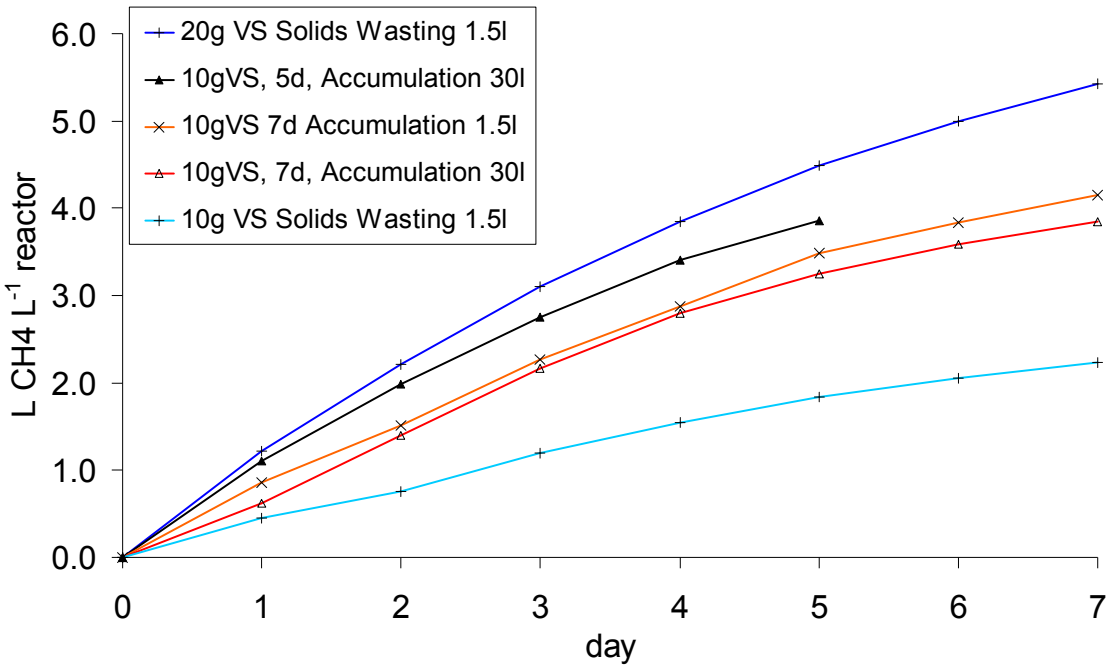


Figure 10.2. Specific methane yield compared for accumulation and solids wasting systems.

Table 10.1. Summary Results all trials

Digester **Trial** No.	Loading gVS L^{-1} [cycle]	Methane Production L L^{-1} [day^{-1}]	VS Destroyed %	Inoculum to Substrate Ratio	Specific CH_4 yield L gVS^{-1} added
T1 R5	10 [29]	2.36	41	2.08	0.236
T1 R6	10 [29]	2.50	51	2.08	0.250
T1 R9	20 [41]	4.57	44	1.04	0.228
T1 R10	20 [41]	5.19	54	1.04	0.260
T2Liquid	10 [7]	1.67 [0.24]	25.5	1.40	0.175
T2 Solid	10 [7]	2.10 [0.30]	23.0	1.49	0.245
T3 Stir	20 [12]	3.77 [0.31]	-	0.71	0.165
T3 Unst	20 [12]	3.61 [0.30]	-	0.64	0.189
T4 R1	10 [7]	3.85 [0.55]	Accumulation	3.5 – 6.3	0.385
T5 R1	10 [5]	3.85 [0.59]		[Ave 5.5]	0.386
T4 R2	10 [7]	4.10 [0.77]	Accumulation	5.7 – 10.4	0.411
T5 R2	10 [5]	3.75 [0.75]		[Ave 9.5]	0.375
T6 All	10 [7]	4.15 [0.59]	Accumulation	3.21	0.415
T7 D9	10 [7]	2.23 [0.32]	24	1.56	0.223
T7 D11	10 [7]	2.20 [0.31]	30	1.35	0.220
T7 D10	20 [7]	5.25 [0.75]	32	0.97	0.263
T7 D12	20 [7]	5.43 [0.76]	30	0.90	0.275

Notes on the table

Bold first column is the trial number then digester number. Second column is loading and cycle length in days. Third column is the methane yield per cycle then daily.

The summary table (Table 10.1) shows the parameters of interest in trials T1 to T7. The accumulation type system (trials T4, T5 and T6) showed a better performance in terms of the specific methane yield. While the best volumetric methane yield was the solids wasting at double the load of the accumulating reactors. Figure 10.2 compares the best performing experiments which were the optimum cycle of the accumulator reactors is compared with the 30 l scale accumulators on both 7 and 5 day cycles, the higher loaded solids wasting reactor is shown as a counterpoint. The solids wasting lower load is shown for reference as all the other reactors bar one are fed at the same rate but the solids are retained. The 5 day cycle may not be very as stable and needs to run for a longer period to find out. The best performer volumetrically does not recover the most energy from the feedstock, this could be a stage in a system. Whether this higher load could be the starting point for an accumulation system at this

load is not clear as there does seem to be the uncoupling denoted by a sag in gas production appears when the load is too high and when I:S ratio is very high. The best performers over a number of parameters, under these conditions are the accumulators – IBLR 10gVS l^{-1} on 7 day feed interval. There seems to be no advantage allowing the I:S ratio to rise above 3.5 though.

Chapter 11

Conclusions

Ryegrass is a slow digesting energy crop and requires a long retention time within the digester to break down to the fullest extent under anaerobic conditions. From the research carried out in this thesis a number of operational modes have been identified.

The key findings were;

- The methane potential of the ryegrass was 0.245 $m^3 CH_4 kg^{-1}$ VS added. This is slightly low compared to other energy crops and the theoretical value of 0.301 $m^3 CH_4 kg^{-1}$ VS added.
- Experiments to determine the first order kinetic constant for methane production showed this varied from 0.0622 d^{-1} to 0.0204 day^{-1} at the range of initial loadings tested and was inversely proportional to loading.
- At the end of the batch digestion period it was found to be beneficial to return the separated fibre to the digester while removing the separated liquid as this allows a longer contact period for the partially digested material that improves the gas yield while also providing the inoculum.
- Stirring showed little advantage over non-stirred conditions in terms of gas yield and, because of the problems associated with mechanical mixing, liquid recirculation was adopted in subsequent trials.
- A novel mode of operation in which feed was added and liquor removed on a weekly basis while solids were allowed to accumulate in the digester gave an elevated specific methane yield. At the loading used the digester could be operated for more than 6 months without emptying. This opens up the possibility of seasonal operation fitting in with the agricultural cycle of annual harvesting and restricted periods for the application of digestate to land.
- Shorter cycle times at higher loadings were attempted and these showed elevated biogas yields, but it is unclear whether this regime could be sustained over long periods.
- When accumulation was started from liquor only inoculum and the digester was fed over 20 cycles the maximum specific methane was found at an inoculum:substrate ratio of 3.5 to 1 on a volatile solids basis. At this ratio the methane production was similar to the larger-scale accumulation experiment at the same OLR, showing the same performance could be achieved at different scales.

- Volumetric methane yield was increased by rejecting separated fibre and retaining the liquor but with a resulting decrease in specific methane yield.
- The first order kinetic constant estimated in the batch accumulation trials was , $k = 0.0796\ d^{-1}$ showing an improvement on the highest value of $0.0662\ d^{-1}$ found previously ($p= 0.001$)

The experimental results can be interpreted either in the context of an ideal plug flow reactor with no dispersion, or as a sequencing anaerobic batch reactor. In either case the findings identified an optimal mode for promoting an elevated specific methane yield while maintaining a continuous elevated volumetric methane yield.

Chapter 12

Future Work

In its document Anaerobic Digestion Shared Goals (DEFRA 2009) sets out a number of areas where AD is seen to be appropriate. The main areas are waste management, agriculture and wastewater. In response to the task for agriculture the NFU has set a goal of 1000 farm based digesters by 2020 and 100 CAD plants with farming links. This is not particularly ambitious considering the growth that Germany experienced when their Feed In Tariff was implemented. The UK's Feed In Tariff follows the German model which rewards electricity generation: the FIT price is 11.5p kWh^{-1}, <500kW and 9p kWh^{-1}, >500kW for electricity (DECC 2010).

There are however pitfalls to wholesale replication of the German model as Lindorfer et al (2008) points out '*In many cases this* [growth] *resulted in copying conventional plant designs. There was no time for integrating new experiences or improvements in the construction of plants.'* If the UK is to learn from the Austrian and German experience it should explore the possibilities already on offer as well as put more effort into specific digester designs and operating protocols for energy crop digestion, drawing on the extensive body of research conducted in Europe to the which the UK has made a significant contribution.

This work here details a number of theoretical or simulated feeding regimes to optimise the specific methane yield of ryegrass digestion. There is no system design here but a set of principles that show advantages over conventional systems. Future work would therefore focus on translating these findings initially into small scale systems that would be fed batch reactors similar to Bekon (www.bekon-energy.de) for example.

Trials of the short cycle (5 day) accumulation regime are needed to discover whether it can be sustained. The work could also be extended to replicate the accumulation model at a higher loading to find whether the inhibition identified remained after acclimation of inoculum to feedstock. This work was intended to inform reactor design, so research and prototyping have to go forward in concert. The attraction of fed batch is that it is modular and there are plenty of proprietary tanks, plumbing and ancillary equipment available, allowing various configurations to be tried without building permanent structures. The design of a tubular or channel plug flow reactor would be

more of a challenge as a wet system may well turn out to be nearer CSTR operation than plug flow.

Self heating as mentioned in relation to large energy crop digesters is of interest as the development of a relationship between size, insulation and loading would be useful in the design of digesters to reduce the parasitic load as CHP may not be the end use for the biogas. With small systems the parasitic heat load is greater but CHP is less of an option and an understanding of how to induce self heating would be valuable.

Ultimately a simple reproducible efficient and appropriate system are required if the UK is to meet its own goals for anaerobic digestion.

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Plug flow anaerobic digestion of ryegrass as an energy crop

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Abstract
In order to find an optimum feed regime for rye grass digestion in plug flow conditions, a series of laboratory-scale trials were conducted using successive cycles of batch digestion. The loading rate and plug flow cycle length were determined from methane potential test with loadings of 5, 10, 15, 20 and 25 gVS l^{-1}. These gave specific methane yields from 0.22 - 0.24 l CH_4 gVS^{-1}. The plug flow simulation used organic loading rates (OLR) of 10 g VS l^{-1} and 20 g VS l^{-1} with minimum cycle lengths of 6 and 12 days respectively, equivalent to an OLR of 1.7 gVS l^{-1} day^{-1}. The use of solid and liquid-only inoculum was compared showing that both facilitate digestion. The liquid-only inoculum produced gas earlier but the solid inoculum gave a higher specific methane yield. This is due to the residual gas yield from the feed solids in the first cycle contributing to the second cycle as inoculum. After an acclimation period there was little difference between the results of trials in stirred and unstirred reactors. The effect of solids retention was further investigated at a 30-litre scale, when liquor only was removed and the reactor allowed to fill over a period of >20 weeks. Retaining all solids resulted in an improved specific methane yield of 0.32-0.34 L CH_4 gVS^{-1}.

Keywords: Anaerobic digestion, liquid recycle, plug flow, ryegrass, solids accumulation, stirred, unstirred.

INTRODUCTION

Historically anaerobic digestion (AD) has been used primarily for waste stabilisation, but the possibilities of energy recovery from both wastes and biomass have become more important with increasing interest in renewable energy and biofuels (Plochl, 2001; Wieland 2000, 2003). This shift in perspective leads to the re-evaluation of process indicators, from reducing the strength and volume of wastes to an environmentally acceptable level to maximising the methane yield from crop materials. AD offers an effective way of gaining renewable energy from crops with improved efficiency when the digestate is used as fertiliser (Salter, 2004).

In the UK, 57% of agricultural land is permanent grassland of some kind with a further 37% considered cropable. Of this 7% is temporary grassland, resulting in 64% of all agricultural land being used for grazing or animal fodder production (DEFRA 2008). Ryegrass *(Lolium perenne)* is not as energy dense as maize *(Zea mays)* or fodder beet *(Beta vulgaris)* but it is equal in its potential for energy production to grains and other green forage plants when used as a feedstock for AD (Wieland 2003), with the advantage that it can be cropped at most growth stages**.** Pasture is well suited to the application of digestate liquor as a nitrogen source, giving the potential for using this in place of artificial fertiliser in a closed loop nutrient cycle.

Ryegrass has, however, a number of problems that make it less attractive as a feedstock for farm digestion. Handling, pumping and mixing are all difficult as ryegrass is bulky, traps gas and floats on the digester contents forming matted solids that can foul stirrers and block pipes. The breakdown of ryegrass is also relatively slow and this is an added

problem at the short retention times common in continuously stirred tank reactor (CSTR) systems. However the low density of ryegrass makes it difficult to overload a digester and this increases the stability. The alkalinity is generally very high and an operating pH of 7.5 is common. As ryegrass is harvested and used as whole crop (all of the plant material above ground level), there does not seem to be a need for extra nutrient addition to maintain stable digestion.

The CSTR is the predominant AD technology in use but it suffers from lower efficiencies than batch digestion due to its hydrodynamic characteristics (Metcalf and Eddy, 2003). The mixing regime and the feed and discharge arrangements on CSTRs leads to bypass, with loss of some undigested feedstock after a period less than the nominal retention time and retention of some fully digested material for longer periods. The effects of this are more noticeable with slow digesting feedstocks and short retention times. Batch feeding is very controllable and provides a guaranteed minimum retention time, but batch reactors cannot be loaded to the same level as a CSTR, and this leads to a reduced volumetric gas yield. Plug flow combines the retention characteristics of batch digestion with the advantages of continuous feeding. Plug flow can be achieved in a number of ways, the simplest of which uses digester geometries that are long compared with their diameter, such as channels or pipes. In a plug flow digester a 'batch of feedstock' - the plug - is placed in the beginning of the digester and is then pushed through as each day's new feedstock is added. In this way the plug remains as a plug and is not dispersed through the reactor. Because of the lack of mixing, inoculum must be added to each batch of feedstock as it enters the reactor. This is the ideal plug flow regime: in practice there is usually some forward and back mixing. The greater the amount of mixing, the more the reactor behaves as a CSTR. Linking CSTRs in series also gives an approach to plug flow as the number of reactors increases (Metcalf and Eddy, 2003).

The aim of the current research was to use plug flow digesters to maximise the specific methane yield from ryegrass by ensuring maximum feedstock transformation. The work considered a number of possible feeding regimes and different inoculation strategies.

METHODS

Determination of the methane potential of ryegrass

The methane potential of ryegrass was determined using 12 no. 2-litre reactors. Each reactor was seeded with 1 litre of sewage sludge, to which was added 0 (control), 5, 10, 15, 20 and 25 g VS l^{-1} of ryegrass (in duplicates). The reactors were then made up to 1.5 l with tap water leaving a 0.5 l headspace. The 12 reactors were run in batch mode until measurable gas production ceased. The average gas production from the control pair was subtracted from the other gas production results in order to remove the contribution due to the inoculum.

Simulation of plug flow

For experimental modelling of ideal plug flow, the substrate was mixed with the inoculum and placed in a batch reactor. This represents day 1. The material then remains in the reactor for the chosen Hydraulic Retention Time (HRT), with each successive day representing the plug moving down a tubular reactor without mixing, as shown in Figure 1. At the start of the second cycle some of the material from the first cycle is returned as inoculum, leading to an increased HRT for the proportion of material retained. For experimental purposes the cycle length can be selected based on

the time required to achieve a certain percentage of the maximum potential methane yield of the substrate as determined in an extended batch experiment.

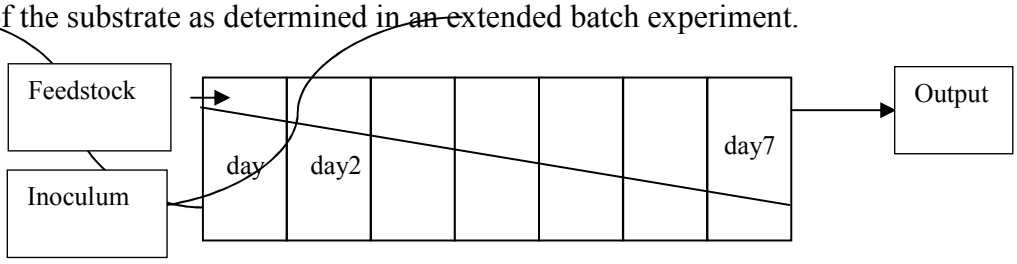


Figure 1. Schematic of the plug flow model

Two plug flow trials were carried out using the method described. The first compared the use of separated solid and liquid fractions as inoculum, and the second looked at the effect of increasing mass transfer by stirring the material.

Comparison of inoculum type

Four 2-litre digesters were used in the trial. Initially each of these received 10 g VS of ryegrass as fresh substrate with the reactor volume made up to 1.5 l using mixed digestate from the batch methane potential test. After one cycle the digestate was separated into solid and liquid portions by passing it through a 1 mm mesh, and the VS content of each fraction were determined. One pair of reactors received the liquid fraction as inoculum, and the second pair received the solid fraction. In practice this meant that each reactor received 10 g VS of ryegrass as substrate. For the liquid-only inoculum the reactor volume was made up to 1.5 litres using the liquid fraction from the previous cycle. For the solid inoculum an equivalent amount of VS to that in the liquid-only inoculum was added to the reactor in the form of retained solids, and the volume made up to 1.5 litres with tap water. In the third and subsequent cycles the amount of solids available to inoculate the solid inoculum reactors was insufficient due to the need to remove material for analysis, and the inoculum solids content was therefore made up by using all the available solid material and supplementing this with VS from the liquid inoculum, then making up the remaining volume to 1.5 litres with tap water. This regime resulted in an Inoculum to Substrate (I:S) ratio of 2.5:1. All reactors were continually stirred throughout.

Effect of mixing on methane yield

A comparison of stirring and not stirring was carried out duplicate pairs of reactors, with one pair completely undisturbed and the other continually stirred at approx 40 rpm. The reactors were set up using 20 g VS l^{-1} with the reactor volume made up to 1.5 l using mixed digestate from the batch methane potential trial.

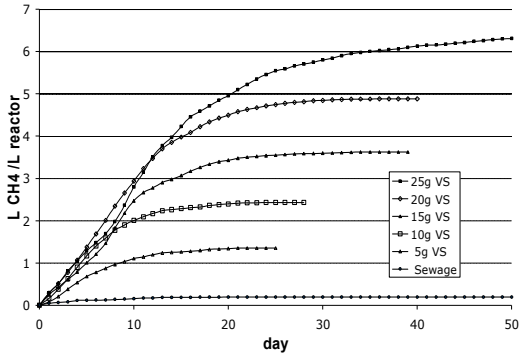
Cumulative feed solids retention reactors

40-litre reactors with a working volume of 30 l were used in this experiment. These were initially full of acclimated digestates derived from ryegrass and sewage sludge, which had different histories resulting in different initial digestate solids concentrations. On the first day of the experiment the liquor was drained from the reactor bottom, and ryegrass added at a load equivalent to 10 g VS l^{-1}. the reactor was refilled with the drained liquor to the working volume and excess liquor discarded after measurement of

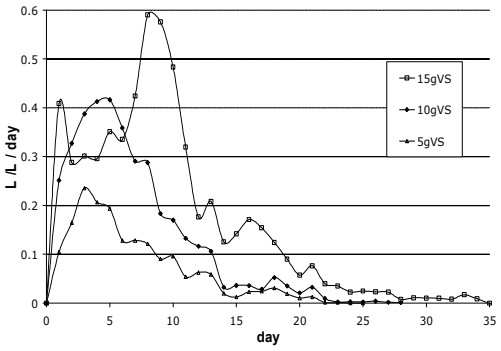
its volume and solids concentration. This procedure was repeated on a 7-day cycle, taking note of the depth to which solids had accumulated in the reactor after draining the liquor. To provide a degree of mixing in the reactor on each of the 6 days between feeding cycles the liquor was recirculated once a day from the base to the top. This helped to recombine the liquid with the solids, which tended to float above the liquid surface as a mat. Cyclic feeding could be continued until the feed addition would exceed the working volume. This would occur at a Solids Volume/ Reactor Volume ratio of less than 1.0 as room is be required for the final feed. As the final feed required approximately 10% of the working volume, the full point ratio was taken as 0.9. In view of the long duration of the trial, the ryegrass was air-dried to ensure a consistent feedstock in each cycle. This material was added to the reactor with four parts of water to give the equivalent water content to fresh grass.

RESULTS AND DISCUSSION

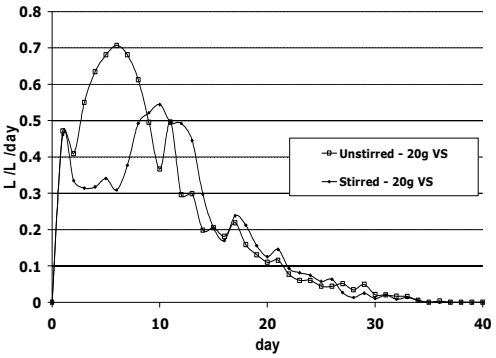
Batch methane potential trial. The results of the trial (Figure 2a) show that the ultimate yields were proportional to the initial substrate loading. The different loadings did, however, show differences in behaviour over the first 10 days. The daily gas production (Figure 2b) shows this more clearly as a lag in the main production peak at 15 g VS l^{-1}. A similar lag appeared in both pairs at 20 g VS l^{-1} and 25 g VS l^{-1} loadings, but was not as severe in one of each pair where a stirrer failure occurred, as shown in Figures 2c and d. Based on these results loadings of 10 and 20 g VS l^{-1} were chosen for subsequent experiments as these gave good gas production without interruption.



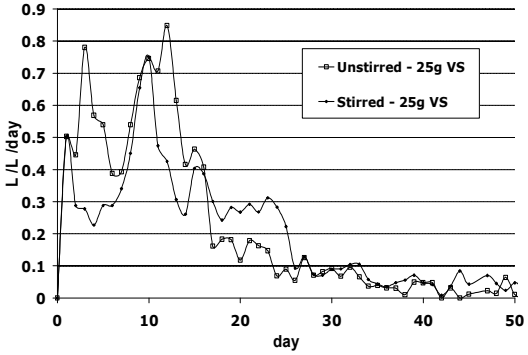
a. Average total production, baseline trail.



b. Daily biogas gas production.



c. Stirred and unstirred at 20 g VS l^{-1} loading.



d. Stirred and unstirred at 25g VS l^{-1} loading.

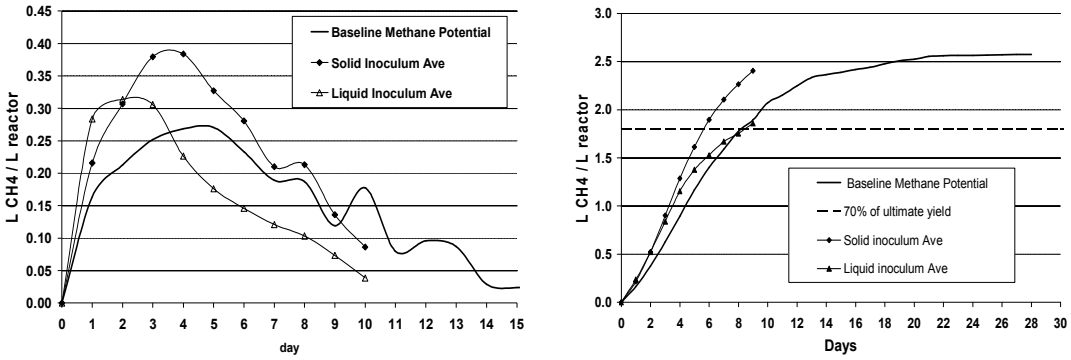
Figure 2. Results of batch methane potential tests

Plug flow experiments

Effect of inoculum type. The liquid-only inoculum showed an improvement in gas production with each successive cycle. The results of the fifth cycle (Figure 3) showed that peak gas production occurred earlier than in the initial cycles, with a methane yield similar to the value obtained in the batch trial. The solid inoculum showed a higher daily gas production peak which occurred later than that of the liquid-only inoculum, and a greater cumulative volume. This indicates that some of the gas production came from the solid inoculum but is less readily converted.

The solid inoculum, once acclimated, produced methane yields similar to those achieved in the batch trial within the first 10 days of the 15-day cycle (Figure 3b). It did not reduce the duration of the main production peak or bring it forward compared to the batch methane potential test (Figure 3a). The liquid-only inoculum produced a peak earlier but with no apparent contribution from the inoculum to gas yield (Figure 3b). This shows that the reuse of the digestate solids as inoculum increases the gas yield by providing a longer retention time.

Effect of mixing. There was initially a difference between gas production in stirred and unstirred reactors, but with successive cycles this reduced until the performance was roughly equal (Figure 4a). This indicates that there was little or no advantage to stirring at a loading of 20 g VS^{-1}.



a) Daily gas liquid, solid inoculum and baseline trial. b) Liquid versus solid inoculum (cumulative).

Figure 3. Comparison of liquid and solid inoculum

Comparison of effects of inoculum type, mixing and initial load. At initial loadings of 10 and 20 gVS l^{-1} in digesters with a 9 and 13 day feed cycle respectively the maximum daily volumetric methane production was similar at the two loadings and in both the stirred and unstirred reactors (Figure 5) but with gas production continuing over a longer period, this is shown in Figure 6 by reference to the daily gas production in the 10 and 20g VS l^{-1} solid inoculum reactors. In both cases gas production was higher than that achieved in the batch methane production tests, the value for which is also indicated in figure 6.

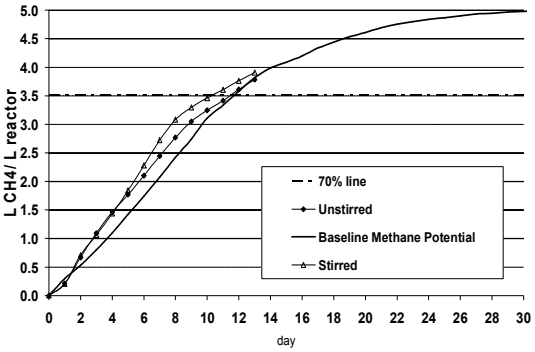


Figure 4. Stirred versus unstirred at 20 g VS l^{-1}

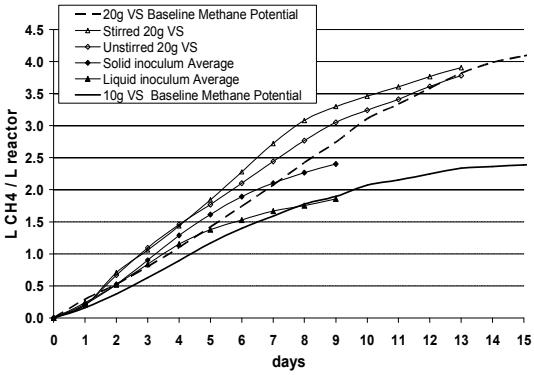


Figure 5. Cumulative gas production stirred and unstirred with solid and liquid inoculum at loadings of 10 and 20 gVS $l^{-1}d^{-1}$

Cumulative feed solids retention reactors. The solids build-up in both reactors was similar and on the basis of the results shown in Figure 7 the duration to projected full point was on the order of 20 weeks. The specific methane yield achieved was 0.32-0.34 l CH_4 gVS^{-1} in this trial. This is far higher than the yield of 0.18-0.23 l CH_4 g VS^{-1} in the 1.5 l trial at the same loading, reflecting the contribution from the retained solids and the increased build up of acclimated microbial inoculum.

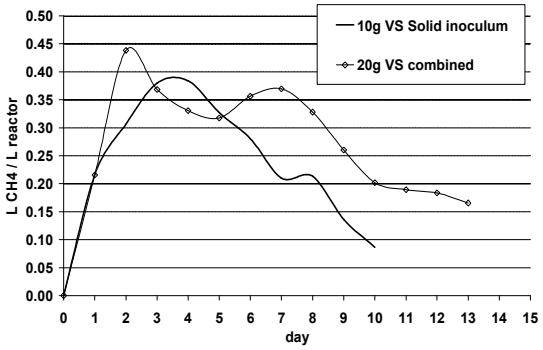


Figure 6. Daily volumetric gas production at 10g and 20 gVS l^{-1} initial loadings.

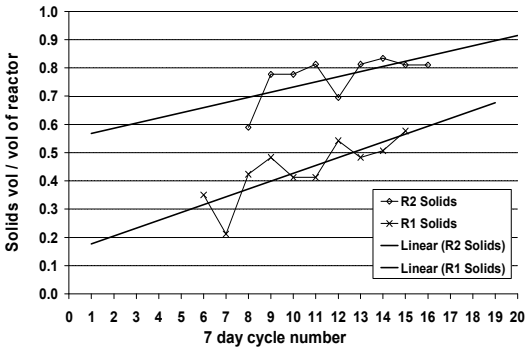


Figure 7. Solids accumulation in digesters over a 17 week period at a loading of 10 gVS^{-1} on a 7 day feed cycle.

A summary of the results from the different feeding regimes, operating conditions, inoculum types and reactor types are shown in table 1

Table 1. Summary results from the reactor trials

Trial, initial load (cycle length)	I:S ratio	HRT (days)	OLR ($g\ l^{-1} day^{-1}$)	Specific yield ($l\ CH_4\ gVS^{-1}$)	Volumetric yield ($lCH_4\ l^{-1}\ day^{-1}$)
Liquid inoculum, 10 g VS l^{-1} (7 day)	2.5	95	1.43	0.178	0.26
Solid inoculum, 10 g VS l^{-1} (7 day)	2.5	95	1.43	0.225	0.30
Stirred, 20 g VS l^{-1} (12 day)	0.86	80	1.66	0.195	0.31
Unstirred, 20 g VS l^{-1} (12 day)	0.86	80	1.66	0.193	0.30
R1 30L, 10 g VS l^{-1} (7 day)	4.8	160	1.43	0.318	0.43
R2 30L, 10 g VS l^{-1} (7 day)	7.5	160	1.43	0.343	0.46

CONCLUSIONS

Plug flow reactors using a solid inoculum showed a higher specific methane yield per cycle than those using a liquid-only inoculum. This is likely to be due to the carry-over of undigested solid material from one cycle to the next in the solid inoculum.

Under conditions of solids recycle an initial load of 10 g VS l^{-1} on a 7-day cycle (equivalent to 1.43 g VS l^{-1} d^{-1}) gave a specific methane yield of 0.225 l g VS^{-1}. This compares with a batch methane potential of 0.243 l g VS^{-1}. Under the optimum conditions of loading in the plug flow reactor the volumetric methane yield was 0.3 $l\ l^{-1}$ d^{-1}. This low volumetric productivity can be attributed to the limited overall load that can be applied to a plug flow reactor using this type of feed material.

Where solids were allowed to accumulate in the reactor, the best specific methane yield of 0.32 - 0.34 l CH_4 gVS^{-1} could be achieved, equivalent to a volumetric methane production of 0.43-0.46 $l\ l^{-1}$ day^{-1}. This mode of operation leads to the digester being full of the undigested fibre component of the ryegrass which will require emptying out once the solids volume / reactor volume ratio reaches 0.9 or above. In practice this could be timed to correspond to digestate application to farmland, leaving the digester ready to receive the subsequent year's crop harvest.

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Appendix C

Hydraulics of reactor flow

The theory of the hydraulic characteristics of reactor flow is summarised in Metcalf and Eddy (2002). The theory is demonstrated using tracer studies where an inert tracer was introduced into a digester either as a pulse input or continuous injection, the output was measured to develop a discharge curve. These curves can be transformed into Residence Time Distribution curves by normalising time; dividing the time axis by the HRT and the concentration of tracer by the initial concentration. The area under the curve is unity representing all the tracer. This type of analysis allows mathematical modelling as well as the comparison of different reactor configurations with each other and the models.

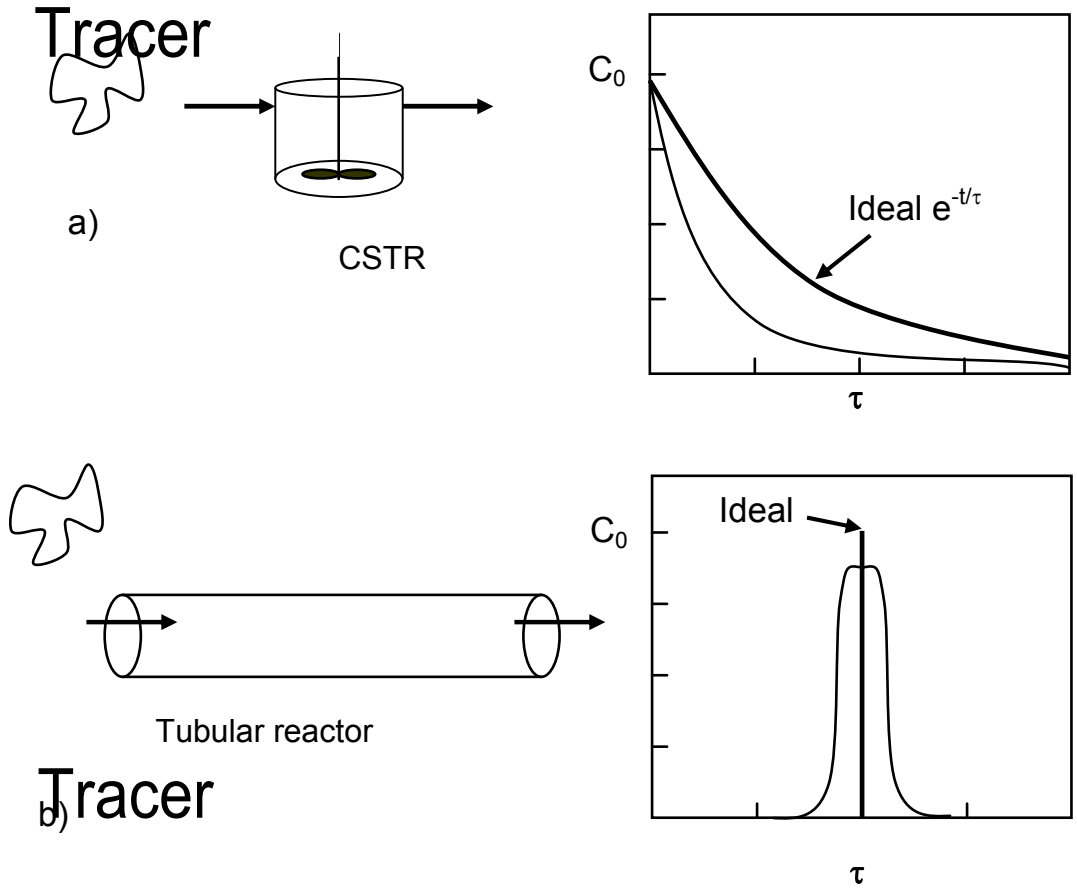

Figure C.1. (after Metcalf and Eddy). Pulse tracer input for continuous feed a), plug flow reactors b), C_0 is the concentration of the tracer and □ is the HRT.

The output curves from the pulse tracer inputs are reproduced in Figure D.1. The curve for a continuously fed CSTR is an exponential depletion of the tracer and it can be shown that after one full HRT 37% of the tracer has not been removed, after two retention times 14% of the tracer remains and after three retention times 5% is still left.

This corresponds to the effect of adding an inert material to a tank and mixing it completely; this effect is compounded by the digestion of feedstock.

Kinetics and washout

To compare the CSTR and batch digestion the decay rates are assumed to be the same, as the data was obtained from a batch test under quiescent conditions at various loadings, a CSTR is not likely to perform better.

First order reaction rate;

$$r_c = \frac{dC}{dt} = -kC \tag{1}$$

r_c is the rate of conversion, $ML^{-3}T^{-1}$.

C is the concentration of material remaining, ML^{-3}.

k is the fist order reaction coefficient, T^{-1}.

t is time.

The integrated form is;

$$\ln \frac{C}{C_0} = kt \tag{2}$$

If a CSTR is loaded in a semi-continuous fashion, a homogeneous parcel of feed is introduced and an equal volume of digestate is removed at each feed interval. The output material is an average of the whole reactor contents at the instant the feed is introduced, assuming that none of the feed has time to mix or move to the exit during this operation. The feed parcel is then fully mixed with the reactor contents and is dispersed over the entire reactor. When the next feed is introduced a portion of the previous feed will exit the reactor, following the washout curve Figure C.1.

When a step change in input tracer concentration is introduced the output resembles Figure C.2. where the concentration on the CSTR increases following an exponential growth curve until the input concentration is approached, but never reached, after nearly three retention times. This response is very slow even when there are no biochemical reactions. The plug flow response is easier to imagine where the move to the feed concentration is immediate if the flow is ideal and slower with increased dispersion. CSTR and batch are two theoretical end points of flow regimes with plug flow in between. Axial dispersion is the factor that moves the hydraulic regime from resembling batch towards fully mixed conditions and at the extreme a plug flow reactor will behave as a CSTR if the dispersion is great enough.

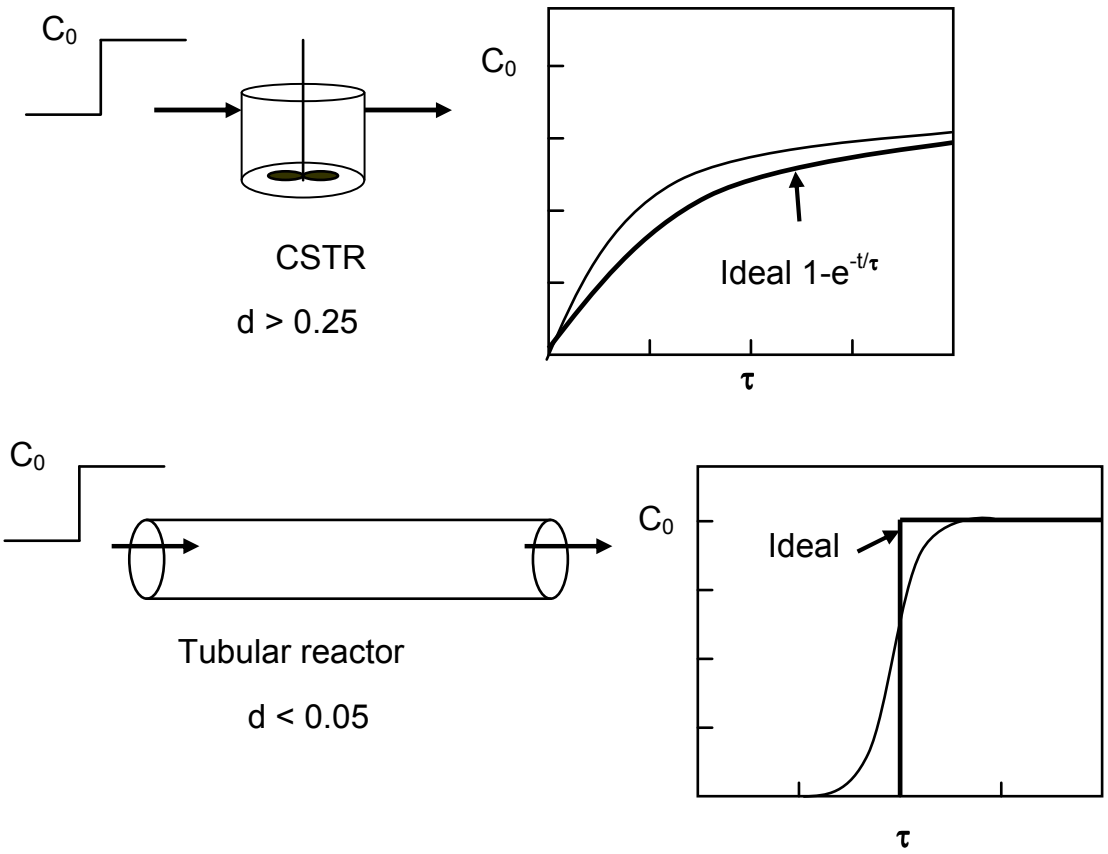

Figure C.2. (after Metcalf and Eddy).Step tracer input for continuous feed a), plug flow reactors b),C_0 is the concentration of the tracer and □ is the HRT.

Dispersion

Dispersion is a key parameter as to how the flow is behaving. Levenspiel (1974) set out the dispersion model based on a dispersion number.

$$D = \frac{u}{L} \tag{3}$$

Where; *D* = molecular diffusivity cm^2s^{-1}

u = average liquid velocity cms^{-1}

L = liquid path length through the reactor cm.

This is significant for the definition of plug flow and Thomlinson and Chambers (1979) defined a D/uL value of 0.2 as a 'large' degree of dispersion while a value of 0.02 as an 'intermediate' degree of dispersion. In an ideal perfectly mixed reactor D/uL = infinity and for perfect plug flow D/uL = 0.

The dispersion can be measured experimentally so it can be compared across reactor configurations. Another useful feature of the dispersion number is associated with its reciprocal, the Peclet number, which is used to show how plug flow can be achieved by

linking CSTRs in series. The Peclet number divided by 2 gives the approximate number of CSTRs in series that correspond to plug flow. A dispersion factor of 0.05 gives a Peclet number of 20 and therefore 10 reactors in series is a close simulation. The OPL system with 8 tanks would have a dispersion number of 0.063 or an intermediate dispersion.

CSTR in series

The transition from the single reactor's residence time curve to the plug flow curve is illustrated in Figure D.4. As the number of reactors in series increases the discharge curve comes to resemble plug flow conditions. This fact enables the modelling of plug flow using a set of standard CSTR digesters such as the ABR configuration.

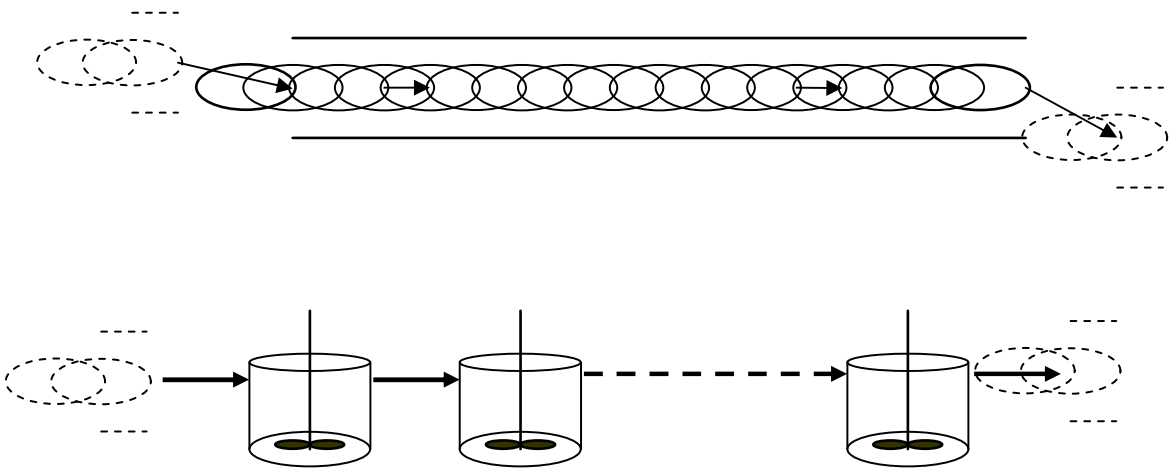

Figure C.3. Plug flow in a pipe and CSTR in series.

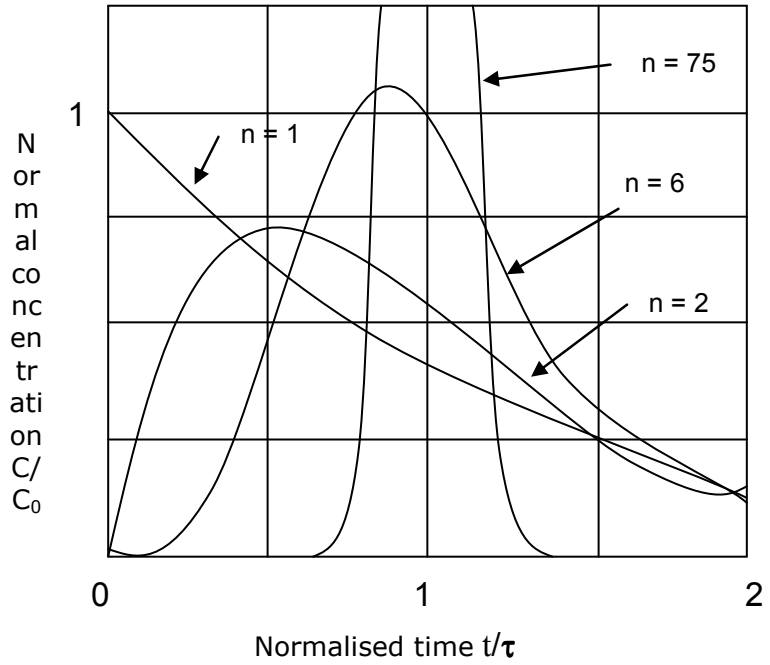

Figure C.4. Effluent concentration curves subject to pulse input to the first reactor in a series. After Metcalf and Eddy.

Appendix D

Thermodynamics and self-heating effects

This section was a preliminary study into the possible issues and applications of thermodynamic work on microbial cultures and its use in quantifing the exothermic reactions, also known as self heating, found in large anaerobic digesters. In a conventional laboratory experiment most of the heat released from the culture is not detected as it is lost to the environment too quickly to be noticed; but at large scale, industrial fermenters may operate nearly adiabatically due to their smaller surface-to-volume ratio (von Stockar and Marison, 1991).

Urs von Stockar and van de Wielen (1997) called for wider use of thermodynamics as a tool to optimise biotechnology. The use of theories involving balances, equilibria and kinetics is well established, while thermodynamics has received less attention. This leads to over-reliance on empirical methods giving less than optimum results. The authors are specialists in the thermodynamics of living systems, using calorimetry to monitor the heat effects in cellular cultures.

Much of the work published by Battley (1994, 1995, 1998a and b, 1999, 2002), Battley et al (1997), and von Stockar et al. (1991, 1994, 1997, 1998, 1999, 2001 a b and c, 2002) has a purely scientific focus, using calorimetry to determine absolute value of various thermodynamic parameters in micro-organisms. One of the applications of calorimetry is to monitor biological processes to optimise them as well as ensure stability while working under specific conditions (Chynoweth, 1997; Koni, 2001). von Stockar et al. (2001) carried out a pilot-scale (200 L) study using on-line monitoring for the production of a bio-pesticide. This was a scaled-up trial based on data from von Stockar and Marison (1998), using glucose yeast medium in aerobic conditions, and

showed that the heat profile of the cooling water could be used for monitoring the metabolic processes within the reactor.

Calorimetry can be carried out at large scale but most work is done at bench scale as conditions can be better controlled. Heat balances conducted at larger scale tend to estimate heat loss to the environment from area and insulation data and in some cases against the outdoor environment (Salter, 2004; 2007, Lindorfer, 2006; Axaopoulos, 2000). This is reasonable but for better results the heat loss is directly measured for the equipment and conditions in the experiment. Calorimetry is an established method of observing the thermodynamic behaviour of materials, substances and processes such as exercise or microbial activity. There are various methods of calorimetry but in terms of investigation of microbial activity both direct and indirect methods have a role (Battley, 1995).

Indirect calorimetry involves the calculation, from experimental data, of the heat exchange from a reaction or process without direct measurement. With direct calorimetry the heat exchange that accompanies a reaction or process is measured. Even this observed measurement needs correction for various factors: the corrections are taken from previous data and therefore make use of indirect calorimetry. The only direct measurement possible is the heat of growth and this comprises free energy, enthalpy and entropy.

D.1 The Bio-calorimeter

An important area of calorimetry is the study of chemical reactions by measuring the heat given out or absorbed by a reaction. There are many types of calorimeter used for this purpose and bio-calorimetry is an extension of thermo-chemistry, used to study living systems. As a lot of the biological systems of interest respire aerobically and these require the supply of nutrients, oxygen/CO2 and stirring; a special form of calorimeter has been developed that can keep a culture alive as well as measure heat flux. The bio-calorimeter, figure D.1. was the equipment used by von Stocker et al (2002) for their work.

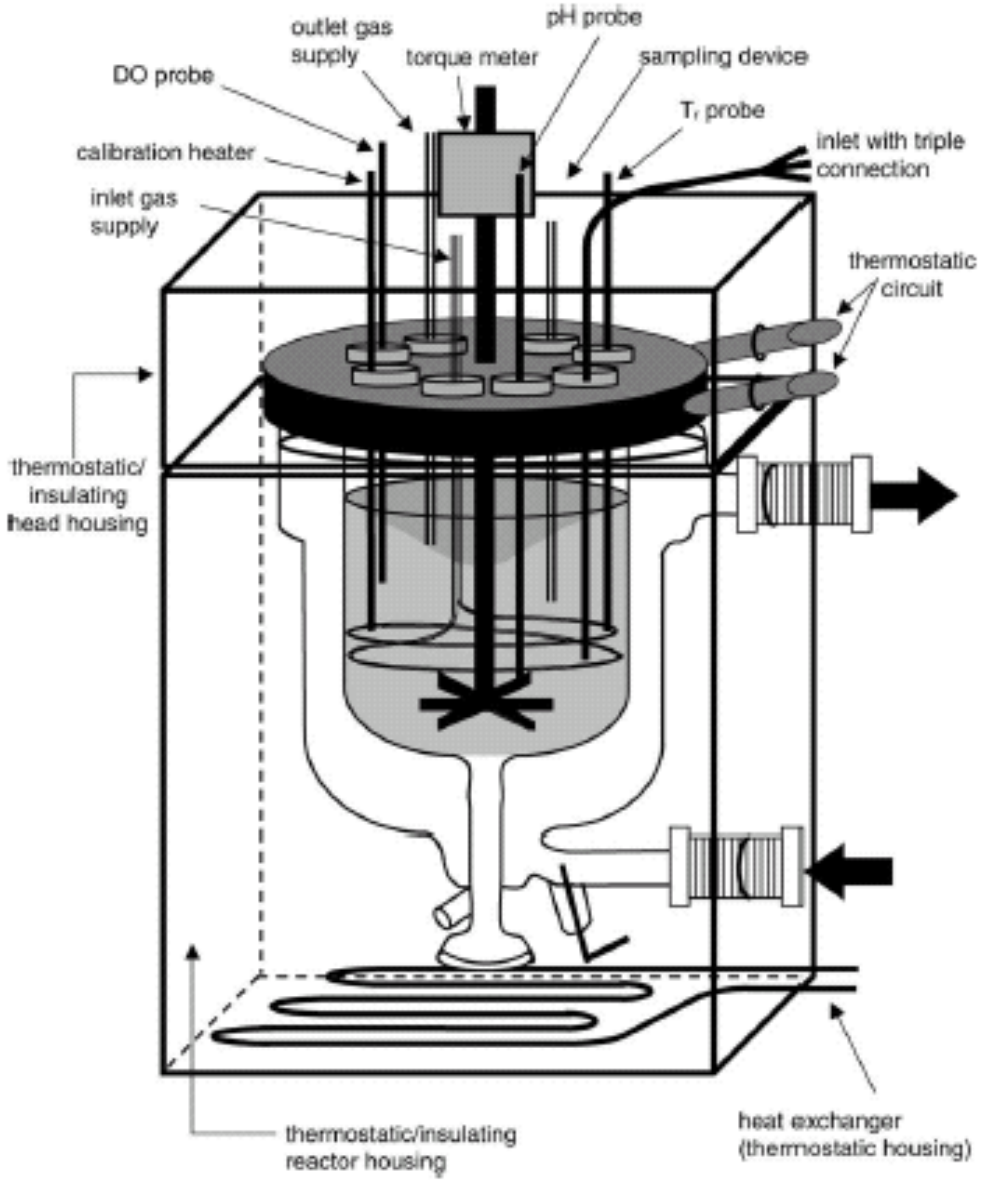

Figure D.1. Schematic representation of RC1 from Mettler-Toledo AG, Switzerland. (von Stockar 2002)

The RC1 is a glass reactor with heated lid in an insulated box. The important feature is the temperature control via the jacket around the reactor. The heat balance is calculated at the inlet and outlet.

$$q_{flux} - q_{baseline} = UA\,(Tr\text{-}Tj) - q_{baseline} = q_{biological} \quad (7)$$

restated becomes;

$$UA\,(Tr_1\text{-}Tj_1) - UA\,(Tr_0\text{-}Tj_0) = q_{biological} \quad (8)$$

where:

U = overall coefficient of heat transfer, W m^{-2} $^oK^{-1}$.

A = cross sectional area through which the heat is lost, m^2.

Tr = temperature of the reactor, ^{o}K.

Tj = temperature difference between the inlet and outlet of the water-jacket, ^{o}K.

$q_{biological}$ = heat evolved by the biological culture in question.

Here the heat flux in the jacket (q_{flux}) minus the heat from the baseline ($q_{baseline}$), the lumped parameters of all the heat sources that influence the reactor, (Tr-Tj) leave the heat caused by biological activity ($q_{biological}$). *UA* is the global heat transfer coefficient and can be measured from a known source such as a resistance heater. The baseline signal comprises stirring, q_s, loss to the environment, q_l, and from additions, q_a, e.g. gas and liquid to the broth. The stirring input can be measured with a torque meter and the heat loss has to be minimised to below the level of noise that could obscure the signal. A more difficult task is to asses the heat of the additions and therefore it is best to avoid them. Gas additions are accounted for in the calibration phase. This calorimeter has a heated head plate to stop condensate causing disturbance in the broth, but the gas exiting the reactor is a heat bridge and so are all the sensors, sampling ports and the stirrer. When all of these are accounted for they can be summed as the baseline signal ($q_{baseline}$).

D.2. Sources of metabolic heat

Life processes are spontaneous (i.e. proceed with an increase in entropy) because they are irreversible and so they form a special case within thermo-chemistry (Metzler, 1977; von Stockar and van de Wielen, 1997). The heat given out by the micro-organisms is a result of their metabolism, including both catabolism of the substrate and the growth of the microbial cells. The sum of catabolism and anabolism is metabolism, catabolism being the larger contributor to heat output in most cases Battley, (2002).

The Gibbs free energy relates the enthalpy, ΔH, the observed energy change and the entropy generated, ΔS. The Gibbs free energy is the theoretical maximum work available from a reaction and the energy necessary for growth. By convention both ΔG and ΔH are negative quantities denoting heat given out from a reaction.

$$\Delta G^0 = \Delta H^0 - T\,\Delta S^0 \qquad (4)$$

Entropy is a property of state and is temperature dependent: it is zero at -273K and increases from there. Entropy is defined in different ways, including the randomness, probability and organisation of molecules in a substance which manifests as absorption of thermal energy. Entropy is a mathematical function having no physical reality characteristic of material bodies, but when multiplied by the temperature for which the entropy has been calculated the product becomes the quantity of thermal energy

needed for a substance to exist above absolute zero (Battley, 1999). This is a statement of the third law of thermodynamics that reactions proceed in one direction and even when they are reversible there is a gain in overall entropy.

Micro-organisms do not violate the laws of thermodynamics in that they do not decrease overall entropy, as they themselves become more ordered maintaining their own entropy level. Internal entropy production associated with the irreversible nature of growth must be transferred to the environment with heat or by producing products of higher entropy than the nutrients (von Stockar et al., 1999). The portion of entropy given out to the environment as heat is the enthalpy term and the entropy change between the reactants and the products is the entropy term.

Battley (1997) investigated the thermodynamic properties of the yeast *Saccharomyces cerevisiae*. This is an interesting choice as this yeast grows both aerobically and anaerobically on glucose and aerobically on ethanol and acetic acid, and these growth patterns can be compared. Figure 2.11 shows graphs for various Gibbs free energy efficiencies and enthalpy conservation efficiencies, the first being the quantity conserved with potential available for non-conservative processes and the second being the enthalpy conservation within the system. With anaerobic systems the conservation of energy includes the formation of external products as well as products stored in the cell. Figure 2.11 illustrates the general pattern of anaerobic fermentation yielding very little energy compared with aerobic reactions on the same substrate, using the specific example of this yeast.

Ethanol fermentation by *K. fragilis* and *S. cerevisiae* has very low heat production and about ¾ of the growth is driven by the chemical entropy change from the breakdown of the large glucose molecules to CO_2 and ethanol. The difference in reaction between the two yeasts seems to be small (von Stockar and Liu, 1999). This shows the expected result that anaerobic fermentations produce less heat than aerobic respiration. This is not the whole picture as there are other metabolic pathways that constitute anaerobic digestion.

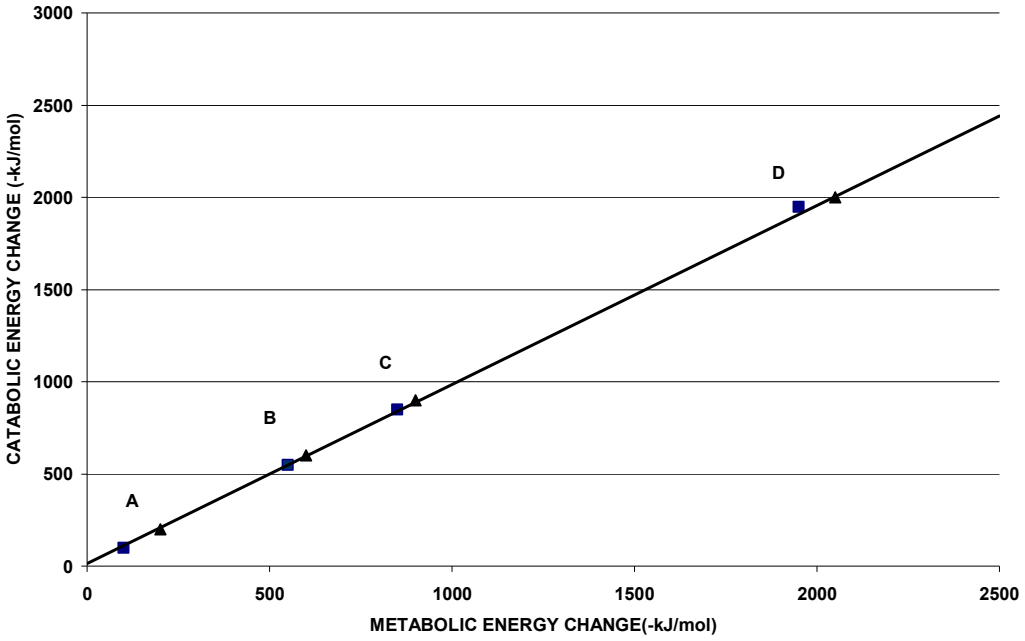

Figure 2.11. Free Energy ■ and enthalpy ▲ for; **A** Anaerobic growth on glucose, **B** aerobic growth on acetic acid, **C** aerobic growth on ethanol, **D** aerobic growth on glucose. (Battley, 1997)

D.3. Methanogenesis

Schill and von Stockar (1994) found that with *Methanobacterium thermoautotrophicum* (a hydrogenotrophic methanogen) the reaction is strongly exothermic.

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O \qquad (5)$$

The reason for the high enthalpy change is the large decrease in chemical entropy during the growth. For spontaneous growth, the enthalpy must not only contribute to the driving force for growth but compensate for the decrease in chemical entropy in the medium, termed entropy retarded growth. Here both chemical entropy and internal entropy is exported as heat. The other main methanogenic pathway, acetoclastic cleavage, has only been investigated indirectly by Heijnen and von Dijiken (1994), who calculated that there should be a net heat uptake during growth.

$$CH_3COOH \longrightarrow CH_4 + CO_2 \qquad (6)$$

Spontaneous growth is possible only because the chemical entropy overcompensates for the retardation of the enthalpy. The enthalpy of the products is richer than the substrate or entropy driven growth.

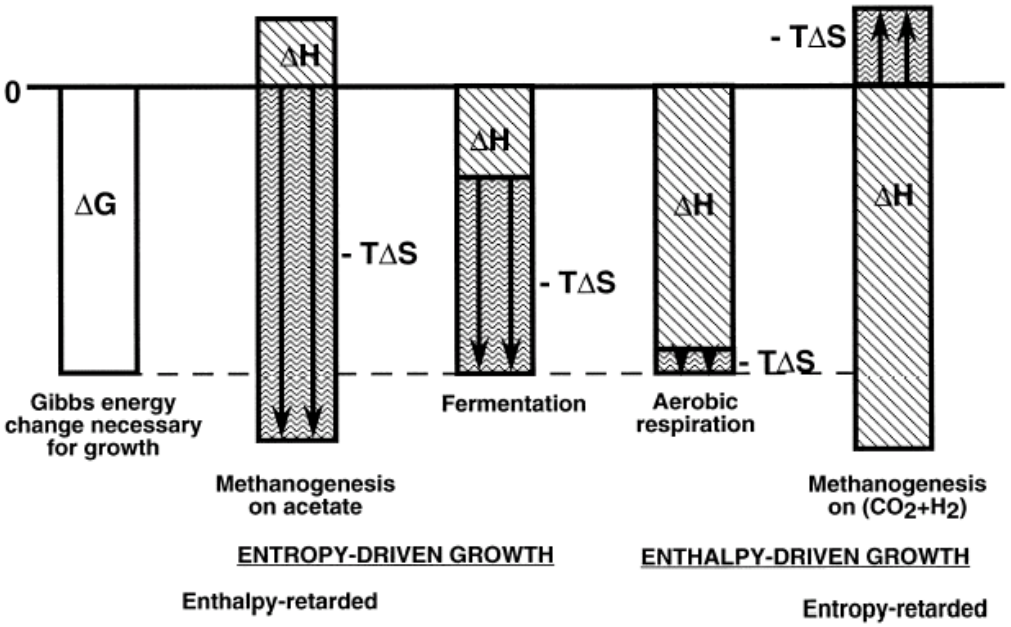

Figure D.2. Schematic of enthalpic and entropic contributions to the driving force of microbial growth. (von Stockar and Liu 1999.)

It is interesting to compare the heat evolution of the various processes as in Figure D.2. The enthalpy part, the measurable heat flux, varies from the extremely exothermic hydrogenotrophic methanogenesis [right] to the endothermic acetoclastic cleavage [left] with aerobic respiration surprisingly in between.

Daverio et al. (2002) applied calorimetry directly to anaerobic digestion of glucose and acetic acid and produced thermograms associated with the microbial activity, showing the heat evolved over time. As microbial activity is directly linked to heat flux (von Stockar 2001), specific processes can be identified. The thermograms show both exothermic and mild endothermic reactions (Figure D.3). After a glucose pulse was fed there was a lag and then a steep peak of heat was detected. Immediately after this glucose peak a small endothermic dip appears associated with the acetate utilisation. The size of this is all the more remarkable since it follows such a large exothermic peak.

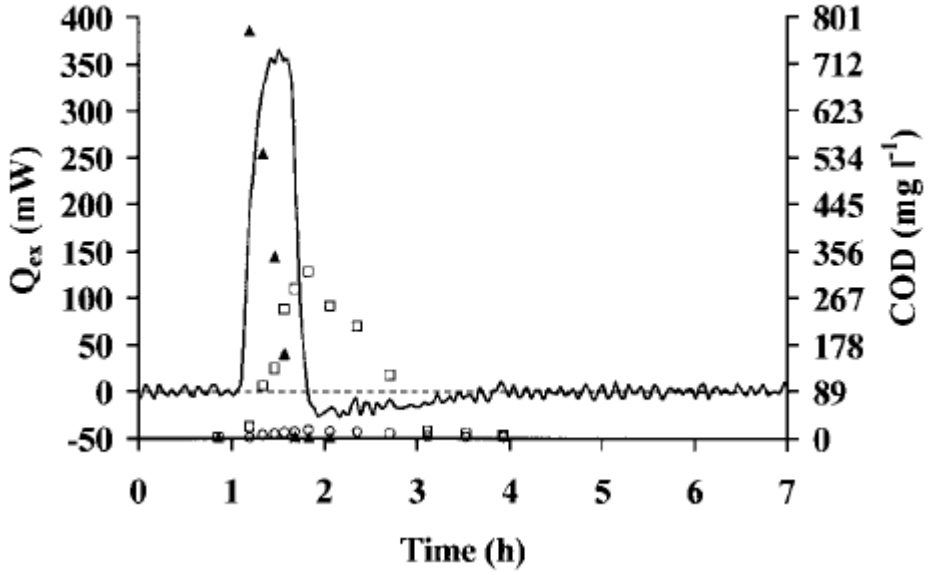

Figure D.3. Comparison between heat production rate with glucose and VFA concentration profiles (35^{O}C): □, glucose;□, acetate; O, propionate. Daverio et al. (2002).

The effect of CO_2 evolution as glucose is fermented and then as acetate is converted is unclear, but is of importance as the reactions involving CO_2 are significant at least in yeast fermentations (Merier-Shneiders 1994).

D.4. Effect of CO_2 and ammonia on heat balance

When using a calorimeter to find metabolic heat unavoidable chemical reactions occur that affect the heat balance. Battley (1994) put the question 'Does CO_2 (aq) affect the energetics [within calorimetry]?'. The CO_2 reaction moving from the liquid to the gas phase and back is a source of non-microbial heat that has to be accounted for as it is exothermic when it moves from gas to liquid and endothermic as it desorbs to the gas phase. The equilibrium position is governed by the partial pressure of the CO_2 in the headspace (Merier-Shneiders 1994).

$$CO_2(g) \longrightarrow CO_2\ (l)\ H_R = -20.3\ kJ\ mol \quad (8)$$

$$H_2O + CO_2\ (l) \longrightarrow H_2CO_3^- + H_3O^-\ H_R = +7.5\ kJ\ mol \quad (9)$$

With fermentations the heat absorbed as CO_2 moves from the liquid to gas phase can produce a large error if CO_2 reactions are not included. The recommended way to avoid this error is to keep the CO_2 transfer rate constant by keeping pH and pressure constant and pre-saturating the broth. The other option is to maintain high partial pressure and high pH. Ammonia has a similar interaction with the digestate and is pH

dependent. Whether this reaction is also significant in heat balances is unclear although the CO_2 term has been added explicitly in the heat balances after 2001 (von Stockar et al., 2002)

D.5 Finding metabolic heat in the laboratory

The application of bio-calorimetry in AD has the problem of low net heat yields and the associated net background heat obscuring the metabolic heat signal. All the methods mentioned are used on continuous cultures that require maintenance of their environment, e.g. heating, stirring, buffering and feeding. All of these interventions disturb the heat balance and have to be quantified and accounted for in the balance. This has led to the design of sophisticated bio-calorimeters that are very sensitive. Determination of whether self heating occurs, however, is a simpler objective than much of the work described. This leads to the question of whether a simpler calorimeter could be used to identify the net heat signal from an active culture.

If interventions can be eliminated leaving only the heat exchange from the microbes with the medium and the chemical interaction with the gas evolution a lot of the noise can be removed. Stafford et al (1983) used an unstirred, unheated plug flow digester and reported a heating effect at the inlet. As gas evolution increases the volume considerably and is the major route for heat loss, if some way of removing the gas and leaving the heat needs could be found and if disturbances are reduced to a minimum it becomes easier and more accurate to determine self heating.

The question arises of how necessary this knowledge is given that heat in AD systems is usually in abundance and has to be dumped. The problem of cooling that comes at large scale is an area where selfheating needs to be arrested but this could also be gained from experience; it is known that digesters in the $1000m^3$ size are candidates for self heating.