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Improvement of the digestion of cattle slurry via the process of co-digestion

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ABSTRACT

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Thesis submitted for degree of Doctor of Philosophy

IMPROVEMENT OF THE DIGESTION OF CATTLE SLURRY VIA THE PROCESS OF CO-DIGESTION

by Marie Cornell

The use of maize (*Zea mays)* as a co-substrate with cattle slurry for the production of biogas was investigated in detail by running several long term digestion trials under different operational conditions in laboratory scale semi-continuous digesters. These conditions included varying the organic loading rate (OLR) from 2 to 6 g VS l^{-1} d^{-1}, the proportion of cattle slurry from 25 to 100%, and the recirculating regime.

Results indicated that the co-digestion of cattle slurry and maize was viable at all loading rates tested with the greatest volumetric methane yield, 1.46 l l^{-1} d^{-1}, produced at a 5 g VS l^{-1} d^{-1} OLR consisting of 40% cattle slurry; this corresponded to a specific methane yield of 0.26 l g^{-1} VS_{added}. Successful digestion was shown at retention times as low as 15 days where a volumetric methane yield of 1.26 l l^{-1} was produced. Co-digestion had a pronounced effect on the volumetric methane yield with improvements of up to 355% when compared to the digestion of cattle slurry alone. Additionally, the OLR could be doubled by the addition of an equal quantity of maize, on a VS basis, with the volumetric methane yield increasing by over 200% without a great loss of the methane potential of the maize.

For each trial undertaken in this research the actual methane yield produced from co-digestion was compared to that calculated to be produced. Support for synergy was shown in the first two trials where the actual methane yield exceeded that predicted however, the method used to calculate the predicted yield was suggested to be an inaccurate determination. To address this inaccuracy a trial was designed testing the digestion of the two substrates alone and together under the same operational conditions and methodology. A comparison between the mono and co-digestion trials indicated that the addition of maize to cattle slurry produced a methane yield that more or less equalled that calculated from the sum of the cattle slurry and maize alone. This brought the early indications of synergy into doubt with suggestions that they were the result of an inaccurate determination of the predicted yield and of inhibition washout.

In the final part of the research an attempt was made to improve the volumetric methane yield by introducing solids recirculation to the co-digestion process with the objective of maintaining the slowly degradable fraction of the maize and cattle slurry in the digester for longer periods. This proved not to be a viable option with the methane production showing a decline; at an OLR of 5 g VS l^{-1} d^{-1}, consisting of 50% cattle slurry, a decline of 0.31 l l^{-1} d^{-1} occurred. Solids recirculation was also introduced to the mono-digestion process to determine whether the differences shown in the co-digestion trial were a result of recirculating the solids of the cattle slurry, the maize or a combination of the two. Results showed that both substrates produced unstable conditions indicating that the co-digestion trial was not the result of just one substrate failing. Liquid recirculation was also tested on the co-digestion of the substrates and while no decline was observed no improvement was produced.

KEYWORDS: Anaerobic digestion, co-digestion, cattle slurry, maize, solids recirculation

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Authors Declaration

I, MARIE CORNELL declare that this thesis entitled IMPROVEMENT OF THE DIGESTION OF CATTLE SLURRY VIA THE PROCESS OF CO-DIGESTION 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:

- this work was done wholly or mainly while in candidature for a research degree at this University;
- where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated;
- where I have consulted the published work of others, this is always clearly attributed;
- where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work;
- I have acknowledged all main sources of help;
- where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself;

Signed: …………………………………………………………………………..

Date:…………………………………………………………………………….

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Abbreviations and Acronyms

BMP	Biochemical Methane Potential
COD	Chemical Oxygen Demand
C:N	Carbon to nitrogen ratio
FVW	Fruit and Vegetable Waste
GHG	Greenhouse Gas Emissions
HRT	Hydraulic Retention Time
IA	Intermediate Alkalinity
IS	Industrial Sludge
OFMSW	Organic Fraction of Municipal Solid Waste
OLR	Organic Loading Rate
SS	Solid Slaughterhouse Waste
PA	Partial Alkalinity
TA	Total Alkalinity
TKN	Total Kjeldahl Nitrogen
TS	Total Solids
VFA	Volatile Fatty Acids
VS	Volatile Solids

1 Introduction

Agriculture is a large sector in the UK accounting for 72% of the land (Defra, 2005) and is a significant contributor towards the production of greenhouse gases, such as methane and nitrous oxide: for example, agriculture in the EU-27 countries was responsible for 9% of the total greenhouse gas emission in 2006 (European Environmental Agency, 2008). In addition to the release of greenhouse gases, agriculture is associated with the loss of nitrogen via the emission of ammonia and leaching of nitrate into the environment. One source of this pollution within the agricultural sector is the production, storage and use of animal wastes; in Europe the quantity of animal slurries produced was 1284 million tonnes per year (EU-27) (Holm-Nielsen, 2007). The release of methane from agriculture is closely related to the number of livestock as methane is the product of the digestive process in animals and the breakdown of their waste products. The release of methane has reduced since 1999 due to reductions in livestock numbers; in the UK the numbers of cattle and calves has reduced by 1428 thousand from 1998 to 2007 (Defra, 2007). Despite this reduction the agriculture sector still produced 0.9 million tonnes of methane in 2006 (Defra, 2006).

Anaerobic digestion is a well known process that can divert the methane which would be released into the environment from raw cattle slurry into a source of bio-energy. The production of bio-energy can be attractive to farmers as it could supply the energy that is required by the farm and provide an additional source of income; anaerobic digestion will also produce a digestate that can be used as fertiliser. Unfortunately, the digestion of cattle slurry alone yields relatively low amounts of bio-energy in comparison to alternative sources of digester feedstock materials, such as energy crops (Weiland, 2006)**.** The low methane yield that can be obtained from cattle slurry is likely to be due to the microbial fermentation that occurs in the rumen of the cattle where the carbon within the feed is converted into methane; this leads to a reduction in the amount of carbon within the faecal residues (Monteny *et al.*, 2006). As a result of the rumen fermentation, cattle slurry usually contain less easily degradable material when compared to material from animals that do not have rumen fermentation, such as pigs or poultry (Hobson *et al.*, 1981). The reduced methane yields from cattle slurry can make the process economically unattractive due to poor income returns. Methods to improve the digestion of cattle slurry include the use of thermophilic conditions, pre-treatment of the substrate and co-digestion. This research aims to investigate the process of co-digestion with maize in terms of the biogas yield; the economic impact of introducing maize will not be studied but it will provide information that could be used in future economic assessment. The process of anaerobic digestion involves the breakdown of organic matter into simple compounds, such as amino acids. It is commonly described as having three main stages: hydrolysis, acidogenesis and methanogenesis. The success of anaerobic digestion is dependent on the successful performance of all three stages to ensure that complete breakdown can occur without any intermediates accumulating that could lead to inhibition. The benefit of using anaerobic digestion is that there are two usable end products: biogas and digestate. The biogas, which consists of methane and carbon dioxide, can be used to supply the energy required by the digestion plant and can also generate an income by providing energy for external sources. The digestate can be used as a fertiliser to enhance subsequent growth of crops and to minimise the use of artificial fertilisers.

1.1 Co-digestion

Co-digestion is defined as the simultaneous digestion of a homogenous mixture of two or more substrates (Braun and Wellinger, 2002); this research is concerned with the co-digestion of cattle slurry with maize (*Zea Mays*). The introduction of maize is an attempt to improve the returns of the anaerobic digestion by the increase in the gas production therefore increasing the potential income for the farmer. The potential benefits of co-digestion can include the presence of positive synergies; an example of a positive synergism could be an improved nutrient composition within the digester as a result of the digestion of a variety of substances (Mata-Alvarez *et al.*, 2000). This presence of synergy can lead to an improved yield of methane when compared to mono-digestion as shown in the research by Machmuller *et al.*, (2007); in this work the digestion of a mixture containing pig slurry, maize and corn cob was studied along with the individual specific methane yields. The results indicated the presence of synergy as the mixture of substrates produced 40% more methane than the yield calculated from the individual methane potentials. A potential disadvantage of co-digesting cattle slurry with energy crops is that farmers may be tempted to replace all of the cattle slurry with energy crops in order to maximise the energy output. It could be beneficial to avoid this as energy crops are not a waste but a source of food; an increase in the use of energy crops can lead to issues to whether crops should be diverted away from food use to energy production.

1.2 Project aims and objectives

Project Aim

The aim of this research is to identify the optimal working conditions that allow the maximum methane production to occur from the combination of cattle slurry and maize. This optimisation process will ensure that the full potential of both substrates is achieved in an attempt to avoid the wastage of maize; it will also consider the presence of any synergy and how this is influenced by different working conditions. In addition it will take into account the influence that the combination of cattle slurry and maize has on the properties of the digestate.

Specific Objectives

The aim of this research will be met by achieving the following objectives:

1. To determine the methane potential of the individual substrates to provide a baseline for comparison to co-digestion trials.
2. To assess how the performance of the digestion of cattle slurry is affected when different quantities of maize are added to a constant load of cattle slurry. This will determine if increasing the load of maize improves the methane yield and to determine if there is a maximum maize load that can be added.
3. To determine how increasing the quantity of maize in a constant loading rate affects the digestion performance. This will determine if increasing the maize but maintaining a constant loading rate has a similar impact to the previous objective where the maize and total loading rate increased.
4. To determine the impact that replacing a winter collected cattle slurry with a summer collected cattle slurry has on the co-digestion process.
5. To investigate the impact that increasing the loading rate of a fixed cattle slurry/maize ratio has on the digestion process and on the synergistic effect. In an attempt to obtain a realistic picture of any synergy, mono-digestion trials will be run in parallel on both cattle slurry and maize. This will allow for a true comparison between mono and co-digestion trials in semi-continuous conditions.
6. To determine the impact that solids recirculation has on the performance of both mono and co-digestion. This is an attempt to maximise the methane yield by retaining the undigested maize within the digester for longer periods therefore achieving the full potential of the maize.

7. To determine the impact that liquid recirculation has on the co-digestion process in terms of the methane yield. This will provide a comparison to solids and no recirculation in an attempt to discover the optimal recirculation conditions.
8. To determine the impact that the addition of maize has on the characteristics of the digestate. This objective will be met by observing the impact that the different working conditions tested in the previous objectives have on the characteristics of the digestate.

2 Literature Review

The aim of this literature review is to provide a background to the digestion of cattle slurry and how introducing an additional substrate can improve the performance; it reviews previous research that has been undertaken on the use of cattle slurry and/or energy crops as co-substrates. In addition it draws attention to the main parameters that should be considered when optimising the co-digestion process and highlights research which indicates the presence of synergies. The final section of this chapter aims to uncover the characteristics of the digestate that can influence the fertiliser quality of the digestate.

2.1 Digestion of cattle slurry

Previous research into the digestion of cattle slurry alone has produced a wide range of specific methane yields. Figure 2.1 provides an overview of the digestion performance of cattle slurry but does not consider the different retention times and organic loading rates (OLR) tested, both of which can influence the digestion performance.

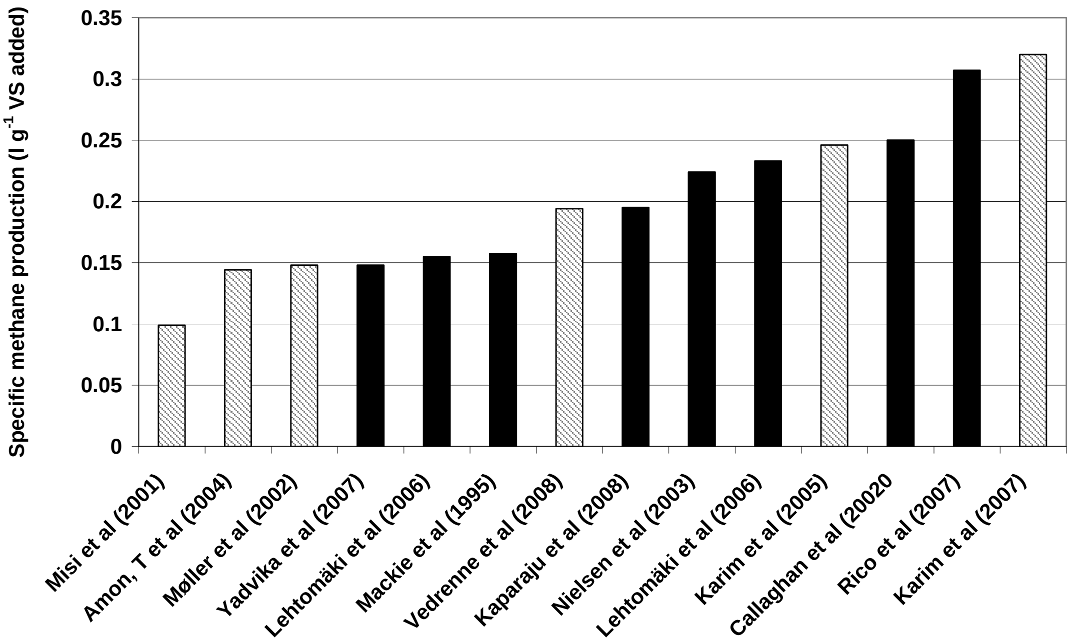


Figure 2.1: Literature values of the specific methane yield of dairy cattle waste at mesophilic temperatures (values are averages of the yields obtained in the research). Striped bars represent batch trial while the filled bars represent long term, continuously fed digesters.

Figure 2.1 shows that the specific methane yield produced from the digestion of cattle slurry as reported in previous literature remained within the range of 0.099 and 0.32 l g^{-1} VS $_{added}$ with an average value of 0.20 l g^{-1} VS. Focusing on the lowest and highest values, it can be seen that Misi *et al*., (2001) produced a yield of 0.067 l g^{-1} VS_{added} while the research by Karim *et al*., (2007) gave a yield of 0.40 l g^{-1} VS_{added}. The high values produced by Karim *et al*., (2007) were obtained an experiment which was unusual in that the digesters were not fed daily, instead feeding occurred every other day. The value 0.40 l g^{-1} VS_{added} is 25% greater than the nearest methane yield of 0.307 l g^{-1} VS_{added} (Rico *et al.*, 2007) and is not repeated elsewhere in the reviewed literature. This suggests that this value is untypical for the digestion of cattle slurry alone; it can also be observed that the specific methane yield of 0.40 l g^{-1} VS_{added} is greater than some methane potentials reported in literature for energy crops. Energy crops typically have a greater ability to produce methane when compared to animal wastes; for example the methane yield of maize has been reported to be within the range 0.338 and 0.422 l g^{-1} VS_{added} (Amon, 2006, Machmüller *et al.*, 2007). This unusual value does question the reliability of the results produced by Karim *et al.*,(2007; there was little discussion to explain the high methane yield: there was a lack of data on the characteristics of the cattle slurry and no details about the cattle were given (i.e. feeding regime, housing conditions). This makes it difficult to determine the reason behind the high value. The research by Misi *et al.*, (2001) provided the lowest methane production, 0.057 l g^{-1} VS and is comparable to the research by Karim *et al.*, (2007) as there was little discussion to explain the low methane yield. The research did not provide data about the cattle slurry used or any information about the cattle. The lack of information makes it difficult to determine the cause behind the poor performance however, from the volatile solids destruction rates it was suggested that it was the hydrolysis stage that was inhibited due to the low rates achieved.

Table 2.1: Operational conditions followed by previous research investigating the digestion of cattle slurry; the volumetric and specific methane yield produced by each condition are also given to provide a comparison between the items of research

Reference	Organic loading rate	Retention time	Volatile solids destruction	Methane yield			Notes
	g VS l^{-1} d^{-1}	days	%	l d^{-1}	l l^{-1} d^{-1}	l g^{-1} VS destroyed	
Callaghan *et al.*, (1998)	5.07	21	54	22.82	1.27	0.46	Approximate values from graphs used
Lehtomäki *et al* (2006)	2	28	25	1.24	0.31	0.62	
Karim *et al.*, (2005)	2	16.2	36.9-63.7	1.94-2.3	0.52-0.62	0.43-0.77	Greatest methane yield produced from the digester mixed by an impeller. Lowest was from the digester mixed by biogas recirculation
Karim *et al.*, (2005)	3.24	16.2	34.8-41.82	2.3-2.9	0.67-0.78	0.53-0.69	Greatest methane yield was produced from the digester mixed by slurry recirculation. Lowest was produced from the unmixed digester
Kaparaju *et al.*, (2008)	5.23	15	n/a	1.61-1.65[1] 1.87-1.76[2]	0.45-0.46[1] 0.43-0.48[2]	n/a	[1]Continuous mixing [2]Various mixing No volatile solids destruction given
Mackie *et al.*, (1995)	3-12	10-20	26.5-46.2	1.87-3.81	0.62-1.27	0.72-0.76	
Karim *et al.*, (2007)	1.11-5.87	4.6-24.4	41-67	1.67-4.47	0.44-1.18	0.30-0.84	Digesters were fed on alternative days

Table 2.1 provides a brief outline of several items of research on mono-digestion and gives the operational conditions tested in the research. A range of OLRs have previously been tested, from 1.11 to 5.87 g VS l^{-1} d^{-1}. In terms of the volumetric methane yield and the specific methane yield (per g VS destroyed) the highest OLR produced the greatest yields. In addition to the OLR a range of retention times have been tested, 4.6 to 28 days. Work by Karim *et al.*, (2007) studied the impact of increasing the loading rate from 1.11 to 5.87 g VS l^{-1} d^{-1} with the retention time declining from 24.4 to 4.6 days. As the loading rate increased the volumetric methane yield followed the trend shown by Figure 2.2 however, in contrast to the trend shown by Figure 2.2 complete failure was not reached.

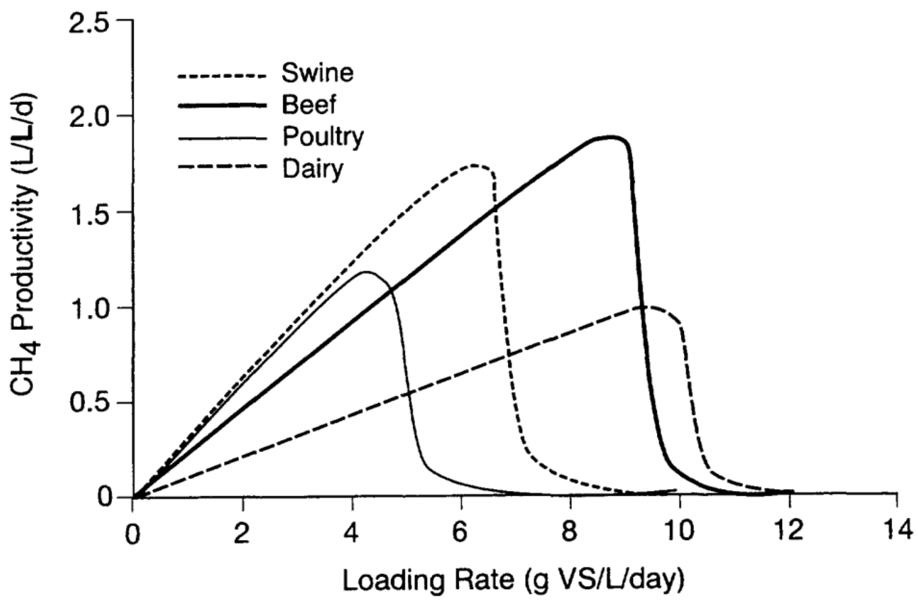


Figure 2.2: Predicted methane productivity for different animal wastes (Husain, 1998)

A parameter that could be influencing the methane production from cattle slurry is the retention time. A low retention time can have a negative influence on the specific methane yield as it can cause the washout of methanogens and allow for undigested material to leave the digester. The affect of a short retention time could be more pronounced in the digestion of cattle slurry since the readily degradable material has already gone as a result of rumen fermentation so what is left is likely to be slow degrading. This would suggest that a long retention time would be required to ensure that the substrates remain in the digester for longer periods allowing for an improved chance of complete degradation. The influence of a short retention time was shown in the research by Karim *et al*., (2007); where the shortest retention time produced the highest volumetric methane yield of 1.181 l l^{-1} d^{-1} but the lowest specific methane yield of 0.20 l g^{-1} VS

$_{added}$. The results produced by Karim *et al.*, (2007) are surprising as each trial tested produced a specific methane yield that was equal of greater than 0.20 l g^{-1} VS $_{added}$, despite the retention time reaching a duration of 4.6 days. For example the work by Lehtomäki *et al.*, (2006) produced a lower specific methane yield at a longer retention time of 20 days. This success at such a small retention time does again question the results produced by Karim *et al.,* (2007). The experiments run by Karim *et al*., (2007) were only run for three retention times meaning that a retention time of 4.6 days was tested for 14 days, which does not provide evidence that long term digestion of cattle slurry at this retention time would be possible.

The trend displayed by Karim *et al*, (2007) identified earlier by Linke, (1997) showed that increasing the retention time corresponded to an increase in the specific methane yield. Linke (1997) thought that a retention time of at least 10 to 15 days would be required for an adequate methane production while Gerardi (2003) said that a retention times of less than 10 days is not recommended as it could lead to a significant washout of bacteria.

One explanation for the variation in the methane yields found in previous research is the diet of the cattle, which can vary throughout the year; this means that the time of year when the sample of cattle slurry is collected can influence the amount of methane produced. An example of how the methane production can vary was shown by Amon *et al.,* (2001) where the yield of methane from a commercial biogas plant decreased as the cattle diet changed from summer grass diet to a winter hay diet. A compound within the feed that can affect the methane yield is lignin, which is a complex component with aromatic polymers joined by links that are difficult to break; it is thought that lignin cannot be broken down by bacteria within anaerobic digesters (Günter Schlegel *et al.,* 1993, Hobson and Wheatley, 1993). An increase in the amount of lignin within the feed will lead to an increase in the concentration that is excreted by the cattle; this can lead a decline in the specific methane production, in terms of VS added, to be observed, as shown by Amon *et al.,* (2007) and Moller *et al.,* (2004).

Amon *et al.,* (2007) looked at the influence of the feeding intensity on the methane production of cattle slurry; six batches of cattle slurry were tested where the diet of the cattle consisted of concentrate, hay, grass and maize silage in different quantities. The results showed as the amount of lignin in the slurry increased from 125 to 190 g kg dry $matter^{-1}$ (DM), a decline in the methane yield from 0.166 to 0.126 l g^{-1} VS $_{added}$ was observed. Moller *et al.,* (2004) studied the methane production from samples of cattle slurry obtained from cattle under different diets. The diets included clover with hay, a mixture of concentrates with roughage and barley, a mixture of concentrates with roughage, and a diet consisting of only concentrates. The highest methane yield of 0.207 l g^{-1} VS $_{added}$ was obtained from the slurry produced from cattle fed on concentrates, roughage and barley, the characteristics of this type of cattle slurry were not provided making it difficult to obtain an explanation for the higher methane yield. The lowest methane yield was 0.100 l g^{-1} VS $_{added}$ produced from the cattle fed on hay with clover, this material also has the greatest lignin concentration. In addition the lowest methane yield was produced from the cattle slurry that had the lowest ammoniacal concentration. From the data provided it was not possible to determine if there was a strong relationship between the ammoniacal concentration and the methane yield. The work by Amon *et al.,* (2007) did not report the total nitrogen content within the cattle slurry tested so a comparison between the literatures in terms of nitrogen can not be made. Vedrenne *et al.,* (2008) undertook batch trials on the digestion of cattle slurry collected from a farm where the cattle were fed with conventional feed and from a farm where the cattle were organically fed. The results showed that in an unmixed digester the slurry produced from organically-fed cattle had a specific methane yield of 0.214 l g^{-1} VS $_{added}$ while the cattle fed with conventional feed produced a slurry with a lower specific methane yield, 0.172 l g^{-1} VS $_{added}$. Unfortunately, no data on the type of feed was given but the different batches of cattle slurry displayed a clear difference in the VFA and the solids content with the conventional fed cattle producing the higher values for both parameters.

2.2 Enhancement of cattle slurry digestion

For the process of anaerobic digestion to be viable the amount of methane produced must be greater than the energy that the process requires. As Section 2.1 showed the yield of methane produced from the digestion of cattle slurry can be as low as 0.05-0.1 l g^{-1} VS $_{added}$. To ensure that anaerobic digestion of cattle slurry is profitable in terms of the quantity of methane produced several methods have been investigated to improve the yield. Co-digestion is the main focus of the current work but, this is not the only method available that can improve the digestion process. This section briefly presents alternative methods that have been tested in previous research.

Pre-treatment: Introducing dilution to reduce the level of inhibitors

The impact of dilution on the digestion of cattle slurry alone (with no inoculum) has been studied by Vedrenne *et al.,* (2008). The purpose of diluting the cattle slurry prior to digestion was to lower the level of inhibitors introduced to the system, for example it was an attempt to maintain the concentration of ammonia below 1500 mg l^{-1}. The effect of dilution was studied in unmixed batch digesters at cattle slurry to water ratios of 1:0 and 1:1; it was shown that the specific methane yield increased as the dilution increased. This improvement in yield was more pronounced in the digestion of the cattle slurry that had the greatest VFA concentration (11.4 g l^{-1}) and which displayed signs of inhibition when digested with no dilution. It was suggested that this inhibition was a result of the high VFA concentration and that this was the cause of the increase in the time required for the digester to reach the final methane yield. Upon dilution to a ratio of 1:1 the methane yield of this sample of cattle slurry increased from 0.172 to 0.257 l g^{-1} VS $_{added}$. This result suggests that pre-treatment by dilution was a viable option for reducing the concentration of VFA's introduced into the digester. In addition to the reduction in VFA's it was suggested that dilution could aid the digestion process by reducing the concentration of ammonia within the system. Unlike the VFA concentration no trend was shown between the concentration of free ammonia and the time required for the total methane yield to be achieved. Despite the lack in relationship between the ammonia and the methane yield it was suggested that cattle slurry should have a dilution that allows for the free ammonia to remain below 100 mg l^{-1}. In terms of the VFA concentration it was suggested that the dilution should ensure that the concentration remains below 5 g l^{-1}.

Eliminating mixing: Reducing energy input

An alternative option to increasing the gas production is to minimise the cost and energy inputs in order to improve the overall energy balance. One approach to reduce the inputs is to eliminate the need for mixing, which will reduce the amount of energy required by the system. Previous research investigating the impact of mixing on the methane yield have produced contradictory results; for example work by Vedrenne *et al.,* (2008) showed a higher methane yield in the unmixed digester when compared to a mixed digester while work by Karim *et al.*, (2005) showed benefits from introducing mixing. Vedrenne *et al.,* (2008) tested cattle slurry at a 1:1 and 1:10 dilution ratio with and without mixing. At the higher dilution, it was found that mixing resulted in the specific methane yield to drop by approximately 0.05 l g^{-1} VS $_{added}$. At the lower dilution the introduction of mixing created a larger decline in the specific methane yield, of approximately 0.15l g^{-1} VS $_{added}$; suggesting that the mixing was creating an inhibition. It was suggested that the reason for the decline in the methane yield was from a greater dispersion of the inhibitors. Research by Kaparaju *et al.,* (2008) investigated three modes of mixing at thermophilic temperature: minimal, intermittent and continuous mixing. In terms of the methane yield it was shown that the minimal mixing (mixing for 10 minutes prior to feeding) produced a yield of 0.246 l g^{-1} VS $_{added}$ which was only slightly greater than 0.217 l g^{-1} VS $_{added}$ produced by the continuous mixing. This indicates that there was no significant difference between mixing and minimal mixing suggesting that mixing did not create an inhibition to the process, unlike that shown by Vedrenne *et al*., (2008)

Research by Karim *et al.,* (2005) suggested that the introduction of mixing to semi-continuous digesters was beneficial. The impact of mixing appeared minimal at low total solids concentrations; however as the solids content within the slurry increased, the impact of the mixing became more pronounced and a significant difference appeared between the mixed and the unmixed digesters. This impact was shown to be positive, with all modes of mixing producing an increase in the methane yield when compared to the unmixed digester. The solids content of cattle slurry can vary throughout the year as a result of different feed so based on the results from Karim *et al.,* (2005) it could be suggested that a mode of mixing should be included in the process to ensure no limitation to the methane production during times of high solid cattle slurry.

Thermophilic temperatures

In an attempt to improve the degradation of slow degrading material, often found in cattle slurry, the working temperature of the digester can be increased from mesophilic to thermophilic (55-70 ^{o}C). A digester run at mesophilic temperatures may achieve solids degradation equal to a digester at thermophilic temperatures, but the latter achieves this solid degradation at shorter retention times (Hobson and Wheatley, 1993). The increase in the ability to degrade solids at the higher temperatures may correspond to an increase in the growth rate of the bacteria. Research has been carried out on thermophilic digestion of cattle slurry (El-Mashad *et al.*, 2004, Nielsen *et al.*, 2004) and a comparison between the digestion performance at mesophilic and thermophilic temperatures has been undertaken by Mackie *et al.*, (1995). Mackie (1995) found higher methane yields at the thermophilic temperatures at all loading rates tested and the results indicated that thermophilic temperatures allowed greater loading rates to be achieved. The highest loading rate of 12 g VS l^{-1} d^{-1} gave a volumetric methane yield that was 85% greater than that achieved at the mesophilic temperatures. Despite the ability to achieve high loading rates at the thermophilic temperatures, increasing the loading to rates of 12 g VS l^{-1} d^{-1} produced a decline in the specific methane yield indicating a reduction in the degree of breakdown of the substrate. This suggests that the use of thermophilic temperatures to allow for higher loads to be achieved is not a suitable method of optimising the digestion of cattle slurry for energy production, as the full methane potential of the slurry is not achieved. The greatest specific methane yield produced at thermophilic temperatures was achieved at the lowest loading rate; at this loading rate increasing the temperature to thermophilic only increased the volumetric methane yield by 13%. The limitation of thermophilic temperatures is the extra energy input that is required to maintain the digester at the higher temperatures. Mackie *et al.*, (1995) briefly discussed the impact of increasing the temperature on the net energy yield of the process and stated that the use of thermophilic temperatures would only be effective at high loading rates with short retention times. This was suggested in despite of the decline observed by the specific methane yield as the loading rate increased under thermophilic temperatures.

2.3. Co-digestion

Co-digestion is the simultaneous digestion of a mixture of two or more substrates and can act as a mechanism to improve the digestion process. It is not a new idea with research into cattle slurry as a co-substrate occurring thirty years ago (Robbins *et al.*, 1979, Hills and Roberts, 1981). The benefits of co-digestion include:

- A well balance nutrient composition: missing nutrients can be supplied by the co-substrate. In addition to the improvement of nutrients co-digestion can allow for a well balanced composition of minerals, such as sodium and manganese
- Economic benefits from sharing equipment
- The co-substrate could improve the moisture content, which could improve the mixing within the system. Combining a high solid material, which can have poor fluid dynamics, with a dilute substrate may allow easier digestion of the solid material.

(Braun and Wellinger, 2002)

To ensure that the co-digestion process produces the greatest volumetric methane yield possible while ensuring that the full potential of both substrates is achieved, optimisation of the process will need to be carried out. This optimisation process must consider the following factors:

- The substrates that should be digested together
- The co-substrate ratio that should be adopted
- The loading rate and retention time

This section of the literature review considers each of these points separately to provide a clear understanding what research on co-digestion has taken place.

2.3.1 Co-substrates

Benefits that have been identified from the use of cattle slurry include:

- Cattle slurry typically has a solid content of 7-10%; low total solids content allow a high percentage of liquid to be introduced to the system. This can be advantageous as it introduces a source of liquid that can aid the mixing conditions of the digester.
- Cattle slurry typically has a high buffering capacity, which can help protect the system against failure as a result of an increase in VFA's and a decline in pH.
- Cattle slurry may be rich in nutrients which can aid in the optimal growth of bacteria

(Angelidaki and Ellegaard, 2003)

Nordberg and Edstöm (1997) showed that the addition of cattle slurry to ley crops was more effective than the addition of a trace element solution as the digestion process reached stability at a loading rate of 6 g VS l^{-1} which was not possible with the trace element solution addition. This suggests that the cattle slurry was providing the system with a suitable quantity of nutrients and possibly with an additional element, compound or co-factor when compared to the addition of trace elements. This item of research highlights that cattle slurry is a suitable co-substrate but it does not specify what the cattle slurry could be introducing to the digester that allows for a greater loading rate to be achieved.

A factor that cattle slurry brings to the digestion system is an improved buffering capacity; the benefit of this has been shown in the co-digestion of cattle slurry with fruit and vegetable waste and solid slaughterhouse waste. The success of the mixtures containing cattle slurry led to the conclusion that 'The manure, which is characterised by a low TS concentration, a high fraction of fibres, many nutrients and a high buffering capacity, acts as an "excellent" carrier co-substrate' (Alvarez and Lidén, 2008). The benefit of the higher buffering capacity is supported by research into the addition of cattle slurry to the digestion of the organic fraction of municipal solid waste (OFMSW). This item of research provided a good example of how an improved buffering capacity can aid mono-digestion mainly by improving the stability of the process. The introduction of just 5% cattle slurry to the digestion of OFMSW, where stability was difficult to achieve, resulted in an increase in the methane yield of approximately $65m^3$ ton^{-1} VS_{added}. (Capela *et al.*, 2007). The positive influence that cattle slurry can have on the buffering capacity was also highlighted by the research of Banks *et al.,* (2010) where is was indicated that the digestion of food waste was improved by the addition of cattle slurry. In addition, the provision of essential elements and a continuous addition of anaerobic microorganisms were highlighted as important contributors to the improved digestion performance.

Cattle slurry has been digested with a range of different substrates at laboratory scale to determine the digestion performance when compared to mono-digestion. Examples of this work can be found in Callaghan *et al.,* (2002) and Misi and Forster (2002). Callaghan *et al.,* (1999) investigated the co-digestion of cattle slurry with several substrates, including chicken manure, fish offal and brewery waste, in batch conditions. In terms of the volumetric methane yield, replacing 20% of the digester content with fruit and vegetable waste proved to be the most effective option with the production of the highest cumulative methane yield, in the range of 11 to 13 l. The poorest performance was produced by the addition of chicken manure; this was considered to be the result of the high free ammonia concentration found in the digester, which reached 1000 mg l^{-1}. There may be the presence of an additional factor within the chicken manure and cattle slurry mix as free ammonia is stated to be manageable if the concentration within the digester remains below 1500 mg l^{-1} and the pH remains below 7 (Gerardi, 2003). In terms of specific methane yield (g of VS destroyed) only the additions of the fish offal and the brewery waste showed an improved performance when compared to the digestion of the cattle slurry alone, 0.08 and 0.005 l g^{-1} $VS_{destroyed}$ (approximate value from graph) improvement respectively.

The majority of previous research shows that co-digestion with energy crops can lead to an increase in the methane yield, both volumetric and specific (VS added). Examples of this includes Kaparaju *et al.,* (2002) where, at farm scale, it was suggested that energy crops are a potential co-substrate. The addition of energy crops to cattle slurry in a 150 m^3 capacity digester was shown to produce a reliable performance with a specific methane yield of 0.22 m^3 kg VS^{-1}_{added}. Comparing this to 0.21 m^3 kg VS^{-1}_{added} produced by the cattle slurry alone does not highlight a large improvement to the performance. Unfortunately, it was not possible to determine how beneficial the addition of energy crops was to the methane yield as there is a lack of information on the total and volumetric methane. In support, Machmüller *et al.,* (2007) concluded from an extensive batch trial, involving the co-digestion of pig slurry with a number of different energy crop mixtures (maize, sugar beet, sunflower, clover and rye), that the digestion of energy crop mixtures should be digested with animal slurry. The major benefit of this research was that it investigated the digestion of the individual substrates and of the different groups under similar operating conditions allowing for an accurate comparison to take place. The weakness of this research is the reasoning behind the conclusion that animal slurry should be added to energy crops. From the wide range of different combinations tested, there was only one mixture that did not contain pig slurry so the actual benefit that animal slurry may have on energy crops is not clearly shown.

A disadvantage of using energy crops is that it is brings up a moral argument on whether crops should be diverted away from agricultural production (Holmes, 2008). An OECD report giving an overview of the potential impact that the growth of energy crops can have on the food crop production suggests that if the EU15 was to produce enough bio-energy to replace 10% of their fuel consumption, 65% of the current land used to produce food crops would have to be turned over to energy crops (OECD, 2006). In addition, the use of crops for energy has been stated to be one of the reasons for the recent increase in the price of crops and this has received widespread negative coverage. For example it was quoted by Pfuderer *et al.,* (2008) that the price of wheat and maize increased by 136 and 31% in March 2008 when compared to March 2007. A report from Defra stated that the demand for bio-energy cannot be solely responsible the increase reported in 2008 as the use of wheat for biofuel is low when compared to maize, which displayed a lower price increase (Pfuderer and Castillio, 2008). This suggests that energy crops do not necessarily need to be eliminated from the bio-energy industry however, given the amount of land that would be needed to contribute towards the 10% target, it is vital that the use of crops is carefully managed and that the full energy potential of the crop is achieved. To ease the demand on energy crops alone, other sources of bio-energy such as wastes should be encouraged; this is where co-digestion could be beneficial.

Figure 2.3 gives the range of specific methane yields for some co-substrates that have been reported by the literature. This graph highlights that a number of co-substrates have been tested by different authors resulting in a difference in the methane yield produced, which could be the result of differences in the operational conditions. To provide support for this Figure, Table 2.2 provides more detailed information on different trials.

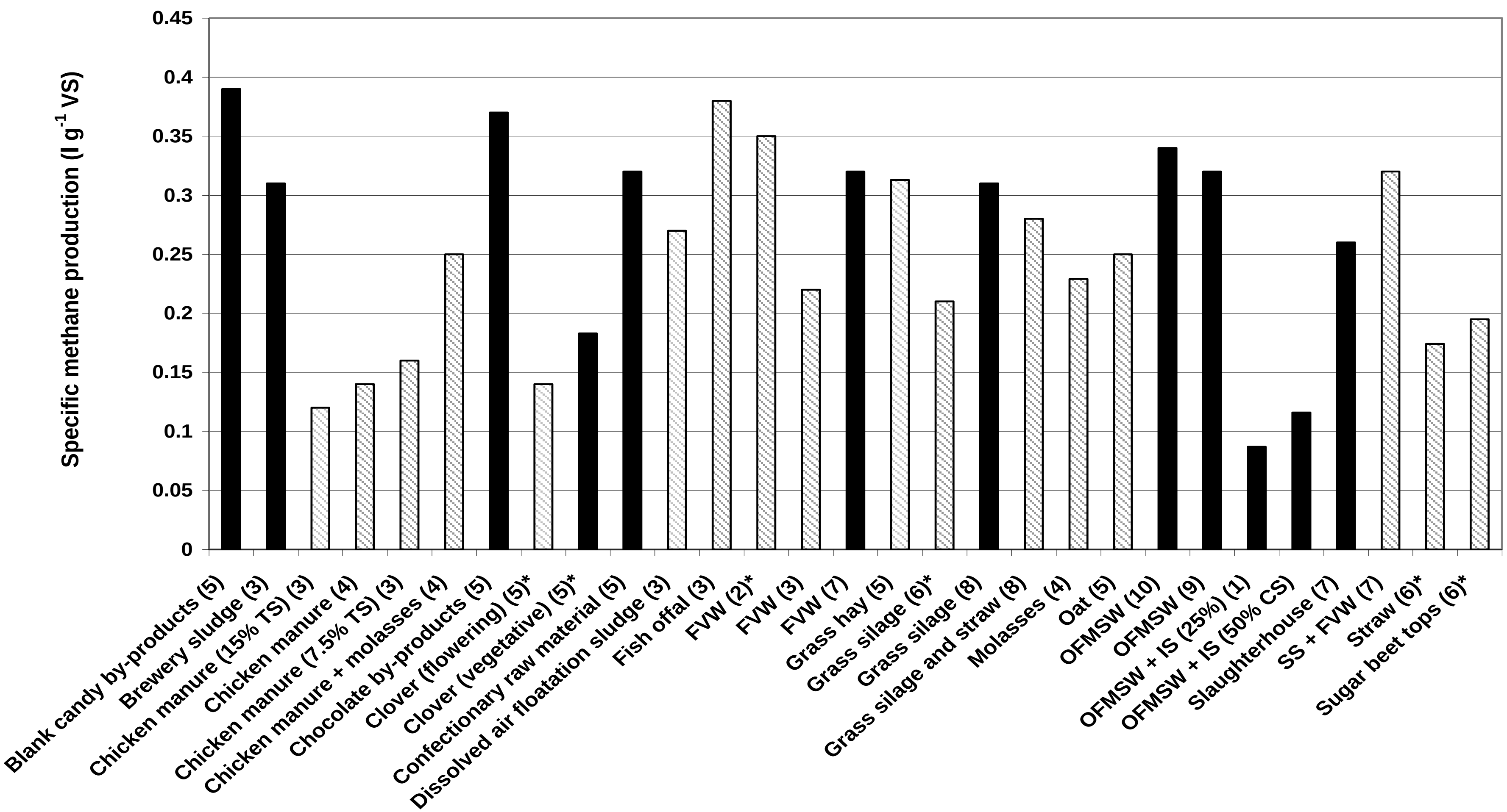


Figure 2.3: A summary of previous co-digestion trials, with the filled bars representing CSTR trials and the striped bars representing batch trials. References: (1): (Capela *et al.*, 2007). (2): (Callaghan *et al.*, 2002), (3): (Callaghan *et al.*, 1999), (4): (Misi and Forster, 2001), (5): (Kaparaju *et al.*, 2002), (6): (Lehtomäki *et al.*, 2006), (7): (Alvarez and Lidén, 2008), (8): (Nordberg and Edström, 1997), (9): (Nordberg and Edström, 2005) and (10): (Hartmann and Ahring, 2005). (NB: * average value)

Table 2.2: Operational conditions followed by previous research investigating the co-digestion of cattle slurry; the volumetric and specific methane yield produced by each condition are also given to provide a comparison between the items of research

Reference	Trial	Co-substrate		Loading rate	Retention time	VS Destruction	Methane yield		Notes
		Substrate	**%**	**g VS l^{-1} d^{-1}**	**days**	**%**	**$l\ l^{-1}$**	**$l\ g^{-1}$ VS_{added}**	
(Alvarez and Lidén, 2008)	Semi-continuous 1.8 litre $35^{o}C$	Slaughterhouse waste (SW) and FVW	66 (equal) VS basis	0.14 – 3.8	10-70	8.7 – 67.6	0.0197 – 0.440	0.12 – 0.34	Greatest methane yield produced by OLR: 0.49 g VS l^{-1} and 70 day retention time
			SW: 67 FVW: 17	1.1-1.3	30	67.3	0.315	0.27	Proportion is based on the VS of the substrates
			SW:17 FVW:67	1.1-1.3	30	67.4	0.357	0.35	
			34 (equal)	1.1-1.3	30	54.2	0.454	0.32	
		FVW	50 VS basis	1.1-1.3	30	51.7	0.461	0.32	
		Slaughterhouse waste	50 VS basis	1.1-1.3	30	51.7	0.305	0.26	

Reference	Trial	Co-substrate		Loading rate	Retention time	VS Destruction	Methane yield		Notes
		Substrate	%	g VS l^{-1} d^{-1}	days	%	l l^{-1}	l g^{-1} VS_{added}	
(Callaghan *et al.*, 1999)	Batch 1 litre 35 °C	Brewery waste	20% of the digester volume	n/s	Trial ran for 17 weeks	33.9	(4.8)		**NB:** Values in brackets are the ***total methane*** value. Values for the methane yield and the VS destruction are approximated readings from graphs
		Dissolved air floatation				45.2	(5.8)		
		FVW				52.1	(12)		
		Fish offal				47.3	(7)		
		Chicken manure (7.5 % TS)				48.9	(5)		
		Chicken manure (1%				81	(7)		
(Callaghan *et al.*, 1998)	Semi-continuous 18 litres 35 °C	Fish offal	22-30 VS basis	5.0-6.33	21	Lowest: 10 Maximum: 59		Lowest: 0.1 Maximum 0.31	Unstable conditions: increasing fish offal resulted in failure.

Reference	Trial	Co-substrate		Loading rate	Retention time	VS Destruction	Methane yield		Notes
		Substrate	**%**	**g VS l^{-1} d^{-1}**	**days**	**%**	**l l^{-1}**	**l g^{-1} VS_{added}**	
(Capela *et al.*, 2007)	Batch 35 °C	Industrial sludge (IS) OFMSW	12.5-90.0 TS basis	n/a	Trial ran for 65 days	10-60		0.025-0.25	Highest methane yield achieved at 75% OFMSW, 12/5% cattle slurry and 12.5 % IS
(Hills and Roberts, 1981)	Semi-continuous 3.4 litres 35°C	Barley straw	Not given	Not given	17	23.4-34.4		(0.31-0.38)	**NB:** Values in brackets are ***per COD destroyed*** Proportions not given by the C:N ratio varied between 12.3 and 40. For the two types of straw the greatest methane yield was produced at C:N of 25; for the rice hull it was a C:N of 32
		Rice straw				27.6-32.9		(0.28-0.36)	
		Rice hulls				12.8-30.6		(0.31-0.36)	

Reference	Trial	Co-substrate		Loading rate	Retention time	VS Destruction	Methane yield		Notes
		Substrate	%	g VS l^{-1} d^{-1}	days	%	l l^{-1}	l g^{-1} VS_{added}	
(Hills and Roberts, 1981)	Semi-continuous 4 litres 35 °C	Grass silage	10-40 VS basis	2-4	16-20	41-53	0.356-0.744	0.178-0.268	The 30% proportion for all substrates produced the greatest yield Increasing the loading rate increased the volumetric but reduced the specific methane yield
		Sugar beet		2	20	28-49	0.298-0.458	0.149-0.229	
		Oat straw		2-4	16-20	33-40	0.290-0.628	0.145-0.213	
(Mähnert and Linke, 2006)	Semi-continuous 2 litres 35 °C	Maize	33 and 67 VS basis	1-4	Not given	Not given	Not given	(0.25-0.80)	**NB**: Values in the brackets are the ***specific biogas production*** An increase in the loading rate caused a decline in the biogas yield

<table>
<tr><th rowspan="2">Reference</th><th rowspan="2">Trial</th><th colspan="2">Co-substrate</th><th>Loading rate</th><th>Retention time</th><th>VS Destruction</th><th colspan="2">Methane yield</th><th rowspan="2">Notes</th></tr>
<tr><th>Substrate</th><th>%</th><th>g VS l^{-1} d^{-1}</th><th>days</th><th>%</th><th>l l^{-1}</th><th>l g^{-1} VS_{added}</th></tr>
<tr><td rowspan="3">(Misi and Forster, 2001)</td><td rowspan="3">Batch
1 litre
35 ^{o}C</td><td>Chicken manure and molasses</td><td>33</td><td rowspan="3">n/a</td><td rowspan="3">Trial ran for 33 days</td><td>30.4</td><td>(5.22)</td><td>0.25</td><td rowspan="3">NB: The values in the brackets are the total methane production</td></tr>
<tr><td>Chicken manure</td><td>50</td><td>26.5</td><td>(3.33)</td><td>0.14</td></tr>
<tr><td>Molasses</td><td>50</td><td>45.3</td><td>(4.78)</td><td>0.229</td></tr>
<tr><td rowspan="3">(Nordberg and Edström, 1997)</td><td rowspan="3">Semi-continuous</td><td>Grass silage</td><td>80
TS basis</td><td rowspan="3">2.5-60</td><td rowspan="3">Data shown for 200 days of operation</td><td rowspan="3">Not given</td><td rowspan="3">Not given</td><td>0.31</td><td rowspan="3"></td></tr>
<tr><td rowspan="2">Grass silage and straw</td><td>Grass: 60
Straw: 20</td><td>0.28</td></tr>
<tr><td>Grass: 70
Straw: 10</td><td>0.29</td></tr>
</table>

The different co-substrates produced a wide range of specific methane yields, ranging from 0.087 l g^{-1} VS $_{added}$ for a mixture containing OFMSW and industrial waste to 0.39 l g^{-1} VS $_{added}$ for the black candy by-products (Capela *et al.*, 2007, Kaparaju *et al.*, 2002). Several of the co-substrates, chicken manure, fruit and vegetable waste, grass and OFMSW, have been tested more than once by different authors. The three trials testing the chicken manure all produced a similar specific methane yield, ranging from 0.12-0.16 l g^{-1} VS $_{added}$; this similarity is repeated with the co-digestion of the OFMSW. In contrast, the digestion of cattle slurry with grass silage and the fruit and vegetable waste (FVW) showed a difference in the specific methane yield found.

Figure 2.3 provides two results for the grass silage, 0.21 l g^{-1} VS $_{added}$ produced in long term semi-continuous conditions while the value of 0.31 l g^{-1} VS $_{added}$ was produced in batch conditions. The value of 0.21 l g^{-1} VS $_{added}$ is an average of four trials testing different ratios of grass silage; the range of this average is given as 0.14 to 0.268 l g^{-1} VS $_{added}$. Apart from the different methodologies followed the main difference between the trials was the percentage of grass silage within the feed. The batch value (Nordberg and Edström, 1997) was produced from a feed consisting of 72% grass silage, on a VS basis, while the semi-continuous trial tested feeds with 20-40% grass silage (Lehtomäki *et al.*, 2006). This suggests that the increasing proportion of grass within the load corresponds to a greater methane potential however, this may not be a viable observation due to the different operational conditions which could be an explanation behind the difference. This is supported by the digestion of fish offal with cattle slurry (Figure 2.3) which was shown to be possible by Callaghan *et al.*, (1999) under batch conditions but failed under semi-continuous conditions (Callaghan *et al.*, 1998). This explanation can also be applied to the difference shown by the digestion of cattle slurry with FVW, but in an opposite trend to the fish offal it was the semi-continuous trial that produced the greatest methane yield, 0.35 compared to 0.22 l g^{-1} VS produced by a batch trial (Callaghan *et al.*, 1999, Callaghan *et al.*, 2002). These differences highlight the need to test co-substrates under long term trials to test its long term feasibility and it questions the reliability of testing co-substrates solely by batch conditions,

2.3.2 Co-substrate ratio

To ensure the maximum methane output it is vital that the ratio of cattle slurry to the co-substrate is chosen carefully; when determining the co-substrate ratio two factors should be taken into consideration: the potential inhibition and benefits that the co-substrates can bring to the system. For example, in terms of the inhibition, the co substrate could be responsible for an increase in the level of free ammonia or VFA's that could lead to a reduction in the total methane production (Callaghan *et al.*, 1998, Callaghan *et al.*, 1999). If this is the case then the ratio would have to favour the substrate that introduces the lowest level of inhibition to the digester. Research by Nordberg *et al*., (2005) highlighted the importance of considering the benefits that a co-substrate can bring to the system. This research tested the impact of increasing the proportion of the energy crops from 45 to 72%, in terms of VS, as a co-substrate to OFMSW; it was shown that this increase corresponded to a decline in the specific methane yield of 0.04 l g^{-1} VS $_{added}$ in laboratory scale digesters and by 0.05 l g^{-1} VS $_{added}$ in pilot trials. This difference in the specific methane yield is not significant but the reduction in energy crops from 72 to 45% allowed a greater loading rate to be achieved.

Lehtomäki *et al.,* (2006) looked at the co-digestion of cattle slurry with grass silage, sugar beet and oat straw in a detailed study investigating the impact of increasing the energy crop proportion. This was achieved in a long term study with each proportion given a suitable time period to stabilise; this allowed for the impact of the change in proportion to be monitored. For each crop an increase in the proportion to 30% resulted in the highest specific methane yield, 0.229 and 0.184 l g^{-1} VS $_{added}$ respectively. At this proportion the volumetric methane yield showed an improvement of 65, 58 and 16% for the sugar beet, grass and straw respectively in comparison with the yield from the digestion of the cattle slurry alone. A further increase in the proportion of energy crop, from 30 to 40%, led to a decline in the specific methane yield in all cases suggesting that the optimal ratio for energy crops and cattle slurry should be 30%. Mähnert *et al.,* (2006) co-digested cattle slurry with maize in semi-continuous trials with 33 and 67% of the total VS added attributed to maize at different OLR. The highest specific biogas, in the range of 0.6 to 1.0 l g^{-1} VS $_{added}$, was produced by the 67% maize proportion while the digestion of cattle alone gave a range of 0.3 to 0.6 l g^{-1} VS $_{added}$. The influence of the OLR on the two co-digestion mixture will be discussed in section 2.3.3. Unfortunately, data on the methane yields was not present so a comparison to the Lehtomäki *et al.,* (2006) cannot be made.

Alvarez *et al.,* (2008) digested a combination of cattle and swine manure with a mixture of FVW and slaughterhouse wastes, with the mixed co-substrate present at 0, 34, 67 and 83% at a wet weight basis (ww). In addition to these combinations, a mixture containing only slaughterhouse waste and FVW at equal quantities was tested producing a specific methane yield of 0.04 l g^{-1} VS $_{added}$ indicating a presence of inhibition. The explanation for the inhibition was the accumulation of VFA, which reached a final value of 8.3 g l^{-1}. The addition of cattle slurry to a mix of slaughterhouse waste and FVW was shown to be successful at all ratios tested with the specific methane yield increasing as the proportion of cattle slurry declined. It was shown that an addition of just 17% of the manure mixture resulted in the highest methane yield, 0.35 l g^{-1} VS $_{added}$, highlighting the benefit of animal manures as a co-substrate.

2.3.3 Organic load and retention time

In addition to the co-substrate ratio the OLR and the retention time must be considered as these two factors can have a significant impact on the co-digestion process. The loading rate must be chosen carefully to avoid overloading to the system resulting in a decline in the methane production. An increase in the loading rate may not always correspond to a decline in the retention time but if this decline is too great failure can occur as a short retention time will enhance the level of nutrient and/or bacteria washout. If a suitable retention time and loading rate is followed failure could still occur as a result of the presence of inhibitors within the feedstock, such as ammonia and VFA's. The trend displayed in Figure 2.2 may also be typical for the co-digestion of energy crops and cattle slurry, although the loading at which failure occurs (e.g. 10 g VS l^{-1} d^{-1} for the digestion of dairy cattle waste) could differ. The process of co-digestion involving the use of cattle slurry is common in Germany and the typical loading rate is usually between 1 and 3 g organic dry matter m^3 d-^{1} with the majority of the digesters running at retention times of 60-90 days (Weiland, 2006). The loading rates tested in experimental co-digestion trials ranged from 1 to 4 g VS l^{-1} d^{-1} and the retention times ranged from 10 to 70 days. It can be difficult to determine the impact that increasing the loading rate has on the co-digestion process as in much of the literature an increased OLR was achieved by increasing the proportion of the co-substrates meaning that two parameters have altered.

Research by Lehtomäki *et al.*, (2006) did consider the impact of the OLR by maintaining the proportion of the energy crop at 40% and increasing the OLR from 2 to 3 g VS l^{-1} d^{-1} and finally to 4 g VS l^{-1} d^{-1}. The increase in OLR was tested on the co-digestion of cattle slurry with grass silage and oat straw; both substrates displayed an increase in the volumetric methane yield confirming that digestion was possible at all loads tested. A clear decline in the specific methane yield of 16 and 26% was found for the digestion of the oat straw and the grass silage respectively as the OLR increased from 3 to 4 g VS l^{-1} d^{-1}. These results indicate that the optimal loading rate in terms of achieving the maximum methane yield from the energy crop was 3 g VS l^{-1} d^{-1}. It was suggested that the decline in the retention time to 16 days at the 4 g VS l^{-1} d^{-1} OLR meant that the time spent in the digester was too short for effective digestion. This was supported by the fact that the higher loads produced higher post-digestion emissions in terms of VS added. The increase in the load did not correspond to an increase in VFA concentration indicating that the hydrolysis stage of anaerobic digestion was the rate limiting stage.

Mähnert *et al.,* (2006) also tested the co-digestion of cattle slurry and maize at two set ratios at different loading rates. This research tested the digestion of cattle slurry and maize alone at a ratio of 66 and 33% (VS basis) at OLR between 1 and 4 g VS l^{-1} d^{-1}. The results showed a decline in the specific biogas at both proportions as the loading rate increased with the results indicating that the specific biogas production was inversely proportional to the OLR range tested. The retention times were not reported and no other information apart from gas yield were given so it is difficult to get a clear picture of the digestion process as a whole as the load increased.

From the literature on co-digestion it can be concluded the ratio of the cattle slurry to co-substrates appears to be an important parameter along with the OLR and retention time on the optimisation of the co-digestion process in terms of the total and specific methane yield. A number of authors have studied the impact of the ratio of the co-substrate but relatively little work has been carries out on the impact of the OLR on a fixed ratio.

2.4 Synergies

Synergy can be an important benefit of co-digestion; a synergy is defined as 'two of more substrates working together to produce a greater effect than the sum of their individual effects'. In anaerobic digestion synergy can occur when two substrates are digested together and the methane yield obtained from the co-digestion process is greater than when the substrates are digested alone. The work on co-digestion of energy crops and animal slurries by Lehtomäki *et al.,* (2006) and by Machmuller *et al.,* (2007) showed the presence of synergies. Lehtomäki *et al.,* (2006) provided evidence of synergy by comparison of the methane yield produced in co-digestion trials with that calculated from the methane potential of the individual substrates. For example the combination of sugar beet and cattle slurry at a 30:70 ratio, in terms of VS, produced 16% more methane than predicted from the individual methane potentials. It was suggested that the increased methane yield was the result of a more balanced nutrient composition within the feedstock, with the energy crops introducing additional carbon to the system The carbon to nitrogen (C:N) ratio within cattle slurry can be low as a result of the rumen fermentation: Umetsu

(2006) gave values of 11-14, which is well below the optimal ratio for anaerobic digestion, stated to be between 25 and 32 (Hills, 1979, Hills and Roberts, 1981). The additional carbon can bring the C:N ratio closer to the optimal for anaerobic digestion. The approach of this trial is not completely conclusive as the co-digestion trials were undertaken in CSTR trials and compared to individual methane potentials obtained from batch trials. As shown in section 2.3.1 these different methodologies can lead to differences, with the batch trial often providing optimal conditions for the digestion process. The apparent increase calculated from this method may therefore give an inaccurate picture of the actual synergy occurring in the co-digestion trials. For example, Lehtomäki *et al.*, (2006) fed one semi-continuous digester solely on cattle slurry and the specific methane yield at a retention time of 20 days was 0.155 l g^{-1} VS_{added}, which was 0.049 l g^{-1} VS_{added} less than that produced from the batch trial after a 20 day period. If the methane yield was taken as that from the semi-continuous digester instead of the value obtained by the batch value of 0.204 l g^{-1} VS added, the improvement produced from sugar beet and cattle slurry (3:4 ratio) was actually 41%. Unfortunately, this trial did not include a semi-continuous digester fed only on the energy crops to provide a closer comparison and a more accurate picture of any synergies present in the digester. Machmüller *et al.*, (2007) studied the digestion of a mixture of energy crops, which included maize, with pig manure. Evidence of synergy was provided by comparing mono and co-digestion trials following the same methodology: batch trials. The research indicated that positive synergies were present as the combination of pig manure with a mixture of crops produced a methane yield 40% greater than the methane yield calculated from the individual values. Mähnert *et al.*, (2006) stated that it was possible to calculate the biogas production from a co-digestion mixture from the sum of the individual biogas yields. This is contradicted by the results of Machmüller *et al.*, (2007) and Lehtomäki *et al.*, (2006) and does not take into account any synergism or antagonism that could occur from the combination of substrates. Mähnert *et al* (2006) also showed signs of synergy in that the maize to be digested at an organic load of 4 g VS l^{-1} d^{-1} when combined with cattle slurry whereas the digestion of maize alone was inhibited above 3 g VS l^{-1} d^{-1}.

Explanations for these improvements in the specific methane yield have included the C:N ratio and improved nutrient composition. The use of a co-substrate can introduce carbon into the system, which can raise the ratio into the optimal range for anaerobic digestion. The effect of the C:N ratio on the anaerobic digestion performance has been studied previously in semi-continuous digesters. Hills *et al.*, (1981) studied the digestion of cattle manure with different quantities of field crop residues (barley straw, rice straw or rice hulls) at different C:N ratios, between 12.3

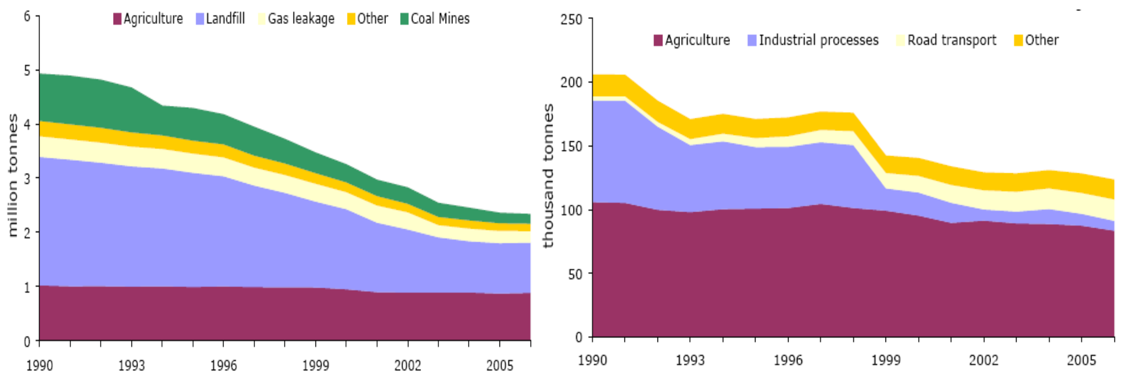
and 40. All digesters displayed a decline in ammonia and total VFA; taking barley straw as an example, the ammonia declined from 715 to 10 mg l^{-1} while total VFA declined from 1010 to 220 mg l^{-1}. The greatest specific methane yield was obtained with C:N ratios between 25 and 32; for the barley straw and rice straw the greatest specific methane production was achieved at a C:N ratio of 25. The rice hulls gave the highest methane production at a ratio of 32; this could be explained by the VFA concentration of the mixes. For the barley and rice straw the digestate at a ratio of 25 had a VFA concentration of 500 and 750 mg l^{-1} respectively while the rice hull mixture (tested at ratio 27) had a greater VFA concentration of 1030 mg l^{-1}. At the ratio of 32 the VFA concentration declined to 720 mg l^{-1}, similar to the value for rice straw at a ratio of 25.

An alternative reason for the synergistic effect is the improvement of the nutrient composition in the digesters; this explanation has been given by several authors, (Lehtomäki *et al.*, 2006, Mata-Alvarez *et al.*, 2000, Nordberg and Edström, 1997). There is, however, little published information on which nutrient/s could be responsible for any synergies and which substrate may be limited in the co-digestion of cattle slurry and maize. Research on the digestion of energy crops (grass and clover) with OFMSW showed that the volumetric and specific methane yield improved when the proportion of OFMSW increased; this was stated to be the result of an increase in cobalt. At a 50:50 ratio (energy crops: solid waste, TS basis) a specific methane yield of 0.38 l g^{-1} VS_{added} was produced compared to 0.33 l g^{-1} VS produced at the 80:20 ratio (Nordberg and Edström, 2005).

2.5 Application of the digestate

As stated previously, anaerobic digestion produces two useable products: biogas and a digestate. The digestate can be used as an organic fertiliser to reintroduce the nutrients that were taken up by the crops back onto the land. This research aimed to discover the impact that the co-digestion of cattle slurry and maize has on the characteristics of the digestate which can influence the quality of the digestate as a fertiliser. To reflect this aim this section of the literature review provides a brief review of the literature on the use of cattle slurry and digestate as fertiliser and highlights the main characteristics of the digestate that can influence the quality.

The agricultural sector in the UK is a large source of environmental pollution via the use of nitrogen fertiliser and via the production, storage and application of animal slurries. This pollution can occur as water pollution, either direct or diffuse, which can lead to eutrophication of freshwaters (Smith *et al.*, 2001a, Smith *et al.*, 2001b) or as air pollution, such as methane, nitrous oxide and ammonia (Chambers *et al.*, 2000). The agricultural sector is the main source of nitrous oxide in the UK with the application of fertiliser responsible for 95% of the agricultural emissions (Defra, 2008a). In terms of the release of methane, landfill and the agricultural sector are the largest contributors to methane emissions in the UK; Figure 2.4 shows the trend in methane and nitrous oxide emissions in the UK from 1990 to 2006 (Defra, 2006).



a) b)

Figure 2.4 Emissions of a) Methane and b) Nitrous Oxide from agricultural and other sources in the UK (Defra, 2008b)

From Figure 2.4 it is clear that the total emissions of methane and nitrous oxide declined throughout the 16 year time period displayed. The decline in total emissions however, did not correspond to a decline in emissions from the agricultural sector, with values for both gases approximately consistent. As a result of the associated environmental risks the application of fertilisers on to land must be carefully managed in terms of the amount applied and the timing of the application. The use of fertilisers will also needs to comply with legislation, including the Nitrate Directive (91/673/EEC), which aims to reduce the level of nitrate reaching waters by limiting total nitrogen application rates to 250 kg ha^{-1} during a 12 month period (Defra, 2009).

Fertilisers can be split into two categories, inorganic and organic; the difference between the two types in terms of gas emission was investigated by Ball *et al.*, (2004). Several organic fertilisers and two types of inorganic mineral fertilisers were applied to land and the emission of nitrous oxide was observed. All fertilisers emitted nitrous oxide, with the conventional inorganic NPK fertiliser producing greater emissions when compared to cattle slurry, at 26.4 kg N ha^{-1} compared to 15.3 kg N ha^{-1}. Two types of inorganic fertilisers were studied in this research, a conventional and a slow-release NPK fertiliser. The slow release NPK fertiliser produced the lowest nitrous oxide emission (3.7 kg N ha^{-1}), suggesting that in terms of post-application emissions the use of organic fertilisers does not necessarily lead to a reduction of pollution. The results of Ball *et al.*, (2004) indicated that cattle slurry emitted the greatest yield of nitrous oxide amongst the organic fertilisers tested, suggesting that attempts should also be made to reduce the pollution potential of organic fertilisers, especially cattle slurry.

The use of inorganic fertilisers does introduce a cost to the farmer and recent increases could promote an increased use of organic fertiliser. Figure 2.5 displays the trend in the price of three types of fertilisers: urea, diammonium phosphate (DAP) and potash; it can be observed that for all three types the cost remained approximately constant from 1995 until 2006, where an increase is shown. An explanation for this is given by the cost of fuel; the production of ammonia, which is the source of the majority of the nitrogen fertiliser, relies on natural gas so the cost of ammonia production will reflect changes in the cost of natural gas, which has increased as a result of the high oil prices (Farmers Guardian, 2008).

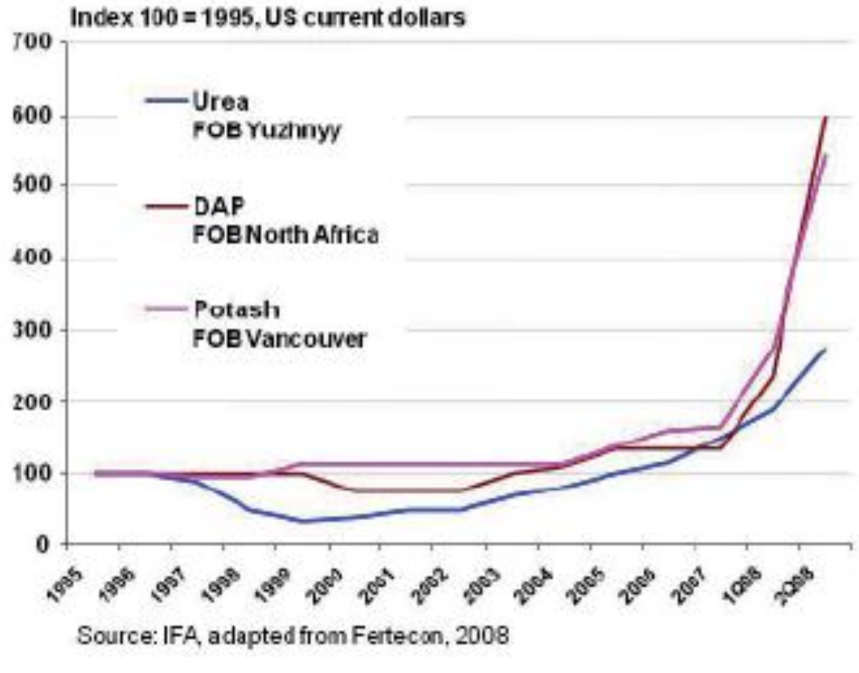


Figure 2.5: Price history of major fertilisers: 1995-2008. (International fertilizer industry association, 2008)

Anaerobic digestion can be looked upon as an option in the abatement of greenhouse gas emissions (GHG), as the capture of methane to act a renewable energy avoids the release of un-used methane into the atmosphere. Research into mitigating the emissions of greenhouse gases from conventional and organic farms has been undertaken by Weiske *et al.,* (2006). In this research greenhouse gas emissions from farms with and without an anaerobic digester were modelled and compared, along with several other mitigating options. Modelled results indicated that the introduction of a digester led to a decline in the greenhouse gas emissions of 96% when compared to the baseline emissions (calculated from emissions from organic and conventional farms on a yearly basis). The total emissions were then presented in the form of three individual gases (methane, nitrous oxide and carbon dioxide) which showed that the reduction in total emissions was a result of a reduction in methane and carbon dioxide (substitution of fossil fuels) while the emission of nitrous oxide were not shown to decline. It was concluded that the use of an anaerobic digester can be beneficial as it allowed the mitigation of greenhouse gases from animal slurries and a reduction in the need for fossil fuels.

Amon *et al.,* (2006a) and Clemens *et al.,* (2006) both compared the greenhouse gas emissions from raw and digested cattle slurry. These studies provide experimental support for the reduction in greenhouse gas emissions shown by the simulated results given by Weiske *et al.,* (2006). Amon *et al.,* (2006a) looked at the emission of greenhouse gases during storage and after field application: untreated, digested, separated, aerobic and straw covered slurries were tested. From all the methods tested it was shown that the greatest reduction in total greenhouse gas emissions was from the digested cattle slurry, which reduced emissions by 59%. This decline in the total emissions was the result of a 67% reduction in methane; in terms of the emission of nitrous oxide it was shown that anaerobic digestion created an increase of 30%. This could prove to be a significant disadvantage of using digested cattle slurry instead of raw cattle slurry as the global warming potential of nitrous oxide is greater than that of methane, at 289 and 72 respectively over a 20 year period (Solomon *et al.*, 2007). Amon B, *et al.,* (2006a) had highlight that 90% of the greenhouse gas emissions associated with cattle slurry originated from methane leading to the conclusion, despite the increase in the nitrous oxide, anaerobic digestion does provide a viable process for the abatement of greenhouse gas emissions. The research by Clemens *et al.,* (2006) confirms the results shown by Amon, B *et al.,* (2006a) by displaying a reduction in the methane yield as the cattle slurry is digested and an increase in the emissions of nitrous oxide. This was shown both at laboratory scale trials and at a pilot scale trial, which was split into a winter and summer experiment. The research of Clemens *et al*., (2006) studied at the influence of co-digestion on post-digestion emissions by measuring the emissions of methane and nitrous oxide from raw cattle slurry, digested cattle slurry and digested cattle slurry/potato starch mix. It was indicated that the introduction of potato starch to the digestion of cattle slurry was beneficial in terms of both, the specific methane yield and post digestion emissions. The specific methane yield (in terms of slurry) increased from 4230 to 8625 l m^{-3} while the emission of nitrous oxide reduced, from 42.7 to 41.6 mg N_2O-N m^{-2}. The retention time in the research was increased from 29 to 56 days for both the digestion of cattle slurry alone and with potato starch. The impact of an increased retention time, but with a constant OLR, was more pronounced in the co-digestion digester with an increase of the specific methane yield by 1725 l m^{-3} compared to 235 l m^{-3} shown by the cattle slurry. In addition the increase in retention time was shown to reduce the nitrous oxide emissions by 27.5%; a decline of this magnitude is not repeated elsewhere in the literature and is not explained by the research. Comparing the digestate with raw cattle slurry it was shown that, with the exception of the co-digestion digestate at a 56 day retention time, the digestate produced higher emissions of nitrous oxide. The digestate from the digestion of cattle slurry alone at the 56 day retention time was not tested for post-digestion emissions so a comparison can not be made

In addition to greenhouse gases, animal slurries like other fertilisers can also lead to loss of nitrogen to the surrounding environment via nitrogen leaching or ammonia volatilisation (Johnson *et al.*, 2005). In terms of ammonia the use of nitrogen fertilisers has been stated to contribute 8% of UK ammonia emissions (Sutton and Harrison, 2002). This can be detrimental to the quality of the fertiliser as it results in a reduction in the level of nitrogen available to the crop. Several authors have provided evidence that anaerobic digestion does not reduce nitrogen losses but in contrast leads to an increase in the amount lost; it has been suggested that the ammonia emissions could be 15% greater upon digestion (Möller and Stinner, 2009, Smith *et al.*, 2001a). Amon, B *et al.*, (2006a) showed that there was little difference in ammonia losses between the digested cattle slurry and the raw cattle slurry (226.7 and 229.9 g m^{-3}) however, there was a difference in the timing of the emissions. The research separated the post-digestion emissions into storage and application emissions and it was shown that the undigested cattle slurry produced a greater quantity of ammonia during the storage stage (41 and 10 g m^{-3}). During the field application stage the digested cattle slurry was shown to produce 18% more ammonia than the undigested cattle slurry. The greater emissions during the 80 day storage period by the raw cattle slurry may be explained by the fact that it contains a greater concentration of easily degradable material when compared to the digested cattle slurry. The higher emissions during field application may be due to the higher level of ammoniacal nitrogen and pH within the digested cattle slurry. These findings were supported by Clemens *et al.*, (2006) who found an increase in ammonia emissions as the cattle slurry was digested alone; this was shown in laboratory-scale trials and during the summer at a pilot scale trial. The co-digestion of cattle slurry with potato starch at a retention time of 29 days produced the greatest ammonia emission while the increase in the retention time to 56 days produced the lowest level. An explanation for the trend in ammonia emissions was not given but the concentrations of ammoniacal nitrogen and total solids content could be put forward as influencing factors on the basis that the addition of potato starch led to an increase in both parameters while the extension of the retention time led to a decline.

An additional benefit of anaerobic digestion is the influence it has on the odour associated with the application of raw cattle slurry, which can be an issue to the farmer. Previous studies have shown that digested cattle slurry had a significantly reduced odour intensity when compared to raw cattle slurry (Powers *et al.*, 1999). The explanation for this is that anaerobic digestion allows time for the intermediates produced by decomposition, such as phenols and VFA's, to be converted to end products that are less odorous.

The purpose of the application of fertiliser is to improve the yield of the crop by providing the nutrients that the crop requires including nitrogen, phosphorus and potassium. It is important to ensure that the use of digested cattle slurry produces an improvement to the crop yield which is similar to that produced by other types of fertiliser. The influence on the crop yield has been investigated by Kocar (2008) where the impact of applying digested cattle slurry to a crop of safflower was compared to the application of mineral fertiliser. This comparison was made by observing the crop yield and the height of the safflower produced from the two types of fertiliser; the results indicated that in terms of these parameters the digested cattle slurry was the most effective fertiliser as it led to an increase in the height and in the yield of seeds produced. In contrast to this, work on the improvement to grass yield by the introduction of fertilisers highlighted that it was the mineral fertiliser that produced a greater yield (Matsunaka *et al.*, 2006). This research investigated several cases of digestate application and a direct comparison with application of the digestate at a standard application during spring with the application of a mineral fertiliser was provided. The results indicated that both types of fertiliser led to an improvement in the dry matter yield of the grass when compared to no fertiliser application however the mineral fertiliser was the most effective. The application of mineral fertiliser led to a grass dry matter of 4200 g m^{-2} while the application of digestate led to a range from 3200 to 3750 g m^{-2} (approximate values taken from graph). Both fertilisers were approximately equal in terms of nitrogen lost via nitrous oxide emissions and leaching, but it was shown that the use of digested cattle slurry led to a higher ammonia emissions. This meant that the application of the digestate provided a lower quantity of nitrogen to the crop compared to the mineral fertiliser.

The main characteristics of the digestate that can influence the fertiliser quality, in terms of the loss of nutrients via leaching and pollution, are the dry matter content, pH and the nutrient content. The application of cattle slurry to soils introduces nitrogen in the form of organic nitrogen and as ammonium; both of which can be used indirectly by the crop. For crop uptake the nitrogen has to be converted to nitrate; this means that the organic nitrogen must undergo mineralisation and the ammonium must undergo nitrification (Monteny *et al.*, 2001). The introduction of nitrogen in the form of ammonium can have positive and negative impact as it can lead to an increase in nitrate which can contribute to an improvement of the crop growth. The disadvantage is that if the ammonium applied to the land leads to greater nitrate concentrations than the crops requirement then leaching can be increased and the unused nitrate, which is mobile, could enter water streams (Johnson *et al.*, 2005). These processes will only occur if the cattle slurry is incorporated into the soil; this is where the importance of the dry matter content comes in. The dry matter concentration can influence the level of infiltration: high dry matter content can lead to the cattle slurry remaining on the surface of the soil for a longer period. This can be detrimental in terms of crop yield and the environment as the amount of ammonia volatilisation can increase which will also lead to a lower level of nitrogen available for the crop. It has been given that if manure is incorporated into the soil within one day 65% of the ammonium nitrogen will be retained, if incorporated after 5 days all of the ammonium will be lost (Johnson *et al.*, 2005). Research into the influence of the dry matter content has been well studied (Smith *et al.*, 2001a, Thompson and Meisinger, 2002); research by Misselbrook *et al.*, (2005) indicated the presence of a significant relationship between the ammonia emissions and the dry matter content, with ammonia emissions increasing at a rate of 3.9% (Total Ammoniacal Nitrogen applied) per 1% of dry matter. Further evidence was provided by Wulf *et al.*, (2002) where the loss of nitrogen in the application of cattle slurry and digested cattle slurry (from co-digestion with biowaste) was investigated. The results showed that the overall emission of ammonia did not vary greatly; however, the initial emissions from the digested slurry after application to the field were greater when compared to the untreated cattle slurry. Emissions from the untreated cattle slurry were shown to continue over a longer period when compared to the digestate as a result of the higher dry matter, which caused the cattle slurry to remain on top of the soil for longer periods (Wulf *et al.*, 2002).

The process of anaerobic digestion produces an increase in the digestate ammoniacal nitrogen and this increase can prove to be a disadvantage when combined with the increase in pH that is often associated with digestion. The equilibrium of ammonium and ammonia, as shown by the following equation:

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

An increase in the pH can cause the balance to shift towards the right-hand side of the equation; this can result in a loss of nitrogen via ammonia volatilisation. In theory a digestate with a higher pH can display an increase in ammonia emission, as shown by Figure 2.6.

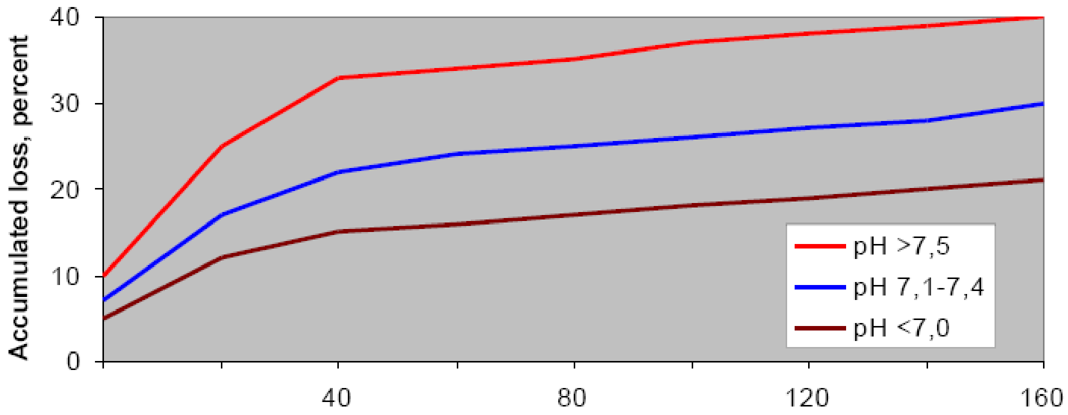


Figure 2.6: The impact of increasing the pH of cattle slurry on the amount of ammonia lost during storage (Sommer *et al.*, 1993)

The influence of the pH shown in Figure 2.6 can be counterbalanced by the impact that anaerobic digestion has on the solids content, which as stated previously can aid the reduction of ammonia volatilisation by increasing the rate of infiltration.

The use of digestate must comply with the same regulations as the application of other organic and mineral fertilisers and in addition, it must follow legislation that applies specifically to the use of anaerobic digestion digestate. The benefit of using animal slurries and crops in the digestion process is that neither substrate are classed as a waste and under current guidelines from the UK Environmental Agency this means that waste regulatory controls do not apply (Environmental Agency, 2008). This is a relatively new approach taken in the UK; previous to this, all digestate from anaerobic digesters was classed as a waste, which required the digester operator to follow waste regulatory controls if it was to be applied to land. As a result of the new approach to the use of digestate the protocol that must be followed, PAS 110:2008, is still a proposed protocol therefore could be subjected to change (British Standards Institute, 2008). From PAS 110:2008 several limits can be quoted; these are shown in Table 2.3

Table 2.3: Upper limits for heavy metals within digestate as given by British Standards (2008)

Parameter	Normal upper limit	Exceptional upper limit
Cadmium	1.5 mg kg^{-1} DM	1.9 mg kg^{-1} DM
Chromium	100 mg kg^{-1} DM	113 mg kg^{-1} DM
Copper	100 mg kg^{-1} DM	125 mg kg^{-1} DM
Lead	200 mg kg^{-1} DM	250 mg kg^{-1} DM
Mercury	1.0 mg kg^{-1} DM	1.3 mg kg^{-1} DM
Nickel	50 mg kg^{-1} DM	63 mg kg^{-1} DM
Zinc	200 mg kg^{-1} DM	250 mg kg^{-1} DM
Organic acids	4000 mg kg^{-1} fresh mass	4500 mg kg^{-1} fresh mass

Overall, it can be stated that digesting the cattle slurry has several benefits, such as a reduction in the methane emitted and in the solids content. There are, however disadvantages, digestion does not reduce the nitrous oxide emissions and in some cases an increase was observed; in addition the increase in pH could potentially produce an increase in ammonia emissions. The use of anaerobically digested cattle slurry has been shown to provide an improvement to the crop yield when compared to no fertiliser indicating that the used of the slurry is viable. In addition anaerobic digestion can reduce the odour problems associated with the application of cattle slurry to fields.

2.6 Proposed research

The literature review has shown that co-digestion is not a new process, but there are few detailed investigations into the combination of cattle slurry and maize. The current research provides new knowledge in this field by carrying out a detailed study of the co-digestion of cattle slurry and maize, as a basis for process optimisation. This research will define optimisation as the working conditions that aim to achieve the greatest methane potential possible without reducing the quality of the digestate and by ensuring that the greatest methane potential from the maize is achieved. In addition to this, the optimisation takes into consideration the potential synergy that could be obtained from combining the two substrates. In terms of economics the maximum energy output option will often be favoured, which lead operators of anaerobic digesters to increase the load of maize and reduce or eliminate the use of cattle slurry. This option would promote the use of energy crops over cattle slurry, adding to the controversy over whether crops should be diverted away from food. This debate was highlighted in this literature review as a disadvantage of using crops for energy: it creates negative publicity to bio-energy and can prove to be a significant barrier in promoting the use of anaerobic digestion for environmentally beneficial purposes such as nutrient management and reduction of greenhouse gas emissions. The advantage of optimising the process to maximise the potential of the energy crops is that it will reduce the level of crop wastage.

In an attempt to ensure that the full potential of the maize is achieved the following points are investigated:

- Impact of different cattle slurry to maize ratio
- Impact of winter and summer collected cattle slurry on the co-digestion process
- Impact of increasing the loading rate
- Impact of solid and liquid recirculation

The impact of the above points is considered in terms of the digestate, the methane yield, the yield of methane contributed from the maize and on any synergies present. The impact that the co-substrate ratio had on the co-digestion trial has been studied previously, as shown by section 2.3 while the impact of increasing the loading rate on a fixed loading rate has only been investigated by a couple of research papers. The process of recirculating the solid fraction is a new proposed method for improving the co-digestion process: in other work the liquid fraction is often recirculated as it is considered to have the higher methane potential. Recirculating the solid fraction may prove to be more beneficial in this co-digestion process as it may allow higher OLR's to be achieved while ensuring that undegraded fractions of maize do not leave the system.

In addition to providing optimal digestion conditions this research looks at the presence and source of any synergies. It has been shown that synergistic effects can occur in the co-digestion process and possible explanations are the improvements to the C:N ratio and nutrient composition. There is a lack of published research providing an accurate picture of synergy, as the identification of this effect is often the result of a comparison of mono and co-digestion trials following different methodologies, e.g. batch and semi-continuous trials. This comparison may not provide an accurate picture as it has been shown in the previous literature that batch and semi-continuous trials can produce different results. This research attempts to provide an accurate picture of any synergies by comparing mono and co-digestion trials that both follow semi-continuous working conditions and similar operational conditions.

3 Materials and methodology

This section will describe in detail the experimental plan and analytical techniques followed

3.1 General

Reagents

Except where otherwise stated all of the chemicals mentioned in this section were of laboratory grade and obtained from Fisher Scientific (Loughborough, UK).

Water

Solutions and standard were prepared with the use of deionised water (Elix electrodeionisation system, 97% ionic rejection, Millipore Corporation, UK), with the exception of the standards for the heavy metals, potassium and phosphorus where Milli-Q water was used (Milli-Q RiOs, resistivity 18.2 MΩ-cm at 25^0C, filter cartridge 0.22 μm, Millipore Corporation, UK).

Laboratory practise

All laboratory operations were carried out using good laboratory practice, the appropriate risk assessments and, where necessary, COSSH assessments. All equipment, laboratory apparatus, and analytical instruments were operated in accordance with the manufacturer's instructions. All glassware was washed using washing detergent followed by rinsing with tap water and deionised water. The glassware used for the acid digestion was soaked in a 10% nitric acid bath for a 24 hour period after which the glassware was rinsed with Milli-Q water.

3.2 Analytical methods

Gas production and composition

Gas composition was measured by a Varian CP 3800 gas chromatograph (Varian USA) which used Argon as the carrier gas at a flow of 50 ml min^{-1}. The GC was fitted with a Haysep C column and a molecular sieve 13 x (80-100 mesh) operated at a temperature of 50 ^{o}C.

Volatile Fatty Acids (VFA)

Samples were initially sieved through a 1 mm mesh and then centrifuged at 13000 rpm (Relative centrifugal force (RCF):17,900) (Eppendofr, Hamburg, Germany) for 40 minutes to get a clear supernatant. The samples were then diluted with deionised water to an appropriate strength to match that of the standards and preserved with 10% formic acid. The diluted acidified sample was then centrifuged for a further 10 minutes to remove any remaining solids. The VFA present in the samples were quantified by a Shimazdu 2010 gas chromatography (GC) instrument, which used a capillary column SGE BP 21 and helium as the carrier gas, the flow of this gas in the column was 1.86 ml min^{-1}. The temperature in the GC increased from 60^{o}C to 210^{o}C in 15 minutes with a holding time of 3 minutes, the temperature in the injector and the detector were 200 ^{o}C and 250 ^{o}C respectively. In each VFA run three standard solutions containing 50, 250 and 500 mg l^{-1} of acetic, propionic, iso-butyric, n-butyric, iso-valeric, valeric, hexanoic and heptanoic acids were used for VFA calibration. These standards were prepared by a laboratory technician and were stored at a temperature of 4 ^{o} C. The concentration of VFA in the digestate and the feedstock will be expressed as the sum of the individual VFA.

From the VFA concentrations the theoretical COD was calculated by the factors given in Table 3.1

Table 3.1: COD conversion factors

Acid	COD factor
Acetic	1.07
Propionic	1.51
Iso-butyric	1.82
Butyric	1.82
Iso-Valeric	2.04
Valeric	2.04
Hexanoic	2.20
Heptanoic	2.34

Soluble COD

Soluble chemical oxygen demand (SCOD) was measured weekly for the initial long term digestion trial and was determined following a modified mercury-free version of the closed tube digestion method. The samples were first sieved through a 1 mm mesh and then centrifuged at 13000 rpm for 40 minutes (Eppendorf, Hamburg, Germany). Following dilution to the correct strength 2 ml samples were added to borosilicate culture tubes, 160 x 10-mm, which were closed with PTFE-lined screw caps; duplicate controls consisting of 2 ml deionised water were prepared for each SCOD run. To each sample, including the controls 3.8 ml modified COD reagent (Ficodox Plus) was added in sequence. The samples were mixed and then heated for 2 hours at 150±2 ºC. After cooling to room temperature, the tube contents were titrated using 0.025 M standard ferrous ammonium sulphate titrant (FAS) with ferroin as indicator. To calculate the molarity of the FAS, 5 ml of a 0.02083 M solution of potassium dichromate was diluted to 60 ml and 15 ml of sulphuric acid was added; this mixture was allowed to cool before ferroin indicator was added and titrated against the FAS. The molarity was calculated by the following equation:

$$\text{Molarity} = \frac{5}{8 \times FAS}$$

Where:

FAS is the volume of FAS used (ml)

The titration was carried out using a Schott Titronic Universal automatic titrator (Schott, Mainz, Germany); the end point was a colour change from blue to red. The SCOD content of the samples was calculated by the following equation:

$$\textbf{COD (mg O}_2\textbf{ l}^{-1}\textbf{) =} \frac{8000(V1 - V2) \times M}{2 \times Dilution}$$

Where

V1 = Volume of FAS titrated against blank (ml)

V2 = Volume of FAS titrated against sample (ml)

M = Molarity of FAS

Alkalinity

The alkalinity of the digestate was measured by titration to endpoints of 5.7, 4.3 and 4.0 representing partial (PA), intermediate (IA) and total (TA) alkalinity. The partial alkalinity represents carbonate alkalinity (Jantsch and Mattiasson, 2004) while intermediate alkalinity represents the VFA buffering. The alkalinity of the digestate samples was measured by titration with 0.25M sulphuric acid using a Schott Titroline Easy automatic titrator (Schott, Mainz, Germany). Magnetic stirring was used to ensure accurate results and cross contamination was avoided by the use of deionised water to clean the pH probe between samples. From the results the ratio of partial to intermediate alkalinity can be calculated to provide an indication of the stability of the process; a ratio shown to be greater than 0.25 indicates a source of disturbance in the process (Ripley *et al.*, 1986).

Alkalinity (mg $CaCO_3$ l^{-1}) = $\frac{V1 \times N \times 50000}{V2}$

Where:

V1 = Volume of sulphuric acid titrated against sample (ml)

V2 = Volume of sample (ml)

N = Normality of the sulphuric acid

Total/Volatile Solids

The total solids content was measured by weighing a sample of digestate and heating the sample at 105 ^{o}C in a fan assisted oven (Vulcan-Hart, USA) for 24 hours. The volatile solids content of the digestate was measured by heating the previously dried sample to 550 ^{o}C in a muffle furnace (Carbolite, UK) for 2 hours (Standard Method 2540 G, APHA 2005).

It is important to note that this method of measuring solids can result in a potential error if the substrate has a high content of volatiles, such as VFA's or alcohols. These volatiles can be lost during the determination of the solids resulting in an underestimate of the solids content (Weißbach and Strubelt, 2008). This could particularly be true for ensiled maize, as ensiling will result in the production of VFA's and alcohols. The impact of this underestimation can be shown in subsequent results, such as an overestimation of the specific methane yield (l g^{-1} VS $_{added}$) and this was shown by the work undertaken by Mukengele and Oechsner (2007). This study investigated the impact of ensiling and the effect that correcting for volatiles had on the specific methane yield of maize. Failure to correct for volatiles resulted in a yield that was 10% greater than that calculated when the presence of volatiles was considered. Correction of the dry matter in this research has not been undertaken so the results presented in the following chapters could be up to 10% greater than the true value.

Ammoniacal Nitrogen

Ammoniacal nitrogen was measured weekly by steam distillation using a Foss Tecator Kjeltec System 1002 distillation unit (Foss Tecator AB, Hoganas Sweden). A sample of approximately 10 ml was taken and diluted up to 100 ml with deionised water; sodium hydroxide was added to raise the pH to above 9. The sample was distilled for 5-7 minutes until 150 ml distillate was collected in a flack containing 25 ml boric indictor, and the colour changed from purple to green. The distillate was then titrated against standardised 0.25 M sulphuric acid using an automatic titrator (Schott, Mainz, Germany) until a reverse colour change occurred. The calculation used for the ammonia concentration is given below.

Ammoniacal nitrogen (mg l^{-1}) = $\frac{14000 \times (V1 - V2) \times N}{V}$

Where:

V1 = Volume of sulphuric acid titrated against sample (ml)

V2 = Volume of sulphuric acid titrated against blank (ml)

V = Volume of sample

In addition a blank which consisted of 100 ml of distilled water and the control which consisted of 10 ml of standard ammonium chloride solution were also analysed.

Total Kjeldahl Nitrogen (TKN)

The TKN content was measured by acid digestion followed by ammonia distillation and titration. A sample of approximately 1 g was weighed into a digestion tube with 12 ml sulphuric acid (low in nitrogen) and a copper catalyst (FOSS, Cu 3.5 g, 0.4g $CUSO_4.5H_20$) was added. This mixture was agitated to ensure the sample and the acid were well mixed and the digestion tube was then heated to 450 ^oC in a heating block (FOSS Tecator 1007 for digestion trials 1-3; Büchi Digestion Unit K-435 for digestion trials 4-6) until the sample was completely digested; this was approximately 2 hours. When cool 75 ml of deionised water was added to each sample tube to prevent crystallisation and then distilled following the method and calculation for ammonia determination.

pH

Determination of the pH used a Jenway 3010 pH meter (Jenway, London, UK) which was calibrated daily using buffers to 7.0 and 9.2. The buffers were made weekly and stored in plastic sealed containers. The pH probe was cleaned in between samples with deionised water to avoid any cross contamination. During the measurement of the pH sample were continuously stirred in an attempt to obtain the pH of the complete sample.

Acid digestion of feedstock and digestate samples for metal and phosphorous recovery

Samples were air-dried and milled to ensure a homogenous sample. Approximately 0.5-1.0 g was weighed and added to 7.5 ml of hydrochloric acid and 2.5ml of nitric acid in glass digestion tubes. This mix was left to digest at room temperature for a minimum of 16 hours during which time the mixture was agitated frequently. After this initial digestion stage the digestion tubes were placed in a heating block and heated to 200 ^{o}C for 2 hours. To aid the digestion of the sample, the digestion tubes were agitated every 15 minutes during the heating period. In addition to the samples a blank containing only the acid mixture was digested.

After the digestion period the samples were allowed to cool before they were filtered by gravity through hardened cellulose paper (15.0 cm diameter, Whatman No. 30) into 50 ml volumetric flasks; the volume was made up with 12.5% nitric acid. The volumetric flasks were thoroughly mixed before the contents were transferred to 50 ml plastic containers for storage before analysis.

Analysis of heavy metals

The metals in the acid digested samples were analysed using a Varian Spectra AA-200 atomic absorption spectrophotometer (AAS) (Varian, Australia). The AAS is based on the absorption of UV or visible light by gaseous atoms. The heavy metals within a sample are measured when they are atomised by an air-acetylene flame; the atoms in the flame then absorb the wavelength that is sent by the light source: a hollow-cathode lamp. Each metal requires a specific lamp designed to emit the required wavelength. Table 3.2 gives the standard conditions required for the determination of the targeted metals

Table 3.2: Standard conditions for the determination of heavy metals

	Targeted Metals					
	Cadmium	**Chromium**	**Copper**	**Nickel**	**Lead**	**Zinc**
Wavelength (nm)	228.8	357.9	327.7	232.0	217.0	213.9
Lamp current (A)	4	7	4	4	5	5

The AAS machine was switched on 20 minutes before the injection of the sample to allow the equipment to stabilise and for the lamp to warm up. At the start of each analysis a calibration curve for each metal was prepared by running 5 standards as shown in Table 3.3.

Table 3.3: Standards for the heavy metals calibration

	mg l^{-1}					
Standard	**Cadmium**	**Chromium**	**Copper**	**Nickel**	**Lead**	**Zinc**
1	0.4	1.0	1.0	0.4	4.0	0.2
2	0.8	2.0	2.0	0.8	8.0	0.4
3	1.2	3.0	3.0	1.2	12.0	0.6
4	1.6	4.0	4.0	1.6	16.0	0.8
5	2.0	5.0	5.0	2.0	20.0	1.0

Once a linear calibration curve was obtained, replicate samples (appropriately diluted where necessary) were injected. A standard was injected between every fourth sample to check the stability of the measurement.

Analysis of potassium

The AAS was used to determine the potassium content of the sample. The acid digested sample was diluted to a suitable factor and 1% of caesium nitrate was added before injection into the machine. The purpose of the caesium addition was to suppress the ionisation of the potassium in the air-acetylene flame. The lamp for potassium determinations emits a wavelength of 766.5 nm. The concentration of the potassium was calculated from a calibration curve that was created from the five standards shown in Table 3.4.

Table 3.4: Potassium standards

Standard	**Potassium mg l^{-1}**	**10% Caesium nitrate ml**
1	0.4	1.0
2	0.8	1.0
3	1.2	1.0
4	1.6	1.0
5	2.0	1.0

A standard was injected between every fourth sample to check the stability of the measurement.

Analysis of phosphorous

The phosphorous content of the acid digested sample was determined by the use of a UV-Visible scanning spectrophotometer (Cecil 3000 series, Cecil Instruments). 2.5 ml of the acid digested sample was added to a 10 ml volumetric flask and a drop of phenolphthalein was added followed by several drops of 40% sodium hydroxide to produce a colour change to pink. When a pink colour was achieved 12.5% nitric acid was added to discharge the colour; sodium hydroxide (1M) was again added to reintroduce the pink colour followed by 1 drop of 0.1M nitric acid to discharge the colour. After all of the additions the solution was made up to 10 ml with deionised water and from this a suitable dilution for the determination was made. The samples were measured against standards prepared at concentrations of 0.25, 0.5, 0.75 and 1.0 mg l^{-1}. To all samples and standards 1.5 ml reagent colour was added and left for 20 minutes to allow colour formation. The composition of the reagent colour is presented in Table 3.5.

Table 3.5: Composition of reagent colour used in the analysis of phosphorous

Reagent name	Quantity (ml)
Sulphuric acid 2.5M	25
Potassium antimonyl	2.5
Ammonium molybdate	7.5
Ascorbic acid solution	15

The UV spectrophotometer was used at a wavelength of 880 nm and was allowed to warm up before use. The sample concentration was determined against a calibration graph using the following equation:

$$\textbf{Concentration (mg l}^{-1}\textbf{)} = \frac{Absorbance \times dilution}{Slope}$$

Elemental Analyser

The quantity of total carbon and nitrogen of the feed and the digestate samples were measured using a FlashEA 1112 Elemental Analyser (Thermo Finnigan, Italy). Samples of the feed and the digestate were air dried and milled to obtain a homogenous sample. Samples of approximately 3-4 mg in size were weighed into standard weight tin disks using a five decimal place analytical scale (Radwig, XA110/X, Poland). The equipment works by flash combustion of the sample in a gas flow temporarily enriched with oxygen resulting in a temperature greater than 1700 ^{o}C and the release N_xO_x, CO_2, H_2O and SO_2 (depending on the composition of the sample). The gas mixture is then an analysed by GC where the different components are measured by appropriate detector. The working conditions of the elemental analyser are presented in Table 3.6.

Table 3.6: Summary of methods and principle of the elemental analyser

		CHN determination
Reactors	**Configuration**	*Oxidation zone:* Chromium oxide *Reduction zone:* Reduced copper *SO_2 removal:* Silvered cobaltous/cobaltic oxide
	Temperature	900 ^oC
Gas chromatographic columns		Multiseparation column
Detector	**Type**	Thermal conductivity detector (TCD)
	Temperature	75 ^oC
Helium	**Reference flow**	100
	Carrier flow	140
Oxygen flow		250

Each run consisted of a calibration curve generated by measuring the carbon and nitrogen content of the following standards. In each run the standards (shown in Table 3.7) were run as unknown samples to check the accuracy of the machine.

Table 3.7: Standards used for the calibration of the elemental analyser

Standard	Carbon (%)	Hydrogen (%)	Nitrogen (%)
Methionine	40.29	7.48	9.44
Cystine	29.94	5.04	11.63
Sulphanilamide	41.65	4.61	16.23

As previously mentioned under the totals solids analysis, failure to account for loss of volatiles could result in an underestimate of the results. When measuring the nitrogen, some of the ammonia may have evaporated before determination of total nitrogen therefore resulting in an underestimation. This can also hold true for the total carbon determination.

3.3 Digesters

Semi-continuous fed 5-litre digesters

The digesters had a total volume of 5 litres and were operated at a working volume of 4 litres. A schematic drawing of a pair of digesters is shown in Figure 3.1. The digesters were constructed of PVC with a top flange to which a top plate was secured using stainless steel bolts and wing nuts. A gas tight seal between the top plate and the digester flange was maintained using a closed-pore neoprene gasket. The top plate was fitted with a gas outlet connector and a feed port sealed with a rubber bung. On the top plate a DC motor was mounted which was coupled to the digester stirrer through a draught tube water gas seal, with the draught tube itself being secured in a gas-tight compression seal. Digestate was removed from the digester via a 15 mm diameter outlet port at the base of the digester. The contents of the digesters were continuously stirred by means of a motorised asymmetric bar stirrer at 40 rpm. Temperature was maintained at 35 ^{o}C +/- 0.5 by water circulating through an external heating coil that surrounded the digesters. When assembled, and before filling, each digester was tested for gas leaks by applying a positive pressure to the digester and submerging in water to ensure there was no gas escape when all ports were sealed. The digesters were connected to gas counters, which continuously measured gas production throughout the digestion period; the gas counters operated by the alternate filling and discharging of a calibrated cell which logged each discharge via a LabJack U12 (LabJack Corporation) to a computer interface. The calibration of each gas counter was checked weekly by attaching the gas counter gas vent to a gas collection bag (SKC Ltd) The volume of gas collected was then measured accurately through a water displacement gasometer and the volume corrected to STP (101.325 kpa, 273.15 K) using the weight method (Walker *et al.*, 2009).

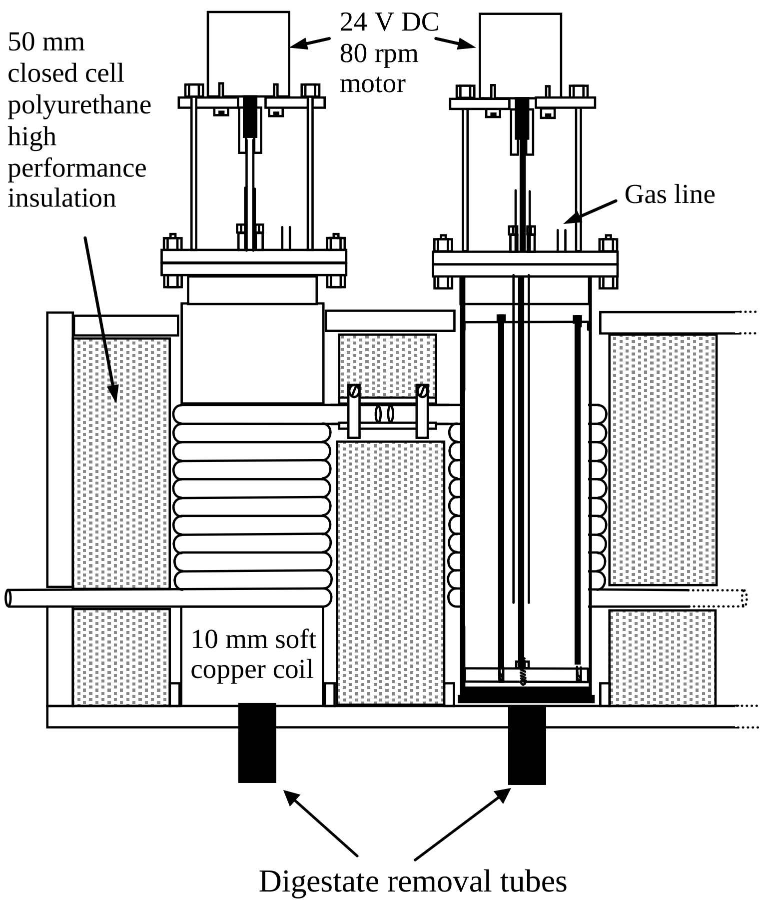


Figure 3.1: Diagram of the 4-litre working volume digester

Batch digesters

Batch fed digesters were used in the determination of biochemical methane potential (BMP). These had a volumetric capacity of 2 litres and a working volume of 1.5 litres. The construction was identical to that of the 5 litre reactors, except there was no discharge port in the base of the digester. Temperature was maintained by immersion in a temperature-controlled water bath at 35 ^{o}C. Biogas was collected in glass liquid displacement gasometers with a barrier solution of 75 % saturated sodium chloride acidified to pH 2 (Walker *et al.*, 2009). Gas production was measured continuously throughout the experiment by recording the pressure in the gasometer using pressure sensors calibrated to the liquid level. Pressures were logged as 10 minute averages using a labjack interface connected to a PC.

3.4 Feedstock

Cattle slurry

The cattle slurry was collected from a dairy farm with a herd size of 100 cattle near Southampton (Parkers Farm, Rownhams, UK). In total five different batches of cattle slurry were collected details of each batch, including the collection date, the housing status and the diet of the cattle, are given in Table 3.8. The dates refer to when the cattle slurry was collected and put into storage. Each batch was 'fresh' cattle slurry, collected directly from the milking area immediately after milking by the use of a tractor-mounted rear scraping mechanism

Table 3.8: Cattle slurry batches collected and the digestion trials in which they were used

Batch	Digestion trial	Date	Housed	Diet
1	1	July 2007	Outdoors	Grass with feed supplement*
2	2	January 2008	Indoors	Maize/grass silage with feed supplement
3	2	May 2008	Outdoors	Grass with feed supplement
4	3 and 4	September 2008	Outdoors	Grass with feed supplement
5	5 and 6	April 2009	Outdoors	Grass with feed supplement

*Actual amount of supplement given is unknown; however it is known that during the winter months (when the cattle are housed indoors) the cattle herd received a greater quantity of feed supplement when compared to the summer diet

The supplement fed the cattle contained the following ingredients:

- Wheatfeed
- Palm kernel, citrus pulp, wheat and molasses
- Rice germ, barley, calcium carbonate, magnesium oxide, salt, vegetable oils, vitamins/minerals
- Copper sulphate

The cattle slurry was stored at a temperature of +4 ^{o}C for all digestion trials with the exception of the second digestion trial where the cattle slurry was stored at ambient outdoor temperatures.

Ensiled maize

The ensiled maize was collected from Downlands and Woolmer farm (Liphook, UK) in spring 2007. Sufficient material to satisfy the needs of this research was collected in one batch to ensure consistency between the digestion trials. After collection the maize was placed in plastic food bags and stored at a temperature of -20 ^{o}C.

Before the maize and the cattle slurry were added to the digesters both substrates were finely shredded via a commercial garbage grinder (S52/010 Waste Disposer, Imperial Machine Company Ltd). This ensured a homogenous feedstock and also allowed the removal of unwanted material such as stones, which could have interfered with the digester stirring mechanism. The characteristics of the feed substrates used are given in Table 3.9.

Table 3.9: Feedstock Characteristics

		Cattle Slurry				
Parameter	**Maize**	**Batch 1**	**Batch 2**	**Batch 3**	**Batch 4**	**Batch 5**
pH		6.7	6.4	6.8	6.7	6.7
Total Solids (%)	33.70	11.07	9.57	12.79	7.68	11.78
Volatile Solids (%)	32.24	7.38	7.95	8.16	4.98	8.08
Total Kjeldahl Nitrogen (g l^{-1})	4.82	3.82	3.11	5.63	3.06	5.19
Ammonia (g l^{-1})	0.69	1.06	1.72	2.28	1.19	1.84
Total Nitrogen (g kg^{-1})	5.59	3.24	2.80	4.34	2.14	3.68
Total Carbon (g kg^{-1})	147.11	39.94	39.25	40.97	26.70	39.95
Carbon to Nitrogen ratio	26.32	12.31	14.01	9.45	12.46	10.85
Volatile Fatty Acids (mg l^{-1})	-------	2366	10536	1603	2938	3160
Potassium (as K_20) (mg g^{-1})	3.94	1.82	3.80	4.89	2.14	6.24
Phosphorus (as P_2O_5 mg g^{-1})	4.06	3.47	2.66	3.22	2.49	3.80
Cadmium (mg kg^{-1} DM)	0.2	0.4	0.2	0.6	3.0	0.8
Chromium (mg kg^{-1} DM)	18	333	13	1724	554	251
Copper (mg kg^{-1} DM)	5	49	50	60	49	52
Nickel (mg kg^{-1} DM)	7	105	10	866	237	108
Zinc (mg kg^{-1} DM)	27	263	210	214	200	201

3.5 Inoculum

In the semi-continuous digestion trials the inoculum for each trial was as detailed in Table 3.10. For the BMP test anaerobic digester sludge obtained from Millbrook Wastewater Treatment Plant (Southampton, UK) was used as the inoculum. On the day of collection the sludge was first sieved through a 1 mm mesh, to remove any large particles present and then added to the digesters and left at 35°C with stirring for 40 hours: until the gas production was minimal.

Table 3.10: Inoculum used in all semi-continuous digestion trials

Digestion trial	Inoculum used
1	Cattle slurry and digestate obtained from a laboratory scale semi-continuous digesters fed only on maize at a loading rate of 3 g VS l^{-1} d^{-1}
2	Digestate from all digesters in digestion trial 1 was mixed and used to provide a homogenous inoculum
3 and 4	Mixture of digestate obtained from digestion trial 2 and fresh cattle slurry
5: Maize	Digestate collected from a commercial size biogas plant that was fed with cattle slurry and maize (Lowbrook Farm, Dorset, UK).
5: Cattle slurry	Digestate from all digesters in digestion trial 4 was mixed and used to provide a homogenous inoculum
6	Combination of fresh cattle slurry and digestate removed from the mono-digestion trials (digestion trial 5)

3.6 Trace element additions

Where digesters were supplemented with a trace element solution, the composition of this was that shown in Table 3.11 (Gonzalez-Gil *et al.*, 2001).

Table 3.11: Composition of the trace element solution used in this research

		Concentration mg l^{-1}	
Compound	**Element**	**Compound**	**Element**
$FeCl_2.4H_2O$	Fe	2000	562
H_3BO_3	B	50	9
$ZnCl_2$	Zn	50	24
$CuCl_2.2H_2O$	Cu	38	14
$MnCl_2.4H_2O$	Mn	500	139
$(NH_4)_6Mo_7O_{24}.4H_2O$	Mo	50	4
$AlCl_3.6H_2O$	Al	90	10
$CoCl_2.6H_2O$	Co	2000	495
$NiCl_2.6H_2O$	Ni	142	35
$Na_2SeO. 5H_2O$	Se	164	56
EDTA		1000	

3.7 Experimental design and set up

To provide an extensive study into the co-digestion of cattle slurry and maize, and to meet the objectives set out in Chapter 1 a number of trials with different operational conditions were set up. A full description of the experiments is given in the appropriate Chapter along with the objective of the trial. All digesters were fed on a daily basis by adding the required wet weights of feed materials to achieve the required loading, with the volume of material removed equal to that needed to maintain the digesters at a constant volume. This led to all digesters, unless noted, to operate under a 'natural' retention time.

Analytical frequency

The analytical techniques described in section 3.2 were applied to all semi-continuous experiments following the frequencies given in Table 3.12 unless stated otherwise.

Table 3.12: Frequency of analysis followed by all semi-continuous trials

Analysis	Frequency
Ammoniacal nitrogen	Weekly
Alkalinity	Twice a week
COD	Twice a week
Gas volume	Daily
Gas composition	Weekly
Solids (TS/VS)	Weekly
pH	Alternative days
TKN	Weekly
VFA	Alternative days (except weekends)

Models

Pseudo-parallel first-order model

To determine the kinetic constants of the substrates tested by the BMP trial the specific methane production was modelled using a pseudo-parallel first-order model (Rao *et al.*, 2000). For this model the specific methane production is given by the following equation:

$$Y = Y_m \left(1 - Pe^{-k_1 t} - (1-P)e^{-k_2 t}\right)$$

where:

Y: cumulative methane yield at time t, m^3 CH_4 kg^{-1} VS added;

Y_m: ultimate methane yield, m^3 CH_4 kg^{-1} VS added;

k_1 is the first order rate constant for the proportion of readily degradable material, d^{-1}.

k_2 is the first order rate constant for the proportion of less readily degradable material, d^{-1}.

P is the proportion of readily degradable material

This model was also applied to the specific residual methane production in digestion trials 5 and 6.

Semi-continuous kinetic model

Mathematical models used in previous literature have included the steady-state anaerobic digestion models proposed by Chen and Hashimoto (1978) and Hill (1991). Both of these models were used and compared to the results produced by the co-digestion trial in Chapter 8. Chen and Hashimoto (1978) proposed that the methane production rate ($l\ l^{-1}$) can be given by:

$$G = B_o L \left(1 - \frac{K}{\mu_m \theta - 1 + K}\right)$$

Where:

B_o = Ultimate methane yield
L = Volatile solids loading rate ($g\ l^{-1}\ d^{-1}$)
K = Dimensionless kinetic parameter
μ_m = Maximum specific growth rate (d^{-1})
θ = Hydraulic retention time (d)

The model by Hill (1991) proposed the following equation to calculate the methane production:

G= $\gamma \times B_o \times \sigma \times I$

I= $0.5 + \left(\frac{1}{2.95}\right)\arctan\left(\frac{\tau - \sigma}{0.211}\right)$

Where:

B_o = Biodegradability factor
γ = Methane production (l g^{-1} VS consumed)
σ = Loading rate
I = Productivity index
τ = Stress Index

Carbon mass balance

A mass balance of the carbon entering and leaving the digesters in each digestion trial was calculated from the destruction of VS, the amount of carbon in the feedstock and composition of biogas. The following equation was used to produce a theoretical methane yield to compare to the actual methane yield.

CH_4 potential = $\left(\frac{VS_g \times C \times VS_{des} \times CH_4}{12}\right) \times 22.4$

Where:

VS_g = Quantity of VS added (g)
C = Carbon content (g)
VS_{des} = VS destroyed (g)
CH_4 = Percentage of methane

12 represents the molecular weight of carbon (g) and 22.4 is the quantity of litres per mol of carbon

VS destruction

The volatile solids destruction was determined from a series of equations aimed at calculating the difference between the VS added to the digester with that removed. The quantity of VS removed was calculated from a combination of the weight of feed added (in terms of ww), the weight of biogas produced and the VS content of the digestate. The series of equation were as followed:

VS destroyed (%) = $\frac{VS_{added} - VS_{removed}}{VS_{added}}$

VS removed (g) = $\left(WetWeight_{added} - Biogas_{produced}\right) \times VS\%$

Biogas produced (g) = $\frac{\left(\left(CH_{4(l)} \times 16\right) + \left(CO_{2(l)} \times 44\right)\right)}{22.4}$

Statistics

Statistics have not been used in this thesis as each operational condition was tested only in duplicate. In the absence of statistics, it is not possible to determine whether a significant difference is present between the different conditions tested. Where necessarily range bars are shown on the graphs to highlight the range of values achieved from the duplicates.

GHG emissions calculator

Salter, (pers.comm, 2010) provided an on-farm energy tool that determines the energy efficiency of a complete farm system by considering the energy consumed in the running of the farm and of the biogas plant along with the energy produced by the biogas plant. In addition it looks at the use of the digestate as a fertiliser and the land required for the application of all digestate produced. The number of cattle and area given for the growth of energy crops can be altered; modification of these factors allows for the amount and proportion of substrates fed to the digester to vary. The tool can be applied to all conditions tested in this research allowing for the associated greenhouse gas emissions to be calculated along with the greenhouse gas emissions saved by the production of biogas.

4 Partial BMP trial

4.1 Objective

The objective was to determine the specific methane yield from the maize and the first batch of cattle slurry. This methane yield is expressed in terms of the volatile solids content of the feedstock material added to the test. The test is carried out in batch mode and is run until such a time that no further biogas is produced relative to an inoculum-only control. The result is sometimes referred to as the biochemical methane potential (BMP) of the substrate and provides a baseline for comparison with the co-digestion trials.

4.2 Methodology

The digesters were run in duplicate following an inoculum to substrate ratio of 3.5:1, based on the volatile solids content. Table 4.1 provides the conditions of the BMP assays, each condition was run in duplicate.

Table 4.1: Operational conditions followed by the BMP trial

Digester	**1** Maize control	**2** Maize	**3** Cattle slurry	**4** Cattle slurry control
Inoculum added (g)	1450	1450	1400	1400
OLR of substrate (g VS l^{-1})	0	10.65	10.28	0
Substrate (g)	0	34.50	35.60	0
Trace element added (ml)	1.45	1.45	1.40	1.40

To ensure an accurate addition of inoculum and consistency between the digesters each empty digester was weighed and filled with the fixed wet weight of inoculum (Table 4.1). The inoculum was kept homogeneous by continuous stirring while sub-samples were taken for loading the digesters. The amount of substrate added to each digester was calculated based on inoculum to substrate volatile solids ratio of 3.5: 1. The required amount of substrate was taken from a well mixed container and added to the digester by placing the digester on a balance and making note of the increase in weight. The required amount of trace element solution was added and the top plates were secured onto the digesters with new gaskets fitted. Each digester was then placed into the heated water bath and attached to its corresponding gas collector.

The barrier solution level in the gas collectors was checked and recorded at least twice a day along with the ambient temperature and pressure to correct the gas volume to standard temperature and pressure. A sample of the gas collected was tested for methane content when the gas collector was full, or after 5 days (whichever was the shorter); the barrier solution level in gas collector was raised to zero by using a vacuum pump.

4.3 Results

The BMP value obtained after 45 days provided a baseline for comparison of the specific methane yields obtained in semi-continuous co-digestion trials. The 45-day test did not provide an ultimate value for the BMP of the substrates but the incubation time was longer than the 33 day maximum retention time used in the semi-continuous digester studies

The results for the two substrates are shown in Figure 4.1 expressed as specific methane yield (l g^{-1} VS_{added}). The cattle slurry used was from batch 1 (Table 3.8)

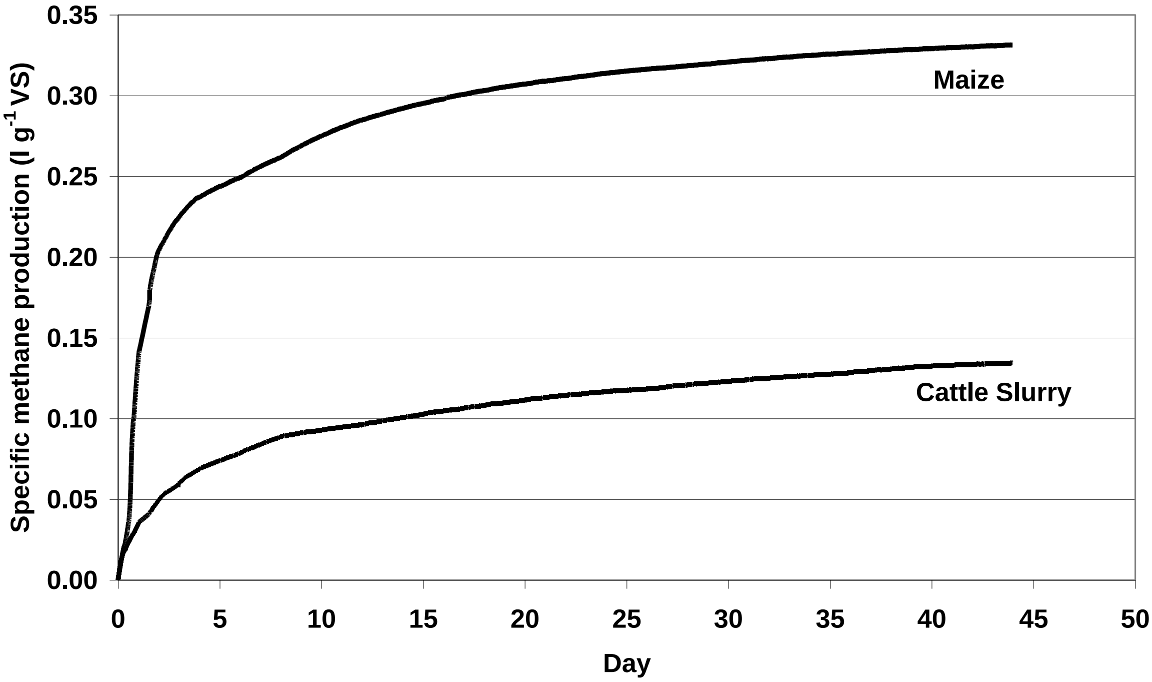


Figure 4.1: Biochemical methane production of cattle slurry and maize following mono-digestion in batch conditions.

The specific methane yields at the end of the 45 days were given to be 0.13 and 0.33 l g^{-1} VS_{added} for the cattle slurry and the maize respectively. From the shape of the graph it can be seen that there was a rapid early methane production. Over half of the methane potential of both substrates was observed within the first 10 days; 69 and 83% for the cattle slurry and the maize respectively. As expected, the results from the BMP trial indicated that the methane potential of the maize was greater than that of the cattle slurry. The value of 0.13 l g^{-1} VS_{added} for cattle slurry was in the mid range of values reported by Amon *et al.*, (2007) of 0.126 to 0.166 l g^{-1} VS_{added} and the value for maize silage of 0.33

$l\ g^{-1}\ VS_{added}$ was in the higher part of the range of 0.268-0.365 $l\ g^{-1}\ VS_{added}$ for maize, depending on the variety and harvest time. The value for maize silage was also very close to the 0.338 $l\ g^{-1}\ VS_{added}$ reported by Machmüller *et al.*, (2007).

The results of the empirical pseudo-parallel model as described in Chapter 3 were used to interpret the test data and the results are given in Table 4.2. The model showed a good fit to the experimental data as can be seen in Figure 4.2 and Figure 4.3.

Table 4.2: Empirical model parameters used for the BMP trial

	Maize	**Cattle slurry**
Methane yield ($l\ g^{-1}\ VS_{added}$)	0.33	0.13
Proportion of readily degradable fraction (P)	0.65	0.35
Degradation rate for the readily degradable fraction (K_1)	0.95	0.75
Degradation rate for the slowly degradable fraction (K_2)	0.08	0.07
R^2	0.997	0.997

The results indicate that as expected the maize silage has the greater proportion of readily degradable material (P) with a higher rate of degradation (K_1) when compared to the cattle slurry. The rate of degradation of the lesser degradable fraction is similar for both substrates but the proportion of this fraction in the cattle slurry is almost double than in the maize silage.

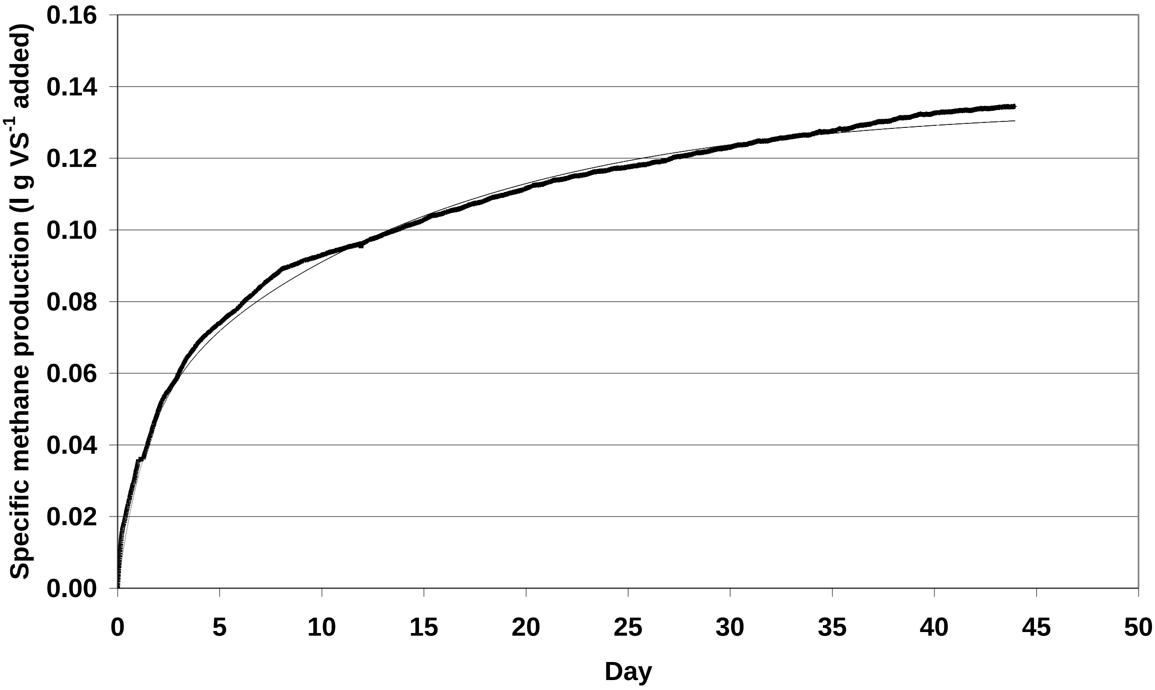


Figure 4.2: Parallel pseudo-first order model for the batch digestion of cattle slurry: Experimental (▬) and model (—) data

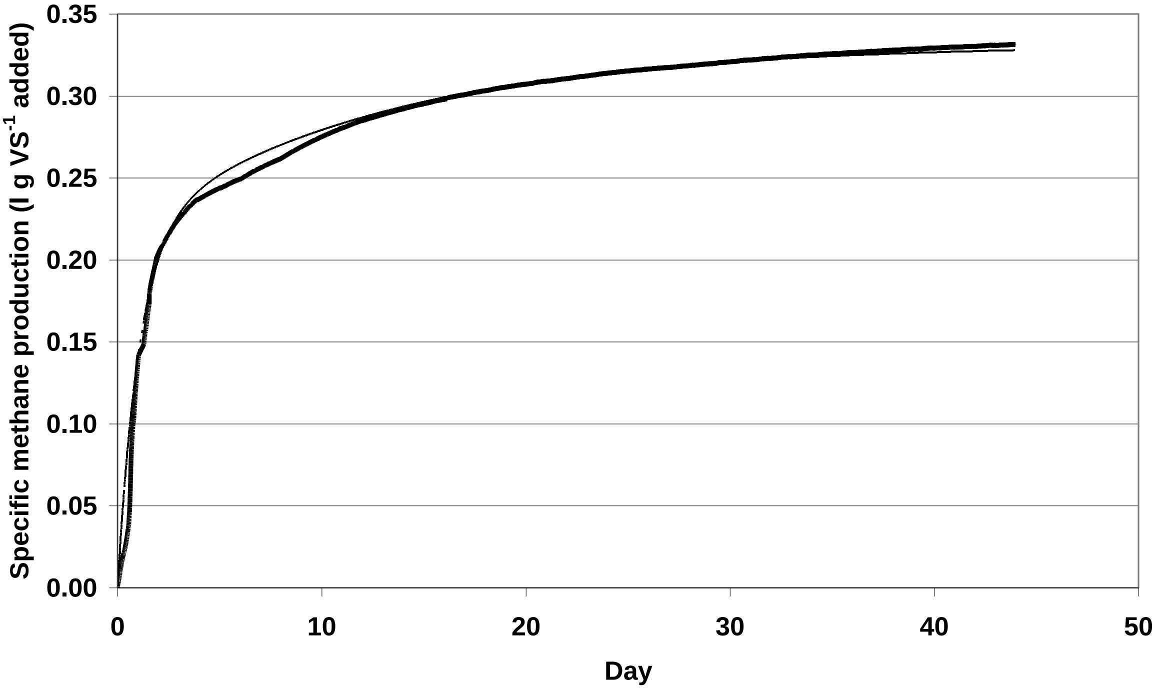


Figure 4.3: Parallel pseudo-first order model for the digestion of the maize: Experimental data (▬) and model data (—)

5 Digestion trial 1: Impact of increasing the quantity of maize added to a constant cattle slurry loading rate.

5.1 Objective

The objective of this trial was to measure the increase in volumetric gas production of the digestion process when a cattle slurry digester is supplemented with maize silage. To achieve this, the volatile solids loading of the cattle slurry component of the feed was kept constant and the extra load was added as maize silage. It was also hoped that the experiment would indicate the presence of any synergy between the two substrates which could improve the combine gas yield when compared to mono-digestion.

5.2 Methodology

Eight 5-litre digesters were used in this trial. One pair of digesters was maintained as a control, fed only with cattle slurry at a OLR of 2 g VS l^{-1} d^{-1}; the remaining three pairs of digesters had an identical OLR of cattle slurry but maize was added to increase their total OLR up to a maximum of 5 g VS l^{-1} d^{-1}. The retention time ranged from 26 to 33 days for the different loading rates as shown in Table 5.1. The cattle slurry used in this trial was batch 1.

Table 5.1: Operational conditions followed by each digester pair in digestion trial 1.

	Cattle slurry		Maize		Retention time
Digester	**g VS l^{-1} d^{-1}**	**g (ww)**	**g VS l^{-1} d^{-1}**	**g (ww)**	**d**
1	2-2.56	121	0	0.0	33
2	2-2.56	121	1	11.9	30
3	2-2.56	121	2	23.8	28
4	2-2.56	121	3	35.7	26

The VS content of the cattle slurry changed slightly during the digestion trial resulting in the actual VS load to vary between 2 and 2.12 g VS l^{-1} d^{-1} up to day 70, after which the average VS of the raw cattle slurry was shown to change from 6.97 to 8.90% . This change resulted in the actual VS cattle slurry load to increase from 2 to 2.56 g VS l^{-1} d^{-1} for the final 69 days of the trial. This could have been the result of insufficient mixing of the raw cattle slurry at the beginning of the trial and it highlights the importance for the cattle slurry to be mixed thoroughly to give a homogeneous feed for the complete trial.

5.3 Results

Biogas and methane production

After 30 days of operation each digester showed a constant biogas production with little variation shown during the trial period with the methane percentage remaining between 55-60%. The pair of digesters fed at the highest OLR showed the greatest average methane yield of 5.8 l d^{-1} for the final 69 days of the trial, which is equivalent to a volumetric methane yield of 1.46 l l^{-1} d^{-1}. The digestion of cattle slurry alone produced a total methane yield of 1.39 l d^{-1}, which is equivalent to 0.35 l l^{-1} ^{1}. The average specific methane yield (l CH_4 $g^{-1}VS_{added}$) of each digester pair for the final 69 days was calculated to allow for a comparison between the digesters. The highest specific methane yield of 0.26 l g^{-1} VS $_{added}$ was obtained at the 5 g VS l^{-1} d^{-1} OLR, of which 3 g VS l^{-1} d^{-1} was contributed by the maize addition. The lowest specific yield of 0.131 l g^{-1} VS was produced by the digestion of cattle slurry alone, Figure 5.1 shows the volumetric and specific methane yields at the different OLR's

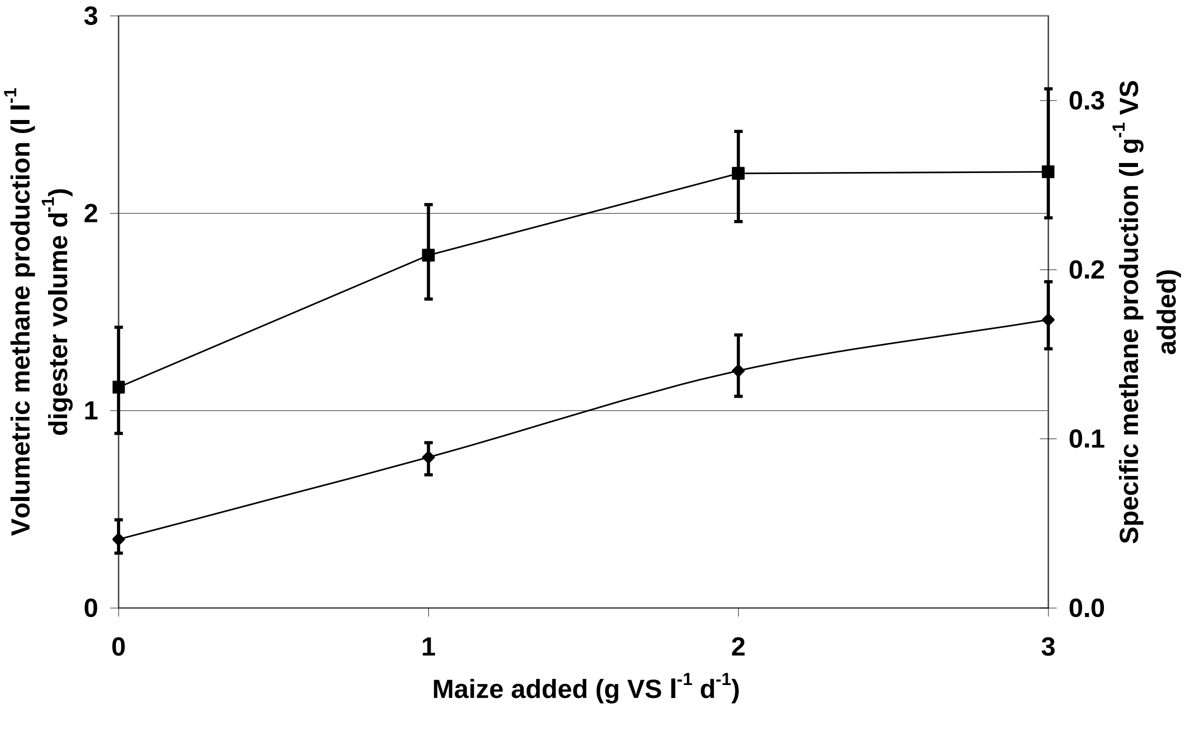


Figure 5.1: Average methane production from each digester pair and at each loading rate in terms of the volumetric methane (♦) and specific methane (■) yields. The values are taken from the final 69 days of the trial; the bars represent the range of values achieved.

By increasing the OLR, both, the volumetric and specific methane yield increased in value indicating that the digestion process was viable at all loading rates. From Figure 5.1 it can be seen that up to the 2 g VS l^{-1} d^{-1} maize addition the volumetric methane production followed an approximate linear relationship at 0.43 l l^{-1} per g VS l^{-1}. Increasing the maize addition from 2 to 3 g VS l^{-1} d^{-1} still produced an improvement to the volumetric methane yield but this was slightly lower than that achieved at the lower loading rates and indicated that not all of the substrate was being utilised at this higher loading. The specific methane yield increased from 0.13 l g^{-1} VS for cattle slurry alone to 0.21 l g^{-1} VS_{added} when 1 g VS l^{-1} d^{-1} maize was added and then to 0.26 l g^{-1} VS_{added} at the higher maize loads. This difference between the maize loads does not appear to be significant, with a similar range given for each maize addition.

The connection of the digesters to gas counters allowed for the daily biogas evolution to be determined; this is shown in Figure 5.2. It can be seen that in each case feeding induced a higher rate of gas production, which declined throughout the day. In the digestion of cattle slurry alone the higher rate of production was observed in the first 4 hours, after which the rate remained approximately linear at 0.018 l g^{-1} VS h^{-1}. In the case of co-digestion the higher rate of degradation was observed over an 8- hour period and comparison between the initial rates of production and the quantity of maize added showed an increasing initial rate as the load of maize increased. At the highest maize addition the initial rate was 0.038 l g^{-1} VS h^{-1} while at 1 g VS l^{-1} d^{-1} it was 0.020 l g^{-1} VS h^{-1}. After this initial period the rate of gas production in all digesters progressively decreased ending in a similar rate to that with cattle slurry alone.

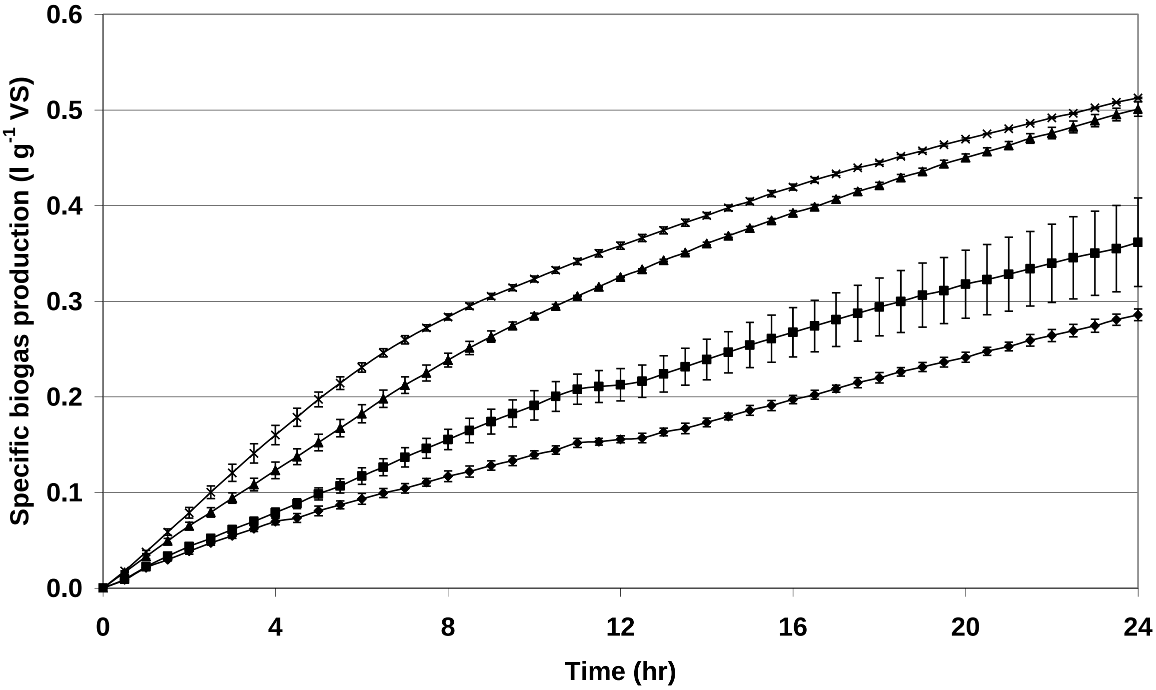


Figure 5.2: Average specific biogas yield produced by each digester pair at all maize loads tested during a 24 hour period at day 138: 0 g VS l^{-1} d^{-1} maize addition (♦), 1 g VS l^{-1} d^{-1} maize addition, (■), 2 g VS l^{-1} d^{-1} maize addition (▲) and 3 g VS l^{-1} d^{-1} maize addition (▬). The bars represent the range of values achieved.

To determine whether the combination of the two substrates created any synergistic or antagonistic effects the volumetric methane yield calculated from the BMP trial was compared to the actual methane yield produced from this digestion trial. This approach has some limitations as batch trials can produce different results to a semi-continuously fed digester (Callaghan *et al.*, 1998). Comparison of the BMP trial in Chapter 4 with the semi-continuous digester fed with cattle slurry alone in this Chapter produced similar specific methane yields, 0.13 and 0.13 l g^{-1} VS $_{added}$ produced from the BMP trial and the semi-continuous trial respectively. It was decided to calculate the total methane yield using the methane yield from slurry digestion in the semi-continuous trial and not from the BMP test to allow similar methodologies to be compared. Unfortunately, a maize-only semi-continuous trial was not undertaken at this stage so the methane potential from the BMP trial was used. The comparison is shown in Figure 5.3; the difference between the two values is shown on the Figure. The actual volumetric methane yield is the average of the digester pairs over the final 69 days.

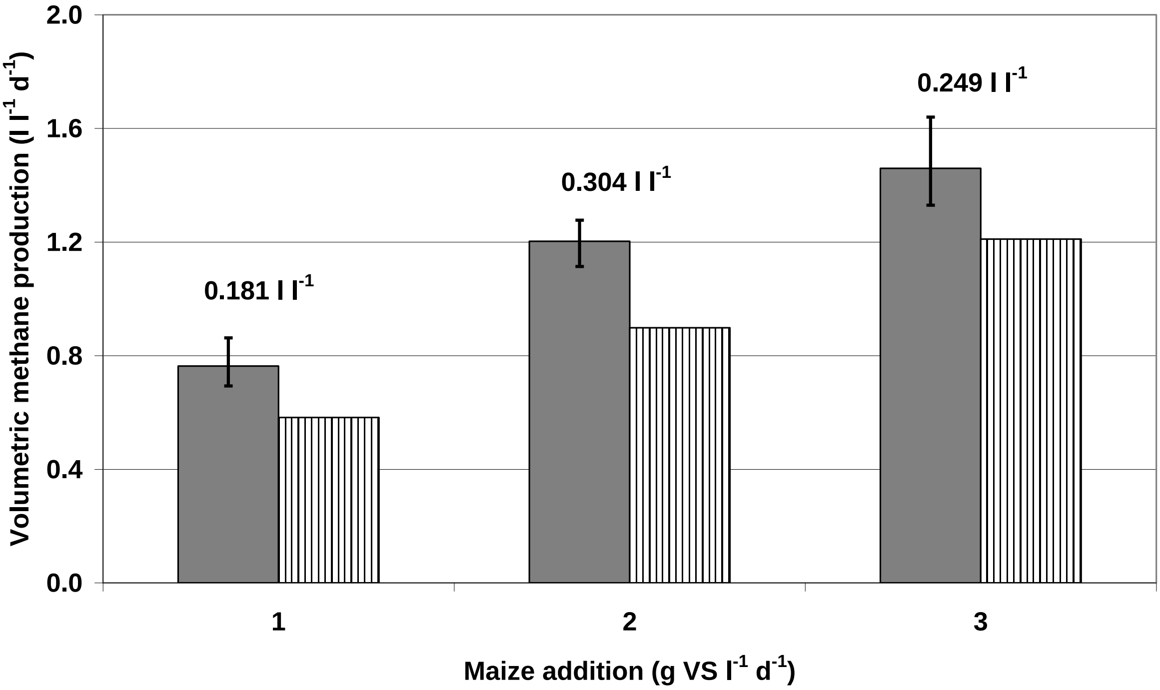


Figure 5.3: Difference in the volumetric methane production (l l^{-1} d^{-1}) between the actual methane production (filled bars) and the yield calculated from combining the methane potential of the maize and of the cattle slurry (striped bars). The actual methane yields are the average of each digester pair taken from the final 69 days of the trial. The numerical differential is displayed and the range of values achieved is represented by the range bars.

Figure 5.3 shows that when calculated in this way the digesters produced a greater methane yield than predicted The smallest differential was at the 1 g VS l^{-1} d^{-1} maize addition, which produced 0.18 l l^{-1} more methane than the theoretical prediction; the greatest improvement was at the 2 g VS l^{-1} d^{-1} maize addition, which produced 0.30 l l^{-1} more than the calculated yield. At the 3 g VS l^{-1} d^{-1} maize addition the differential reduced to 0.25 l l^{-1}. The range of values achieved from all replicates remained greater than that calculated, as shown by the range bars.

The difference in the amount of methane produced that could be attributed to the maize component of the co-digestion feedstock is shown in Figure 5.4. Here the specific methane production attributable to the cattle slurry has been subtracted from the overall specific methane production in the co-digestion trials. For comparison the methane potential of the maize from the BMP test is also shown on the graph.

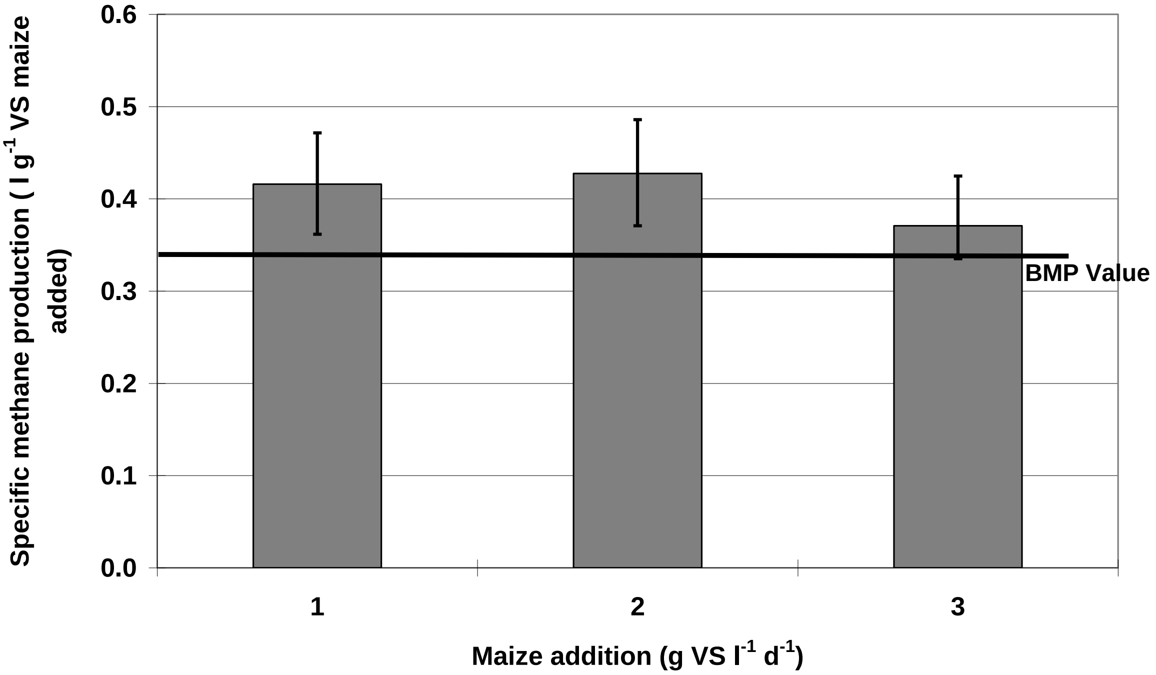


Figure 5.4: Specific methane production attributable to the maize by the subtraction of specific methane yield of the cattle slurry from the overall specific methane yield. These are the average of each digester pair at each loading rate tested from the final 69 days tested. The range of the specific methane production is given by the bars while the methane potential of the maize calculated from the BMP trial (Chapter 4) is given for comparison

The addition of maize to cattle slurry appears to improve the average specific methane yield of the maize compared to the batch BMP test. The highest specific yield was 0.43 l g^{-1} VS $_{added}$ of maize produced by the 2 g VS l^{-1} d^{-1} maize addition, closely followed by the 1 g VS l^{-1} d^{-1} maize addition (0.42 l g^{-1} VS of maize). The maize at the 3 g VS l^{-1} d^{-1} was calculated to contribute the lowest average yield of 0.37 l g $VS^{-1}{}_{maize}$. The bars indicate that the range of the specific methane yield does remain above the BMP value with the exception of the highest maize load where the lower range equals that of the BMP value. As with the overall specific methane yields shown in Figure 5.1 the difference between the maize loads is minimal with the ranges being almost equal. From Figure 5.3 and Figure 5.4 it is likely that a further increase in the maize load would further reduce the differential between the actual and predicted methane yield and in the specific methane yield of the maize

Digestate properties

The digestate properties are summarised in Table 5.2; these are the average of the digester pairs taken from the final 69 days.

Table 5.2: Characteristics of the digestate at all maize additions tested; given values are averages of the digester pairs taken from the final 69 days of the digestion trial

Maize addition g VS l^{-1} d^{-1}	**0**	**1**	**2**	**3**
pH	7.5	7.4	7.4	7.4
TKN g l^{-1}	3.4	3.4	3.7	3.8
Ammonia g l^{-1}	1.3	1.4	1.3	1.3
% of TKN	38.6	40.7	34.5	33.
Soluble COD g l^{-1}	3.9	4.0	5.7	6.2

The results for the digestate of the control digester that only received cattle slurry indicated that digestion increased the pH of the raw cattle slurry from 6.7 to 7.5, accompanied by an increase in the concentration of ammonia from 1.1 to 1.4 g l^{-1}. With the addition of maize the pH of the digestate remained constant at 7.4 along with a consistency in the ammonia content, 1.3-1.4 g l^{-1}. The amount of total nitrogen (TKN) in the digestate displayed an increase in concentration from 3.4 to 3.8 g l^{-1} as the load of maize increased. The lower ammonia content and the higher TKN values are highlighted by the decline in the percentage of TKN accounted for as ammonia. A mass balance of the nitrogen is shown in Table 5.3.

Table 5.3: Mass balance of the nitrogen entering the digester and the nitrogen leaving the digester at a daily basis. Values are based on the average value for the raw cattle slurry, the maize silage and the average of each digester pair over the final 69 days of the digestion trial.

Maize load	Daily digestate removal	Nitrogen (g)		Difference	
(g l^{-1} VS d^{-1})	l	Input	Output	g	%
0	0.12	0.46	0.41	-0.06	-12.1
1	0.13	0.52	0.43	-0.09	-16.9
2	0.14	0.58	0.50	-0.08	-13.6
3	0.15	0.63	0.56	-0.08	-12.6

Parameters which did not appear to reach a steady state value over the duration of the trial was the solids content; the trend shown by the solids are shown in Figure 5.5 and 5.6..

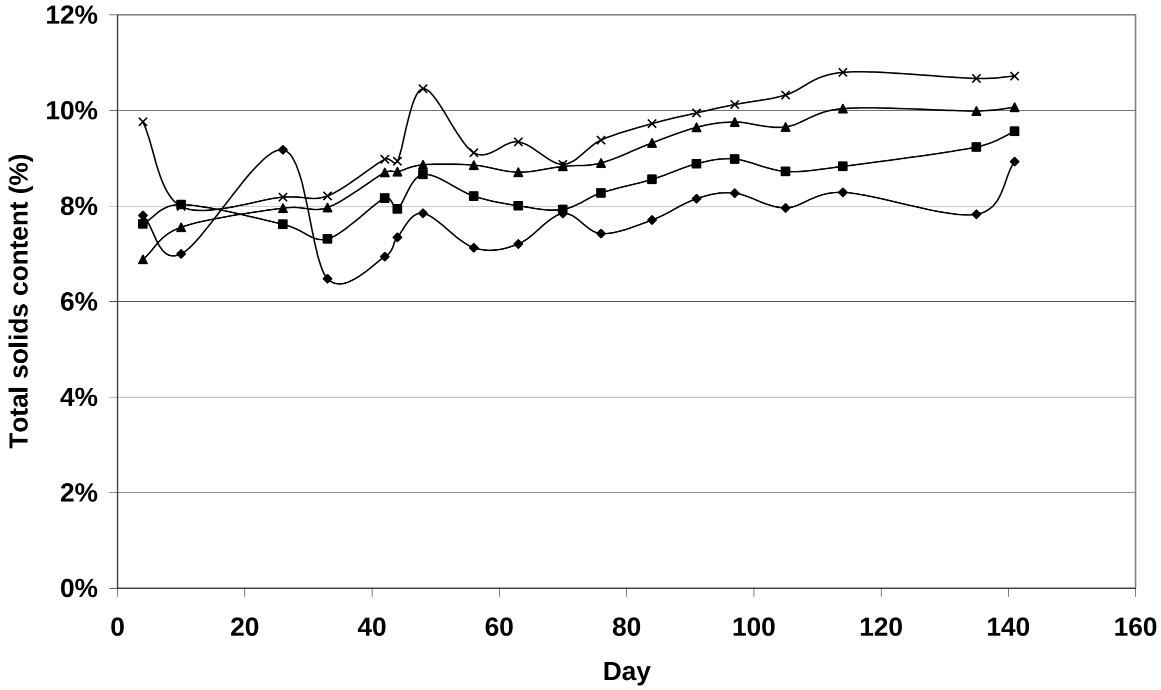


Figure 5.5: Average total solids content of each digester pair during the digestion period and at each loading rate tested: 0 g VS l^{-1} d^{-1} maize addition (♦), 1 g VS l^{-1} d^{-1} (■), 2 g VS l^{-1} d^{-1} maize addition (▲) and 3 g VS l^{-1} d^{-1} maize addition (X)

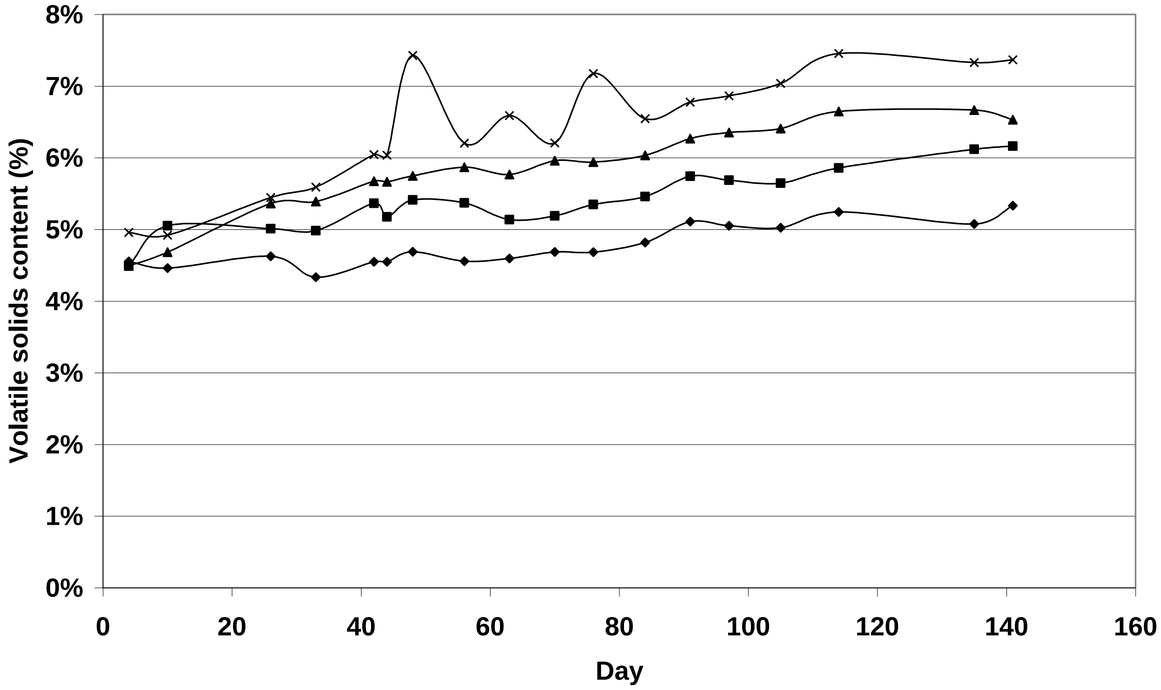


Figure 5.6: Average volatile solids of each digester pair during the digestion period: 0 g VS l^{-1} d^{-1} maize addition (♦), 1 g VS l^{-1} d^{-1} (■), 2 g VS l^{-1} d^{-1} maize addition (▲) and 3 g VS l^{-1} d^{-1} maize addition (X)

The total and volatiles solids slowly increased at all maize loads with an indication that this parameter was beginning to stabilise by the final 25 days. This increase in the volatiles solids could be the result of the inconsistency of the VS content of the raw cattle slurry (Table 5.1). Taking the average of the digester pairs over the final 25 days it was shown that digestion of the cattle slurry led to a reduction in the total solids from 11.07% to 8.34%, corresponding to a 24.70% decline. The digesters fed on a mix of cattle slurry and maize all showed lower average TS concentrations than raw cattle slurry but as the maize load increased, so did the solids content up to a maximum of 10.73%, which is only 0.34 % below that in raw cattle slurry. The relationship between total solids concentration and maize addition was strongly linear (R^2 = 0.989) with an increase of 0.80 % TS per g VS l^{-1} d^{-1} of maize added.

The VS destruction was determined from a mass balance as described in Chapter 3. Figure 5.7 and Table 5.4 show that the greatest volatile solids destruction occurred at the highest maize addition, with the final 69 days showing an average destruction of 55%. The digestion of the cattle slurry alone produced the lowest volatile solids destruction of 42.1%.

Table 5.4: Mass balance of the VS content of each digester pair at all loading rates; values are based on the average VS input, output and methane yield from the final 69 days of the trial

Maize addition (g VS l^{-1} d^{-1})	**VS Input (g)**	**Digestate removed (g d^{-1})**	**VS output (g)**	**VS destruction (%)**	**Specific methane yield (l g^{-1} $VS_{destroyed}$)**
0	10.3	118	6.0	42.1	0.32
1	14.3	126	7.1	50.3	0.43
2	18.8	135	8.6	54.5	0.47
3	22.8	145	10.2	55.4	0.46

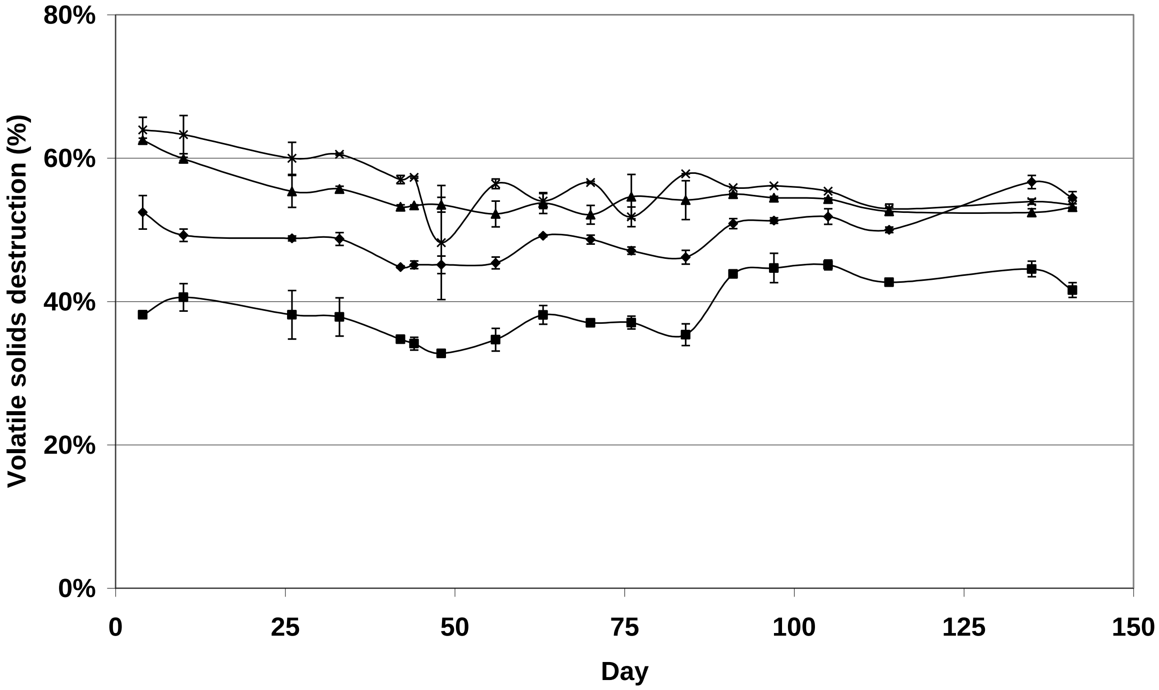


Figure 5.7: Average volatile solids destruction of each digester pair during the digestion period: 0 g VS l^{-1} d^{-1} maize addition (♦), 1 g VS l^{-1} d^{-1} (■), 2 g VS l^{-1} d^{-1} maize addition (▲) and 3 g VS l^{-1} d^{-1} maize addition (X)

An additional parameter that did not show consistency during the trial was the concentration of the total VFA. It can be seen that in all digesters the concentration of total VFA remained below 250 mg l^{-1} and, as Figure 5.8 shows, there was little difference between the digesters. The majority of the VFA within the digestates were short chain acids, mainly acetic acid with small concentrations of propionic. This consistently low concentration indicates that the accumulation of acids was avoided in all conditions tested.

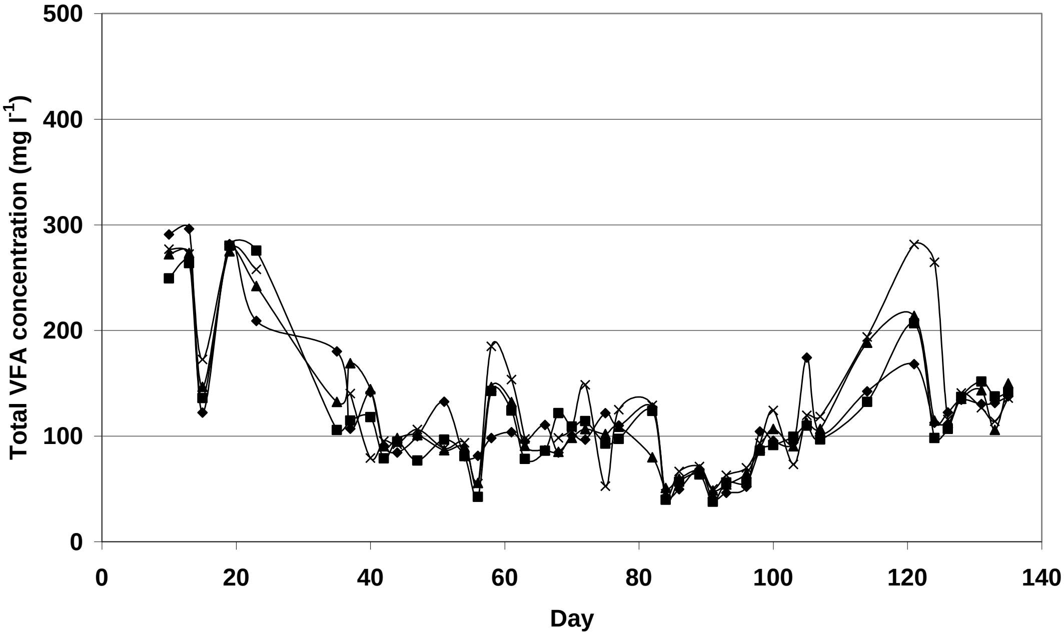


Figure 5.8: Average concentration of total volatile fatty acids of each digester pair during the digestion period for all maize additions tested. 0 g VS l^{-1} d^{-1} maize addition (♦), 1 g VS l^{-1} d^{-1} (■), 2 g VS l^{-1} d^{-1} maize addition (▲) and 3 g VS l^{-1} d^{-1} maize addition (X)

Theoretical COD values based on the VFA concentrations were calculated to allow prediction of the digestate methane potential based on the stoichiometric equivalence of 1 g of COD to 0.35 l CH_4; the results are shown in Table 5.5.

Table 5.5: Methane potential of the digestate based on the theoretical COD concentration

Maize addition g VS l^{-1} d^{-1}	Theoretical COD g l^{-1}	Methane l l^{-1}
0	0.13	0.04
1	0.12	0.04
2	0.12	0.04
3	0.13	0.04

From knowing the volatile solids destruction and the carbon content of both the maize and the cattle slurry the theoretical potential methane yield from each digester can be calculated and compared to the actual methane yield. This also provides a mass balance of the carbon entering and leaving the system taking into account the methane produced.

There appears to be a trend in the degree of agreement with the increase in the maize addition as Table 5.6 shows. There is good agreement for the two higher maize loads however, a negative balance is shown for the cattle slurry alone and the 1 g VS l^{-1} d^{-1} maize load. This negative result may be the result of an inaccuracy in the collection and measurement of the actual methane yield, an error in the measurement of the carbon and/or the VS destruction rate. The potential calculated for the digestion of cattle slurry could be the unrealistic value as this is equivalent to a potential specific methane yield of 0.28 l g^{-1} VS_{added}, which is high for cattle slurry alone.

Table 5.6: Comparison of the average methane yield of each digester pair over the final 69 days of the digestion trial with the potential methane yield calculated from the quantity of carbon entering the digesters.

	Methane (l l^{-1} d^{-1})		
Maize Addition (g VS l^{-1} d^{-1})	**Potential**	**Actual**	**Difference**
0	0.55	0.35	-36.4%
1	0.76	0.89	-13.8%
2	1.20	1.21	-0.5%
3	1.46	1.46	0.0%

5.4 Discussion

As indicated by the results, the co-digestion of maize and cattle slurry was possible at all maize additions tested with each digester reaching apparently stable conditions in terms of the gas production after the initial 30 days of running. The maximum maize addition was 3 g VS $l^{-1}d^{-1}$, giving a total OLR of 5 g VS l^{-1} d^{-1}. Digestion was still possible at this loading rate and showed the greatest volumetric methane yield. This positive influence of the maize load was repeated in the specific methane yield where an increase was shown as the maize loads increased up to 2 g VS l^{-1} d^{-1}. The final maize increment to 3 g VS l^{-1} d^{-1} showed no improvement in the specific methane yield. This supports the work by Lehtomäki *et al.*, (2006) where increasing the proportion of energy crop (grass silage, sugar beet and straw) to cattle slurry increased the specific methane yield. In Lehtomäki *et al.*, (2006), energy crops were tested at proportions 10, 20, 30 and 40%, based on VS; and it was shown that as the proportion increased from 30 to 40% a decline in the specific methane yield occurred. A decline in the specific methane yield was not seen in the current research however, as shown by Figure 5.1, there was no improvement at the highest maize load (60% maize). The lack of improvement in the specific methane yield at the OLR of 5 g VS l^{-1} d^{-1} was thought to be the result of overloading of the system, and further increases in the maize addition could cause the specific methane yield to decline even more.

Comparing the methane yield from this digestion trial with the calculated methane yield, based on the maize BMP and the semi-continuous control digester showed that each digester maintained a methane yield greater than that predicted (Figure 5.3). When cattle slurry was the only component the methane yield was similar to that calculated from the BMP test while in the co-digestion trials the difference reached a maximum of 0.30 l l^{-1} d^{-1}, achieved at the 2 g VS l^{-1} d^{-1} maize addition. Comparison between the calculated and actual methane yield highlighted the decline in digestion performance at the 3 g VS l^{-1} d^{-1} maize addition, with the difference between the two yields declining from 0.30 l l^{-1} d^{-1} at the 2 g VS l^{-1} d^{-1} to 0.25 l l^{-1} d^{-1}.

As the cattle slurry load remained constant in all the digesters the amount of methane contributed from the maize could be calculated. The results showed that the specific methane yield predicted from the maize contribution was greater than the methane potential calculated from the BMP test and also greater than typical values quoted in the literature ((Amon *et al.*, 2007, Machmüller *et al.*, 2007). The highest contribution from maize was produced at the 2 g VS l^{-1} d^{-1} maize addition, which gave a specific methane yield attributable to the maize of 0.43 l g^{-1} VS maize. This apparent benefit did not show a clear difference between the loads with similar ranges produced at all maize loads. The method used for calculating the methane contributed by the maize makes two assumptions which may or may not be true. Firstly, it assumes that the specific methane yield obtained for maize in the BMP test is correct. This value was used as there was no control semi-continuous digestion trial in which maize was the only substrate; if this trial had been carried out and given a different value for specific methane yield this would have altered the above results. Secondly, it assumes that the improvement is only as a result of the improved methane production of maize, whereas the improvement could actually be due to the cattle slurry or a combination from both substrates. If the results from the maize BMP test are correct, the improvement in overall gas production indicates that synergy is occurring at all of the loading rates tested, including the highest maize loading. The reduction in the apparent synergistic effect at the greatest maize load could be the result of a general system overload or as the proportion of maize increases to around 60% of the feed the synergistic effect is lost as the balance of nutrients necessary for this becomes less favourable.

The results indicate that continuously increasing the maize added to a constant load of cattle slurry in an attempt to increase the energy output of the system is a viable option as the volumetric methane yield is shown to increase. For maximising the energy yield per tonne of organic matter, however, there is a limit to the amount of maize that should be added to cattle slurry as the 3 g VS l^{-1} d^{-1} maize addition failed to improve the specific methane yield. This suggests that further increments in the maize could reduce the specific yield indicating that an addition of 3 g VS l^{-1} d^{-1} is the maximum maize load that should be added to cattle slurry.

The digestion of cattle slurry alone resulted in a rise in pH as a result of an increase in the ammonia concentration from 1.07 to 1.33 g l^{-1}. As a result of this, digested cattle slurry could produce higher ammonia emissions compared to those from raw cattle slurry. This is supported by the work of Amon *et al.*, (2006b) which showed that initial emissions from digested cattle slurry were 18% greater than the emissions from untreated cattle slurry. The decline in the total solids content of the digestate by 28% compared to raw slurry can offset this to some extent, as it allows the digestate to filter into the soil more quickly than the higher solids raw cattle slurry. It was shown by Wulf *et al.*, (2006) that higher initial emissions were obtained from treated slurry while the raw cattle slurry was shown to emit ammonia over a longer time period. One explanation given for this was the extended period that the cattle slurry was exposed to the air due to the slower filtration rate. On the addition of maize the solids content increased from 8.1 to 10.2% with a decline in pH and a reduced ammonia concentration to 1.27 g l^{-1}. This still corresponds to an 18% higher ammonia concentration compared to raw cattle slurry although it is 6% lower than digested cattle slurry alone. This decline in ammonia could reduce the overall ammonia emissions but the proportional reduction is relatively low and at all maize additions the ammonia concentration in the digestate was greater than the raw cattle slurry. At the maize load of 2 g VS l^{-1} d^{-1} (shown to be optimal for methane yield) the solids content increased to 9.8% indicating that the potential for more rapid soil infiltration may be counteracted when using the digestate produced at optimal loading conditions and this may prove to be a disadvantage in terms of ammonia emissions when compared to digestate produced from cattle slurry alone. It could also prove to be a disadvantage as extended periods on the surface can reduce the amount of nitrogen entering the soil therefore becoming available for the crop.

6 Digestion trial 2: Operation of cattle slurry/maize silage digesters at a constant load using varying proportions of the two components

6.1 Objective

This trial had three objectives:

1. To determine if the co-digestion trial is affected by differences in cattle slurry collected in winter and summer.
2. To assess the effect on the digestion performance of increasing the proportion of maize in the feed while maintaining a constant digester load
3. To compare specific methane yields from the first trial conducted at a fixed cattle slurry load and variable total load to those at a variable cattle slurry load but a fixed total load.

6.2 Methodology

Eight digesters were used in this trial and operated as duplicate pairs. The OLR of this trial was maintained at 4 g VS l^{-1} d^{-1}. The proportions of cattle slurry and maize in the feed to three pairs of digesters were calculated to give the required loading based on the maize making up from 1 to 3 g VS l^{-1} d^{-1} (respectively 25 to 75% of the load). One pair of digesters were maintained as controls and fed only on cattle slurry at an OLR of 4 g VS l^{-1} d^{-1}. The digesters were fed on a daily basis and were run at a 'natural' retention time, which ranged from 22 to 50 days as shown in Table 6.1. A load consisting of 50% maize was omitted from this trial to avoid repetition of the first digestion trial, and a load of 65% was used instead.

Over the course of this trial, two batches of cattle slurry were used. The first batch of cattle slurry was collected in the winter months and was used over the first 114 days and the second batch was collected in the summer months and was used for the final 87 days of the trial. The first batch of cattle slurry is referred to as winter cattle slurry while the second batch is referred as summer cattle slurry. These two batches relate to batch 2 and 3 in Table 3.9.

Table 6.1: Operational conditions followed by digestion trial 2

Digester	Cattle slurry g VS l^{-1} d^{-1}	Cattle slurry g (ww)	%	Maize g VS l^{-1} d^{-1}	Maize g (ww)	Retention time d
1	4	208	100	0	0	22
2	3	156	75	1	13.0	27
3	2.6	135	65	1.4	18.2	30
4	1	52	25	3	39.1	50

6.3 Results

6.3.1 Winter cattle slurry

Biogas and methane production

After 18 days constant gas production was observed by all digesters treating the mixed substrate but the digester fed on cattle slurry alone required a longer period to stabilise. The average volumetric methane yield of each digester pair is shown in Figure 6.1.

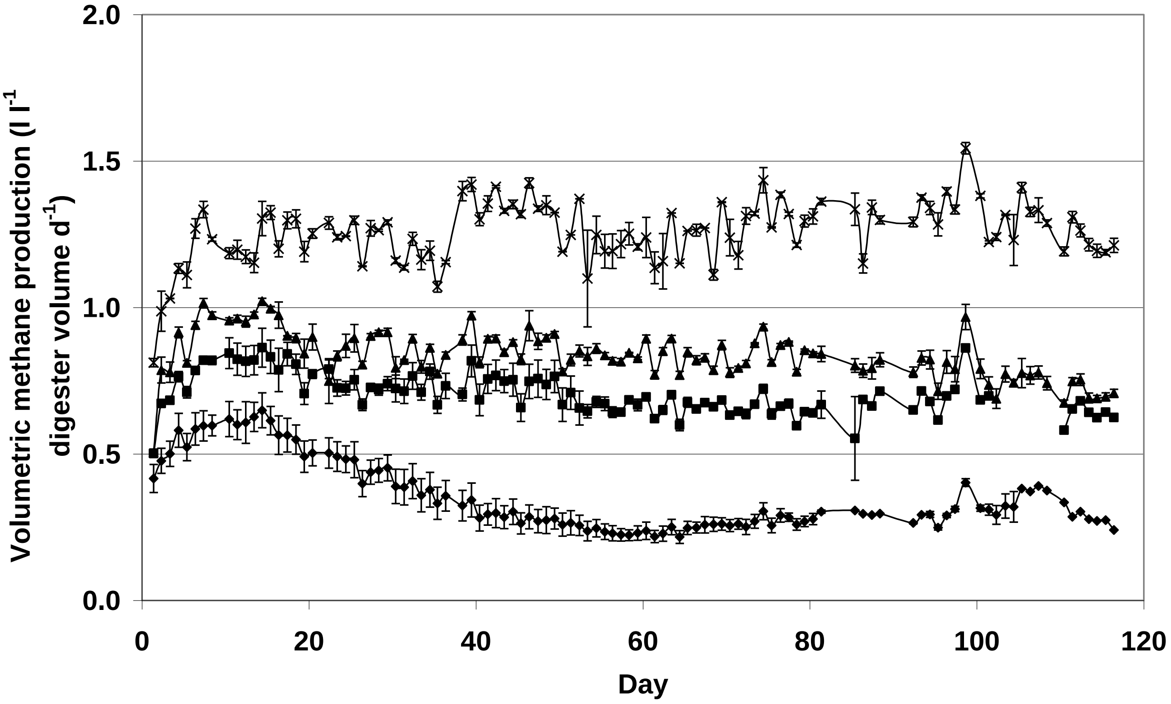


Figure 6.1: Average volumetric methane production of each digester pair at all working conditions tested while fed with the winter cattle slurry. 0 g VS l^{-1} d^{-1} maize addition (♦), 1 g VS l^{-1} d^{-1} maize addition (■), 1.4 g VS l^{-1} d^{-1} maize addition (▲) and 3 g VS l^{-1} d^{-1} maize addition (X). The bars represent the two replicates tested at each loading rate.

The cattle slurry digesters required 50 days to reach consistent gas production and during this period there was a decline in the volumetric methane yield, from 0.55 l l^{-1} d^{-1} at day eighteen to approximately half of this yield, 0.28 l l^{-1} d^{-1}, at the end of the trial. This decline in performance during the initial period was not seen when the cattle slurry was digested with maize.

When comparing the digesters with different maize proportions a clear difference in the volumetric methane yield can be seen. The highest productivity was 1.28 l l^{-1} d^{-1} at the highest maize load. Comparing this value with the volumetric methane yield produced from the cattle slurry alone shows that the replacement of 3 g VS l^{-1} d^{-1} of the loading rate with maize led to an increase by over one l l^{-1} d^{-1}. The specific methane yield also increased as seen by Figure 6.2. The digestion of cattle slurry alone gave a specific methane yield of 0.07 l g^{-1} VS $_{added}$; this is low when compared to the specific methane yield produced by the cattle slurry in the previous digestion trial (0.13 l g^{-1} VS) and when compared to literature values for cattle slurry. Explanation for the difference between the two digestion trials could be due to the greater total VFA concentration in the raw cattle slurry, 2.37 and 10.54 g l^{-1} respectively (Table 3.9).

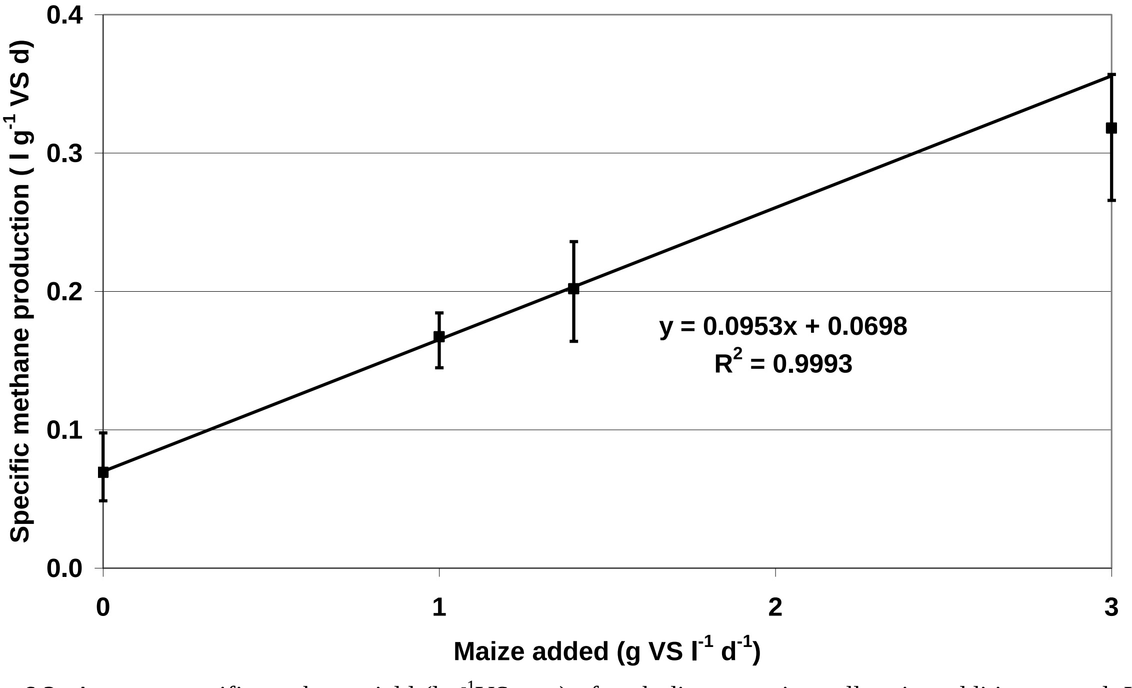


Figure 6.2: Average specific methane yield (l g^{-1}VS $_{added}$) of each digester pair at all maize additions tested. Values are taken from daily readings over the final 61 days of the digestion trial. The linear relationship between the maize addition and the specific methane yield up to the maize load of 1.4 g VS l^{-1} d^{-1} is shown to highlight the reduced average specific methane yield at the 3 g VS l^{-1} d^{-1}

The replacement of 1 g VS l^{-1} d^{-1} of the load with maize led to an increase in the specific methane yield to 0.17 l g^{-1} VS $_{added}$; this is over double the yield achieved by the cattle slurry alone. The highest proportion of maize produced the greatest specific methane yield of 0.31 l g^{-1} VS $_{added}$, which is greater than the maximum specific methane yield of 0.26 l g^{-1} VS $_{added}$ achieved in the first digestion trial. The near linear relationship between the methane yield and the maize additions does however, suggest that the 3 g VS l^{-1} d^{-1} maize load is approaching the system capacity as it is seen to deviate from the relationship with a lower average methane yield.

Table 6.2 compares the C:N ratio at the different maize proportions along with volumetric methane yield and biogas composition. Increasing the amount of maize within the feed led to an increase in the C:N ratio and it can be seen that the volumetric methane yield increased with the ratio; the percentage of methane however, declined from 57 to 54%.

Table 6.2: Carbon to nitrogen ratios tested in digestion trial 2 along with the volumetric methane yield produced.

Maize addition g VS l^{-1} d^{-1}	C:N ratio	Volumetric methane l l^{-1} d^{-1}	% Methane in the biogas
0	14.0	0.28	56.9
1	15.8	0.66	55.4
1.4	16.6	0.80	55.5
3	21.4	1.27	54.4

The average daily biogas production on day 77 for each digester pair is shown by Figure 6.3. As in the first digestion trial, biogas was produced at a higher rate immediately after feeding and this rate reduced towards the end of the 24 hour cycle. In all cases it was observed that both the rate of production and the length of the initial high-rate period increased as the proportion of maize increased. The digestion of cattle slurry alone produced an initial rate of production of 0.007 l g^{-1} VS h^{-1} for a period of 5 hours while the digester fed with 3 g VS d^{-1} maize produced biogas at a rate of 0.028 l g^{-1} VS h^{-1} for a longer period of 13 hours. After the initial period the rate achieved from the digestion of cattle slurry alone was 0.004 l g^{-1} VS h^{-1} while the 3 g VS maize addition produced biogas at a rate of 0.019 l g^{-1} VS h^{-1}. The increase in the rate of gas production reflects the higher content of readily degradable components in the maize (Chapter 4, Table 4.2).

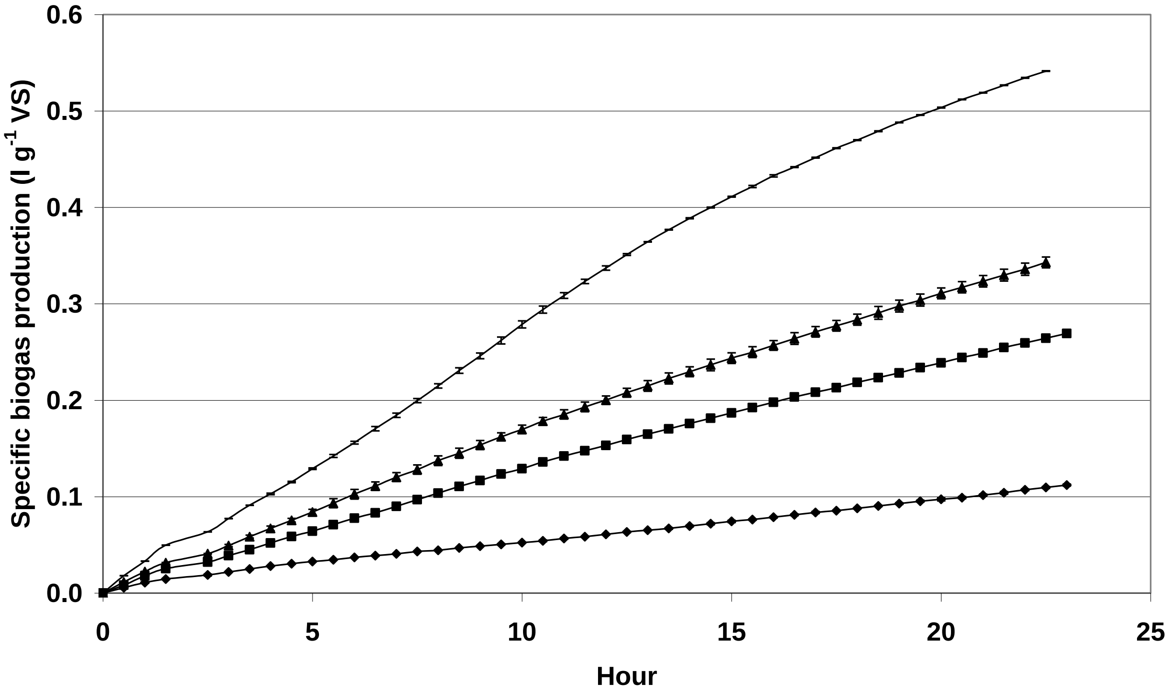


Figure 6.3: Average specific biogas yield produced by each digester pair during a 24 hour period: 0 g VS l^{-1} d^{-1} maize addition (♦), 1 g VS l^{-1} d^{-1} maize addition, (■), 2 g VS l^{-1} d^{-1} maize addition (▲) and 3 g VS l^{-1} d^{-1} maize addition (▬)

The estimated potential methane production was calculated from the maize BMP (Chapter 4) and from the specific methane yield from the cattle slurry (0.072 l g^{-1} VS $_{added}$). The comparison between the calculated and the actual methane yield is shown in Figure 6.4. The average yield from the co-digestion was greater that its predicted value, giving 0.14 l l^{-1} more than that calculated at the lowest maize load and 0.21 l l^{-1} more than that calculated at the highest maize addition.

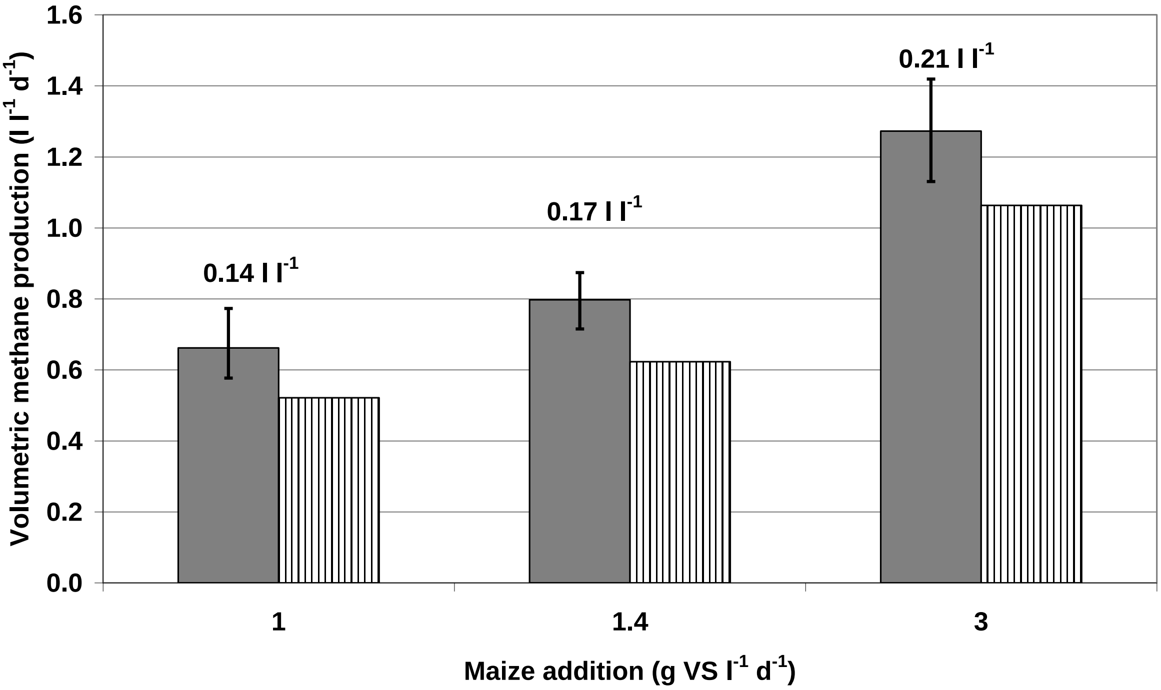


Figure 6.4: Difference in the average volumetric methane production (l l^{-1} d^{-1}) between the actual methane production (filled bars) and the yield calculated from combining the methane potential of the maize and of the cattle slurry (striped bars). The actual methane productions are the average of each digester pair from the final 61 days of the digestion trial. The numerical difference is given in each case along with range achieved at each maize load tested.

A comparison of the specific methane yield from the 1 and 3 g VS l^{-1} d^{-1} maize additions at different cattle slurry additions in the first and second trial is given in Table 6.3. The results indicate that at the 1 g VS l^{-1} d^{-1} maize addition the increase in cattle slurry from 2 to 3 g VS l^{-1} d^{-1} led to a decline in the specific methane yield estimated to be derived from the maize. The specific methane produced from the complete load also declined in value as the load of cattle slurry increased from 66 to 75%, with values of 0.21 and 0.17 g VS l^{-1} at the 2 and 3 g VS l^{-1} d^{-1} cattle slurry loads respectively. A decrease in the specific methane yield attributed to the maize was also shown at the maize load of 3 g VS l^{-1} d^{-1} when the cattle slurry increased from 4 to 5 g VS l^{-1} d^{-1}. This could be due to the increase in the total loading rate, which also led to a significant reduction in the retention time from 50 to 26 days. This comparison however, relies on the assumption that the properties of the cattle slurry used in the two trials (Batch 1 and 2, Table 3.9) are similar: the difference in the specific methane productivities of the cattle slurries used in each trial (0.13 for trial 1 and 0.07 l g^{-1} VS for trial 2) indicates that this was not the case.

Table 6.3: Comparison of specific methane yield produced by the 1 and 3 g VS l^{-1} d^{-1} maize additions attributable to the maize calculated from subtracting the methane yield of the cattle slurry from the overall methane yield. The values are the average of each digester pair collected from the final 69 and 61 days of digestion trial 1 and 2 respectively.

Digestion trial	Maize g VS l^{-1} d^{-1}	Cattle slurry g VS l^{-1} d^{-1}	OLR g VS l^{-1} d^{-1}	Specific methane yield l g^{-1} VS maize added	% Cattle slurry
1	1	2	3	0.42	66
2	1	3	4	0.33	75
1	2	3	5	0.37	40
2	2	2	4	0.40	25

Digestate properties

Table 6.4 shows the average values for the digestate characteristics; these are the average of each digester pair taken over the final 61 days.

Table 6.4: Characteristics of the digestate at all maize additions tested; given values are averages of each digester pair over the final 61 days.

Maize g VS l^{-1} d^{-1}	0	1	1.4	3
pH	7.7	7.6	7.6	7.6
TS %	8.5	8.4	8.8	10.4
VS %	6.9	7.1	7.2	8.3
VS destruction (%)	17.8	31.1	36.9	60.9
TKN g l^{-1}	4.3	4.4	4.4	4.5
NH_3 g l^{-1}	2.6	2.4	2.4	1.8
% of TKN	60	56	54	40
Total alkalinity g l^{-1}	15.8	15.3	15.1	12.7
IA/PA	0.38	0.33	0.36	0.33

The cattle slurry digestate had a solids content of 8.5% compared to 9.6% for the raw cattle slurry. Replacement of the cattle slurry with maize produced the same trend shown in the initial digestion trial (Chapter 5) with the total solids content increasing from 8.5 to 10.4%. The stability shown by the volatile solids content is shown by Figure 6.5.

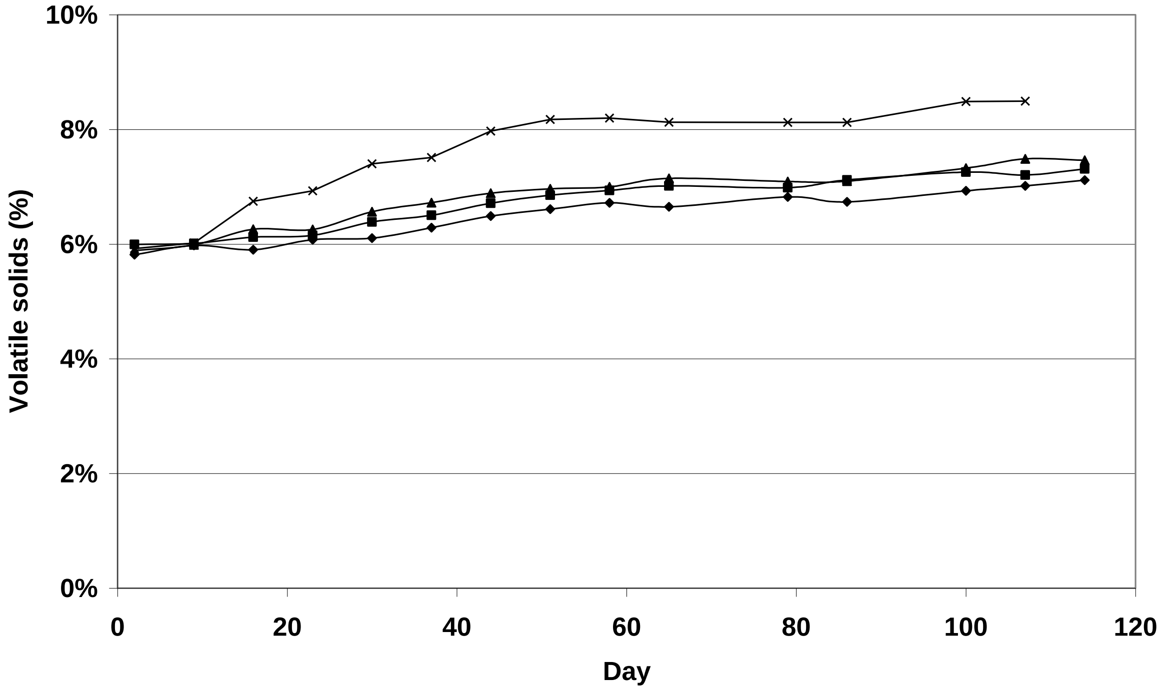


Figure 6.5: Average volatile solids content (%) of each digester pair at all maize additions tested while fed with winter cattle slurry: 0 g VS l^{-1} d^{-1} maize addition (♦), 1 g VS l^{-1} d^{-1} maize addition (■), 1.4 g VS l^{-1} d^{-1} maize addition (▲) and 3 g VS l^{-1} d^{-1} maize addition (X).

The volatile solids destruction shown in Table 6.5 and Figure 6.6 indicates that the lowest destruction was at the cattle slurry digester, 17.8%, corresponding to the low specific methane yield, 0.07 l g^{-1} VS d^{-1}; this represents a low rate of destruction when compared to the 42% VS destruction achieved in the first trial. As with the initial digestion trial increasing the quantity of maize resulted in an increase in the volatile solids destruction, up to the maximum of 60.9%.

Table 6.5: Mass balance of the VS content of each digester pair at all maize loads tested. Values are based on the average VS input, output and methane yield of the digester pair over the final 61 days.

Maize addition (g VS l^{-1} d^{-1})	VS Input (g)	Digestate removed (g d^{-1})	VS output (g)	VS destruction (%)	Specific methane yield (l g^{-1} VS $_{destroyed}$)
0	17.2	206	14.1	17.8	0.37
1	16.9	163	11.6	31.1	0.40
1.4	16.8	147	10.6	36.9	0.51
3	16.7	79	6.5	60.9	0.50

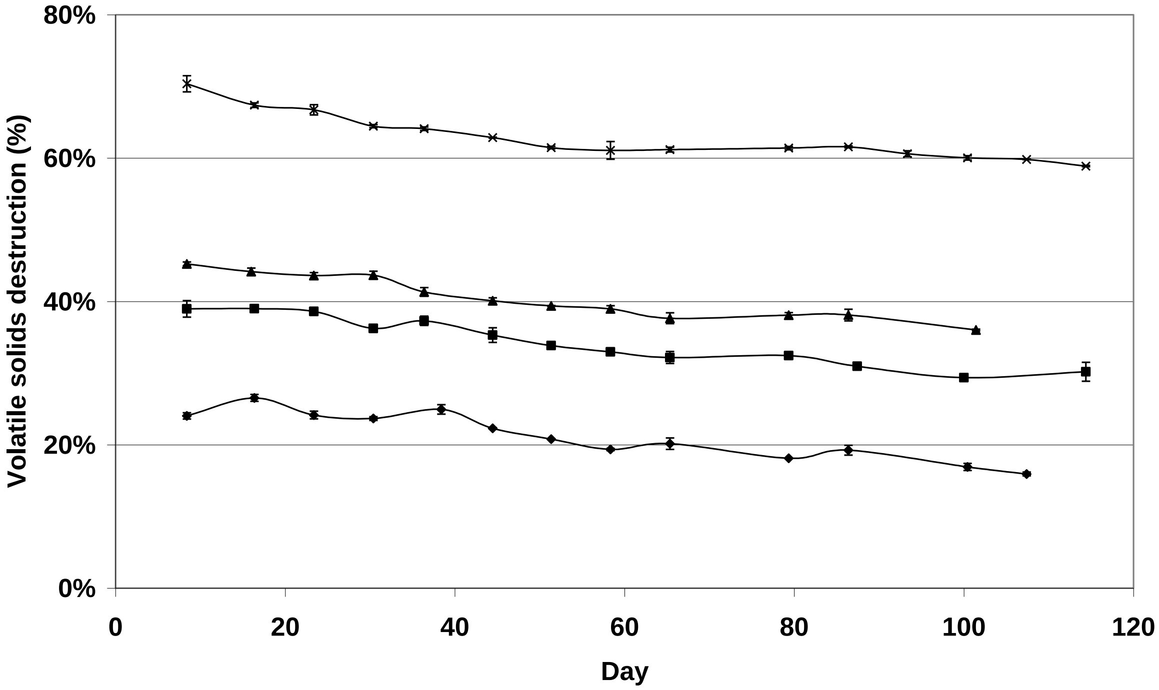


Figure 6.6: Average volatile solids destruction for each digester pair at all maize proportions based on weekly measurements. 0 g VS l^{-1} d^{-1} maize addition (♦), 1 g VS l^{-1} d^{-1} maize addition (■), 1.4 g VS l^{-1} d^{-1} maize addition (▲) and 3 g VS l^{-1} d^{-1} maize addition (X)

The potential methane yield as calculated from the carbon input and the volatile solids destruction is compared to the actual methane yield; this can be seen in Table 6.6. This calculation used the average VS destruction and methane yield of each digester pair from day 58 as it was from this date that VS destruction showed approximate consistency.

Table 6.6: Comparison of average methane yield of each digester pair over the final 61 days, based on daily measurements, with the potential methane yield calculated from the quantity of carbon entering the digesters.

	Methane ($l\ l^{-1}$)		
Maize (g VS l^{-1} d^{-1})	**Potential**	**Actual**	**Difference**
0	0.39	0.28	-28.3%
1	0.65	0.53	-18.1%
1.4	0.76	0.80	+ 4.9%
3	1.21	1.27	+ 5.4%

The comparison shows that this mass balance produced both negative and positive balance with the cattle slurry alone and the lowest maize load producing a lower yield than the potential. The 1.4 and 3 g VS l^{-1} d^{-1} maize loads produced a methane yield equalling the potential calculated (+6.0%). The negative balance indicates potential errors which could be result of the failure to consider the loss of volatile components resulting in the inaccurate measurement of carbon and the VS destroyed

(Mukengele and Oechsner, 2007, Weißbach and Strubelt, 2008). For example, the VS of the input and output may be an underestimate of the true value resulting in an overestimation of the VS destroyed therefore an overestimation of the potential methane yield. The trend matches that shown in the first trial (Table 5.6) with an increase in agreement as the maize increases; this could suggest that results for the raw cattle slurry loads may not be truly representative of the batch of cattle slurry used. It was shown in the first trial that cattle slurry during storage can vary over time; this could mean that the VS content may be too low or the carbon content may be too great.

As well as increasing the solids content, increasing the quantity of maize in the feedstock caused a reduction in ammonia from 2.6 to 1.8 g l^{-1}. The TKN concentration increased from 4.27 to 4.53 g l^{-1} when maize was added. This change in the nitrogen is shown by a mass balance in Table 6.7

Table 6.7: Mass balance of the nitrogen entering the digester and the nitrogen leaving the digester at a daily basis. Values are based on the average values for the raw cattle slurry, the maize silage (Table 3.9) and the average of each digester pair over the final 61 days of the digestion trial.

Maize load	Daily digestate removal	Nitrogen (g)		Difference	
g VS l^{-1} d^{-1}	g	Input	Output	g	%
0	0.21	0.81	0.88	+0.07	+8.1
1	0.16	0.67	0.71	+0.04	+6.0
1.4	0.15	0.61	0.65	+0.04	+5.4
3	0.08	0.39	0.36	-0.03	-8.9

The concentration of VFA in the digestate did not appear to reach a steady state (Figure 6.7); this is in contrast to the first digestion trial, where all of the digesters showed VFA concentrations remaining below 300 mg l^{-1}. In this trial total VFA concentrations slowly increased throughout the digestion period reaching values up to 3500 mg l^{-1}, with the exception of the highest maize addition. An explanation for this is the high VFA concentration of 10535 mg l^{-1} inherent in the winter cattle slurry used. Over the first 30 days the VFA concentration in all digesters remained low, after which an increase was observed. This increase was most pronounced when the feedstock was only cattle slurry and reached 3337 mg l^{-1} while the feed with 3 g VS l^{-1} d^{-1} maize only reached a concentration of 835 mg l^{-1}.

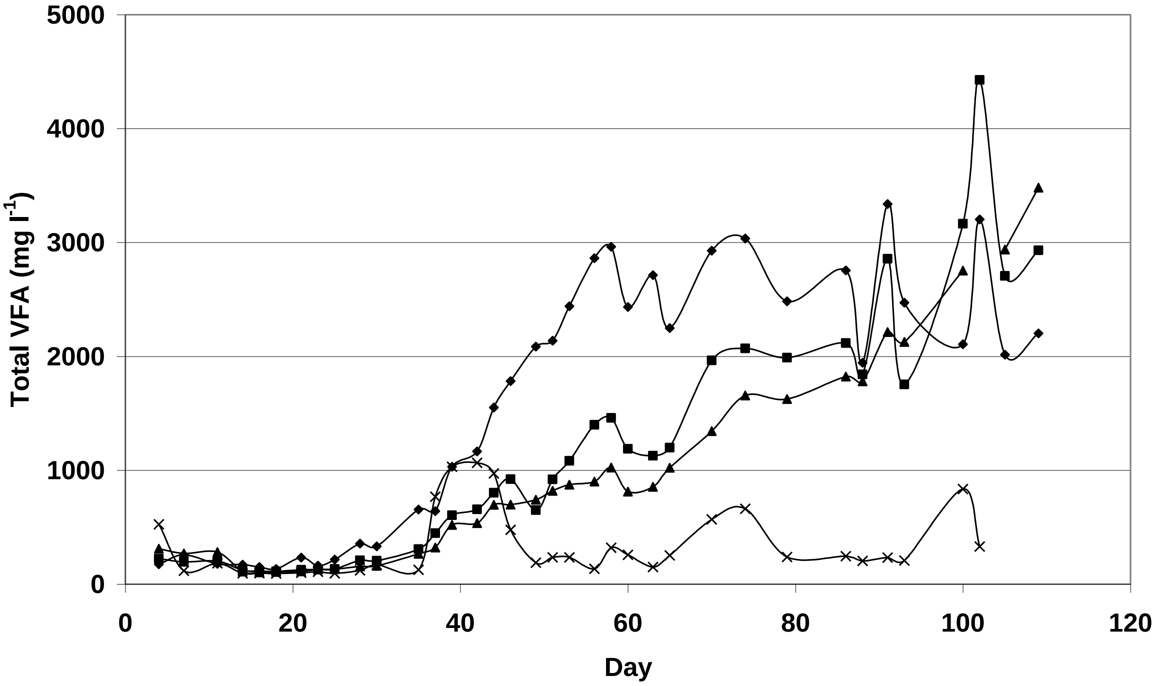


Figure 6.7: Concentration of total volatile fatty acids during the digestion period for all maize additions tested. 0 g VS l^{-1} d^{-1} maize addition (♦), 1 g VS l^{-1} d^{-1} maize addition (■), 1.4 g VS l^{-1} d^{-1} maize addition (▲) and 3 g VS l^{-1} d^{-1} maize addition (X)

Table 6.8 shows the concentration of heavy metals, potassium and phosphorus in the digester feedstock; quadruple samples of the digestate were taken to measure the heavy metal concentrations and the concentrations in Table 6.8 are the average of each digester pair in terms of dry matter (DM). The potassium and phosphorus concentration are the average of each digester pair.

Table 6.8: Concentration of heavy metals, potassium and phosphorus in the digestate produced by all maize proportions.

Maize (g VS l^{-1} d^{-1})	**0**	**1**	**1.4**	**3**
Cadmium mg kg^{-1} DM	0.4	0.5	0.6	0.3
Chromium mg kg^{-1} DM	355	165	210	457
Copper mg kg^{-1} DM	66	48	52	41
Nickel mg kg^{-1} DM	218	83	110	207
Zinc mg kg^{-1} DM	263	261	216	162
Potassium (as K_20 g kg^{-1})	4.2	3.6	3.7	3.9
Phosphorus (as P_2O_5 g kg^{-1})	3.0	2.8	2.8	3.2

A comparison of the heavy metal concentrations in Table 6.8 with the PAS110 digestate standards given in Table 2.3 indicates that the concentration of chromium, nickel and zinc are above the acceptable limits. The exception to this was the zinc concentration in the digestate at the highest maize proportion. This suggests that these metals could pose a potential problem when applying the digestate to land.

The results show that the concentrations of both phosphorus and potassium in the digestate were similar whatever proportion of cattle slurry was replaced by maize, reflecting the similar concentrations of these two materials in each of the feedstock's (Table 3.9). A mass balance of the two elements is shown in Table 6.9 where it is shown that an approximate balance was possible for both elements (+/-15%) at all maize loads.

Table 6.9: Mass balance of potassium and phosphorus at each maize loading. Values are based on the average daily digestate removal over the final 61 days and the average concentration of the raw feedstock (Table 3.9) and the digestate of each digester pair (Table 6.8)

Maize	Input		Output		Difference (%)	
Addition g VS l^{-1} d^{-1})	Potassium g (as K_2O)	Phosphorus g (as P_2O_5)	Potassium g (as K_2O)	Phosphorus g (as P_2O_5)	Potassium g (as K_2O)	Phosphorus g (as P_2O_5)
0	0.79	0.55	0.85	0.62	+8.1	+11.6
1	0.65	0.47	0.58	0.45	---	-10.2
1.4	0.59	0.43	0.55	0.40	-6.3	-6.8
3	0.35	0.30	0.31	0.25	-12.7	-15.5

A mass balance of the heavy metals was attempted for all metals however the results did not show a good agreement with only copper and zinc showing agreement at all maize loads within +/- 15%.

6.3.2 Summer cattle slurry

Over the final 80 days the digesters were fed with summer cattle slurry; otherwise all operational conditions remained the same and a direct comparison between the summer and winter cattle slurry was possible.

Biogas and methane production

Figure 6.8 shows the volumetric methane yield for the final period of 20 days on the winter cattle slurry followed by 80 days on summer cattle slurry. It can be seen that during the duration of the trial a consistency in gas production was achieved by all trials after the initial 22 days.

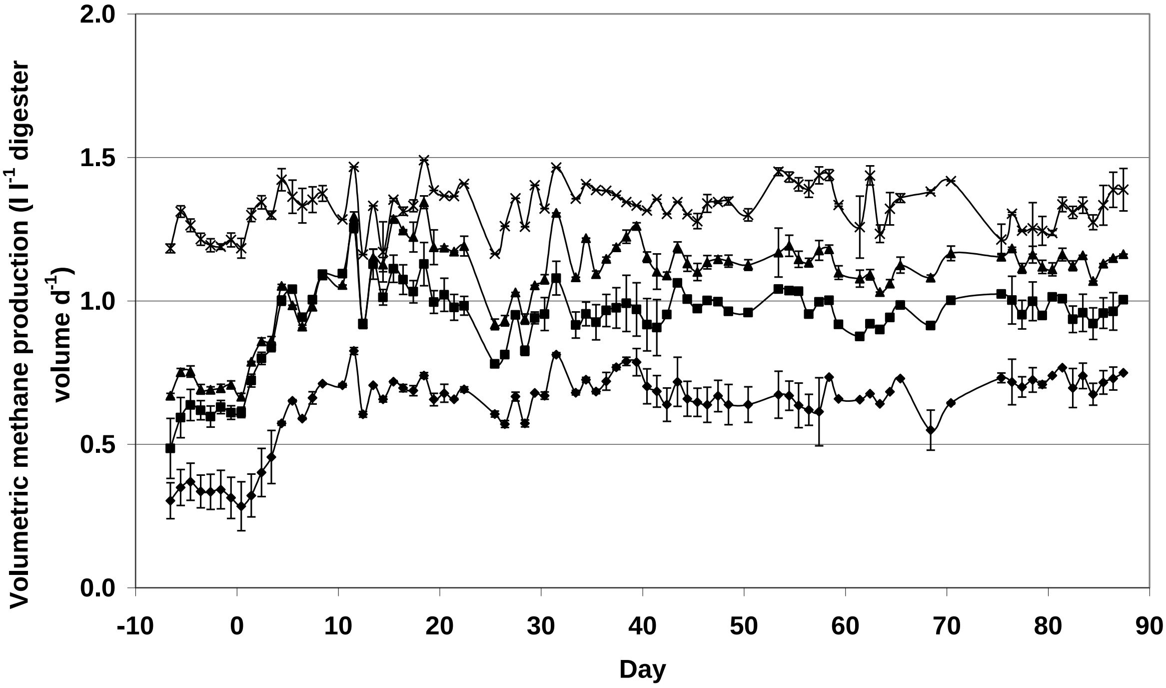


Figure 6.8: Average volumetric methane production of each digester pair during the summer cattle slurry digestion period. 0 g VS l^{-1} d^{-1} maize addition (♦), 1 g VS l^{-1} d^{-1} (■), 1.4 g VS l^{-1} d^{-1} maize addition (▲) and 3 g VS l^{-1} d^{-1} maize addition (X). The bars represent the two replicates tested at each loading rate.

The trend in the volumetric methane yield is comparable to the trend shown by the winter cattle slurry with the volumetric yield increasing with the maize proportion up to a maximum yield of 1.34 l l^{-1} d^{-1}. During the initial 22 days it can be observed that the volumetric methane yield in the cattle slurry and the two digesters receiving the two lowest maize proportions increased and then stabilised at a constant value. The digester receiving the highest maize addition of 3 g VS l^{-1} d^{-1} showed no clear change. The average specific methane yield for each digester pair is shown in Figure 6.9; these are the average values from day 30 to 87.

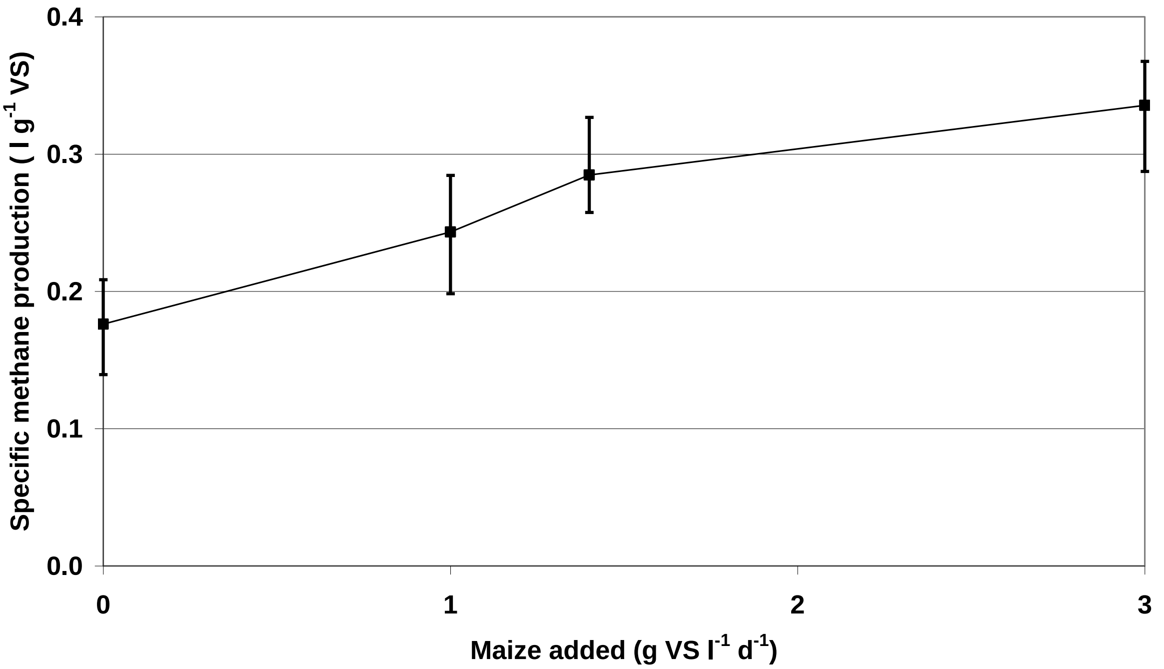


Figure 6.9: Average specific methane yield (l g^{-1} VS $_{added|}$) of each digester pair at all maize additions tested taken from daily readings over the final 57 days of the digestion trial. The range of values achieved at each maize addition is represented by the bars.

Using the summer cattle slurry increased the specific methane yield, which again showed an approximate linear relationship to the proportion of maize in the feedstock mix. The impact of increasing the proportion of maize in the fixed load was less pronounced than the impact displayed when the digesters were fed with the winter cattle slurry: replacing 1 g VS l^{-1} d^{-1} of the feed with maize led an improvement of 0.07 and 0.09 l g^{-1} VS $_{added}$ respectively. An increase from 0.24 to 0.29 l g^{-1} VS $_{added}$ when the maize load increased from 1 to 1.4 g VS l^{-1} d^{-1} suggests an improved performance when the maize load increased by 0.4 g VS l^{-1} d^{-1}. The ranges of specific methane yield achieved at each maize addition do show an overlap suggesting that there is a similar performance at all additions tested.

The impact that changing the batch of cattle slurry had on the gas production can be seen in Table 6.10 and Figure 6.10 in terms of volumetric and specific methane yield respectively.

Table 6.10: Comparison between the average volumetric methane yields produced by each digester pair when fed with the summer and the winter cattle slurry. The average for the winter fed digesters was taken from the final 61 days while for the summer cattle slurry the average was from the final 57 days.

	Volumetric methane yield ($l\ l^{-1}\ d^{-1}$)		
Maize g VS l^{-1} d^{-1}	**Winter cattle slurry**	**Summer cattle slurry**	**Improvement caused by the summer cattle slurry**
0	0.28	0.69	+ 0.41
1	0.66	0.96	+ 0.30
1.4	0.80	1.14	+ 0.34
3	1.27	1.34	+ 0.07

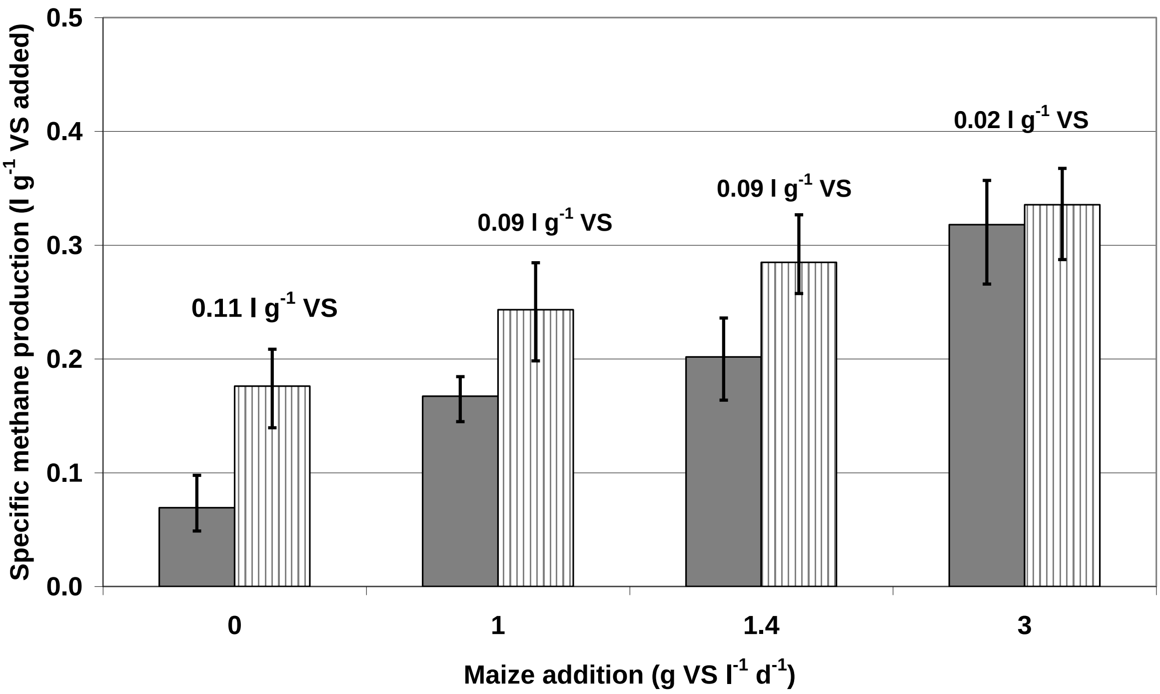


Figure 6.10: Difference in the average specific methane yield of each digester pair between the winter cattle slurry fed digesters (filled bars) and the summer cattle slurry fed digesters (striped bars). The average values are based on the final 61 and 57 days of the digestion trial for the winter and summer cattle slurry fed digesters respectively. The range of values achieved at each maize addition is represented by the bars.

There is a clear difference between the two batches of cattle slurry with the summer cattle slurry giving a greater average gas production at all loads. For the digestion of cattle slurry alone the specific methane yield from the summer cattle slurry was over double than that from the winter cattle slurry. This improvement is shown to decline as the maize load increased with the 3 g VS l^{-1} d^{-1} maize load producing a similar volumetric methane yield and range of specific methane yield to the winter cattle slurry feeding.

The carbon to nitrogen ratio of the feed for each digester was calculated and compared to the volumetric methane yield and biogas composition as shown by Table 6.11.

Table 6.11: Carbon to nitrogen ratios tested in this digestion trial along with the volumetric methane yield produced. The C:N ratio was calculated from the given values in Table 3.9 while the volumetric methane yield was the average of each digester pair from the final 57 days of the digestion trial

Maize Proportion g VS l^{-1} d^{-1}	C:N ratio	Volumetric methane l l^{-1} d^{-1}	% Methane in the biogas
0	9.5	0.69	66.2
1	11.1	0.96	59.2
1.4	12.0	1.14	59.1
3	17.8	1.34	54.7

The results here show that the relationship between the ratio, total methane and composition of methane followed the same trend displayed by the previous trials, with the total methane yield increasing as the ratio increased. From this observation it could be suggested that the improvement in the gas production displayed when summer cattle slurry was introduced would correspond to an increase in the carbon to nitrogen ratio entering the digesters. This however, can be shown to be incorrect as the introduction of the summer cattle slurry created a decline in the carbon to nitrogen ratio. For example, the load containing 1 g VS l^{-1} d^{-1} had a C:N ratio of 14.3 when fed with the winter cattle slurry but a ratio of 11.1 when fed with the summer cattle slurry.

The average daily gas production for each digester pair at day 54 is shown in Figure 6.11 and indicates a similar trend to the winter cattle slurry. Increasing the level of maize within the feeding load led to an increase in both the biogas production and the length of the initial period over which there was a higher rate of production. Comparing Figure 6.3 (daily gas production from the winter fed digesters) and Figure 6.11 it can be seen that the rate of production throughout the daily cycle is greater when fed with summer cattle slurry. For example, the rate of production displayed for mono-digestion of the summer cattle slurry after feeding is 0.0048 l g^{-1} VS h^{-1} greater than the rate displayed by the mono-digestion of the winter cattle slurry.

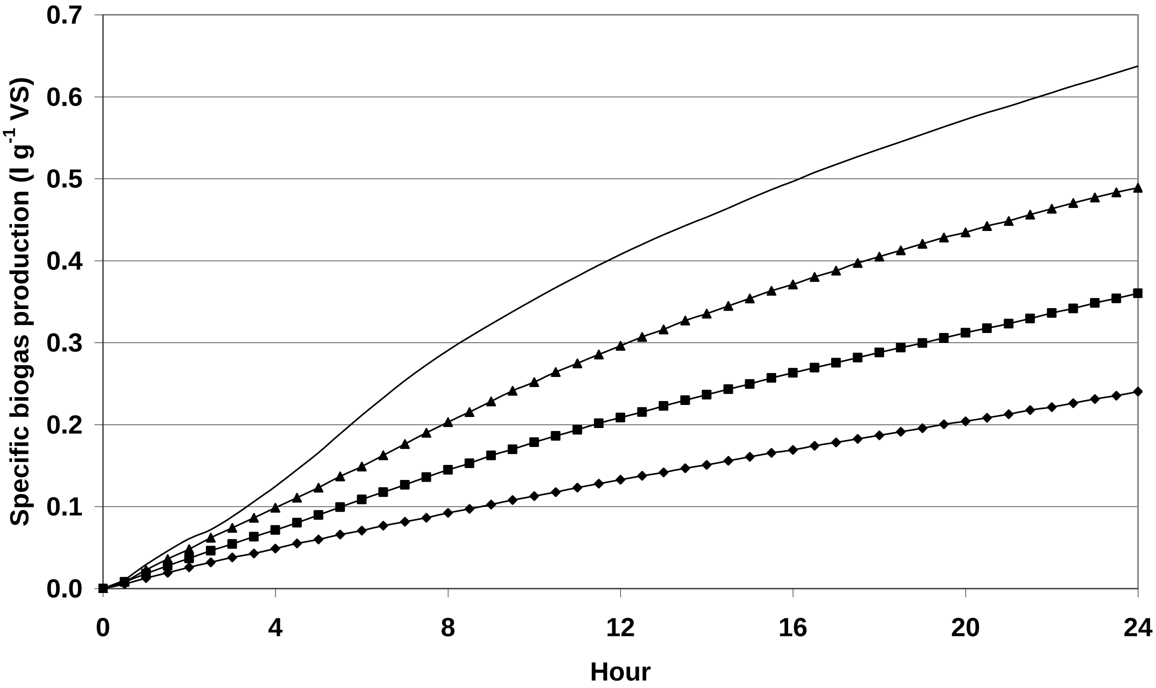


Figure 6.11: Specific biogas yield produced by all working conditions tested during a 24 hour period: 0 g VS l^{-1} d^{-1} maize addition (♦), 1 g VS l^{-1} d^{-1} maize addition, (■), 2 g VS l^{-1} d^{-1} maize addition (▲) and 3 g VS l^{-1} d^{-1} maize addition (▬)

Figure 6.12 compares the volumetric methane yield from the digesters with the volumetric methane yield calculated from the maize BMP and the specific methane yield of the summer cattle slurry produced from the control digester, 0.18 l g^{-1} VS. In all cases, the actual average methane yield was greater than the calculated value but only the 1.4 g VS l^{-1} d^{-1} maize load had a range of methane yield greater than the calculated yield. The smallest differential was shown at the lowest maize addition of 1 g VS l^{-1} d^{-1} producing 0.13 l l^{-1} more methane than predicted by calculation. Increasing the maize load by 0.4 g VS l^{-1} d^{-1} led to a doubling in the differential between actual and calculated methane yields.

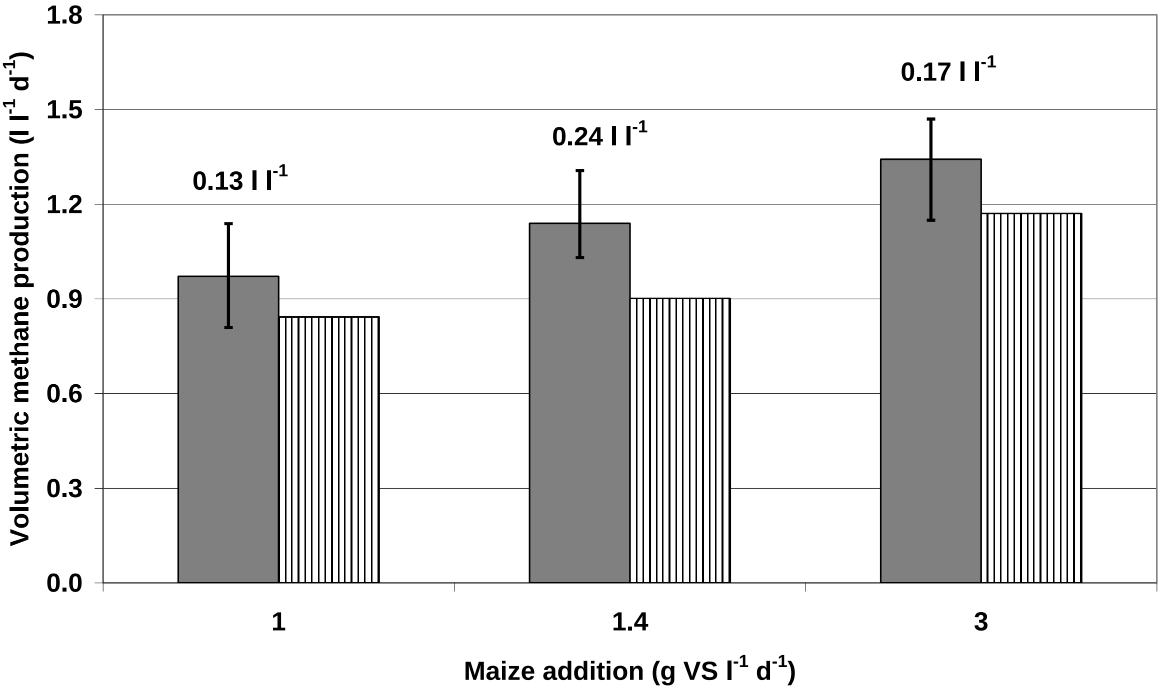


Figure 6.12: Difference in the average volumetric methane production (l l^{-1} d^{-1}) between the actual methane production (filled bars) and the yield calculated from combining the methane potential of the maize and of the cattle slurry (striped bars). The actual methane productions are the average of each digester pair from the final 57 days of the digestion trial. The numerical difference is given in each case along with the range of methane production produced at each addition.

In an attempt to determine if a change in the batch of cattle slurry had an impact on the differential between the actual and calculated volumetric methane Table 6.12 compares the values from Figure 6.12 with the winter cattle slurry.

Table 6.12: Difference between the actual volumetric methane yield produced and the methane yield calculated from the maize BMP (0.32 l g^{-1} VS) and the mono-digestion of cattle slurry (0.18 and 0.07 l g^{-1} VS for the summer and winter cattle slurry respectively): a comparison between the winter and summer cattle slurry

Maize g VS l^{-1} d^{-1}	Improvement to calculated methane yield (l l^{-1})	
	Winter cattle slurry	Summer cattle slurry
1	0.14	0.13
1.4	0.17	0.24
3	0.21	0.17

This comparison indicates that despite the improvement in the methane production caused by the introduction of the summer cattle slurry only one condition, 1.4 g VS l^{-1} d^{-1} maize, displayed a greater apparent synergistic effect than the winter cattle slurry fed digesters. Using this comparison as a means of determining the digestion performance has a number of potential problems. Firstly, the BMP of the maize may not be completely representative of the maize when digested in semi-continuous conditions. In addition the comparison used the methane yield of the cattle slurry at a load of 4 g VS l^{-1} d^{-1}, which had a shorter retention time than all of the maize loads (Table 6.1) and may not be representative of the cattle slurry when digested a longer retention times.

Table 6.13 gives a comparison between 1 and 3 g VS l^{-1} d^{-1} maize additions in the first digestion trial and the summer cattle slurry in this trial. There appears to be a small difference between the loading rates with the trend supporting that shown by the winter cattle slurry in that increasing the cattle slurry reduced the methane yield attributed to the maize. Unfortunately, the specific methane relies on the maize BMP and as with the prediction of synergy this may not be representative of the maize when digested in semi-continuous trials

Table 6.13: Comparison of specific methane yield produced by the 1 and 3 g VS l^{-1} d^{-1} maize additions attributable to the maize calculated from subtracting the methane yield of the cattle slurry from the overall methane yield. The values are the average of each digester pair collected from the final 69 and 57 days of digestion trial 1 and 2 respectively.

Digestion trial	Maize g VS l^{-1} d^{-1}	Cattle slurry g VS l^{-1} d^{-1}	OLR g VS l^{-1} d^{-1}	Specific methane yield l g^{-1} VS maize added	% Cattle slurry
1	1	2	3	0.45	66
2	1	3	4	0.41	75
1	2	3	5	0.37	60
2	2	2	4	0.39	50

Digestate properties

Differences between the two batches of cattle slurry, as shown by Table 3.9 led to differences in the digestate which changed gradually over the 80 days with summer cattle slurry feedstock. The results are therefore shown graphically for the whole period in which summer cattle slurry was used together with the last 20 days of the winter cattle slurry to provide a comparison. The mass balance of the VS and the volatile solids destruction (%) is shown in Table 6.14 and Figure 6.13, and as with the winter cattle slurry, the overall destruction was greater as the proportion of maize in the feedstock increased.

Table 6.14: Mass balance of the VS content of each digester pair at all maize loads tested. Values are based on the average VS input, output and methane yield of the digester pair over the final 57 days.

Maize addition (g VS l^{-1} d^{-1})	VS Input (g)	Digestate removed (g d^{-1})	VS output (g)	VS destruction (%)	Specific methane yield (l g^{-1} $VS_{destroyed}$)
0	17.0	204	10.0	40.8	0.40
1	16.9	162	8.8	48.0	0.46
1.4	16.8	145	8.7	49.6	0.51
3	16.7	79	6.3	62.3	0.51

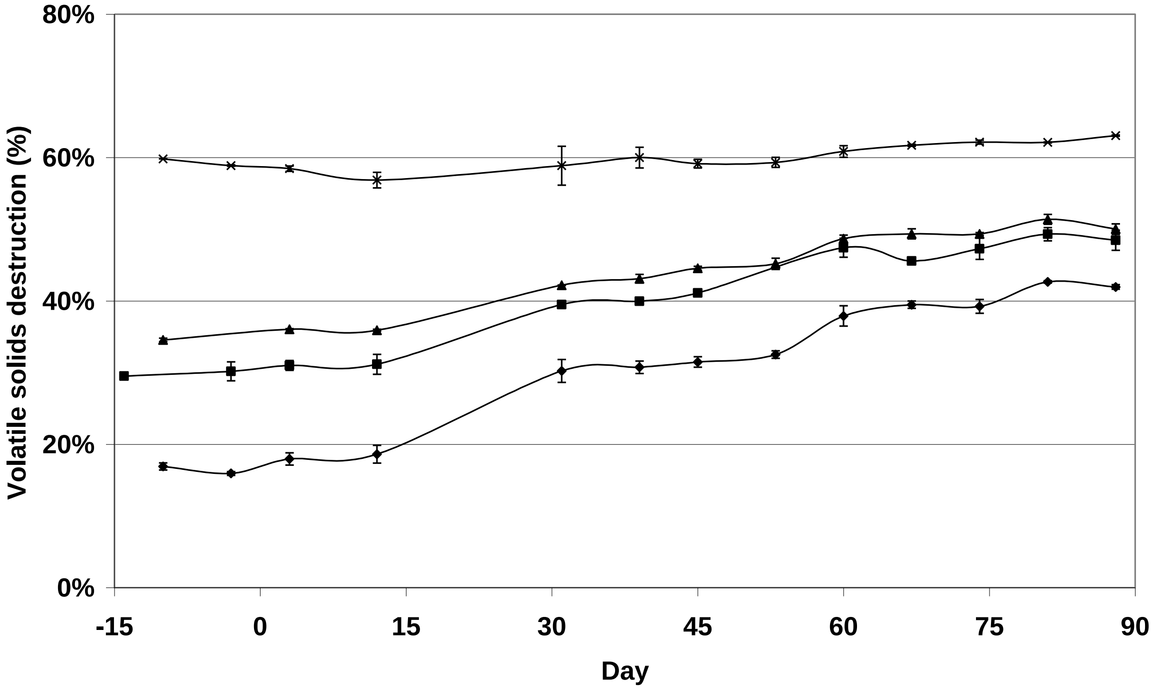


Figure 6.13: Average volatile solids destruction during the digestion period of each digester pair. 0 g VS l^{-1} d^{-1} maize addition (♦), 1 g VS l^{-1} d^{-1} (■), 1.4 g VS l^{-1} d^{-1} maize addition (▲) and 3 g VS l^{-1} d^{-1} maize addition (X)

Figure 6.13 shows that an increase in destruction occurred within 20 days of changing the cattle slurry; this increase is shown to be more pronounced in the digestates where the feedstock has no maize or a lower proportion of maize. The mono-digestion of the winter cattle slurry showed around 15% VS destruction during the final 20 days of the trial; when summer cattle slurry was used this increased to around 42%, a rise of 28% with a concurrent increase in the volumetric methane productivity, 0.42 l l^{-1} d^{-1}. As the proportion of maize increased the volatile solids destruction increased but by reducing amounts and at the 3 g VS maize proportion no increase in VS destruction occurred.

The potential methane yield as calculated from the carbon input and the volatile solids destruction is compared to the actual methane yield; this can be seen in Table 6.15. This calculation used the average VS destruction and methane yield from day 66 as it was from this date that VS destruction showed approximate consistency.

Table 6.15: Comparison of the volumetric methane yield against the potential methane yield calculated from the quantity of carbon entering the digesters.

	Volumetric methane ($l\ l^{-1}$)		
Maize ($g\ VS\ l^{-1}\ d^{-1}$)	**Potential**	**Actual**	**Difference**
0	1.12	0.69	-38%
1	1.15	0.94	-19%
1.4	1.16	1.07	-7%
3	1.25	1.32	+5%

There is an obvious difference in the mass balance at the cattle slurry alone and the lowest maize proportion indicating the presence of an incorrect measurement. This could be the carbon content of the feedstock, the VS measurement or/and the methane measurement. It is unlikely that the methane yield is incorrect as a potential methane yield of 4.49 l at the mono-digestion of cattle slurry would equal a specific methane yield of 0.28 $l\ g^{-1}\ VS_{added;}$ which is high for cattle slurry alone. This leaves uncertainty in the VS destruction and the carbon content of either the cattle slurry or the maize. One suggestion made during the winter cattle slurry was that the measurement of VS was not truly representative of the batch of cattle slurry used for the complete trial and this again could be suggested for an explanation.

The digesters when fed with winter cattle slurry produced a lower volumetric methane yield than when fed with summer cattle slurry; this is shown not to be the case for all digesters in terms of the methane yield per VS destroyed. In Table 6.16 it can be seen that a similar specific methane yield is observed when comparing the batches at the 1 and 3 $g\ VS\ l^{-1}\ d^{-1}$ maize proportions. The cattle slurry alone and the 1.4 $g\ VS\ l^{-1}\ d^{-1}$ maize proportion produced a greater yield when the feed consisted of summer cattle slurry.

Table 6.16: Comparison of the specific methane yield, expressed in terms of VS destroyed, between the maize proportions and the different batches of cattle slurry

Maize addition	**Specific methane yield (l g^{-1} VS $_{destroyed}$)**			
g VS l^{-1} d^{-1}	**0**	**1**	**1.4**	**3**
Winter	0.38	0.48	0.49	0.50
Summer	0.40	0.46	0.51	0.51

Figure 6.14 shows the average digestate total solids content in each digester pair. With the exception of the 3 g VS d^{-1} maize load, the total solids content increased immediately after the change in cattle slurry followed by a decline and then a short period of stability. The initial increase in the total solids content can be explained by the higher solids content of the summer cattle slurry and the decline by the greater solids destruction which became more or less stable by day 60 (Figure 6.13). This may indicate some residual inhibition on solids degradation caused by the winter cattle slurry while the digester still contained a relatively high proportion of it and before washout had reduced the concentration.

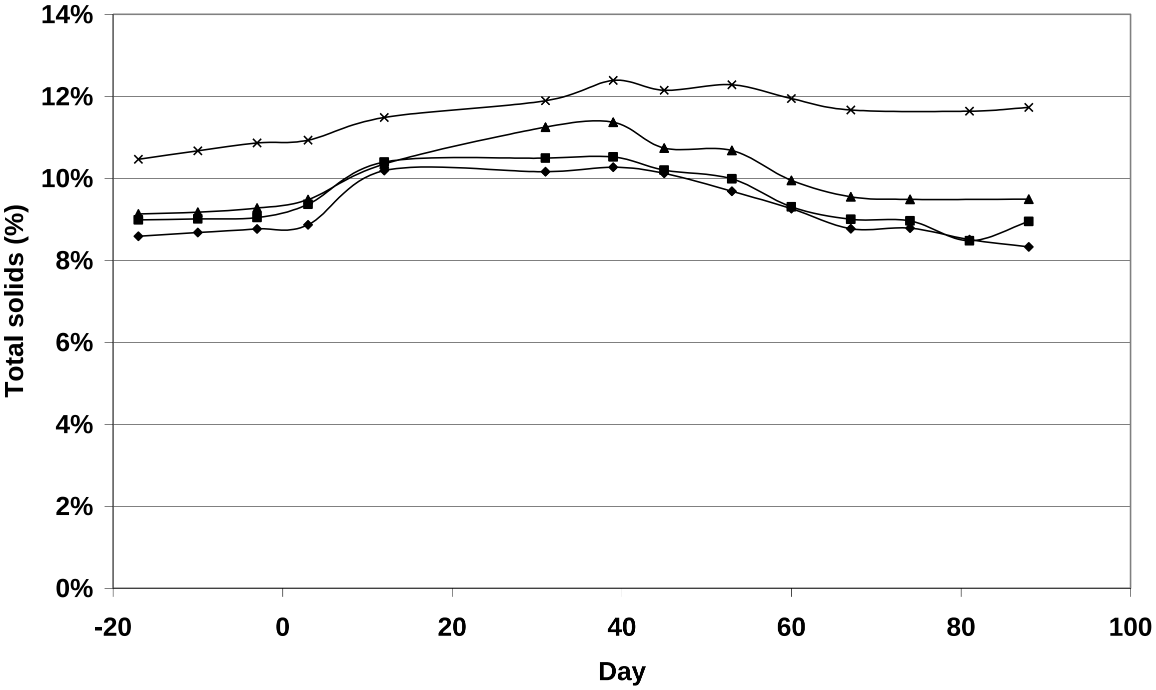


Figure 6.14: Average total solids content of the digestate from each digester pair during the digestion period. 0 g VS l^{-1} d^{-1} maize addition (♦), 1 g VS l^{-1} d^{-1} (■), 1.4 g VS l^{-1} d^{-1} maize addition (▲) and 3 g VS l^{-1} d^{-1} maize addition (X)

The ammonia concentration in the digestate is shown in Figure 6.15. The change from winter to summer cattle slurry increased the concentration of ammonia in the slurry mono-digestion from 2.25 to 3.19 g l^{-1}. The upward trend in the ammonia concentration was seen in all digesters with the lowest concentrations shown at the higher maize proportions. The increase is explained by the higher ammonia content of the summer cattle slurry, which was 2.25 g l^{-1} compared to 1.65 g l^{-1} for the winter cattle slurry.

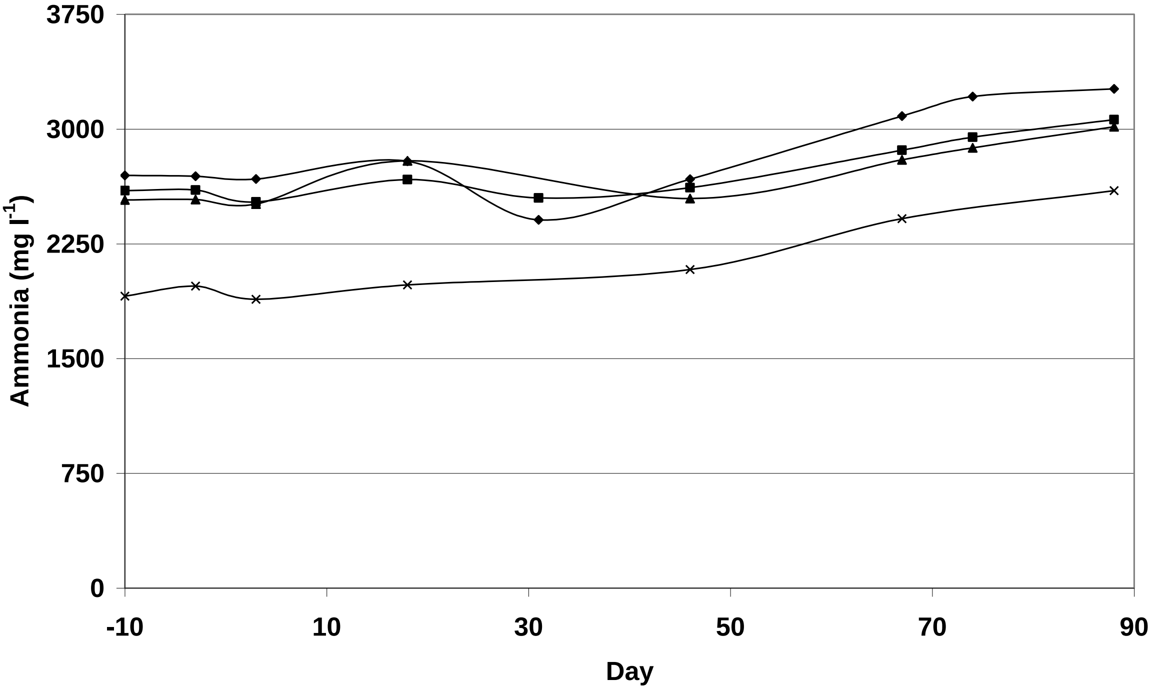


Figure 6.15: Average concentration of ammonia within each digester pair at different points during the digestion period. 0 g VS l^{-1} d^{-1} maize addition (♦), 1 g VS l^{-1} d^{-1} (■), 1.4 g VS l^{-1} d^{-1} maize addition (▲) and 3 g VS l^{-1} d^{-1} maize addition (X)

The TKN concentration (graph not shown) in all digesters also increased reflecting the difference in concentration between the cattle slurry batches, 3.10 and 5.62 g l^{-1} for the summer and winter cattle slurry respectively. The maximum TKN concentration reached in the individual digesters reflected the proportion of maize within the feed and was between 5.60 to 6.06 g l^{-1}. The mass balance shown in Table 6.17 shows the change in the nitrogen content.

Table 6.17: Mass balance of the nitrogen entering the digester and the nitrogen leaving the digester at a daily basis. Values are based on the average value for the raw cattle slurry, the maize silage and the average of each digester pair over the final 57 day of the digestion trial.

Maize load	Daily digestate removal	Nitrogen (g)		Difference	
(g l^{-1} VS d^{-1})	l	Input	Output	g	%
0	0.20	1.17	1.23	+0.06	+5.2
1	0.16	0.94	0.93	-0.01	-1.4
1.4	0.14	0.85	0.83	-0.02	-2.0
3	0.08	0.48	0.44	-0.04	-9.1

The total alkalinity in the digesters ranged from 12.6 to 15.5 g l^{-1} when the feed contained winter cattle slurry, with the highest alkalinity found when the cattle slurry was digested alone (Table 6.4). Total alkalinity increased during the summer cattle slurry trial as shown by Figure 6.16; as expected, as the proportion of maize in the feedstock increased there was a decline in the total alkalinity, giving values ranging from 18.4 to 21.9 g l^{-1} at the end of the trial. The ratio of intermediate to partial alkalinity (IA:PA) of the digester when fed with the winter cattle slurry ranged from 0.33 to 0.42, decreasing in value as the quantity of maize increased (Table 6.4). When using the summer cattle slurry the intermediate alkalinity remained constant but the partial alkalinity increased. As a result the IA:PA ratio ranged from 0.27 to 0.33. In contrast to the winter cattle slurry fed digesters the ratio was shown to decline as the quantity of maize declined.

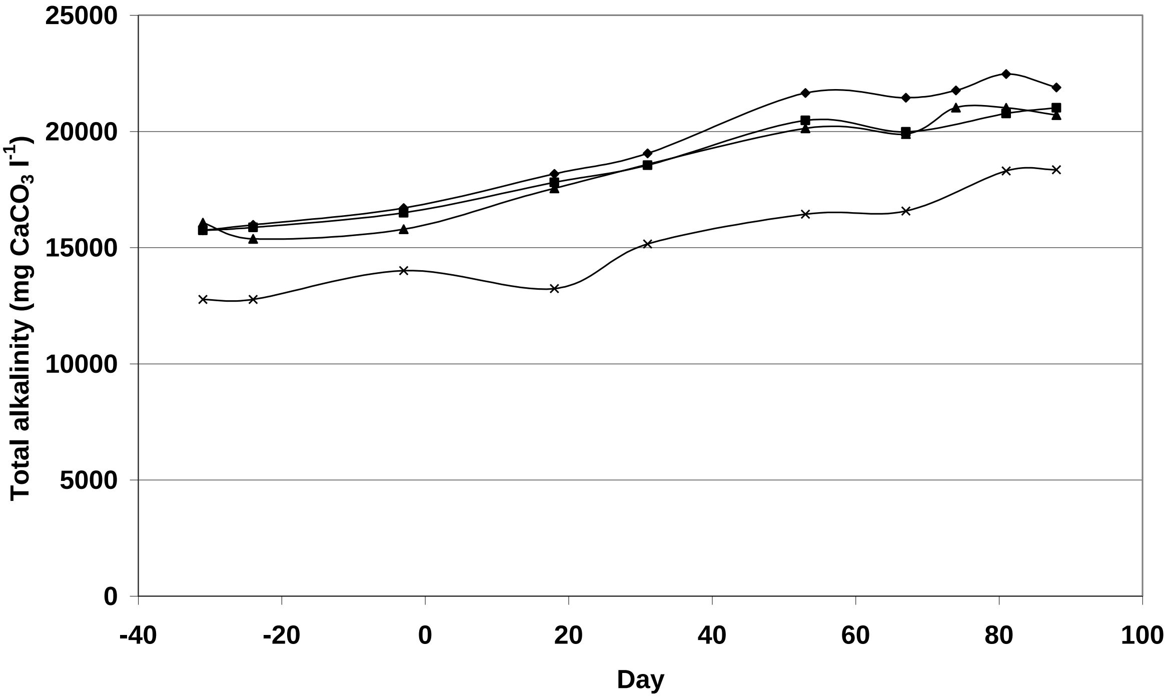


Figure 6.16: Average total alkalinity of the digestate of each digester pair at different points during the digestion period. 0 g VS l^{-1} d^{-1} maize addition (♦), 1 g VS l^{-1} d^{-1} (■), 1.4 g VS l^{-1} d^{-1} maize addition (▲) and 3 g VS l^{-1} d^{-1} maize addition (X)

The VFA concentration in the digestate, and in particular acetic and propionic acid, rose towards the end of the feeding trial using winter cattle slurry. When the summer cattle slurry was used the total VFA concentration declined from initial values of 2250 to 3500 mg l^{-1} to values that remained below 1000 mg l^{-1} in all digesters with the exception of 3 g VS l^{-1} d^{-1} maize load where an initial decline was followed by an increase to around 1300 mg l^{-1}**.** In all cases the decline in the total VFA started first with a reduction in acetic acid concentration followed by a slower reduction in the propionic concentration. The initial decline in the total VFA concentrations can be explained by the different

VFA concentrations of the two batches of cattle slurry; 10 and 1.4 g l^{-1}, for the winter and the summer cattle slurry respectively. The increase in the total VFA at the 3 g VS l^{-1} d^{-1} maize proportion suggests that some instability is being introduced to the digester; this is not reflected by the gas production or the other parameters measured where approximate consistency was shown in the last 20 days.

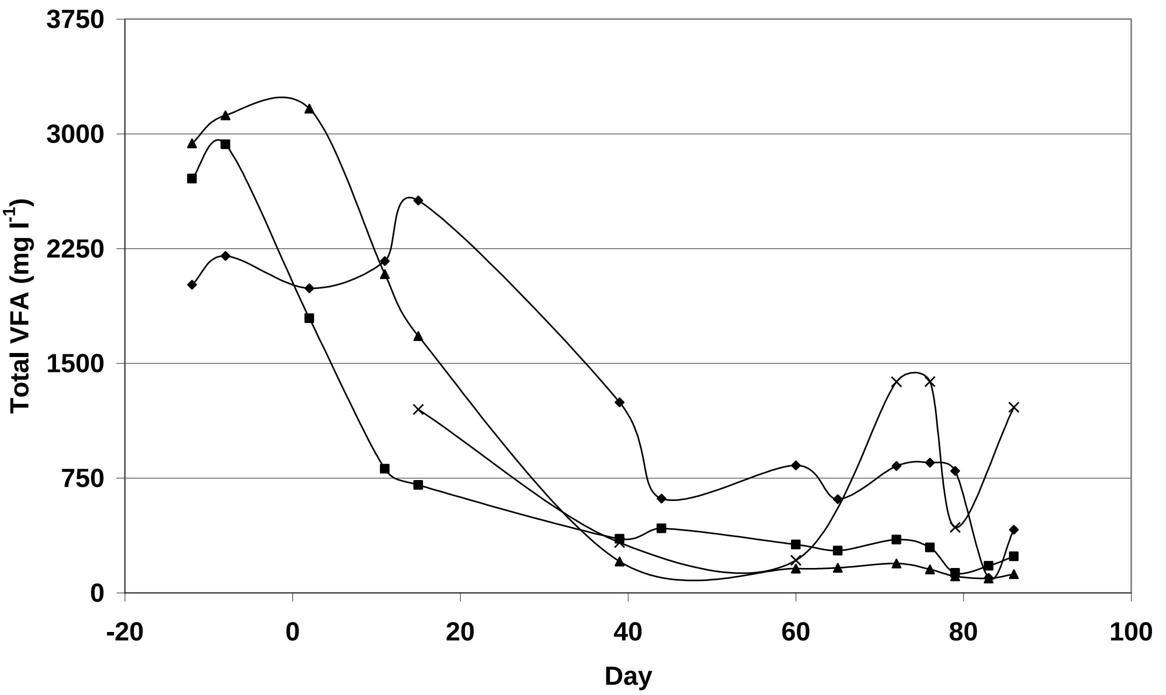


Figure 6.17: Average concentration of the total VFA within each digester pair during the digestion trial. 0 g VS l^{-1} d^{-1} maize addition (♦), 1 g VS l^{-1} d^{-1} (■), 1.4 g VS l^{-1} d^{-1} maize addition (▲) and 3 g VS l^{-1} d^{-1} maize addition (X)

6.4 Discussion

The results showed that co-digestion was possible under the operational conditions used and with both winter and summer cattle slurries. Increasing the proportion of maize within the feed led to an increase in the specific methane yield: for the winter cattle slurry this ranged from 0.07 to 0.32 l g^{-1} VS $_{added}$ and from 0.18 to 0.34 l g^{-1} VS $_{added}$ for the summer cattle slurry. The greatest specific methane yield obtained from this digestion trial was 0.34 l g^{-1} VS $_{added}$ which was obtained at the 3 g VS l^{-1} d^{-1} maize proportion while fed with the summer cattle slurry. This specific methane yield is within the range previously reported for rice straw and barley straw (Hills and Roberts, 1981) and greater than sugar beet, straw and grass when co-digested with cattle slurry (Lehtomäki *et al.*, 2006). This value is also comparable to some results for maize only (Amon *et al.*, 2007, Machmüller *et al.*, 2007). Increasing the proportion of maize within the constant load has the benefit of increasing the retention time, which can benefit the digestion process, and the increase was shown to have a pronounced effect on the volumetric methane yield. The introduction of maize at a 1 g VS l^{-1} d^{-1} proportion to the winter cattle slurry increased the volumetric methane yield by 141%, shown by Table 6.4; this was lower in the summer cattle slurry with an increase of 40%. This indicates that only a small addition of maize is needed to produce an increase in the methane productivity giving the farmer an improved return on the investment in the digester without the need to replace all of the cattle slurry with energy crops. The benefit of the addition of a small quantity of maize to cattle slurry was shown in the first digestion trial (Chapter 5) where an addition of 1 g VS l^{-1} d^{-1} maize to a 2 g VS l^{-1} d^{-1} load of cattle slurry maintained the specific methane yield but increased the volumetric methane yield by 120%. The improvement shown during feeding with the winter cattle slurry indicates that the addition of maize during times of poor quality cattle slurry, in terms of methane production, could prove to be vital in the running of a digester.

The results indicated that the methane production from an anaerobic digester is strongly influenced by the cattle slurry used and this may reflect the diet and housing conditions of the cattle. The mono-digestion of the winter cattle slurry produced a specific methane yield of 0.07 g^{-1} VS compared to 0.18 l g^{-1} VS produced by the summer cattle slurry. Amon *et al*., (2001) found that the methane yield obtained from a winter cattle slurry was less than from a summer cattle slurry and it was shown that the diet of the cattle can have an impact on the methane yield. In contrast to these results, research by Callaghan *et al*., (1999) gave a higher methane yield from the slurry collected from cattle kept outdoors when compared to indoors. The literature review in Chapter 2 presented methane yields in the range of 0.07 to 0.40 l g VS^{-1} for the mono-digestion of cattle slurry. The yield produced by the winter cattle slurry falls in the lower end of the range suggesting that some characteristic of the winter cattle slurry is causing a disturbance to digestion performance. The low specific methane production of the digesters fed on feed mixes containing winter cattle slurry was highlighted when the feed was switched to mixes with summer cattle slurry. When this change took place there was a 47% increase in the volumetric methane yield observed in the digester fed with the lowest proportion of maize. This improvement became less pronounced as the proportion of maize within the feed increased, with the 3 g VS l^{-1} d^{-1} maize proportion producing an improvement of just 0.07 l l^{-1} d^{-1} (5.6%). An additional observation was the influence that the different cattle slurries had on the biogas composition. A comparison between the two different feed mixes indicates a greater methane percentage when the mix contained the summer cattle slurry, 56 and 66% for the digestion of the winter and summer cattle slurry respectively.

A carbon to nitrogen ratio in the range of 25 to 32 has been suggested as optimal for anaerobic digestion (Hills and Roberts, 1981) while values quoted for cattle slurry are often in the range of 11 to 14 (Umetsu *et al.*, 2006). It could be suggested that a cattle slurry with a higher C:N ratio would provide more optimal conditions of anaerobic digestion. This is unlikely to be the case here as the summer cattle slurry had a less favourable ratio of 9.7 compared to 14.4 for the winter cattle slurry. An alternative explanation could be the VFA concentration, which was shown to differ with concentrations of 10536 and 1397 mg l^{-1} given for the winter cattle slurry and the summer cattle slurry respectively. When the digesters were fed with winter cattle slurry VFA concentrations increased, and this was more pronounced in the digester fed with cattle slurry alone. The introduction of the summer cattle slurry resulted in a decline in the VFA concentration, which reflects the increase in the methane yield indicating that the VFA concentration within the raw cattle slurry is an important parameter to consider when determining the success of the digestion process.

The influence of VFA additions on the biogas yield was shown by Siegert *et al.*, (2005) where an increase from 1 to 10 g l^{-1} (i.e. similar concentrations to the winter and summer cattle slurry in this research) added to the batch digestion of cellulose and glucose resulted in the volume of biogas to decline by 2.26 and 1.31 l for cellulose and glucose respectively. A breakdown of the VFA into the individual acids highlighted that for both cattle slurry batches acetic and propionic acid made up the majority of the total concentration. The concentration of acetic acid was 7766 and 1246 mg l^{-1} for the winter and summer cattle slurry respectively while propionic acid was at 1246 and 204 mg l^{-1}. The high concentration of propionic acid in the winter cattle slurry and the subsequent accumulation of propionic acid in the digesters could result in inhibition. Wang *et al.*, (2009) investigated the impact that individual acids had on the methanogenic bacteria by testing acetic acid, propionic and butyric acids at different concentrations. Increasing the acetic acid to 2400 mg l^{-1} produced no significant inhibition but increasing propionic to the maximum concentration of 900 mg l^{-1} showed inhibitory effects on both the acidogenic and methanogenic bacteria which consequently reduced the methane production. The high concentration of acetic acid in the winter cattle slurry could also be contributing to the reduced digestion performance by inhibiting the degradation of propionic; acetic acid at concentrations of 2000 mg l^{-1} has been shown to inhibit the degradation of propionic leading to the accumulation of propionic (Mawson *et al.*, 1991).

Work by Vedrenne *et al.*, (2008) investigated the impact that dilution had on the digestion of cattle slurry that contained a high concentration of VFA's. It was shown that dilution was beneficial as it improved the digestion performance as a result of a reduction of the VFA's entering the system. This is comparable to the impact on the digestion performance caused by replacing a proportion of the winter cattle slurry with maize; the addition of maize acted as a form of dilution as it reduced the level of cattle slurry therefore reducing the quantity of VFA's entering the digesters. The positive impact of dilution can only be applied to the 1 and 1.4 g VS l^{-1} d^{-1} maize proportions as an increase the VFA was shown at the 3 g VS l^{-1} d^{-1} maize load (Figure 6.17). This increase took place at the end of the trial so it is not known if the VFA continued to increase to inhibitory levels.

The initial digestion trial in Chapter 5 suggested the presence of synergy by a comparison of the actual methane yield with that calculated with the maize BMP and the specific methane yield calculated from the mono-digestion of the cattle slurry. An identical comparison was made in this trial with both batches of cattle slurry and in each case an improvement to the calculated yield was shown (Figure 6.4, Figure 6.12). The greatest difference was shown by both batches of cattle slurries at the 1.4 g VS l^{-1} d^{-1} maize proportion; 15 and 27% improvement for the summer and winter cattle slurry respectively. Despite the poor performance produced by the winter cattle slurry alone it was this batch of cattle slurry that created the greater apparent synergy. The success of a low methane producing cattle slurry during co-digestion was shown by research by Misi *et al.*, (2001) where the methane production of cattle slurry alone was poor, 0.09 l g^{-1} VS, however when it was co-digested with chicken manure at a 50:50 ratio an improvement to the specific methane yield was observed.

Identifying synergy by comparing the actual and calculated methane yields can be problematic, it relies on a prediction based on two specific methane yields which are usually obtained in conditions different from those occurring when the substrates are digested together. For example use of the specific methane yield from the mono-digestion of cattle slurry makes the assumption that the cattle slurry will produce the same specific methane yield when co-digested with maize. This may not be accurate for the winter cattle slurry as a reduction in the cattle slurry load effectively reduced the inhibitory factor entering the digester. This could mean that the cattle slurry contributed more methane when digested with maize than predicted from the 4 g VS l^{-1} d^{-1} mono-digestion meaning that the improvement shown in Figure 6.4 was the result of diluting the cattle slurry with maize.

The summer cattle slurry appeared not to be inhibited with an improvement in the methane production occurring 22 days after introducing this batch of cattle slurry (Figure 6.8). The lack of inhibition suggests that the influence of diluting the feedstock with maize will be lower than that shown by the winter cattle slurry. This is supported by the reduced effect of the maize on the volumetric methane yield as the proportion of the maize increased. Introducing 1 g VS l^{-1} d^{-1} of maize to the winter and summer cattle slurry improved the methane yield by 0.38 and 0.28 l l^{-1} d^{-1}

respectively. This reduction in the influence of dilution is an example of how an apparently synergistic effect could be the due to an alternative explanation.

An alternative explanation for the improvement shown in the average volumetric methane yield, which applies to both batches, is the increase in the retention time as the maize proportion increased. The mono-digestion of cattle slurry had a shorter retention time when compared to the maize additions; 19 days compared to 44 days at the 3 g VS l^{-1} d^{-1} maize proportion. The longer retention times could be increasing the methane contribution from the cattle slurry as the cattle slurry is retained in the digesters for longer periods allowing a greater proportion to undergo digestion. The influence of retention time has been shown in a number of studies with suggestions that increasing the retention time will lead to an improved specific methane yield (Karim *et al.*, 2007, Linke, 1997). An additional weakness in the determination of synergy used in this research was the use of a maize BMP value produced from the batch trial in Chapter 4, which may not be an accurate representation of maize when digested in semi-continuous conditions. This can be concluded from evidence in literature (Callaghan *et al.*, 1998, Callaghan *et al.*, 1999, Lehtomäki *et al.*, 2006) where it was shown that batch trials produce different results to semi-continuous trials. These arguments suggest that it is unrealistic to conclude that synergy is present in this trial as the improvement could be the result of a reduction of inhibitory factors, an increase in the retention time or/and the use of the maize BMP. This uncertainty in the apparent methane yield improvement when compared to a calculated yield leads to the requirement for an improved method to be in place to determine if synergy is actually present. An improved method could be to use the same operational conditions (e.g. semi-continuous, same retention time) when determining a baseline methane yield for comparison to co-digestion trials. This could eliminate some of the uncertainty shown in this trial.

One benefit of anaerobic digestion is that it reduces the total solids concentration in the digestate allowing for improved infiltration into the soil and therefore minimising the exposure time of the slurry to the air. A 1.0 % reduction in totals solids was obtained in the mono-digestion of winter cattle slurry and 4.2% with the summer cattle slurry. When maize was also fed to the digesters there was an increase in the total solids of 3% as the maize load increased from 0 to 3 g VS l^{-1} d^{-1} when the digesters were fed with the summer cattle slurry and 1.9% when fed with the winter cattle slurry. The total solids for the digesters fed with summer cattle slurry remained below the solids content of the raw cattle slurry, but this was not the case for the digesters fed with winter cattle slurry where the total solids content at the 3 g VS l^{-1} d^{-1} maize proportion was 10.4% compared to 9.6% for the raw cattle slurry.

The ammonia concentration in the digestate declined by 0.7 g l^{-1} as the maize increased from 0 to 3 g VS l^{-1} d^{-1}; the summer cattle slurry showed a similar trend with a decline 0.7 g l^{-1}. This decline in concentration occurred along with a decline in the amount of digestate removed from the digesters leading to a reduced quantity of ammonia removed on a daily basis (Table 6.7, Table 6.17). This reduction in the ammonia suggests that the load containing the higher proportion of maize is beneficial in terms of immediate ammonia emissions and in situations where readily available nitrogen needs to be reduced. In contrast, this decline could be a disadvantage to the crop yield as it is reducing the amount of nitrogen that is readily available. Despite this decline in ammonia, the digestate at the higher loads still provides a greater quantity of ammonia when compared to the raw cattle slurry. Potassium and phosphorous were measured in the digestate during the winter cattle slurry trial and it was shown that the addition of maize to the feed did not alter the digestate concentration. The concentrations of potassium and phosphorus in the raw cattle slurry were 1.2 and 3.8 g l^{-1} and those of the digestate of the cattle slurry alone were 1.3 and 4.2 respectively. A balance of +/- 15% was achieved for both elements, shown by the mass balance in Table 6.9.

The possible role of the VFA concentration in the decline in specific methane yield produced from the winter cattle slurry has already been described. Despite the accumulation shown during the winter cattle slurry feeding it can be seen that at all conditions the VFA concentration was reduced from its initial concentration of 10536 mg l^{-1}. For the digestion of cattle slurry alone, the average VFA concentration of the digester pair for the final 30 days of digestion was 2602 mg l^{-1} which represents a decline in the VFA concentration by 75%. This was repeated by the digestion of the summer cattle slurry alone where the VFA concentration was reduced by 59%. It has been previously noted that the level of VFA within the digestate declined as the quantity of maize increased resulting in a higher percentage removal. This greater VFA removal indicates that the digestion of cattle slurry and the addition of maize can be beneficial as it can aid the reduction in the odours that are related to VFA's (Powers *et al.*, 1999).

The key points that can be taken from this trial are:

- The introduction of a small quantity of maize to cattle slurry has positive benefits to the farmer as an increase in the volumetric methane yield is observed; 141% and 36% respectively for the winter and summer cattle slurry. This addition could prove to be particularly important in the successful running of a farm digester during times of poor quality cattle slurry.

- A clear difference in the methane performance was shown when two different batches of cattle slurry are compared with the introduction of the summer cattle slurry resulting in an increase in the methane yield within 22 days of operation.

7 Digestion trial 3: Determination of the relative contributions of feedstock components to biogas production, and the effect of increasing the loading rate on digesters fed with equal proportions of cattle slurry and maize silage.

7.1 Objective

The objective of this trial was to determine the impact that increasing the loading rate of a fixed cattle slurry/maize ratio had on the digestion process. Following on from the results produced by the initial digestion trials a ratio of 50:50 had been chosen.

7.2 Methodology

Twelve digesters were used in this trial and operated as duplicate pairs. The same batch of cattle slurry was used throughout the trial to ensure consistency in the feed. The first part of this trial tested the effect of increasing the OLR in digesters fed either with maize or cattle slurry and the second part focused on co-digestion. To improve accuracy of measurement of retention time and loading, the digesters were operated so as to maintain a constant weight rather than a constant volume (as in trial 1 and 2); this was achieved by weighing the digesters once a week. The cattle slurry used in this trial corresponds to batch 4 (Table 3.9).

Mono-digestion kinetics

To provide an accurate baseline for the co-digestion trial, initial single (mono) substrate trials were carried out. These used the same OLR's and retention times as those planned for the co-digestion trials. To achieve this two pairs of digesters were set up: one pair fed on maize and the other on cattle slurry. The OLR was fixed within the range of 1.5 to 3.0 g VS l^{-1} d^{-1} and the retention times were made to match those of the proposed co-digestion trial by the addition of water containing a 1 mg l^{-1} trace element solution. The different loading rates were not tested in parallel; instead the OLR for each pair increased upon stabilisation; Table 7.1 highlights the different operational conditions followed by each pair of digesters during the trial.

Table 7.1: Operational condition followed by digestion trial 3: mono-digestion

Digester	Cattle slurry		Maize		Water	Retention time
	g VS l^{-1} d^{-1}	g WW	g VS l^{-1} d^{-1}	g WW	ml	d
1A	1.5	117	0	0	18.7	29
1B	2.0	156	0	0	24.9	22
1C	2.5	195	0	0	31.1	18
1D	3.0	273	0	0	37.3	15
2A	0	0	1.5	18.7	117	29
2B	0	0	2.0	24.9	156	22
2C	0	0	2.5	31.1	195	18
2D	0	0	3.0	37.3	273	15

Co-digestion kinetics

In this part of the trial the digesters were fed with feed consisting of cattle slurry and maize in a 50:50 ratio on a VS basis. In this trial the OLR of the digesters was increased from 3 to 6 g VS l^{-1} d^{-1} with 1.5 g VS l^{-1} d^{-1} of the initial load being supplied equally by both components. This load was raised in equal increments with each component supplying 3 g VS l^{-1} d^{-1} of the final load of 6 g VS l^{-1} d^{-1}. As in the first mono-substrate part of the trial the digesters had retention times ranging from 15 to 29 days. The operational conditions for this trial are shown in Table 7.2.

Table 7.2: Operational conditions followed by digestion trial 3: co-digestion

Digester	Cattle slurry		Maize		Retention time
	g VS l^{-1} d^{-1}	g WW	g VS l^{-1} d^{-1}	g WW	d
1	1.5	117	1.5	18.7	29
2	2.0	156	2.0	24.9	22
3	2.5	195	2.5	31.1	18
4	3.0	273	3.0	37.3	15

7.3 Results

7.3.1 Mono-digestion

Biogas and methane production

Figure 7.1 shows the average volumetric methane yield from the cattle slurry and the maize for each pair of digesters at all loading rates tested.

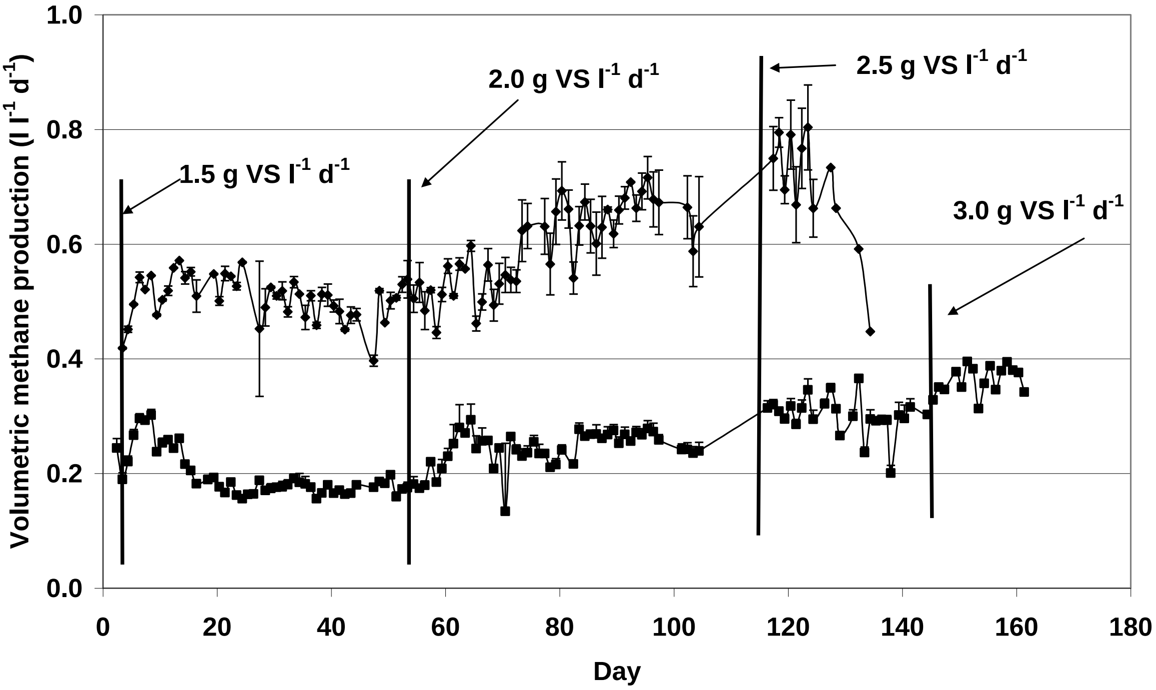


Figure 7.1: Average daily volumetric methane yield of each digester pair produced at all loading rates tested for both maize (■) and the cattle slurry (♦). The lines represent the increment in the loading rate.

Methane production appeared to remain constant for both substrates during the 1.5 g VS l^{-1} d^{-1} loading rate trial with the maize producing the greatest volumetric methane yield. The increase in load from 2 to 2.5 g VS l^{-1} d^{-1} produced an increase in the methane yield by the cattle slurry but methane production from the maize declined sharply and the digester failed in terms of the pH and the gas production. The cattle slurry was tested at a loading rate of 3 g VS l^{-1} d^{-1} but only for one retention time due to lack of material. It was decided not to continue the trial with a new batch of cattle slurry as the results from the second trial clearly showed that digester performance could vary significantly between feed batches. Table 7.3 provides the volumetric and the specific methane yield produced from the two substrates at the different loading rates. These are the average values taken from the final 20 days of the digestion trial.

Table 7.3: Volumetric and specific methane produced by the individual substrates at the different loading rates tested. The values are the average of each digester pair from the final 20 days of the digestion trial

OLR	**Maize**		**Cattle slurry**	
g VS l^{-1} d^{-1}	**Volumetric methane $l\ l^{-1}\ d^{-1}$**	**Specific methane $l\ g^{-1}$ VS $_{added}$**	**Volumetric methane $l\ l^{-1}\ d^{-1}$**	**Specific methane $l\ g^{-1}$ VS $_{added}$**
1.5	0.51	0.34	0.21	0.14
2.0	0.64	0.32	0.25	0.13
2.5	---	---	0.30	0.12
3.0	---	---	0.36	0.12

It is indicated that increasing the OLR increases the volumetric methane yield but decreases the specific methane yield, as expected. For cattle slurry the reduction in the specific methane is low, with a difference of only 0.015 l g^{-1} VS shown between the 1.5 and 3 g VS l^{-1} d^{-1} loading rates, corresponding to 11% of the larger value. For the maize, the difference in the specific yield for the two successful loading was greater at 0.02 l g^{-1} VS, although this is only a 6% change in the larger value. The failure of the maize digestion at a loading of 2.5 g VS l^{-1} d^{-1} could be due to the short retention time of 18 days which would lead to rapid washout of alkalinity, nutrients and prove more detrimental to the digestion of maize when compared to the cattle slurry where these are more plentiful (Table 3.9)

The purpose of this mono-digestion trial was to allow for the prediction of the quantity of methane produced when the cattle slurry and maize were digested together at loading rates of 3, 4, 5 and 6 g VS l^{-1} d^{-1}. This was achieved by combining the specific methane yields provided in Table 7.3 to give a total methane value; these values are shown in Table 7.4 Because no results were obtained for maize at the two higher loadings, the specific methane yield from the BMP test after 18 and 15 days was used to calculate the 5 and 6 g VS l^{-1} d^{-1} loading rates.

Table 7.4: Predicted methane yields calculated by addition of the specific methane yields of cattle slurry and maize as a baseline for comparison to the co-digestion trials. Values in brackets represent calculated methane yield based on addition of the specific methane yield of the cattle slurry at semi-continuous conditions and the maize BMP.

Loading rate (g VS l^{-1} d^{-1})	**Calculated methane yield (l l^{-1})**
3	0.72 (0.68*)
4	0.89 (0.87*)
5	(1.06*)
6	(1.25*)

* Using values for specific methane yield taken from BMP test data as follows:
0.32 l g^{-1} VS $_{added}$ from the BMP trial after 29 days
0.31 l g^{-1} VS $_{added}$ from the BMP trial after 22 days
0.30 l g^{-1} VS $_{added}$ from the BMP trial after 18 days
0.30 l g^{-1} VS $_{added}$ from the BMP trial after 15 days

Digestate properties

Digestate characteristics were determined for the two mono-digestion trials. The level of TKN and ammonia at all loading rates can be seen in Figure 7.2 and Figure 7.3. For both the cattle slurry and the maize the concentration of ammonia and TKN declined as the loading rate increased. The TKN of the maize feedstock was 4820 mg l^{-1} and in the digestate this was reduced at all loading rates with a minimum value of 766 mg l^{-1} at the 2.5 g VS l^{-1} d^{-1} loading rate, equivalent to a reduction of 84%. The loss of TKN can also be seen in the digestate from cattle slurry but to a lesser extent with only a 28% difference.

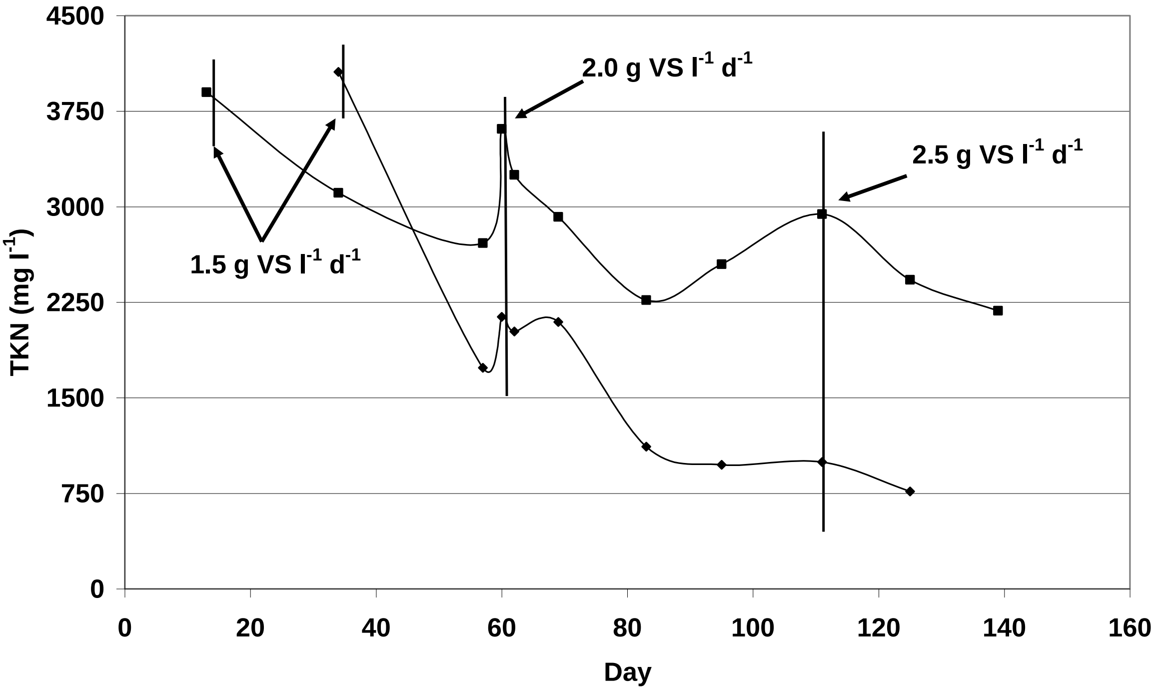


Figure 7.2: Average concentration of total kjeldahl nitrogen of each digester pair at all loading rates tested for both maize (■) and the cattle slurry (♦). The lines represent the increase in the loading rate

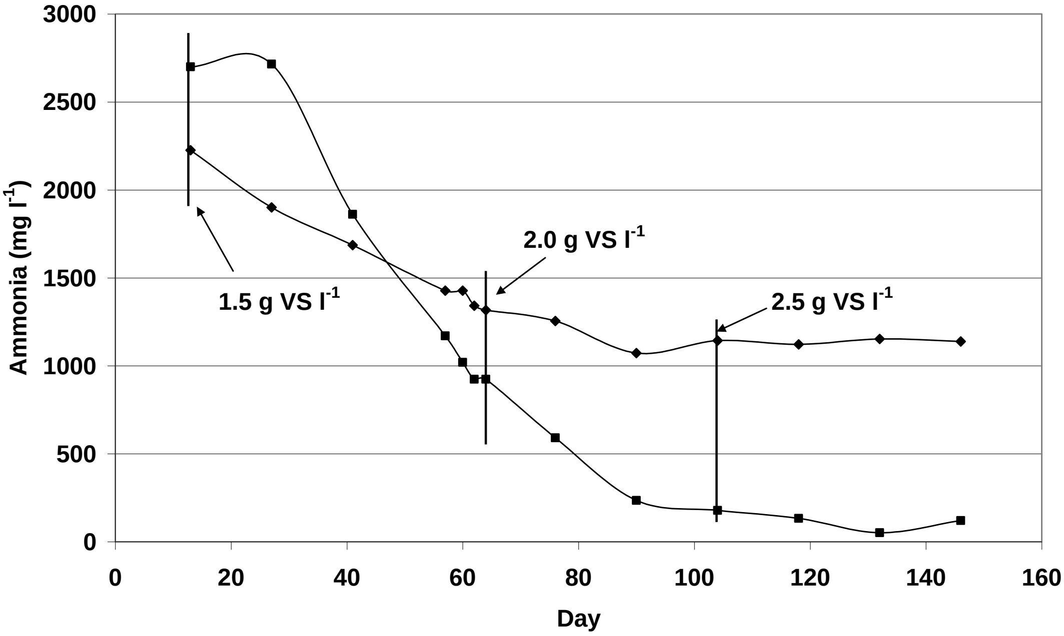


Figure 7.3: Average concentration of ammonia of each digester pair at all loading rates tested for both maize (■) and the cattle slurry (♦). The lines represent the increase in the loading rate.

A sharp decrease in the ammonia concentration was observed in the digestates from both maize and the cattle slurry and was again more pronounced in the case of the maize feedstock. The ammonia concentration in the cattle slurry digestate was either equal or greater to the initial ammonia concentration of the raw cattle slurry (depending on the loading rate). For the maize it is shown that the ammonia concentration failed to remain above 690 mg l^{-1} (concentration of the maize). Consistency of the ammonia concentration was reached at the 2.5 g VS l^{-1} d^{-1} loading rate at concentrations below 100 mg l^{-1}, indicating that in contrast to the cattle slurry the digestion of maize causes the ammonia concentration to decline. This is likely to be the result of washout as the addition of water is increasing the amount of material removed from the digester on a daily basis.

The total and volatile solids of both the maize and the cattle slurry digestion declined as shown by Figure 7.4 and Figure 7.5. The more pronounced decline shown by the maize can again be explained by the washout: the addition of water increases the level of solids leaving the digester.

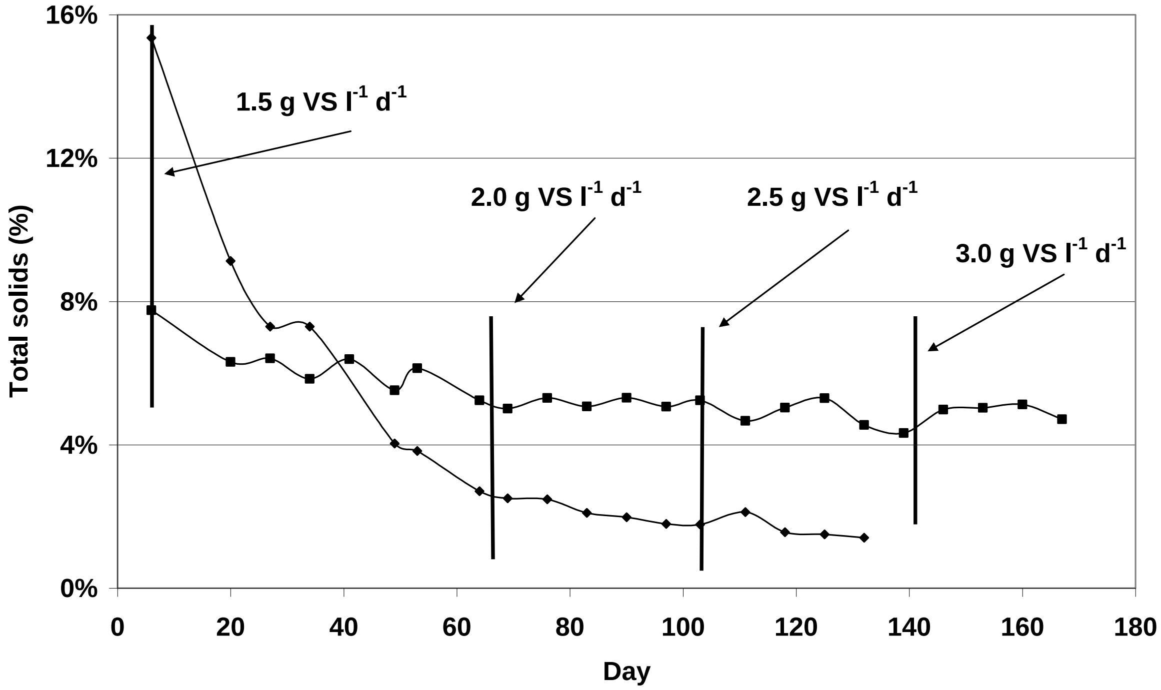


Figure 7.4: Average total solids content of each digester pair during the digestion period: maize (♦) and cattle slurry (■). The lines represent the increment in loading rate;

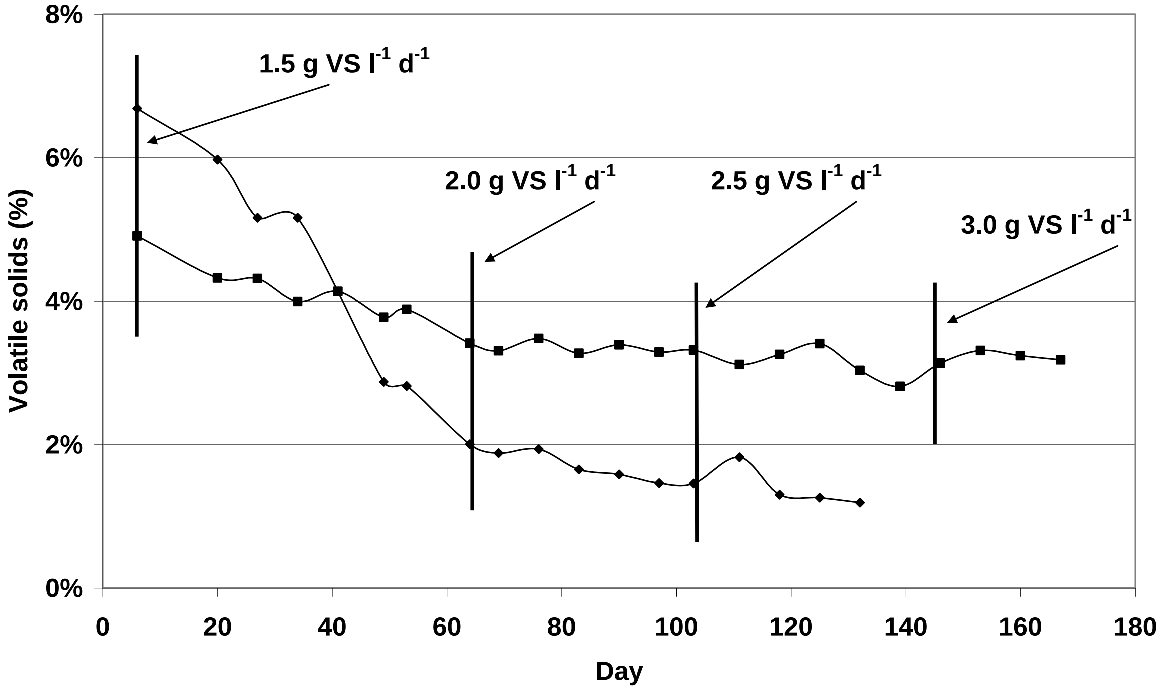


Figure 7.5: Average volatile solids content of each digester pair during the digestion period: maize (♦) and cattle slurry (■). The lines represent the increment in loading rate

The decline in the volatile solids up to the 2.5 g VS l^{-1} d^{-1} OLR is reflected in the increase of the volatile solids destruction, shown by the mass balance in Table 7.5 and Table 7.6. The final increment of the cattle slurry led to a decline of the VS destruction from 41.2 to 36%.

Table 7.5: Mass balance of the VS content of the maize fed digester. Values are based on the average VS input, output and methane yield of the digester pair. For the lowest loading rate stability was not shown so the final two values were taken as an average. For the higher loads the average was taken from the complete duration of that loading rate

Loading rate (g VS l^{-1} d^{-1})	VS Input (g)	Digestate removed (g d^{-1})	VS output (g)	VS destruction (%)	Specific methane yield (l g^{-1} VS $_{destroyed}$)
1.5	6.0	13.3	0.32	94.7	0.37
2.0	8.0	18.7	0.31	96.1	0.33
2.5	10.0	22.9	0.30	97.0	----

Table 7.6: Mass balance of the VS content of the cattle slurry fed digester. Values are based on the average VS input, output and methane yield of the digester pair. For the lowest loading rate stability was not shown so the final two values were taken as an average. For the higher loads the average was taken from the complete duration of that loading rate

Loading rate (g VS l^{-1} d^{-1})	VS Input (g)	Digestate removed (g d^{-1})	VS output (g)	VS destruction (%)	Specific methane yield (l g^{-1} VS $_{destroyed}$)
1.5	5.8	115.0	4.19	28.1	0.49
2.0	7.8	154.2	5.10	34.4	0.37
2.5	9.7	192.5	5.72	41.2	0.30
3.0	11.7	230.0	7.47	36.0	0.35

The total alkalinity and the IA:PA ratio are shown in Figure 7.6. Alkalinity decreased in both digesters irrespective of the loading changes. The alkalinity in the maize digester was 1177 mg l^{-1} compared to 8655 mg l^{-1} in the cattle slurry digester. The IA:PA in the cattle slurry digester decreased whereas in the maize digester it increased and remained below 0.30 until the loading exceeded 2.5 g VS l^{-1} d^{-1} and the digester failed. None of the digesters displayed high concentrations of VFA at any of the loading rates tested. The concentration remained under 100 and 250 mg l^{-1} for the cattle slurry and maize respectively. The decline in alkalinity, as with the ammonia, could be the result of washout and it is likely that it was this that led to the failure of the maize digester.

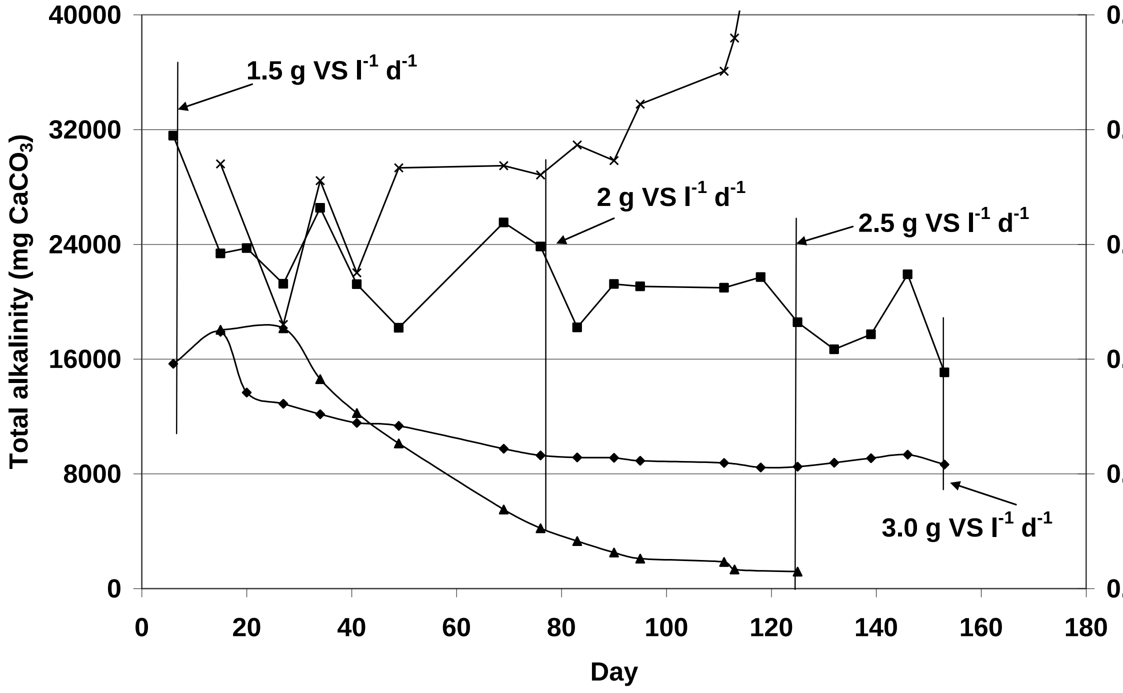


Figure 7.6: Total alkalinity and IA/PA at all loading rates for both substrates. Total alkalinity: cattle slurry (●) and maize (▲). IA/PA: cattle slurry (■) and maize (X). The lines represent the increment in the load.

7.3.2 Co-digestion

Biogas and methane production

The volumetric methane yield can be seen in Figure 7.7. The inoculum used for this trial was made up from a mixture of digestate from the second digestion trial and fresh cattle slurry (Table 3.9). Figure 7.7 indicates that this was not a high quality inoculum due to the low production at the beginning of the trial; however, it is shown that a good recovery is achieved with the volumetric yield increasing from 0.58 l l^{-1} d^{-1} at day 5 to 0.95 l l^{-1} d^{-1} at day 24 for the 5 g VS l^{-1} d^{-1} loading rate.

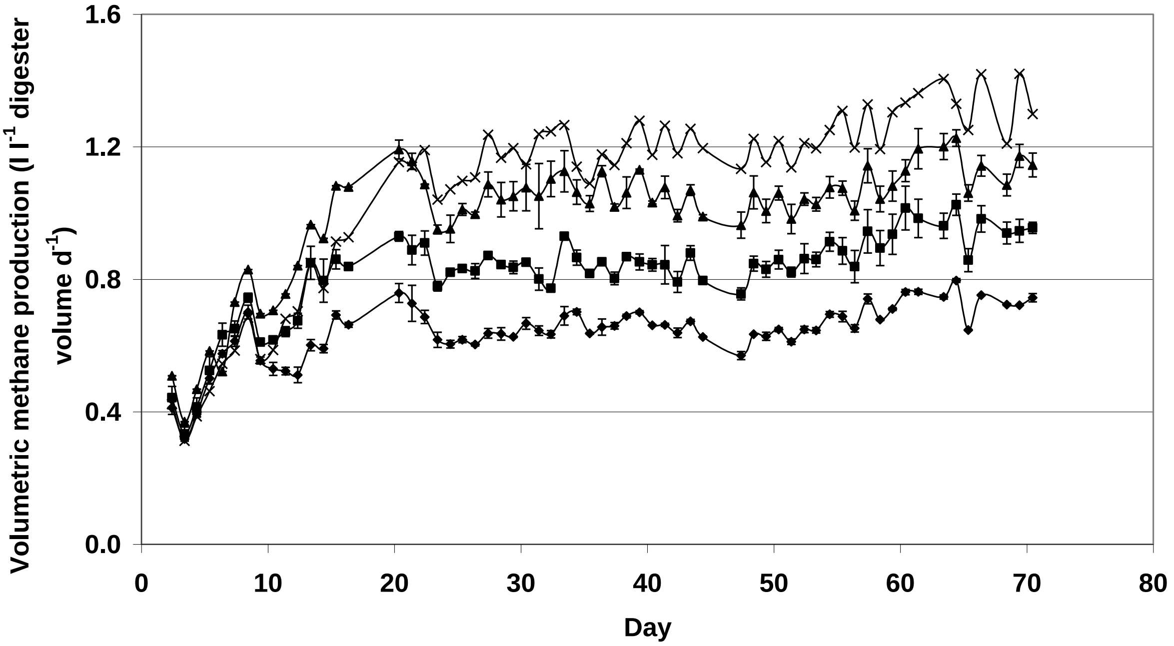


Figure 7.7: Average daily volumetric methane yield of each digester pair during the digestion period for all loading rates tested. 3 g VS l^{-1} d^{-1} (♦), 4 g VS l^{-1} d^{-1} (■), 5 g VS l^{-1} d^{-1} (▲) and 6 g VS l^{-1} d^{-1} (X). The bars represent the two replicates tested at each loading rate.

The loading rate of 3 g VS l^{-1} d-[1] produced the lowest volumetric methane production of 0.67 l l^{-1} d^{-1} while the highest production of 1.26 l l^{-1} d^{-1} was produced at the load of 6 g VS l^{-1} d^{-1}. This indicates that a doubling of the loading rate did not lead to a doubling of the volumetric methane yield.

Figure 7.8 shows the average volumetric and specific methane production for each digester pair from the final 20 days of trial. The volumetric methane production shows a linear relationship of 0.20 l l^{-1} per g VS $_{added}$ l^{-1} d^{-1} (R^2 = 0.993) but it is observed that the improvement to the production reduces as the load increased. Increasing the OLR from 5 to 6 g VS l^{-1} d^{-1} only increased the production by 0.18 l l^{-1} d^{-1} compared to an increase of 0.24 l l^{-1} d^{-1} when the load was increased from 3 to 4 g VS l^{-1} d^{-1}. Figure 7.8 show that there is little difference in the specific methane yields with each load producing a similar range. The highest average specific methane yield of 0.23 l g^{-1} VS $_{added}$ d^{-1} was achieved at a loading of 3 g VS l^{-1} d^{-1} but this was only 0.02 l g^{-1} VS d^{-1} greater than the lowest specific methane yield at the loading rate of 6 g VS l^{-1} d^{-1}.

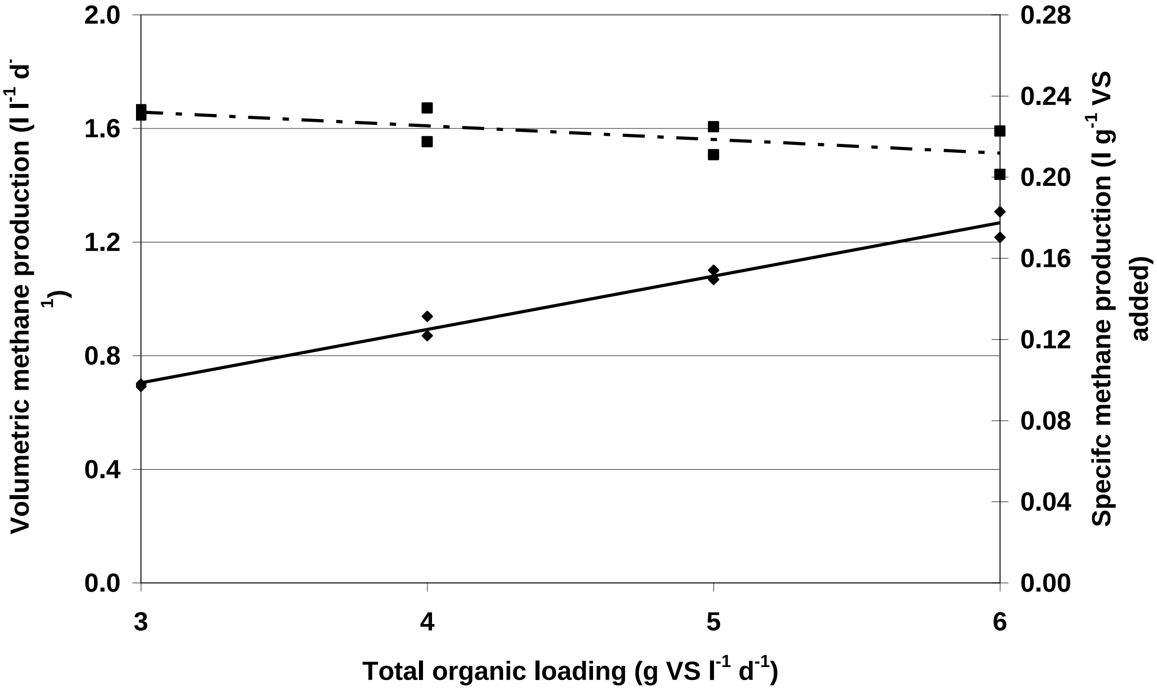


Figure 7.8: Average methane production for each digester pair and at each loading rate in terms of the volumetric methane (♦) and specific methane (■) yields. The values are taken from the final 20 days of the trial

It is shown by Table 7.7 that the addition of an equal quantity of maize to the digestion of cattle slurry caused the volumetric methane yield at all cattle slurry loads to increase by over 200%; the addition of 2.5 g VS l^{-1} d^{-1} maize produced the greatest improvement.

Table 7.7: Improvement in the volumetric methane yield by the addition of an equal quantity of maize to the cattle slurry at all cattle slurry loads tested.

Cattle slurry loading rate (g VS l^{-1} d^{-1})	Volumetric methane yield ($l\ l^{-1}\ d^{-1}$) Mono-digestion	With an equal addition of maize	Improvement $l\ l^{-1}\ d^{-1}$	%
1.5	0.21	0.67	0.46	219
2.0	0.25	0.90	0.65	260
2.5	0.30	1.09	0.79	263
3.0	0.36	1.26	0.90	250

The daily biogas production for day 60 of the co-digestion trial, in the steady state period, is shown in Figure 7.9. There was little difference in the biogas production at all loading rates. All the digesters displayed a higher rate of production of 0.030 l g^{-1} VS in the initial 8 hours after feeding compared to of 0.012 l g^{-1} VS over the latter part of the daily feed cycle.

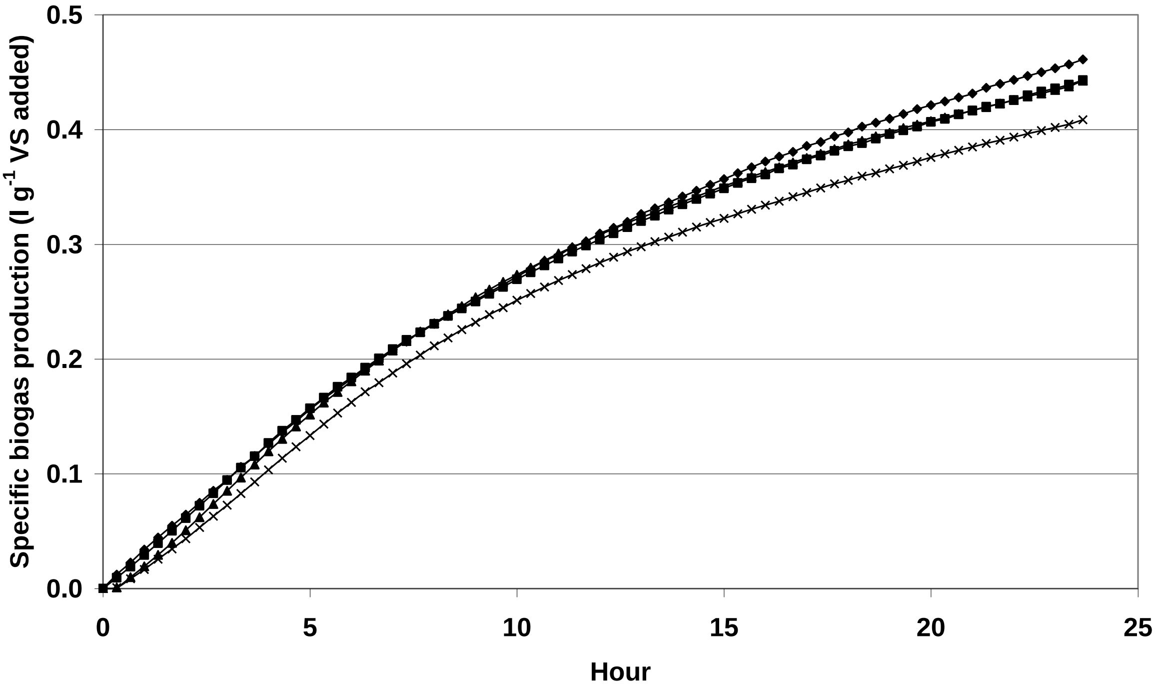


Figure 7.9: Average specific biogas yield produced of each digester pair at all working conditions tested during a 24 hour period at day 60: 3 g VS l^{-1} d^{-1} (♦), 4 g VS l^{-1} d^{-1}, (■), 5 g VS l^{-1} d^{-1} (▲) and 6 g VS l^{-1} d^{-1} (X)

The experimental data shown in Table 7.8 was fitted to the mathematical models of Chen and Hashimoto (1978) and Hill (1991) as described in Chapter 3 (Section 3.7). The results are plotted in Figure 7.10 and in the case of both models the experimental data did not give a good fit. The failure of the Hill's model could be because the values used for parameters, B_o and τ were those recommended for the use with dairy cattle slurry alone. To improve the fit of the Hill model the biodegradability factor was increased to 0.67 and the stress index was declined to 6.9; these adjustments gave a better fit with the experimental data, as shown in Figure 7.10. This match with the experimental data also supports the idea that a loading rate of 6 g VS l^{-1} d^{-1} is the maximum that can be achieved.

Table 7.8: Summary of the parameters used for the Chen and Hashimoto and the Hill kinetic model

Model	Model parameters
Chen and Hashimoto	$\mu_m = 0.34\ d^{-1}$ K = 0.80 $B_o = 0.23\ l\ g^{-1}$ VS (average of the cattle slurry and maize specific methane yield)
Hill	$\mu_m = 0.33\ l\ g^{-1}$ VS destroyed (average value of cattle slurry and maiz $B_o = 0.2292$ (value recommended by for dairy cattle slurry)* *and* = 0.67 (adjusted parameter achieve a better fit with experimental data) τ = 10.12 (value recommended for dairy cattle slurry)* *and* = 6.9 (adjusted parameter to achieve a better fit with experimenta data)

*Husain (1998)

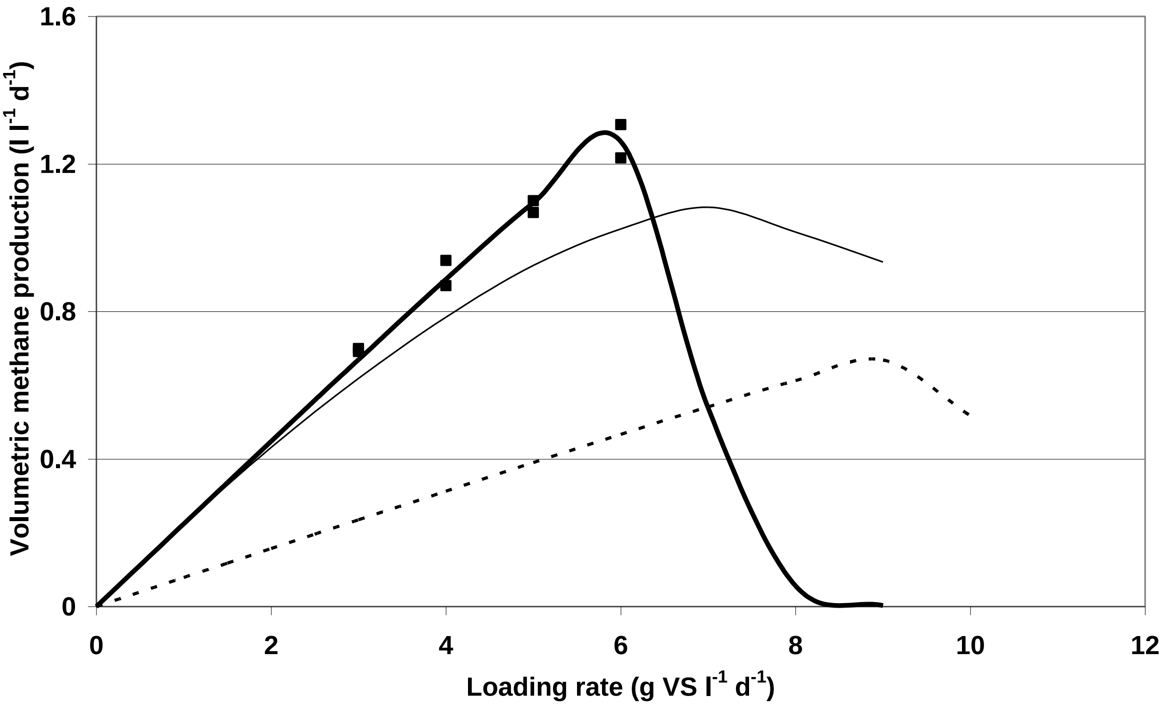


Figure 7.10: Comparison of the experimental methane production (■) with the predictions of Chen and Hashimoto (—) and Hill model for dairy cattle slurry (---) and modified Hill model parameters (**▬). The experimental data is the average** volumetric methane yield taken from the final 20 days of the digestion trial

The previous co-digestion trials (Chapter 5 and 6) compared the actual methane yields with those calculated from the methane potential of the maize from the BMP trial, and of the cattle slurry, achieved by the control semi-continuous digester. As already noted this may not provide an accurate basis for interpretation regarding any possible synergies and the current trial was an attempt to overcome the uncertainties associated with this comparison. For this purpose the methane yields from the co-digestion part of this trial were compared to the predicted methane yields based on the mono-digestion trial (Table 7.4). This comparison is shown in Figure 7.11.

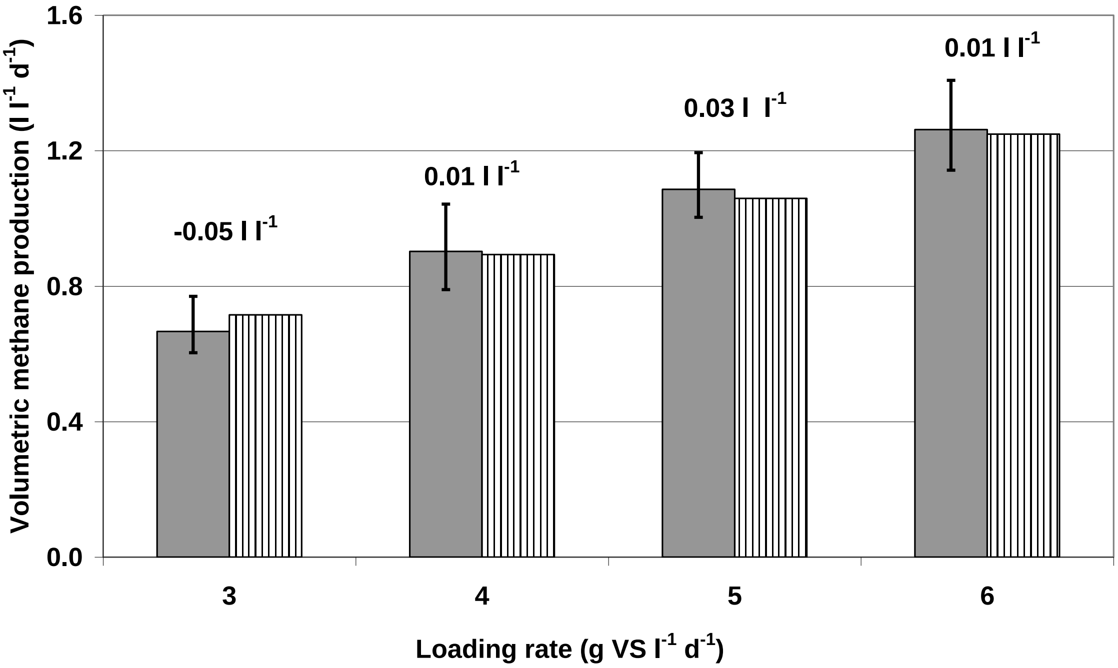


Figure 7.11: Difference in the volumetric methane production (l l^{-1} d^{-1}) between the average methane production of each digester pair (filled bars) and the yield calculated from combining the methane potential of the maize and of the cattle slurry (Table 7.4) (striped bars). The numerical difference and the range of methane yields achieved are shown in each case

It can be seen by Figure 7.11 that the methane yield produced by the digesters was approximately equal to that calculated from the methane potential of the individual substrates indicating no synergy present. This suggests that the apparent synergy shown in Chapter 6 could have been the result of a poor determination of the calculated yield. It is likely that the improvement shown in the previous chapter was the result of the improved retention time and for the case of the winter cattle slurry, a reduction of inhibition.

It is shown in Figure 7.12 that the methane yield calculated to be attributed to the maize was similar at the 3 and 4 g VS l^{-1} d^{-1} loads with a yield approximately equal to that of the BMP value. Increasing the load past 4 g VS l^{-1} d^{-1} led to a decline from 0.33 to 0.30 l g^{-1} VS maize d^{-1} at the 6 g VS l^{-1} d^{-1} loading rate. This reduction in the average specific methane yield at the higher loads is likely to be the result of the decline of the retention time; increasing the load from 4 to 6 g VS l^{-1} d^{-1} corresponded to a decline of 7 days. This will lead to an increase in the washout therefore an increase in the removal of alkalinity and ammonia; both of these were shown to be important parameters in the mono-digestion section of this trial. The wide range of methane yields achieved at each load indicate an overlap suggesting that there is little difference between the loads indicating that increasing the load from 3 to 6 g VS l^{-1} d^{-1} results in an improvement in the volumetric methane yield by 0.6 l l^{-1} d^{-1} without losing the methane yield of the maize as it is shown that the specific methane stays approximately constant.

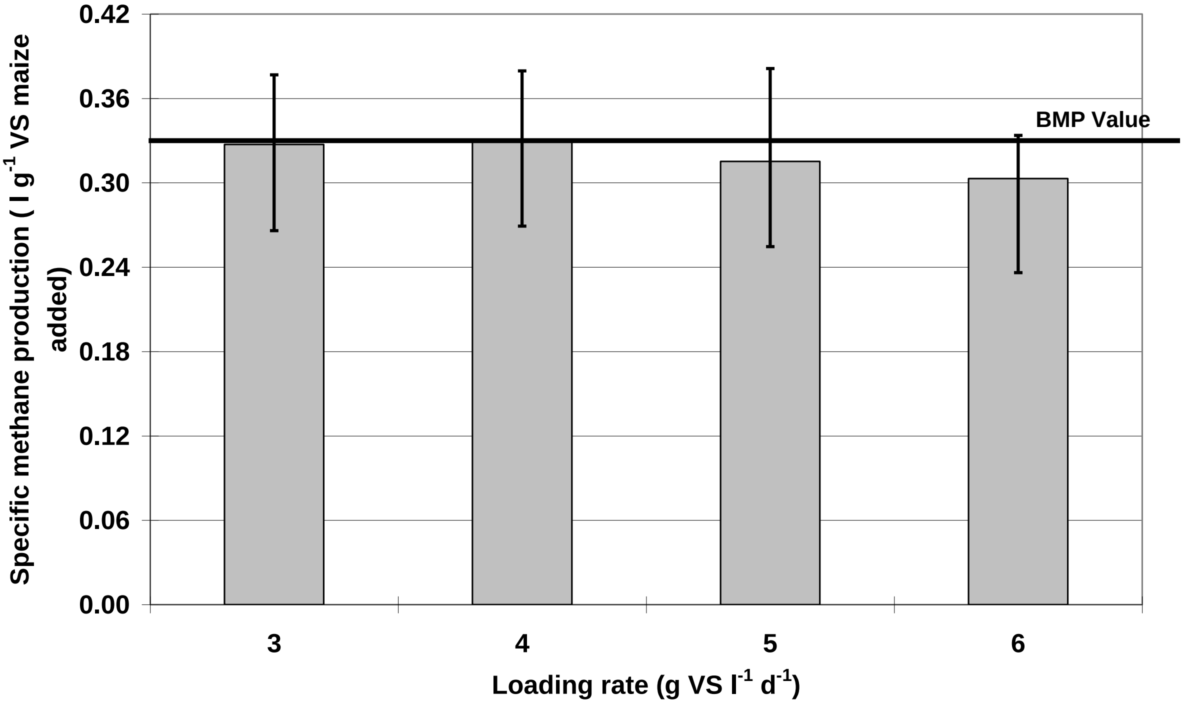


Figure 7.12: Specific methane production attributable to the maize by the subtraction of specific methane yield of the cattle slurry from the overall specific methane yield. These are the average of each digester pair at each loading rate tested from the final 50 days of the trial. The range of the specific methane production is represented by the bars.

Table 7.9 gives the carbon to nitrogen ratio for all the loading rates tested along with the methane composition; to provide a comparison the mono-digestion of maize the C:N ratio of the maize is also shown. Literature has highlighted that an improved C:N ratio is an important benefit of co-digestion; however, it can be seen here that it is not necessarily pivotal to its success as it is shown that co-digestion had an improved performance when compared to the maize mono-digestion despite the lower C:N ratio.

Table 7.9: Carbon to nitrogen ratios tested in this digestion trial along with the volumetric methane yield produced and methane composition

Loading rate g VS l^{-1} d^{-1}	C:N ratio	Volumetric methane ($l\ l^{-1}\ d^{-1}$)	Methane composition (%)
3	16.53	0.67	55.6
4	16.53	0.90	54.8
5	16.53	1.09	54.9
6	16.53	1.26	54.3
Maize	26.32	n/a	n/a

From the methane results achieved in the mono-digestion and co-digestion trials the following observations can be made:

- Washout appeared to be the source of failure in the digestion of the maize at the short retention times highlighting that ammonia and alkalinity are important factors for digestion at short retention time.
- The loading rate of a cattle slurry digester can be increased from 3 to 6 g VS l^{-1} d^{-1} with the volumetric methane yield more of less doubling in quantity while maintaining a constant specific methane yield. This is in despite of the 14 day decline in the retention time.
- Synergy was shown not to occur bringing into doubt the apparent synergy shown in Chapters 5 and 6.

Digestate properties

The digestate properties were constant from day 50; Table 7.10 gives the properties of the digestate from each digester.

Table 7.10: Characteristics of the digestate at all loading rates tested; given values are averages of each digester pair taken from the final 20 days of the digestion trial

OLR g VS l^{-1} d^{-1}	3	4	5	6
pH	7.4	7.3	7.2	7.2
TS %	7.4	7.8	8.3	8.4
VS %	5.0	5.2	5.4	5.5
VS destruction %	55.2	45.6	43.1	41.5
TKN g l^{-1}	3.4	3.3	3.3	3.3
NH_3 g l^{-1}	1.3	1.2	1.1	1.0
% of TKN	37	36	32	31
Total Alkalinity g l^{-1}	10.7	9.8	9.4	9.1
IA:PA	0.38	0.34	0.35	0.39
VFA mg l^{-1}	203	165	173	170

Increasing the loading rate slightly increased the TS and VS within the digesters with the highest loading having a total solids content 1% higher than the lowest loaded digester. Using maize in the feed at a 50:50 ratio (in terms of VS) gave the digestate a higher total solids content than the 7.68% of raw cattle slurry. For comparison, in the first initial trial a 50:50 ratio of cattle slurry to maize at a loading of 4 g VS l^{-1} d^{-1} gave a digestate 1.6% lower in TS than raw cattle slurry; in this trial at the same loading the TS was 3% higher than raw cattle slurry.

An increase in the loading rate resulted in a decline of the volatile solids destruction from 47 to 41% as shown by the mass balance in Table 7.11. The specific methane in terms of VS destroyed remained approximately constant with a slight increase from 0.46 to 0.50 l g^{-1} VS $_{destroyed}$.

Table 7.11: Mass balance of the VS content of each digester pair. Values are based on the average VS input, output and methane yield of the digester pair for the final 50 days of the trial.

Loading rate (g VS l^{-1} d^{-1})	VS Input (g)	Digestate removed (g d^{-1})	VS output (g)	VS destruction (%)	Specific methane yield (l g^{-1} VS $_{destroyed}$)
3	12.3	129.5	6.5	47.3	0.46
4	16.4	172.3	8.9	45.5	0.49
5	20.5	216.2	11.7	43.0	0.49
6	24.5	260.3	14.4	41.2	0.50

A mass balance of carbon using the results in Table 7.11 along with the average methane yield from the final 50 days of the trial is shown in Table 7.12 where an approximate balance at all loads is shown. The mass balance in the previous two trials (Table 5.6, Table 6.6 and Table 6.15) showed an imbalance indicating the presence of an inaccurate measurement. The balance shown here suggests an improvement in the accuracy of the carbon, VS content of the raw cattle slurry or/and methane measurements.

Table 7.12: Comparison of the average methane yield of each digester pair over the final 50 days of the digestion trial with the potential methane yield calculated from the quantity of carbon entering the digesters.

	Methane (l l^{-1} d^{-1})		
Loading rate (g VS l^{-1} d^{-1}	**Potential**	**Actual**	**Difference**
3	0.71	0.67	-6.1%
4	0.91	0.90	-1.0%
5	1.08	1.09	+0.8%
6	1.30	1.26	-2.7%

Initial VFA concentrations were over 1500 mg l^{-1}, as shown by Figure 7.13, and it was not until day 24 stability was reached, after which the VFA concentration remained below 200 mg l^{-1}. This corresponds to the recovery shown by the volumetric methane production (Figure 7.7).

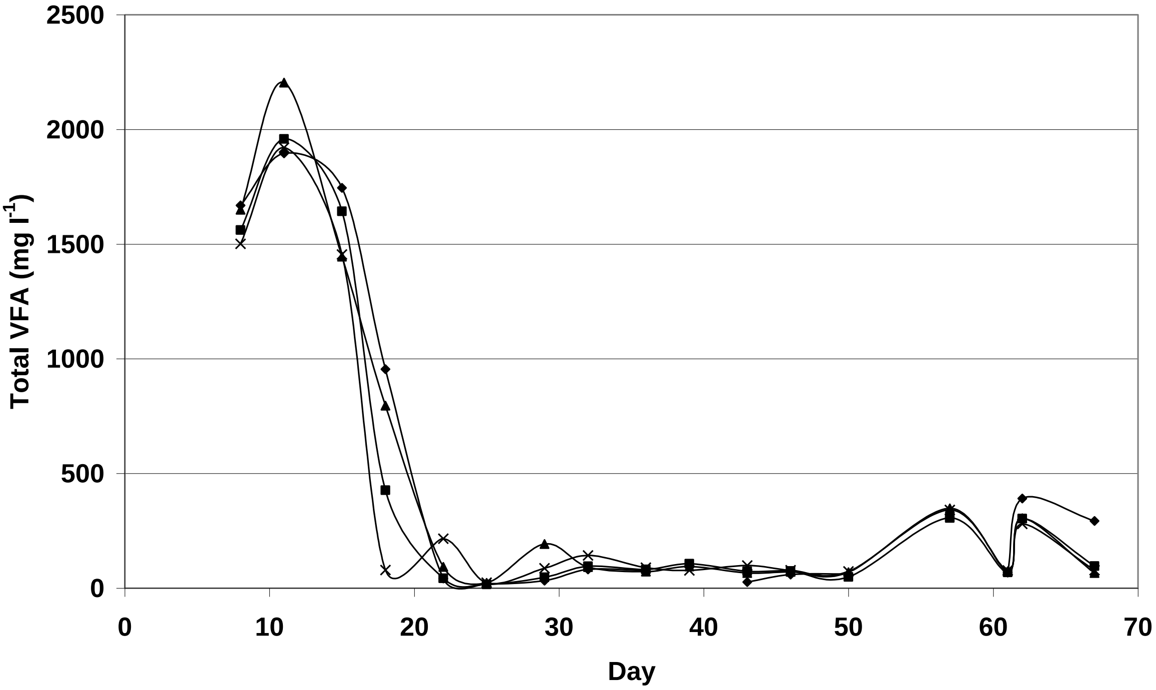


Figure 7.13: Average VFA concentration of each digester pair during the digestion trial at all loads tested: 3 g VS l^{-1} d^{-1} (♦), 4 g VS l^{-1} d^{-1}, (■), 5 g VS l^{-1} d^{-1} (▲) and 6 g VS l^{-1} d^{-1} (X)

The impact that digestion had on the nitrogen concentration, in terms of the TKN and ammonia is shown by the mass balance shown in Table 7.13. Upon digestion, in all cases the concentration of ammonia reduced and the TKN increased.

Table 7.13: Daily nitrogen mass balance using the average TKN and ammonia concentration of the feedstock and the average of each digester pair from the final 20 days at all loads.

Loading rate	Daily digestate removal	Nitrogen (g)		Difference	
g l^{-1} VS d^{-1}	l	Input	Output	g	%
3	0.16	0.45	0.44	-0.01	-1.0
4	0.20	0.60	0.56	-0.04	-6.5
5	0.22	0.75	0.72	-0.03	-4.0
6	0.26	0.90	0.87	-0.03	-3.4

The mono-digestion trial indicated that failure was the result of the increase in the washout, which reduced the buffering capacity of the system. The importance of the ammonia and alkalinity was shown by comparing the two mono-digestion trials; this is repeated by comparing the mono-digestion of maize at the 2.5 g VS l^{-1} d^{-1} load with the co-digestion trial at a load of 5 g VS l^{-1} d^{-1} It can be seen in Table 7.14 that replacing the water with cattle slurry significantly increased the ammonia concentration and therefore the alkalinity of the system indicating that maize can be digested at loads of 2.5 g VS l^{-1} d^{-1} and short retention times if there is adequate buffering.

Table 7.14: Comparison of ammonia and alkalinity between mono and co-digestion trials at loading rates of 2.5 and 5 g VS l^{-1} d^{-1} respectively

Parameter	**Maize (2.5 g VS l^{-1} d^{-1})**	**Cattle slurry (2.5 g VS l^{-1} d^{-1})**	**Co-digestion (5 g VS l^{-1} d^{-1})**
Ammonia g l^{-1}	0.09	1.14	1.05
Total Alkalinity g l^{-1}	1.26	8.69	9.12
IA/PA	0.63	0.22	0.36

An approximate balance of phosphorus and potassium is shown by Table 7.15 with the potassium at the 3 and 4 g VS l^{-1} d^{-1} showing the greatest difference, suggesting inaccuracy in the measurements at these loads.

Table 7.15: Mass balance of potassium and phosphorus at each maize loading. Values are based on the average daily digestate removal over the final 20 days and the average concentration in the raw feedstock (Table 7.15) and the digestate of each digester pair

Maize	Input		Output		Difference (%)	
Addition g VS l^{-1} d^{-1})	Potassium g (as K_2O)	Phosphorus g (as P_2O_5)	Potassium g (as K_2O)	Phosphorus g(as P_2O_5)	Potassium (as K_2O)	Phosphorus (as P_2O_5)
3	0.33	0.37	0.38	0.40	+9.7	+15.2
4	0.43	0.49	0.50	0.53	+8.3	+9.5
5	0.54	0.61	0.59	0.68	+11.3	+11.1
6	0.64	0.73	0.64	0.80	+8.6	+9.4

The concentration of the heavy metals are shown in Table 7.16 in terms of DM, these are the average of each digester pair. A comparison of these measurements with the PAS110 digestate standards given in Table 2.3 indicates that chromium and nickel are above the acceptable limits; this supports the results on Chapter 6 for the winter cattle slurry. It was difficult to achieve a balance of these two metals, as noted in the previous Chapter suggesting that these values may not be accurate. The difficulty in achieving a balance for chromium and nickel has been experienced by other members of the research group at the University of Southampton and from personal communication this has been attributed to stainless steel part of the digesters stirrer.

Table 7.16: Concentration of heavy metals within the digesters at the different loading rates

Loading rate (g VS l^{-1} d^{-1})	3	4	5	6
Cadmium mg kg^{-1} DM	----	0.1	0.8	1.0
Chromium mg kg^{-1} DM	208	246	517	239
Copper mg kg^{-1} DM	55	49	46	51
Nickel mg kg^{-1} DM	104	95	223	98
Zinc mg kg^{-1} DM	180	179	150	157

7.4 Discussion

7.4.1 Mono-digestion

The mono-digestion trial showed that cattle slurry could be digested at all loading rates tested, even at a retention time of 15 days which corresponded to the higher loading. The volumetric methane yield increased with the loading rate in agreement with the work by Linke *et al.,* (1997) which stated that 15 days provides an adequate retention time for methane production. Doubling the loading rate from 1.5 to 3 g VS l^{-1} did not double the volumetric methane yield, however, with an increase from 0.21 to 0.36 l l^{-1} suggesting that a load of 3 g VS l^{-1} d^{-1} is around the maximum for the system. In contrast to the volumetric methane yield there was a minimal impact on the specific methane yield, with a decline from 0.14 to 0.12 l g^{-1} VS with the increase in loading from 1.5 to 3 g VS l^{-1} d^{-1}. Maize was successfully digested at loading rates of 1.5 and 2 g VS l^{-1} d^{-1} producing a specific methane yield of 0.34 to 0.32 l g^{-1} VS $_{added}$. The maize failed within 6 days of increasing the load to 2.5 g VS l^{-1} d^{-1}.

This failure at the high loading rates is in contrast to the previous co-digestion trials where maize was able to digest at a load of 3 g VS l^{-1} d^{-1} when co-digested with cattle slurry. In the initial digestion trial a 3 g VS l^{-1} d^{-1} maize loading rate was digested with a 2 g VS l^{-1} d^{-1} cattle slurry loading rate where a specific methane yield of 0.26 l g^{-1} VS was produced. In comparison, the second digestion trial tested a 3 g VS l^{-1} d^{-1} maize loading rate with a 1 g VS l^{-1} d^{-1} cattle slurry loading rate and this condition proved to be the optimal in terms of the volumetric methane yield. These comparisons suggest that the failure of the mono-digestion at the 2.5 g VS l^{-1} d^{-1} loading rate could have been the result of the difference in the retention time, 18 days compared to 26 and 50 days and/or the absence of cattle slurry within the feed with its replacement by water containing trace elements only. The short retention is likely to be the cause of the failure as washout of alkalinity and nutrients can occur; it was shown that as the retention time decreased both, the alkalinity and the ammonia declined.

To explain the success of the cattle slurry but the failure of the maize to digest at the 2.5 g VS l^{-1} d^{-1} loading rate the ammonia and alkalinity can be compared. The cattle slurry digestate had a higher ammonia concentration at this loading rate than the maize digestion, with values of 1.14 and 0.09 g l^{-1} respectively; and the total alkalinity was also greater than for the maize at 8820 and 920 mg $CaCO_3$ l^{-1} respectively. This confirms the presence of the high concentration of ammonia therefore the higher alkalinity is an important parameter in the success of the digestion at the short retention times.

7.4.2 Co-digestion

The co-digestion trial showed that digestion was possible at all loading rates tested with the volumetric methane yield increasing with loading rate. Figure 7.8 shows the trend in volumetric methane yield and indicates that the maximum loading capacity of the system was not exceeded. In terms of the specific methane yield it can be observed that the digestion was starting to decline at the 4 g VS l^{-1} d^{-1} however the decline shown in Figure 7.8 was not significant with little difference between the ranges of methane yields produced at each loading rate. A further increment in the load may still be possible in terms of the production in the methane but the results indicate that the average specific methane yield will continue to decline with a greater proportion of the potential of the maize lost. One clear explanation for the decline shown at the 6 g VS l^{-1} d^{-1} loading rate can be drawn from the methodology for this trial: the short retention time. As the loading rate increased the retention time fell to 15 days, which is at the lowest range for the digestion of cattle slurry (Linke, 1997).

A key result produced from this trial is the impact that the addition of maize had on the volumetric methane yield of the cattle slurry digesters. Comparing the yields of the co-digestion trial with those produced from the digestion of the cattle slurry alone indicated that the addition of an equal load of maize to the cattle slurry increased the yield by over 200% at all maize loads. This indicates that the farmer does not require large quantities of maize to increase the methane output of the digesters: a 1.5 g VS l^{-1} d^{-1} maize addition to a 1.5 g VS l^{-1} d^{-1} cattle slurry load resulted in an increase of 219% (Table 7.7). Additionally, it was shown that the maximum load tested in the cattle slurry mono-digestion trial could successfully be doubled by adding an equal quantity of maize without a decline in the specific methane yield and as shown by Figure 7.12 no significant decline in the methane attributable to the maize. Further discussion of this improvement to the volumetric methane yield will be given in the final summary Chapter of this research to allow for a comparison of all trials.

The results showed no evidence of synergy with all digesters producing a methane yield that was comparable to that calculated to be produced. The addition of cattle slurry did however, allow digestion of the maize at loadings of 2.5 and 3 g VS l^{-1} d^{-1}, which failed under mono-digestion conditions. The results produced from the mono and co-digestion trials in this Chapter indicated that the main explanation for this was the washout of alkalinity and ammonia when water was added in place of the cattle slurry. This highlighted the importance of the ammonia and alkalinity that the cattle slurry brings to the system indicating that these are important parameters especially when digesting at high loads and short retention times. A similar result was shown by Mähnert *et al.,* (2006) where it was shown that it was only possible for the maize to digest at loads greater that 3 g VS l^{-1} d^{-1} when it was combined with cattle slurry. A direct comparison can not be made due to the difference in the methodology as Mähnert *et al.,* (2006) did not add water to the mono-digestion trial. Minimal explanation behind the failure and success of maize at loads greater than 3 g VS l^{-1} d^{-1} was given so it is not known if the washout of ammonia and alkalinity played an important role.

The mono-digestion trial highlighted two factors that could be drawn from the failure of the maize-only digestion at a 2.5 g VS l^{-1} d^{-1} loading rate and the success at a 3 g VS l^{-1} d^{-1} loading rate when co-digested with cattle slurry: the shorter retention time or the absence of cattle slurry. It can now be stated that the success of the maize to digest at the 3 g VS l-1 d^{-1} loading rate in the previous trials was the result of the presence of the cattle slurry, not as a result of a longer retention time. This can be concluded as it was shown that maize could successfully be digested at a load of 2.5 g VS l^{-1} d^{-1} and at a retention time of 18 days when cattle slurry was added to the system. The addition of cattle slurry can bring to the system a number of factors that can be leading to the successful digestion of maize, such as nutrients, ammonia, buffering and a source of inoculum, The results here show the importance of the high concentration of ammonia that the cattle slurry introduced to the system: introducing cattle slurry to a 2.5 g VS l^{-1} d^{-1} loading rate of maize increased the ammonia from 0.1 to 1.1 g l^{-1} and the alkalinity by 1.3 to 9.9 g l^{-1}.

A comparison between this trial and the initial digestion trial (Chapter 5) is possible as both tested a 4 g VS l^{-1} d^{-1} loading rate at a maize to cattle slurry ratio of 50:50 and the batches of cattle slurry used were similar in their methane potential, 0.131 and 0.126 l g^{-1} VS respectively. At the 4 g VS l^{-1} d^{-1} load the initial trial produced a volumetric and specific methane yield of 1.20 l l^{-1} d^{-1} and 0.26 l g^{-}

^{1} VS while this trial produced 0.92 l l^{-1} d^{-1} and 0.23 l g^{-1} VS. The lower performance of the 4 g VS l^{-1} d^{-1} loading rate in this current trial could be explained by the shorter retention time, or the different properties of the cattle slurry. As noted, there was little difference in the methane yield between the batches of cattle slurry and the characteristics of the two batches of cattle slurry highlighted only one main difference: the volatile and total solids content (Table 3.9). As a result of the difference in the total solids the amount of cattle slurry required for a 2 g VS l^{-1} d^{-1} loading rate will differ; Table 7.17 provides a comparison between the two batches of cattle slurry and how the characteristics of the total feed differs.

Table 7.17: Comparison of the feed input in the 4 g VS l^{-1} d^{-1} loading rate tested in this digestion trial and in the initial digestion trial

Parameter	Digestion trial 1	Digestion trial 3
Cattle slurry (g d^{-1})	120	156
Ammonia (g d^{-1})	0.13	0.19
Total nitrogen (mg d^{-1})	0.40	0.35
Total carbon (mg d^{-1})	5.13	4.45
Cadmium (mg d^{-1})	0.01	0.04
Chromium (mg d^{-1})	4.42	6.64
Copper (mg d^{-1})	0.65	0.58
Nickel (mg d^{-1})	1.39	2.41
Zinc (mg d^{-1})	3.49	2.40

The above table shows that the quantity of cattle slurry does increase by 36 g d^{-1} however there does not appear to be any other clear difference between the batches of cattle slurry that would explain the difference. The difference in the amount of raw cattle slurry fed to the digester resulted in a difference in the retention time with this trial having a lower retention time than the initial trial, 22 days compared to 28 days. Reducing the retention time will increase the level of washout, including undegraded material, which could be an explanation for the lower specific methane yield displayed here.

The addition of maize in the previous trials has been shown to be both positive, in terms of the reduction of the ammonia, and negative, in terms of the increase in the total solids. This trial has indicated that increasing the loading rate had a similar impact, with the solids increasing from 7.44 to 8.38%, and the ammonia declining from 1.27 to 1.02 g l^{-1}. The increase in the total solids was not as defined as the increase shown by previous trials, for example increasing the loading rate from 3 to 6 g VS l^{-1} d^{-1} (i.e. increasing the maize from 1.5 to 3 g VS l^{-1} d^{-1}) increased the solids by 0.94% while increasing the proportion of maize from 0 to 3 g VS l^{-1} d^{-1} in the second digestion trial produced an increase of 1.94% (winter cattle slurry). Despite the less defined impact of the loading rate on the total solids it can be observed that the only loading rate shown to produce a digestate with a lower solids content than the raw cattle slurry was the 3 g VS l^{-1} d^{-1} load however, this was only 0.3% lower. This result along with the difference on the methane yield displayed by the comparison of the 4 g VS l^{-1} d^{-1} loading rate in this trial and the first digestion trial highlights how the digestion of cattle slurry can vary. Variation of the cattle slurry can include the concentration of nutrients and the quality of the slurry as an inoculum, both of which have the potential to influence the methane production. The methane recovery however, can be influenced by a less subtle variation such as a difference in the TS and VS, which will affect the retention time.

The effect of increasing the loading rate was to cause a decline in digestate ammonia concentration, from 1.27 to 1.02 g l^{-1} with the 6 g VS l^{-1} d^{-1} loading rate producing the lowest concentration, which was 0.17 g l^{-1} lower than the raw cattle slurry. The reduced ammonia concentration is cancelled out by the increase in digestate removal observed at the higher loads (Table 7.13) resulting in higher quantities of ammonia leaving the digester, 0.16 and 0.26 g d^{-1} for the 3 and 6 g VS l^{-1} d^{-1} loads respectively.

Increasing the loading rate to 6 g VS l^{-1} d^{-1} may have increased the volumetric yield but it can be suggested that this load is not the optimal: increasing the loading rate from 5 to 6 g VS l^{-1} d^{-1} produced the greatest decline in the average specific methane yield and led to a greater loss of the methane potential of the maize, with the specific methane yield attributed to the maize reducing to 0.30 l g^{-1} VS maize d^{-1}. In the 3 to 5 g VS l^{-1} d^{-1} loading range the specific methane yields remain similar; with the increase shown by the volumetric methane yield it can be suggested that the optimal load should be the 4 or the 5 g VS l^{-1} d^{-1} loading rate. It could be argued that the 5 g VS l^{-1} d^{-1} loading rate is optimal, based on the methane yield rate; a disadvantage of this loading rate is that it can lead to a low retention time and so to a reduction in the amount of methane attributable to the maize. In addition the higher loading rate will require the diversion of a greater quantity of maize from food or fodder to energy production. With the debate on-going about the use of energy crops it could prove to be beneficial to the digester operator to feed at a 4 g VS l^{-1} d^{-1} load and a 50:50 maize cattle slurry ratio, which also has the benefit of a lower solids content.

The main conclusions from this trial are:

- The addition of maize to an equal quantity of cattle slurry in terms of VS can produce an improvement in the volumetric methane yield with no significant reduction in the retention time and the issue of washout was avoided. In addition it maintains the specific methane yield, which avoids any loss of the energy value of the maize.

- As with the previous trials, the addition of small quantities of maize can improve the methane output of a cattle slurry digester: addition of 1.5 g VS l^{-1} d^{-1} to an equal load of cattle slurry increased the volumetric methane yield by 219%.
- A comparison between the mono and co-digestion sections of this Chapter indicates that the digestion of maize and cattle slurry did not result in the presence of synergy. It could be concluded that the apparent synergy shown in the previous Chapters was the result of an inaccurate or inappropriate determination of the calculated methane yield. In the case of the winter cattle slurry the apparent synergy was likely to be due to the washout out of inhibitors.

8 Digestion trial 4 and 5: Impact of introducing solids recirculation to co-digestion and mono-digestion

8.1 Objective

The objective of introducing solid recirculation to the co-digestion process was to determine whether the process could be improved by retaining the slowly degradable fraction of the maize and cattle slurry for longer periods. In addition to the co-digestion trial a mono-digestion trial was set up with an aim to determine how and if the impact of solids recirculation differs between the digestion of the maize and of the cattle slurry.

8.2 Methodology

The operational conditions in digestion trial 4 were the same as in digestion trial 3, with the use of the same batch of cattle slurry allowing direct comparison between no recirculation (Chapter 7) and solids recirculation. In addition this also allowed comparison with the mono-digestion trials in Chapter 7. Digestion trial 5 consisted of the mono-digestion of cattle slurry and maize following both solids recirculation and no recirculation. The loading rate chosen was 2.5 g VS l^{-1} d^{-1} at a retention time of 29 days.

Digestion trial 4*: *Digestate solids recirculation in co-digestion of cattle slurry and maize silage

Eight digesters were used in this trial and operated as duplicate pairs. The same batch of cattle slurry was used throughout the trial and this was the same as the batch used in digestion trial 3 (batch 4, Table 3.9). The digesters were operated to maintain a constant weight and the operational conditions were the same as those for digestion trial 3 (Table 7.2). Solids recirculation was achieved by sieving the digestate through a 1 mm mesh to achieve the weight of digestate liquid required; the sieved solids were returned back to the digester.

Digestion trial 5: Digestate solids recirculation in mono-digestion of cattle slurry and maize silage

Digestion trial 4 revealed differences caused by the recirculation of solids in the digesters. This trial was designed to investigate if those differences were a result of recirculating the solids of the cattle slurry, the maize or a combination of the two. Eight 5 l digesters were used in two sub-trials (1 and 2) and operated as duplicate pairs.

Subtrial 1: Digestion of cattle slurry alone with and without solid recirculation.

Subtrial 2: Digestion of maize alone with and without solid recirculation.

In each subtrial the OLR on the digesters was 2.5 g VS l^{-1} d^{-1}, and the retention time was set at 28 days by adjusting the volume of feed, using water containing a 1 ml l^{-1} trace element supplement. The quantity of feed and trace element supplement added is given in Table 8.1. The cattle slurry used in this trial relates to batch 5 in Table 3.9.

Table 8.1: Operational conditions followed by digestion trial 5

Digester	Cattle slurry g wet weight	Maize g wet weight	Water ml	Recirculation
1	119	0	31.1	No
2	119	0	31.1	Yes
3	0	31.1	119	No
4	0	31.1	119	Yes

Determination of the residual methane production

After feeding had stopped in digestion trial 5, the residual methane from the digestate was measured. This was achieved by transferring the digestate from one of each pair of the 5 litre digesters into the 2 litre digesters as used in the BMP trial. The gas produced from each 2 litre digester was collected in a 3-litre tedlar bags and the volume and composition of the gas were measured each time the tedlar bag filled, or after 2 weeks if the bag had not filled in this period. The purpose of this was to determine whether the introduction of solids recirculation affected the post-digestion methane production potential

8.3 Results

8.3.1 Co-digestion: digestion trial 4

Biogas and methane production

Figure 8.1 shows the average daily volumetric methane yield of each digester pair during the digestion trial. It can be clearly seen that the introduction of solids recirculation caused a decline in the volumetric methane yield; the magnitude of this decline varied with the different loading rates and was greater as the loading rate increased. At the 3 g VS l^{-1} d^{-1} loading rate there was almost no change in the volumetric methane yield with solids recirculation, while at the 6 g VS l^{-1} d^{-1} loading rate the volumetric methane yield declined by 0.42 l l^{-1} d^{-1}. The decline observed by the higher loading rates resulted in all loads producing a similar volumetric methane yield in the final 20 days of the digestion trial.

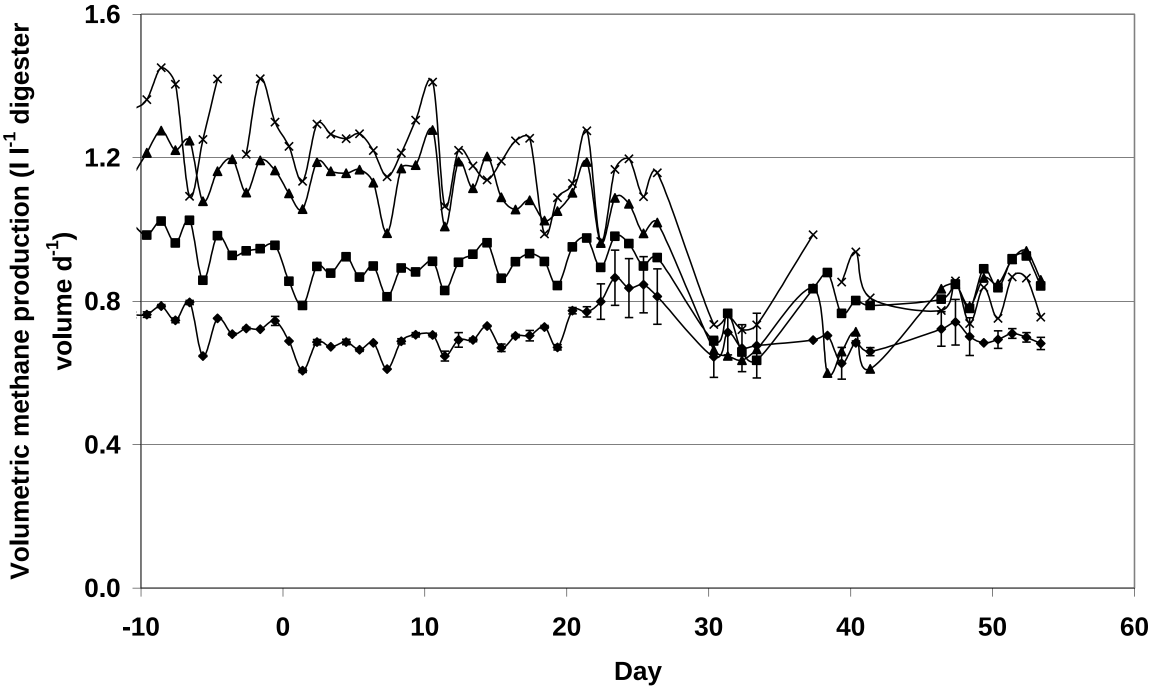


Figure 8.1: Average daily volumetric methane yield of each digester pair during the digestion period for all loading rates tested. 3 g VS l^{-1} d^{-1} (♦), 4 g VS l^{-1} d^{-1} (■), 5 g VS l^{-1} d^{-1} (▲) and 6 g VS l^{-1} d^{-1} (X). The average volumetric methane yield produced during the final 10 days under no recirculation is included for comparison.

Figure 8.2 and Figure 8.3 presents the volumetric and specific methane yield at all loading rates, with both solids and no recirculation, based on the average methane yield from the final 20 days of the digester trial. The specific methane yield under no recirculation was approximately constant as the loading rate increased, while under solids recirculation the specific methane yield declined with increasing loading rate, from 0.23 l g^{-1} VS at the lowest loading rate to 0.14 l g^{-1} VS d^{-1} at the 6 VS l^{-1} d^{-1} loading rate.

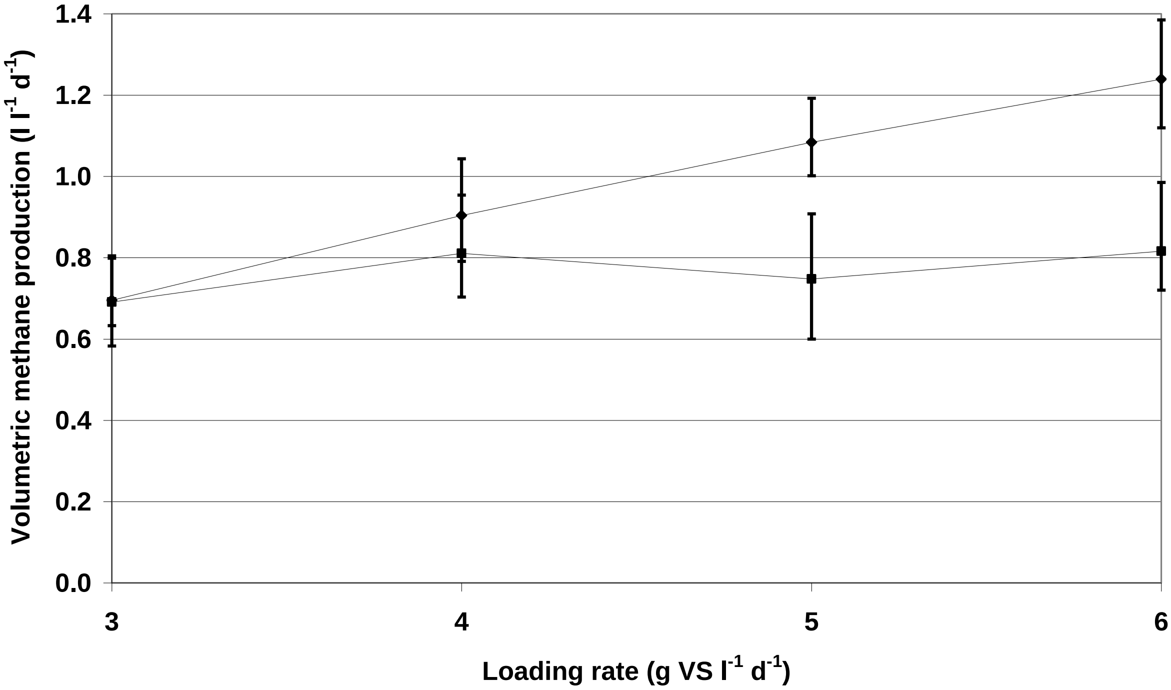


Figure 8.2: Comparison of no recirculation (from trial 3)and solids recirculation at all loading rates tested in terms volumetric methane (no recirculation (♦) and solids recirculation (■)). Values are the average methane yields from the final 20 days of both no recirculation and solids recirculation. The range of each digester pair is shown by the bars.

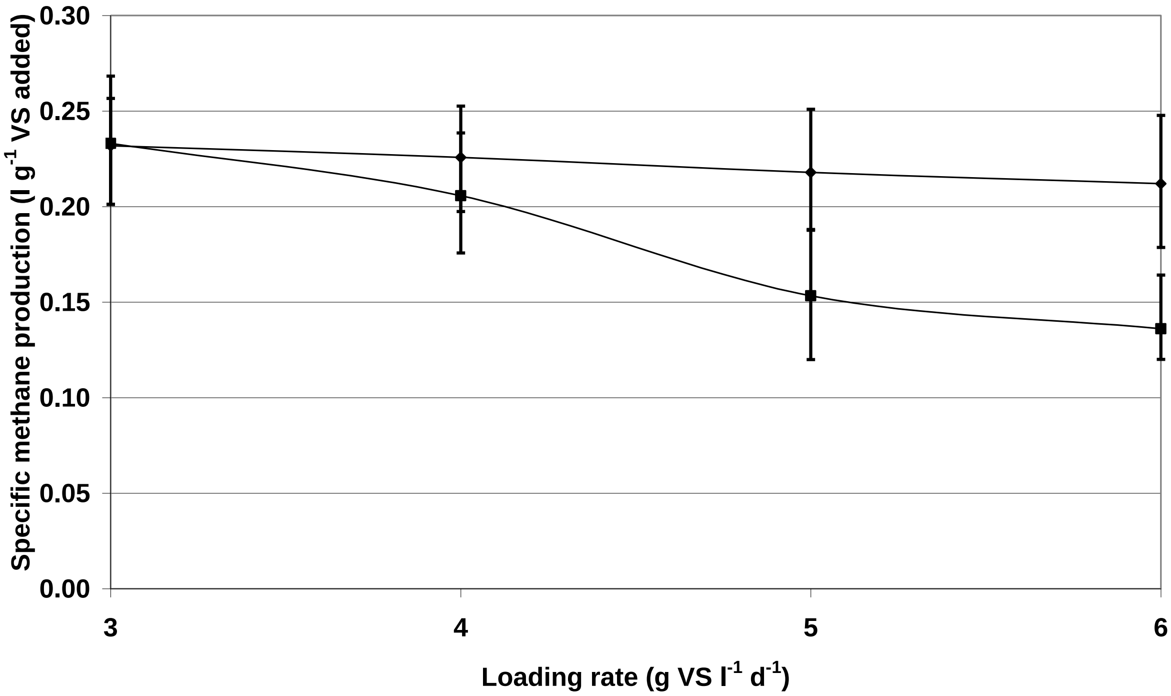


Figure 8.3: Comparison of no recirculation and solids recirculation at all loading rates tested in terms specific methane (no recirculation (♦) and solids recirculation (■)). Values are the average methane yields from the final 20 days of both no recirculation and solids recirculation. The range of each digester pair is shown by the bars.

The decline in performance can also be seen comparison of the volumetric methane yield with the yields calculated from the mono-digestion trials (Chapter 7). This comparison is presented in Figure 8.4; the values shown represent the difference between the two volumetric methane yields. At each loading rate the actual methane yield was lower than the calculated yield with the 6 g VS l^{-1} d^{-1} loading rate presenting the greatest difference of 0.43 l l^{-1}.

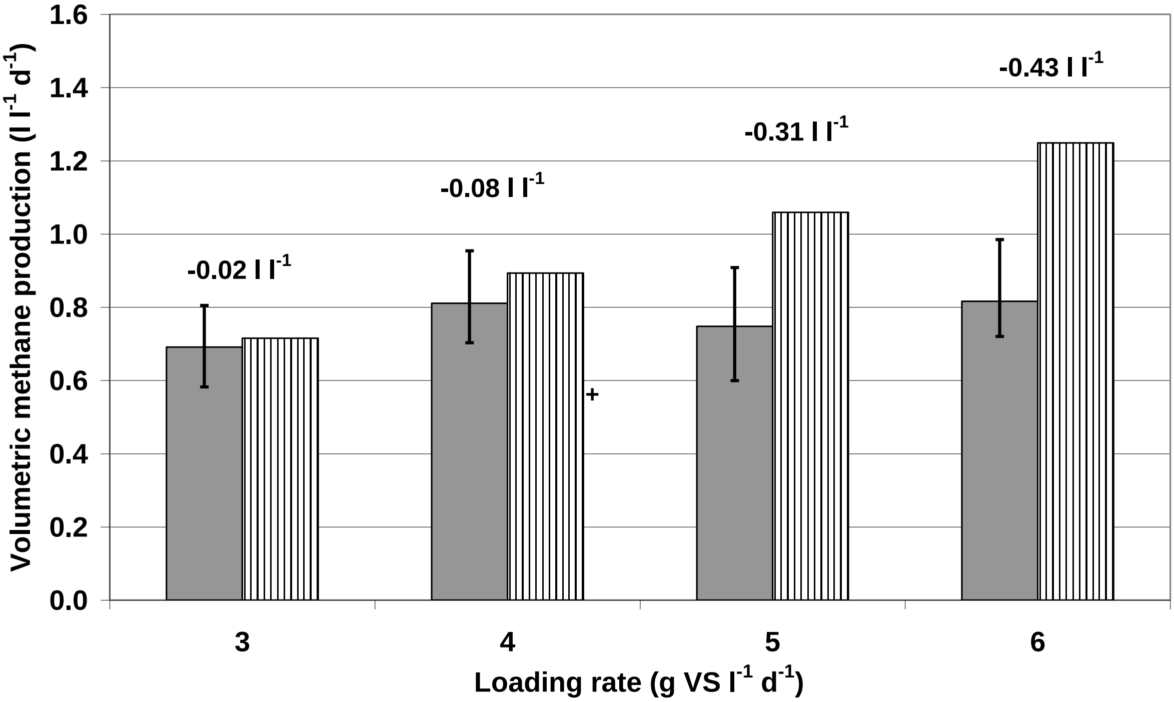


Figure 8.4: Difference in the volumetric methane production (l l^{-1} d^{-1}) between the average methane production of each digester pair (filled bars) and the yield calculated from combining the methane potential of the maize and of the cattle slurry (Table 7.4) (striped bars). The numerical difference and range of yields achieved are also shown.

Despite the decline in the digestion performance it was still possible for maize to be co-digested with cattle slurry at the loading rates of 2.5 and 3 g VS l^{-1} d^{-1} ; in contrast it was shown in Chapter 7 that maize failed to digest at these loading rates under mono-digestion conditions with water replacing the cattle slurry. This indicates that cattle slurry still provided a benefit to the digestion of maize under unstable conditions. The methane production results showed that solids recirculation is not a viable option for improvement of the co-digestion of cattle slurry and maize due to the decline in performance observed. This suggests that the accumulation of the maize solids, cattle slurry solids or a combination of the two created an inhibition to the process.

Digestate properties

In an attempt to discover the cause behind the decline in the specific and volumetric methane yield the digestate characteristics were compared to those of digestate produced when no recirculation was applied. Table 8.2 provides the average values for digestate characteristics of each digester pair at all loading rates under no recirculation (digestion trial 3, Chapter 7) and under solids recirculation. The values are the average of each digester pair from the final 20 days of both digestion trials. The values for pH, total solids and the alkalinity showed instability during the digestion period and this data is presented in Figure 8.5 to Figure 8.7.

Table 8.2: Comparison of digestate characteristics produced at all loading rates following no recirculation and solids recirculation. These are the average of each digester pair from the final 20 days of each digestion trial

Loading rate	**3 g VS l^{-1} d^{-1}**		**4 g VS l^{-1} d^{-1}**		**5 g VS l^{-1} d^{-1}**		**6 g VS l^{-1} d^{-1}**	
Recirculation	None	**Solids**	None	**Solids**	None	**Solids**	None	**Solids**
Ammonia g l^{-1}	1.3	**1.2**	1.2	**1.1**	1.1	**1.1**	1.0	**1.1**
TKN g l^{-1}	3.4	**3.1**	3.3	**3.1**	3.3	**3.1**	3.3	**3.1**
pH	7.3	**7.3**	7.3	**7.2**	7.2	**n/a**	7.2	**n/a**
Cadmium mg kg^{-1} DM	----	**0.6**	0.10	**0.9**	0.83	**1.0**	0.96	**1.0**
Chromium mg kg^{-1} DM	208	**344**	246	**308**	516	**272**	239	**395**
Copper mg kg^{-1} DM	55	**50**	49	**46**	46	**40**	51	**50**
Nickel mg kg^{-1} DM	104	**187**	95	**170**	223	**133**	98	**198**
Zinc mg kg^{-1} DM	108	**155**	179	**144**	150	**128**	157	**121**

*pH for 5 and 6 g VS l^{-1} d^{-1} are not shown due to instability (see Figure 8.5)

Table 8.2 shows that there is no clear difference between the two conditions in terms of the ammonia and TKN concentrations but a difference in the heavy metal concentration can be observed. From the Table it can be seen that the introduction of solids recirculation caused an increase in the level of chromium and nickel, with the exception of the 5 g VS l^{-1} d^{-1} loading rate, which displayed a decline in concentration. As a result of this increase it is shown that solids recirculation does not improve compliance with the PAS110 limits, with chromium and nickel exceeding the upper limits.

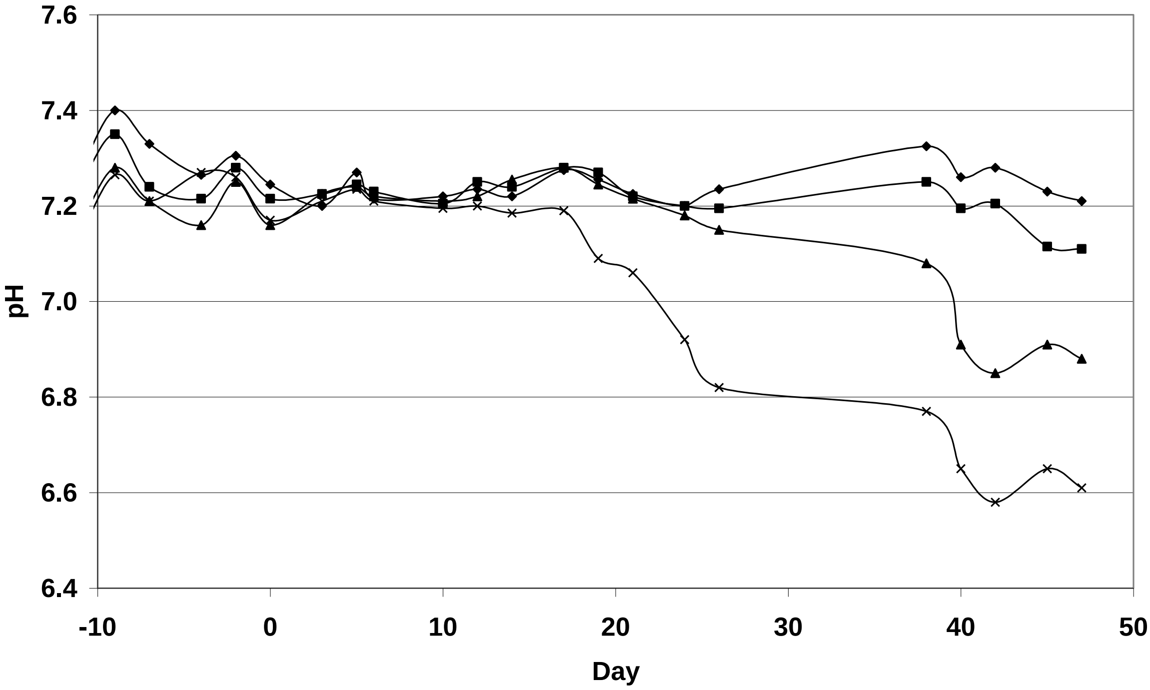


Figure 8.5: Average pH values of each digester pair during the digestion period at all loading rates: 3 g VS l^{-1} d^{-1} (♦), 4 g VS l^{-1} d^{-1} (■), 5 g VS l^{-1} d^{-1} (▲) and 6 g VS l^{-1} d^{-1} (X). The average pH values produced during the final 10 days under no recirculation is included for all loads for comparison.

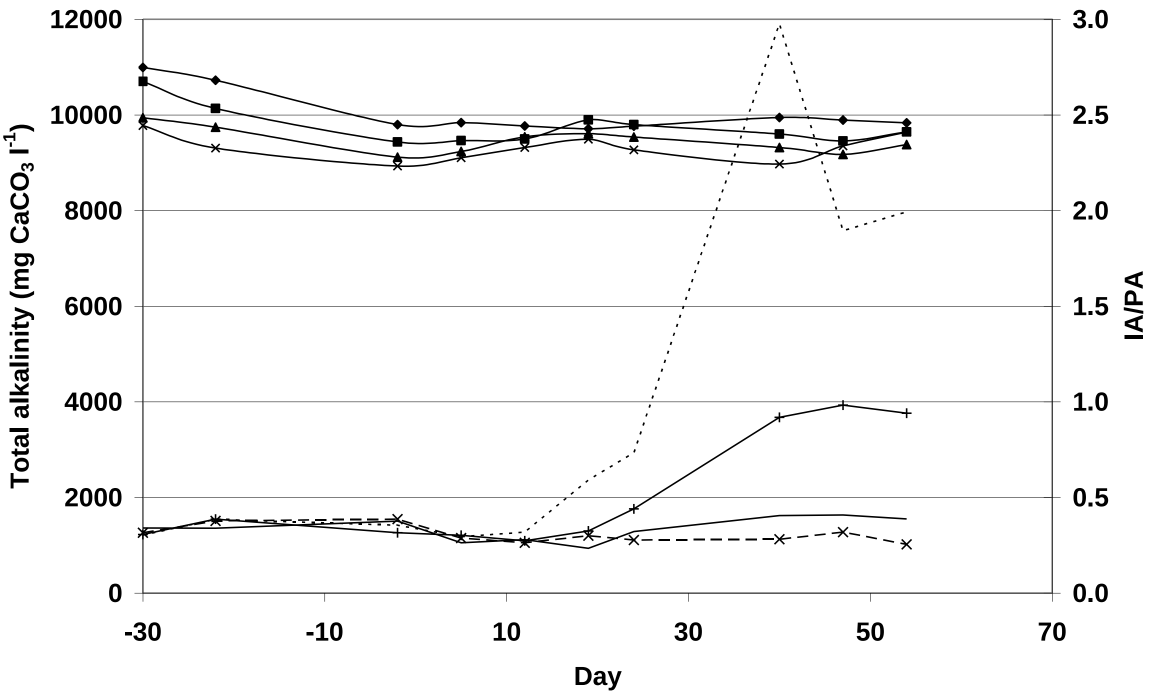


Figure 8.6: Average total alkalinity and IA:PA of each digester pair during the digestion period: total alkalinity (3 g VS l^{-1} d^{-1} (●), 4 g VS l^{-1} d^{-1} (■), 5 g VS l^{-1} d^{-1} (▲) and 6 g VS l^{-1} d^{-1} (X)) and IA:PA (3 g VS l^{-1} d^{-1} (--X--), 4 g VS l^{-1} d^{-1} (—), 5 g VS l^{-1} d^{-1} (+) and 6 g VS l^{-1} d^{-1} (--)). The average values produced during the final 20 days with no recirculation is included for all loads for comparison.

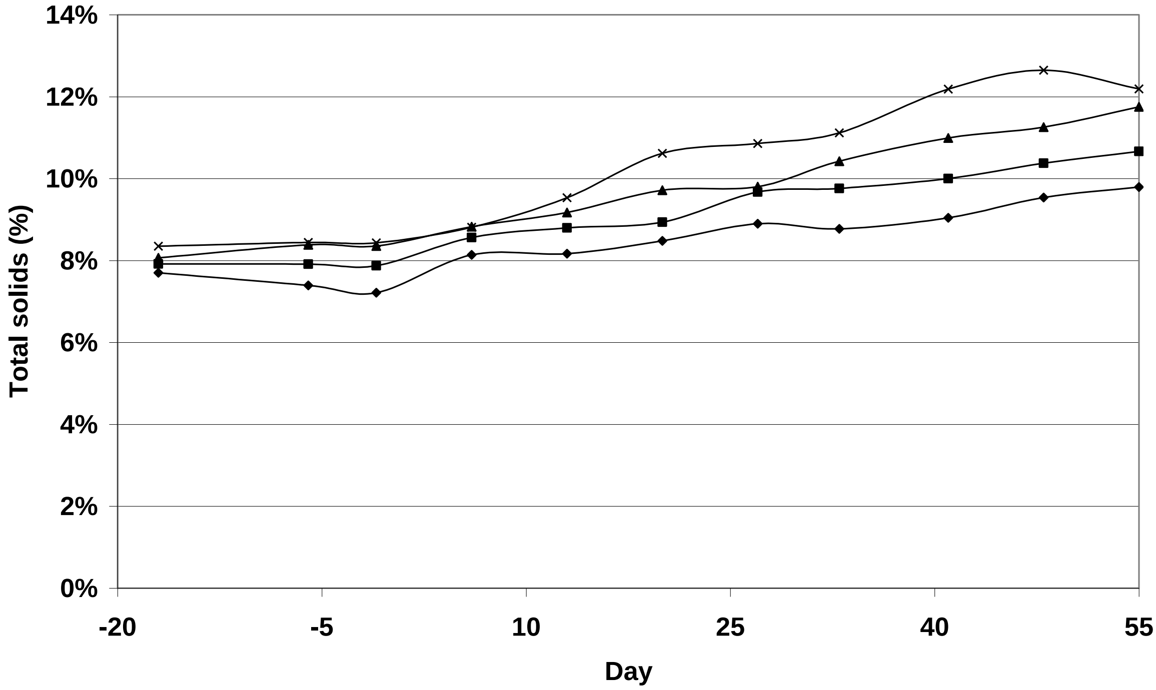


Figure 8.7: Average total solids content of each digester pair throughout the digestion period: 3 g VS l^{-1} d^{-1} (■), 4 g VS l^{-1} d^{-1} (▲), 5 g VS l^{-1} d^{-1} (♦) and 6 g VS l^{-1} d^{-1} (X). The final two TS measurement from the no recirculation trial are included for each load to provide a comparison.

A decline in pH occurs at both the 5 and 6 g VS l^{-1} d^{-1} loading rates, appearing first at the 6 g VS l^{-1} d^{-1} loading rate. From the sharp decline shown it could be predicted that if the digestion period was extended past 55 days the pH would fall below 6, which could result in failure. In addition, it can be seen that at the end of the digestion period the pH at the 3 and 4 g VS l^{-1} d^{-1} loading rates started to decline and it may be at longer digestion periods the lower loading rates could also reach low pH values. In terms of the total alkalinity no significant change can be seen, but the IA:PA ratio at the 5 and 6 g VS l^{-1} d^{-1} loading rates increased up to a maximum value of 3, indicating the disturbance present at the higher loading rates. In terms of the solids content, recirculation led to an increase of total solids within the digester as shown by Figure 8.7. This increase appeared to be steady, with the highest solid content of 12.7%, observed at the highest loading rate. The concentration of VFA within the digesters when there was no recirculation was found to remain constant and below 100 mg l^{-1}. The introduction of the solids recirculation led to this to alter with all loads displaying an increase in concentration and only the 3 and 4 g VS l^{-1} d^{-1} loading rates appearing to stabilise at the end of the trial, as shown in Figure 8.8.

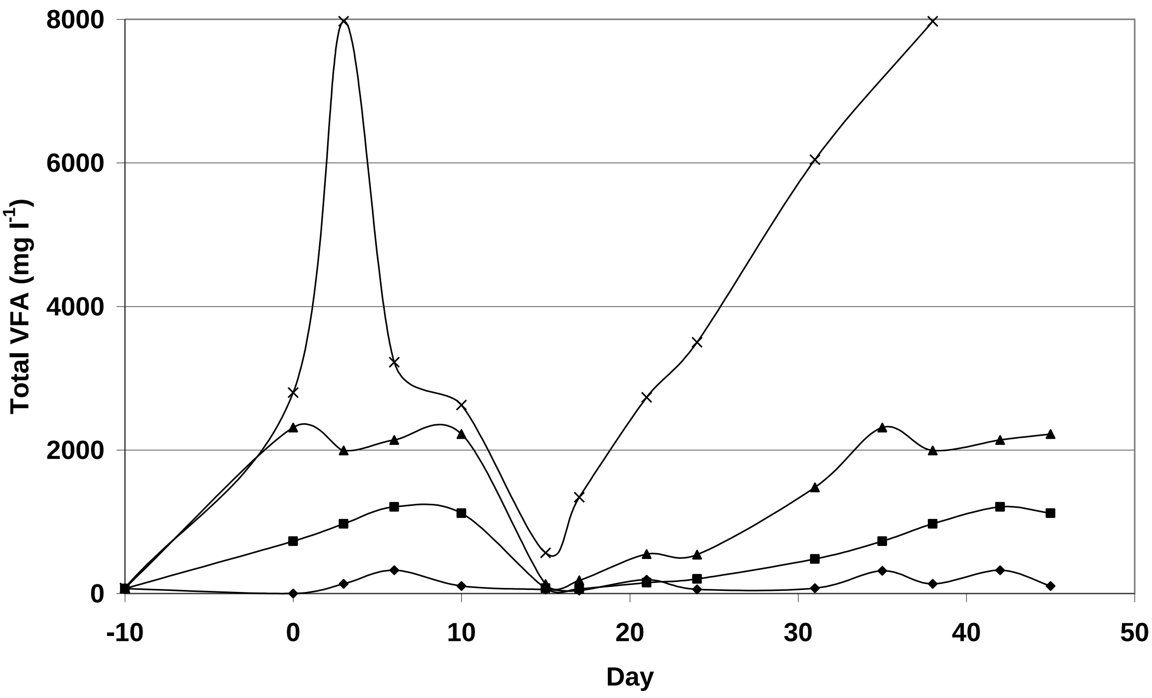


Figure 8.8: Average concentration of the total VFA of each digester pair at all loading rates: 3 g VS l^{-1} d^{-1} (♦), 4 g VS l^{-1} d^{-1} (■), 5 g VS l^{-1} d^{-1} (▲) and 6 g VS l^{-1} d^{-1} (X). The final two measurements from the no recirculation trial are included for each load to provide a comparison.

In line with the decline in the methane yield, the 5 and 6 g VS l^{-1} d^{-1} loading rates displayed the highest VFA concentration; in both sets of digesters it was propionic that was the dominant VFA. This accumulation of acids and the decline in the methane production suggests the methanogenesis stage could have been inhibited due to the failure of the acids to be converted.

The potassium and the phosphorous concentration were also measured with the mass balance shown in Table 8.3.

Table 8.3: Mass balance of potassium and phosphorus at each maize loading. Values are based on the average daily digestate removal over the final 20 days and the average concentration in the raw feedstock (Table 3.9) and the digestate of each digester pair

Maize	Input		Output		Difference (%)	
Addition g VS l^{-1} d^{-1})	Potassium g (as K_2O)	Phosphorus g (as P_2O_5)	Potassium g (as K_2O)	Phosphorus g(as P_2O_5)	Potassium (as K_2O)	Phosphorus (as P_2O_5)
3	0.33	0.37	0.40	0.40	22.3	8.3
4	0.43	0.49	0.51	0.48	17.8	-2.3
5	0.54	0.61	0.55	0.62	1.4	1.5
6	0.64	0.73	0.61	0.80	-6.7	9.1

In terms of the phosphorus, comparing the digestate with the cattle slurry indicates that there was a small difference with an approximate balance shown at all loads. The potassium also showed an approximate balance at the two higher loads however, the 3 and 4 g VS l^{-1} d^{-1} loads produced a digestate that gave a potassium concentration that was greater than that fed to the digester. It could put suggested that an error occurred in the potassium analysis at these two loads. A comparison of the digestate to the raw cattle slurry indicates that the application of the digestate to the field would provide a greater concentration of both elements as a result of the addition of maize. For example, applying 0.22 litres of the digestate produced from the 5 g VS l^{-1} d^{-1} (daily removal rate) would provide 0.55 and 0.63 g of potassium and phosphorus; an equal amount of the raw cattle slurry would provide 0.47 and 0.55 g.

8.3.2 Mono-digestion: digestion trial 5

The purpose of this trial was to attempt to discover the source behind the decline in the methane production observed in the co-digestion trial and to determine the difference made by the introduction of solids recirculation on the digestion of maize and of cattle slurry. This trial used a different batch of cattle slurry (batch 5, Table 3.9) to that in the co-digestion trial so a direct comparison cannot be made but the results were intended to indicate whether one fraction of the feed is responsible for the decline in the co-digestion trial. As indicated in the methodology, each mono-digestion trial was run in duplicate; under no recirculation the duplicate digesters for both cattle slurry and of maize were shown to mirror each other. Under solids recirculation the duplicates did not behave consistent and this section therefore presents the results for digesters with no recirculation as an average of the duplicates but the results with solids recirculation are presented for the two digesters, not as averages.

Biogas and methane production

The gas production from the maize and cattle slurry with no recirculation stabilised within 30 and 10 days respectively. The volumetric methane yield from the maize and the cattle slurry are shown in Figure 8.9 and Figure 8.10 respectively.

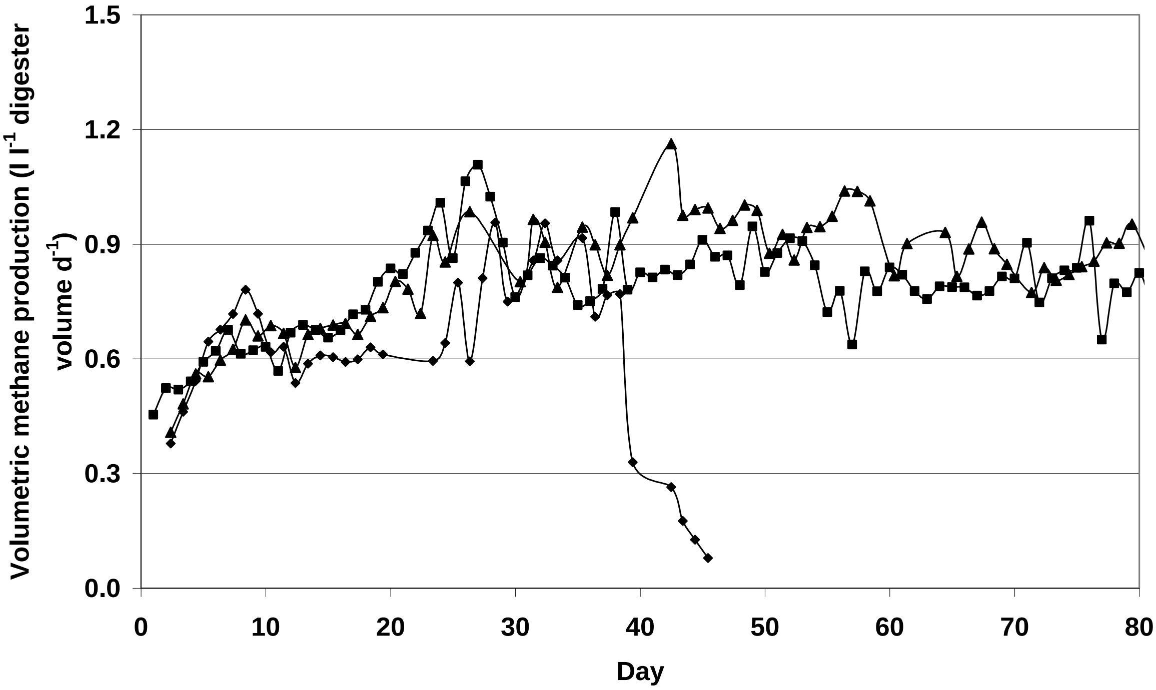


Figure 8.9: Daily volumetric methane yield during the digestion period for maize with no recirculation (■) and with solids recirculation: solid digester 1(▲) and solid digester 2 (♦)

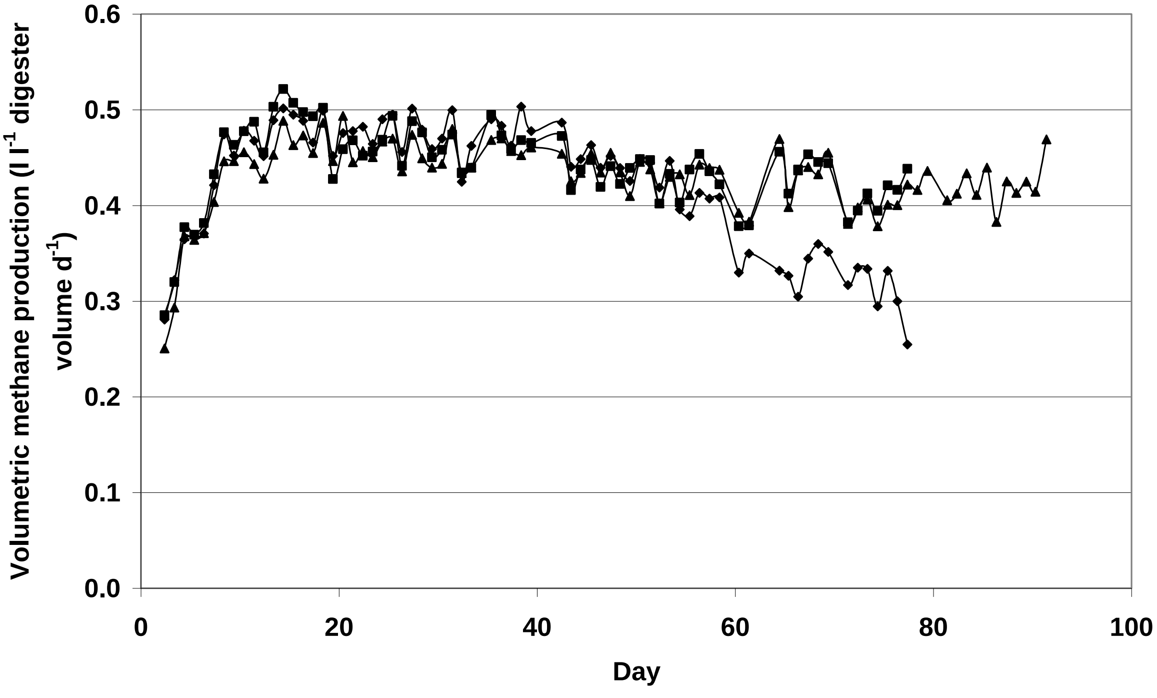


Figure 8.10: Daily volumetric methane yield during the digestion period for cattle slurry with no recirculation (■) and with solids recirculation**:** solid digester 1(▲) and solid digester 2 (♦)

Focusing on the digestion of the maize under solids recirculation it can be seen that one of the duplicate digesters produced a slight increase in the volumetric methane yield, 0.68 l l^{-1} d^{-1} at day 16 to 0.96 l l^{-1} d^{-1} at day 31. In contrast the second duplicate displayed clear signs of failure after 36 days where a sharp decline in the volumetric methane yield was observed from 0.77 to 0.32 l l^{-1} d^{-1} and then downwards. A similar trend can be seen by the digestion of the cattle slurry; however solids recirculation only produced a decline in one of the duplicates and not complete failure in methane production. This decline appeared after 53 days, after which the volumetric methane yield fell from 0.43 to around 0.26 l l^{-1} d^{-1}. The impact of the solid recirculation on the digestion performance is highlighted in Table 8.4, which shows the specific methane yield obtained from the mono-digestion trials. The values represented for the maize solids recirculation are from the digester that did not fail; two specific methane yields are shown for the cattle slurry under solid recirculation due to the different behaviour shown in Figure 8.10 with the second value representing the average methane produciton during the final 3 days for the failing duplicate.

Table 8.4: Specific methane yield and methane composition produced from both substrates following solids recirculation and no recirculation. The values for no recirculation are the average of each digester pair from the final 50 days of the digestion trial. The value for the maize digester under the solids recirculation is the average of the successful digester from the final 50 days; for the cattle slurry the first values is the average of the successful digester from the final 50 days while the second values is the average of the final 3 days of the failing duplicate.

Feed	**Specific methane (l g^{-1} VS added)**		**Methane composition (%)**	
Recirculation?	**None**	**Solids**	**None**	**Solids**
Cattle slurry	0.17	0.17/0.12	58.6	58.9
Maize	0.31	0.36	52.3	53.1

These results indicate that solids recirculation does have an impact on the mono-digestion of the maize and of the cattle slurry as indicated by the difference in methane production. The evidence is conflicting however, as on the introduction of solids recirculation for both substrates, one of the duplicate digesters produced a performance similar to that with no recirculation while the other showed a decline and even failure. The purpose of this trial was to determine if the decline in performance caused by solids recirculation was due to recirculating the solids of the cattle slurry, the maize or both. Despite the conflicting results, both substrates showed evidence of unstable conditions under solids recirculation and it can therefore be deduced that the decline was the result of recirculating solids from both.

An additional result from this trial was the successful digestion of maize at a 2.5 g VS l^{-1} d^{-1} loading rate; this loading rate was shown to fail in the kinetic mono-digestion trial (Chapter 7). This may be explained by the difference in retention time; in digestion trial 3 (Chapter 7) this loading rate had an addition of water resulting in a retention time of 18 days compared to 28 days tested in this current trial.

At the completion of the digestion trial the residual methane of the digestate from all mono-digestion conditions was tested with the results presented in Table 8.5 for the specific methane yield and Figure 8.11 for the volumetric methane yield. The results here represent the residual methane produced from the digestate from one of each digester pair; for the solids recirculation the duplicates that showed success were tested. The residual volumetric methane yield ranged from 5.5 to 11.0 l l^{-1} digestate with the lowest value corresponding to the digestion of cattle slurry alone while the maize under solids recirculation produced the greatest yield. It can be seen that the introduction of solids recirculation led to an increase in the residual volumetric methane yield in both substrates with the increase being more prominent with the digestion of the maize. This increase however, was the result of the greater VS content of the digestate from solids recirculation with Table 8.5 showing that the specific residual methane yield declined as solids recirculation was introduced. The difference between the maize digesters is minimal, only 0.01 l g^{-1} VS but for the cattle slurry the specific methane yield was 0.04 l g^{-1} VS less than the digestate from the cattle slurry under no recirculation.

Table 8.5: Specific residual methane production from cattle slurry and maize with no recirculation and with solids recirculation. The specific methane is in terms of the g VS present in the digester.

Digester	Cattle slurry		Maize	
	No recirculation	Solids recirculation	No recirculation	Solids recirculation
Digestate tested (g)	3005	3075	3041	2876
Final VS measurement (%)	4.33	7.21	3.61	5.82
VS present (g)	130	222	110	168
Methane (l)	17.2	20.4	22.3	32.1
Specific methane yield (l g^{-1} $VS_{present}$)	0.13	0.09	0.20	0.19

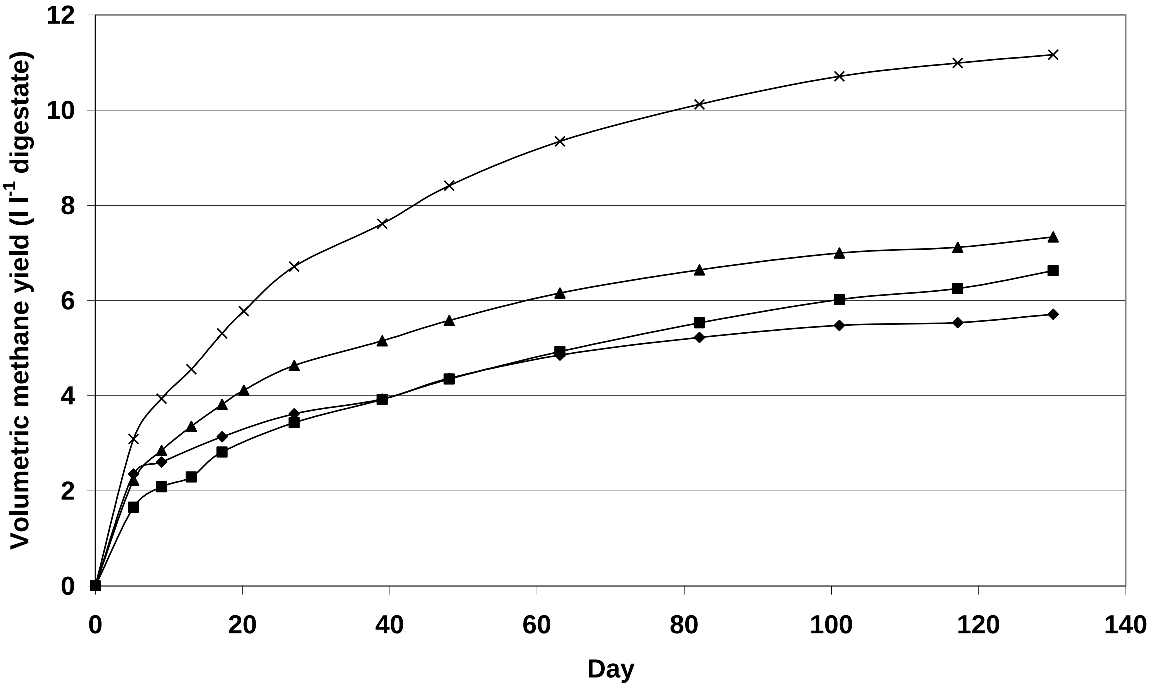


Figure 8.11: Residual methane produced from all digestates: Cattle slurry (♦), cattle slurry with solid recirculation (■), maize (▲) and maize with solid recirculation (X)

Appling the kinetic model, as described in Chapter 3 (section 3.7), a difference in the kinetics constants is observed with the digestates from the digesters under no recirculation giving the highest proportion of readily degradable fraction and the higher rates of degradation.

Table 8.6: Empirical model parameters used for residual methane production of the digestates

	Cattle slurry		**Maize**	
Recirculation	**None**	**Solids**	**None**	**Solids**
Volumetric methane yield ($l\ l^{-1}$)	5.7	6.6	7.3	11.16
Proportion of readily degradable fraction (P)	0.35	0.20	0.30	0.20
Degradation for the readily degradable fraction (K_1)	0.35	0.20	0.35	0.20
Degradation for the slowly degradable fraction (K_2)	0.023	0.02	0.024	0.026
R^2	0.996	0.996	0.999	0.998

Digestate properties

The methane results indicated that stability for both substrates was reached under no recirculation while instability was shown under solids recirculation. In terms of the digestate characteristics stability was shown in all digesters with the exception of the maize digester that showed failure. Table 8.7 gives the digestate characteristics; in line with the methane results the digesters following no recirculation are represented by the average of the duplicates while the solids recirculation conditions are represented by both digesters. Focusing on the digestate obtained under normal conditions (no recirculation) it is observed that the digestion of the cattle slurry produced a decline in the total solid content, 11.8 to 6.9% along with a decline in the TKN concentration, 5.2 to 4.0 g l^{-1}. The concentration of the ammonia fell from 2.0to 1.9 g l^{-1}. These trends were replicated by the digestion of the maize, with the solids content reducing from 34.08 to 4.3% and the TKN values from 4.8 to 2.1 g l^{-1}. Comparing the digestate from the maize and cattle slurry digestion it can be observed that the maize produced a digestate with a lower solids content, ammonia and TKN concentration. The VFA within both digesters remained below 200 mg l^{-1} with the maize digestate displaying the higher concentration

Table 8.7: Digestate properties for both substrates following solids recirculation and no recirculation. Values are the average from the final 50 days with the exception of the maize solid recirculation digester 2, where the values represent the final value achieved.

	Cattle slurry			Maize		
Recirculation	**None**	**Solid digester 1**	**Solid digester2**	**None**	**Solid digester 1**	**Solid digester2**
pH	7.7	7.7	7.7	7.0	7.0	5.2
TS %	6.9	10.4	10.3	4.3	6.3	7.3
VS %	4.4	7.0	7.1	3.6	5.4	6.2
TKN g l^{-1}	4.0	3.6	3.7	2.1	2.4	2.5
NH_3 g l^{-1}	1.9	2.0	2.0	0.7	0.7	1.2
% of TKN	48.1	55.7	53.6	31.8	29.4	29.2
Total alkalinity g l^{-1}	16.1	15.7	5.7	6.5	6.6	7.3
IA:PA	0.2	0.2	0.2	0.4	0.3	0.5
VFA mg l^{-1}	66.3	15.3	58.5	122.7	151.4	1595.1

To determine the impact that solids recirculation has on the digestate a comparison between the different working conditions can be made. In terms of the cattle slurry the introduction of solids recirculation produced a digestate similar to that under normal condition apart from a higher solids content. This is true for both duplicates, with no sign of disturbance in the second duplicate corresponding to the observed decline in methane production. For the maize there was little difference between the digestate properties under no recirculation and with the first maize duplicate digester under solids recirculation. The digestate in the second duplicate digester, where failure occurred, showed a clear difference in terms of its VFA concentration. In addition to the increase in VFA's the second duplicate had an ammonia concentration of 1.2 g l^{-1}, almost double than the first duplicate. The TKN concentration did not show a significant change, leading to the percentage of the TKN accounted for as ammonia to increase from 29 to 49%. The previous trial indicated that introducing solids recirculation to co-digestion led to an increase in the concentration of the heavy metals analysed, in particular nickel and chromium. Table 8.8 gives the heavy metal concentration for each digester.

Table 8.8: Heavy metal concentration within the digesters for both substrates and at both working conditions.

Feed	Cattle slurry			Maize		
Recirculation	None	Solid digester 1	Solid digester 2	None	Solid digester 1	Solid digester 2
Cadmium mg kg^{-1} DM	2	1	1	1	1	1
Chromium mg kg^{-1} DM	352	284	228	124	120	362
Copper mg kg^{-1} DM	70	72	55	73	63	54
Nickel mg kg^{-1} DM	165	121	103	51	48	139
Zinc mg kg^{-1} DM	250	226	218	181	142	142

The heavy metal concentrations shown in Table 8.8 show that there is no clear difference between the cattle slurry digesters. Comparing the digestate produced from the maize digesters it is clear that the main difference is the concentration of chromium and nickel and these metals only appeared to vary in the digestate from the second duplicate digester. The concentrations of nickel and chromium were 88 and 238 mg l^{-1} greater in the failed maize digester when compared to the concentration in the digestate produced without recirculation. Comparing the values with the limits given by PAS110 (Table 2.3, Chapter 2) shows compliance with the exception of the chromium for all digestates and of nickel for the cattle slurry digestate. This was also shown in digestion trial 2 and 3 (Table 6.8 and Table 7.16) indicating that could be a problem with applying the digestate to land. This will be discussed further in the final summary Chapter.

8.4 Discussion

8.4.1 Co-digestion

The idea behind the solids recirculation was to retain the slowly degradable fraction of the maize and the cattle slurry within the digester for longer periods to allow for further degradation. The introduction of recirculation maintained the hydraulic retention time but increased the solids retention time with only the solid fraction below 2 mm (mesh size) leaving the system. The literature suggests that increasing the solids retention time may lead to an improvement in the digestion process for a number of reasons. An increase in the solid retention time can improve the retention of bacteria within the system (de la Rubia *et al.*, 2006). Retention time is also important as it may help in maintaining buffering capacity to aid the digester against shocks, e.g. decline in pH (Gerardi, 2003). Climenhaga *et al.*, (2008) reported the onset of stable and successful performance when solids recirculation was introduced to the digestion of food waste.

In the current research introducing solids recirculation produced a negative impact: a decline in performance was found at all OLRs with the exception of 3 g VS l^{-1} d^{-1} where a constant methane yield was observed with and without recirculation (Figure 8.1). Increasing the OLR past 3 g VS l^{-1} d^{-1} led to a decline in both the specific and volumetric methane yield. The greatest decline was shown at the 6 g VS l^{-1} d^{-1} OLR with the specific methane yield falling from 0.20 l g^{-1} VS $_{added}$ without recirculation to 0.14 l g^{-1} VS $_{added}$ with solids recirculation. At this loading rate the actual methane yield was 0.4 l l^{-1} d^{-1} less than that predicted by calculation. The Hill model in Chapter 7 (Figure 7.10) suggested that under normal conditions the maximum system load is 6 g VS l^{-1} d^{-1}. From the results of this trial it can be deduced that the introduction of solids recirculation lowered the loading capacity of the system, from a loading rate of 6 g VS l^{-1} d^{-1} to 3 g VS l^{-1} d^{-1}. It is clear that the introduction of solids recirculation does not offer a viable option for the optimisation of the co-digestion of cattle slurry and maize.

To determine the source of this decline in performance several parameters were compared in digesters with and without recirculation. It was noted that the introduction of solids recirculation led to an accumulation of VFA's, especially propionic. This suggests that the decline in methane yield could be the result of an inhibition to the methanogenesis; either because an inhibiting factor was accumulating within the digester with the retained solids or because the removal of a slightly larger proportion of liquid led to the more rapid removal of an element that is vital to the digestion performance. Methanogens can be inhibited by a number of different factors, such as ammonia, heavy metals and potassium (Chen *et al.*, 2008). No clear differences were seen between the digesters with and without solids recirculation (Table 8.2), apart from the concentration of chromium and nickel, both of which displayed an accumulation when solids recirculation was introduced with the greatest concentration of both metals occurring at the 6 g VS l^{-1} d^{-1} loading rate. The concentrations failed to reach toxic values, reported as 50-150 mg l^{-1}, for chromium (Alkan *et al.*, 1996, Gerardi, 2003)) and 250 m l^{-1} for nickel (Muñoz *et al.*, 1996, Sanchez *et al.*, 1996). It was mentioned in Chapter 3 that the values for these two metals may be inaccurate due to the failure of the mass balance with the digestate shown to have a higher concentration than that fed to the digesters.

The main difference between the loading rates was the total solids, which was increased from 9.2% to 11.8% at the 3 and 6 g VS l^{-1} d^{-1} loading rates. The solids recirculated back into the digester could contain a high content of slowly degradable or undegradable material (i.e. lignin) resulting in an accumulation of recalcitrant solids. Increasing the loading rate led to an increase in the amount of liquid removed therefore increasing the proportion of these solids in the digester. Evidence that this increase was interfering with the mixing system was shown at the 6 g VS l^{-1} d^{-1} where the motor was shown to slow down. It is known that mixing can affect methane production with Karim *et al*., (2005) indicating that digesters fed with cattle slurry (10% TS content) produced a greater specific and volumetric methane yield than digesters that were unmixed. Reduced methane production has been shown to occur at high solids content; Callaghan *et al.,* (1999) showed that the digestion of chicken manure at a 7.5% solids content produced a methane yield of 0.16 l g^{-1} VS_{added} compared to 0.12 l g^{-1} VS_{added} produced from manure with a 15% solids content. Forster-Carneiro *et al.,* (2008) supported this by showing that the digestion of food waste produced a lower cumulative methane yield as the total solids increased

Another possibility for the decline in performance at the higher loading rates could be the impact that that the solids recirculation had on the bacterial community. Increasing the proportion of recalcitrant solids could be beneficial to bacteria as it increases the amount of surfaces for them to grow. This could lead to a greater production of acids that could be creating an imbalance between the acetogenic and methanogenic stages leading to the quantity of acid to exceed the capacity that the population of methanogens can successfully survive. This is speculative as microbiology assays were not carried in this research so the actual impact that solids recirculation may have on the bacteria communities is unknown; this suggests an area for future work.

8.4.2 Mono-digestion

The mono-digestion trial was set up to discover if the cause of the decline in performance with solids recirculation could be narrowed down to one substrate. This mono-digestion trial produced inconsistent results for the digestion of both maize and cattle slurry, with duplicate digesters failing to show the same behaviour. This inconsistency suggests that the digestion of both substrates under solids recirculation at a load of 2.5 g VS l^{-1} d^{-1} is possible but working conditions are unstable and this load is near the limit of the system capacity. This suggests that the decline in the co-digestion trial was in response to recirculating the solid fraction of both feed substrates.

In the co-digestion trial the decline in performance corresponded to an increase in total solids and the concentration of nickel and chromium; the increase in these two metals was repeated in the maize digester that failed but as with the co-digestion trial concentrations did not reach values described as toxic in the literature. It was also suggested above that the increase in total solids content of the digestate could be a contributing factor as it can inhibit mixing; in the maize digesters the motor was observed to slow down and on some occasions to stop completely. This is not a strong argument, however, as previous studies on the impact of mixing have shown inconsistent results. Furthermore the maize digester that failed had a lower total solids content than the cattle slurry and co-digestion digesters. Despite both substrates showing a negative response to the recirculation of solids, it was the maize that showed failure with the cattle slurry only showing a decline in the methane production during the three retention times tested. Explanations for this can include: the lower buffering capacity or/and the absence of the introduction of bacteria via the cattle slurry. Both the mono-digestion of cattle slurry and the co-digestion trial at the 5 g VS l^{-1} d^{-1} loading rate had a greater total alkalinity than the digestion of maize and it has previously been shown that alkalinity is important in the successful digestion of the maize (Chapter 3). The potential input of bacteria via the cattle slurry can be suggested as an explanation as it could be introducing a consortium of bacteria, including methanogens and the benefit of this has been shown by a number of studies (Gijzen *et al.*, 1986, Kivaisi and Eliapenda, 1995). Again, this is only a speculative explanation and requires further work.

One further observation is that the digestion of maize alone with no recirculation was possible at the 2.5 g VS l^{-1} d^{-1} loading rate; this is in contrast to the results in Chapter 7 where maize digestion failed at the loading rate of 2.5 g VS l^{-1} d^{-1}. The discussion in the previous chapter suggested that the cause of failure was the short retention time and/or the presence of cattle slurry; comparison with the co-digestion trial in that Chapter suggested that the presence of cattle slurry prevented failure. The success of the mono-digestion of the maize in this current chapter at the load of 2.5 g VS l^{-1} d^{-1} but with a longer retention time, 28 compared to 18 days, confirms that extending the retention time in the absence of cattle slurry also leads to an improvement in the digestion performance.

9 Digestion trial 6: Comparison of digestate liquid and solids recirculation in co-digestion of cattle slurry and maize silage

9.1 Objective

It had been shown that recirculating the solid fraction does not provide a viable option to improve the co-digestion process. The objective of this trial was to determine if liquid recirculation provided an alternative option in the improvement of the digestion performance. In addition, a comparison between the performance of solids and liquid recirculation may aid in determining the cause behind the failure of the solids recirculation.

9.2 Methodology

Four 5-litre digesters were used in this trial and operated as duplicate pairs. One pair operated with solids recirculation as described in digestion trial 4. The second pair operated with liquid recirculation which was achieved by following the method detailed in digestion trial 4 but with the digestate liquid returning to the digester. Each digester was fed at a OLR of 5 g VS l^{-1} d^{-1} with a feed containing a 50:50 ratio mix of cattle slurry and maize. As with the previous trials the digesters were fed on a daily basis following a natural retention time of 26 days; Table 9.1 gives the operational conditions for this trial.

Table 9.1: Operational conditions of digestion trial 6

Recirculation	Cattle slurry		Maize		Retention time
	g VS l^{-1} d^{-1}	g (ww)	g VS l^{-1} d^{-1}	g (ww)	d
Solids	2.5	119	2.5	31.1	26
Liquid	2.5	119	2.5	31.1	26

The recirculation of the solid fraction was repeated in this trial as it allowed for the two types of recirculation to be tested with the same batch of cattle slurry; this provides a more accurate comparison between the two types of recirculation. The cattle slurry used in this trial refers to batch 5 (Table 3.8). This batch is the same as that used in the mono-digestion trial in Chapter 8 allowing for a comparison.

9.3 Results

Biogas and methane production

The volumetric methane production for both conditions is shown in Figure 9.1. A clear difference can be seen, with methane production for the digesters under solids recirculation decreasing to a value of 0.27 l l^{-1} d^{-1} at the end of the digestion period. With liquid recirculation methane production was constant at 0.89 l l^{-1} d^{-1} for the first 30 days and then increased and stabilised at 1.44 l l^{-1} d^{-1}.

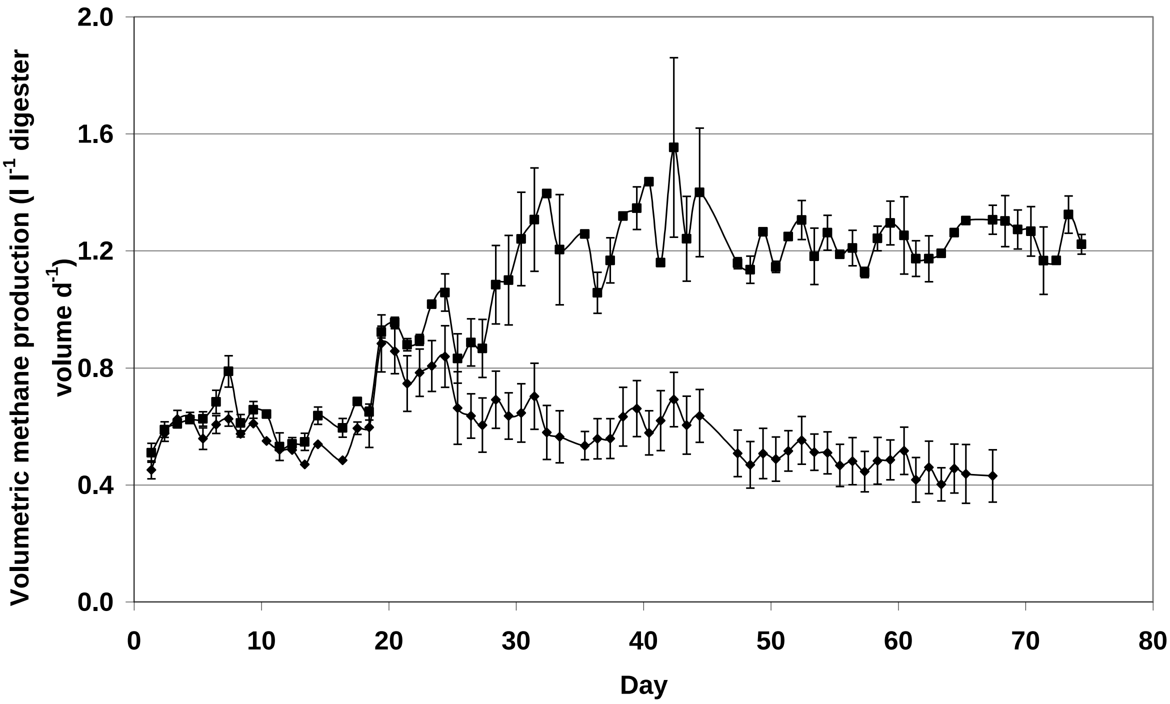


Figure 9.1: Average daily volumetric methane production of each digester pair during the digestion period under both solids (♦) and liquid (■) recirculation. The range of each digester pair is represented by the bars.

The decrease in volumetric methane production seen in the digester pair with solids recirculation confirmed the result from the previous trial providing additional confirmation that solids recirculation is not a viable option. In contrast, the results suggest that liquid recirculation could possibly improve digestion as no failure to the process occurred. The specific methane yield for the two conditions, along with the methane composition is given in Table 9.2 and shows that the value of 0.10 l g^{-1} VS_{added} from the digester with solids recirculation is lower than the methane yield produced from the digestion of cattle slurry alone, given to be 0.17 l g^{-1} VS d^{-1} by the mono-digestion trial. The specific methane yield of 0.25 l g^{-1} VS_{added} obtained from the liquid recirculation is greater than the cattle slurry alone and is similar to the yield produced by the 5 g VS l^{-1} d^{-1}

produced in Chapter 3 (Figure 7.8). This indicates that liquid recirculation does not create an inhibition to the methane production.

Table 9.2: Volumetric and specific methane yields produced from the co-digestion process under solids and liquid recirculation. These values are the average of each digester pair taken from the final 28 days

Recirculation	Volumetric methane $l\ l^{-1}\ d^{-1}$	Specific methane $l\ g^{-1}\ VS_{added}$	Methane composition %
Solids	0.48	0.10	46.1
Liquid	1.22	0.25	56.1

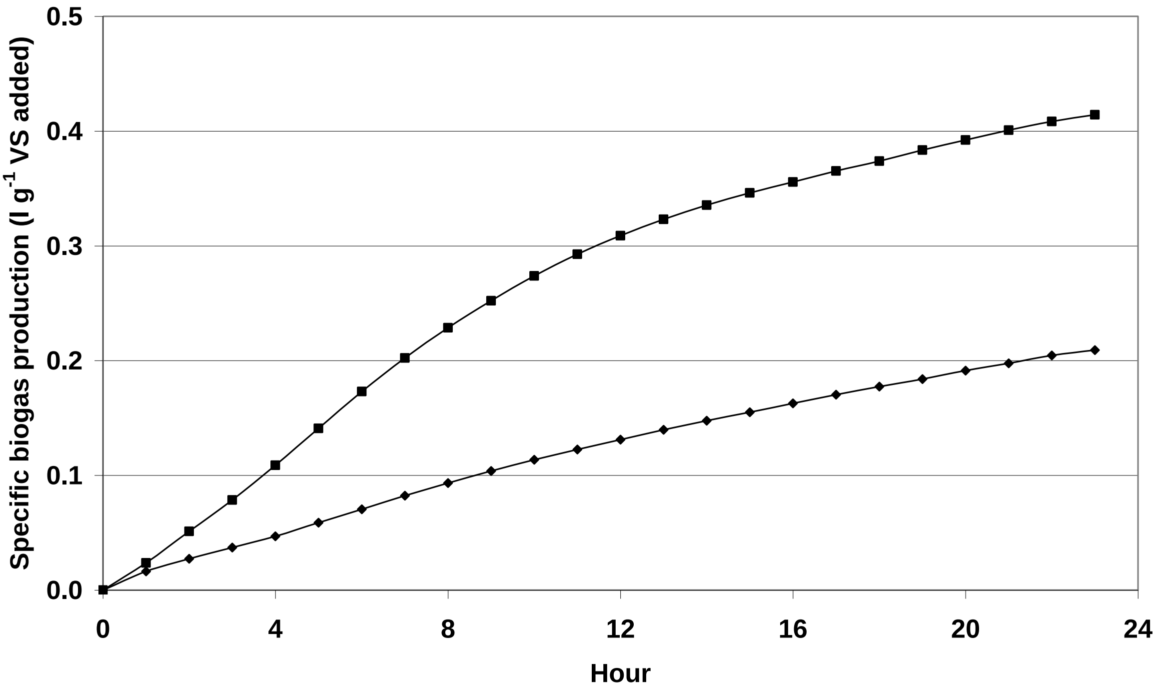


Figure 9.2: Average specific biogas yield produced by each digester pair at both working conditions tested during a 24 hour period at day 54: solids (♦) and liquid (■) recirculation.

Figure 9.2 shows the daily biogas production curve for each condition at day 54. The digesters operating with liquid recirculation followed the same trend displayed by the previous co-digestion trials with the methane production having an initial high rate followed by a lower rate. The initial high rate of 0.027 g^{-1} VS hr^{-1} lasted for a period of 12 hours and was different to the rate of methane production displayed by the digestion trial 3 with the same loading rate but under no recirculation (Chapter 7). In that trial the initial higher production rate lasted for only 6 hours (Figure 7.9) indicating that liquid recirculation may be increasing the quantity of easily/partially degradable substrates available within the system to give a longer period of rapid methane evolution. Over the final 12 hours the rate of production fell to 0.009 l g^{-1} VS hr^{-1}. The digesters operated with solids recirculation gave a rate of production that followed an approximate linear relationship at a rate of 0.01 l g^{-1} VS hr^{-1} over the full 24 hour cycle. The lack of rapid methane evolution after feeding indicates that initial hydrolysis into intermediate products is being inhibited.

The volumetric methane yield was compared to the calculated methane yield of 1.24 l l^{-1}, calculated from the specific methane yields shown in Table 8.4, for digesters operating without recirculation. The results are shown in Figure 9.3 and it is indicated that liquid recirculation is not detrimental to the digestion process but also does not improve the anticipated methane production.

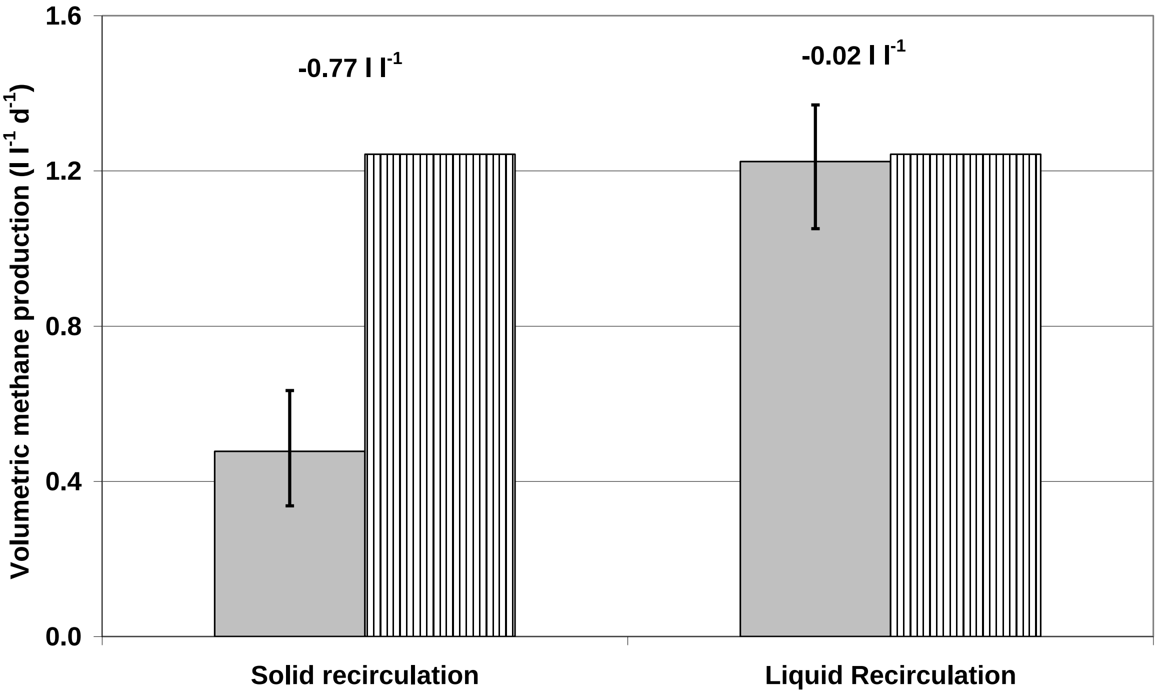


Figure 9.3: Difference in the volumetric methane production (l l^{-1} d^{-1}) between the average methane production of each digester pair over the last 28 days (filled bars) and the yield calculated from combining the methane potential of the maize and of the cattle slurry (striped bars). The numerical difference and the range of the yields achieved are both shown.

At the end of the digestion trial the residual methane production from the digestates was determined over 130 day period and the results are presented in Table 9.3 and Figure 9.4 in terms of the specific and volumetric residual methane production respectively.

Table 9.3: Specific residual methane production from solids and liquid recirculation. The specific methane is in terms of the g VS present in the digester

Recirculation	Solids recirculation	Liquid recirculation
Digestate tested (g)	2686	2450
Final VS measurement (%)	15.9	5.1
VS present (g)	427	130
Methane (l)	23.2	22.0
Specific methane yield (l g^{-1} $VS_{present}$)	0.05	0.17

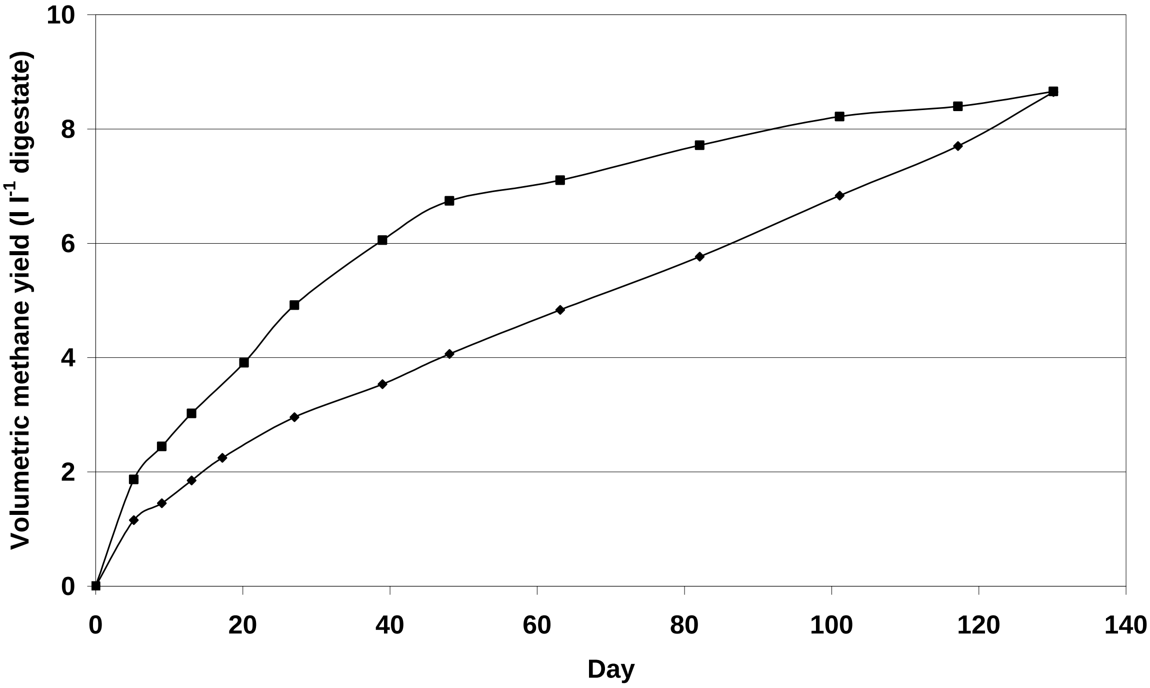


Figure 9.4: Residual methane produced from all digestates: solid recirculation (♦) and liquid recirculation (■)

Table 9.4: Empirical model parameters used for residual methane production of the digestates

Recirculation	**Solids**	**Liquid**
Volumetric methane yield (l l^{-1})	8.65	8.66
Proportion of readily degradable fraction (P)	0.08	0.15
Degradation for the readily degradable fraction (K_1)	0.013	0.10
Degradation for the slowly degradable fraction (K_2)	0.013	0.026
R^2	0.984	0.998

The digestates from solids and liquid recirculation produced very similar 130-day volumetric residual methane yield of 8.65 and 8.66 l l^{-1} digestate. It is clear however, that the residual specific methane yield differed with the digestate from liquid recirculation having a specific yield that was 0.15 l g^{-1} VS greater than that of the solids recirculation. Applying the kinetics model used in the BMP trial (Chapter 3, section 3.7) to the residual methane yield indicated a difference in the kinetics with differential rates of production, as shown by Table 9.4. The slow production of residual methane from the solids recirculation resulted in the cumulative production not reaching a plateau at the 130 day mark suggesting that the methane production would continue.

Digestate properties

In an attempt to determine the reason for the failure of the solids and success of the liquid recirculation several of the digestate properties are compared as shown by Table 9.5 and Figure 9.5,

Figure 9.6 and Figure 9.7. The values in Table 9.5 are the average values of each digester pair from the final 28 days of the trial

Table 9.5: Comparison of digestate characteristics produced by both recirculation regimes. Values are the average of each digester pair over the final 28 days of the digestion trial

Recirculation	Solids	Liquid
Ammonia g l^{-1}	2.7	2.2
TKN g l^{-1}	5.1	5.1
TS (%)	14.9	9.0
Cadmium mg kg^{-1} DM	0.7	1.1
Chromium mg kg^{-1} DM	238	635
Copper mg kg^{-1} DM	49	80
Nickel mg kg^{-1} DM	108	256
Zinc mg kg^{-1} DM	191	279

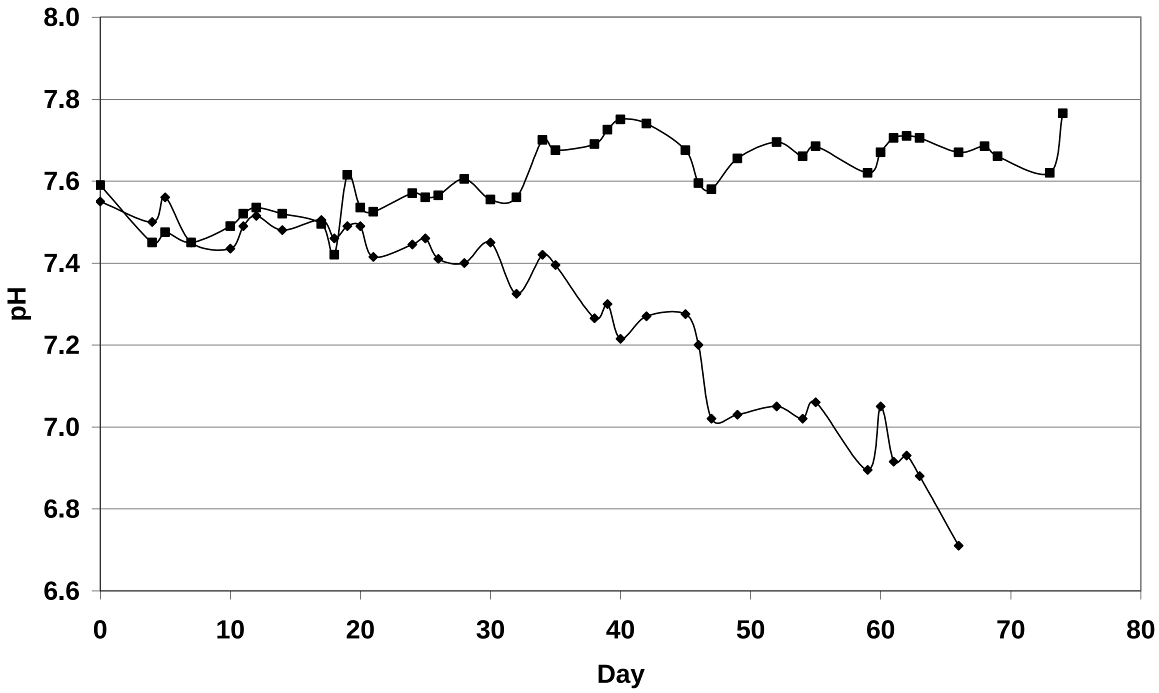


Figure 9.5: Average pH of each digester pair against time for the duration of the digestion trial at both working conditions: solids (♦) and liquid (■) recirculation

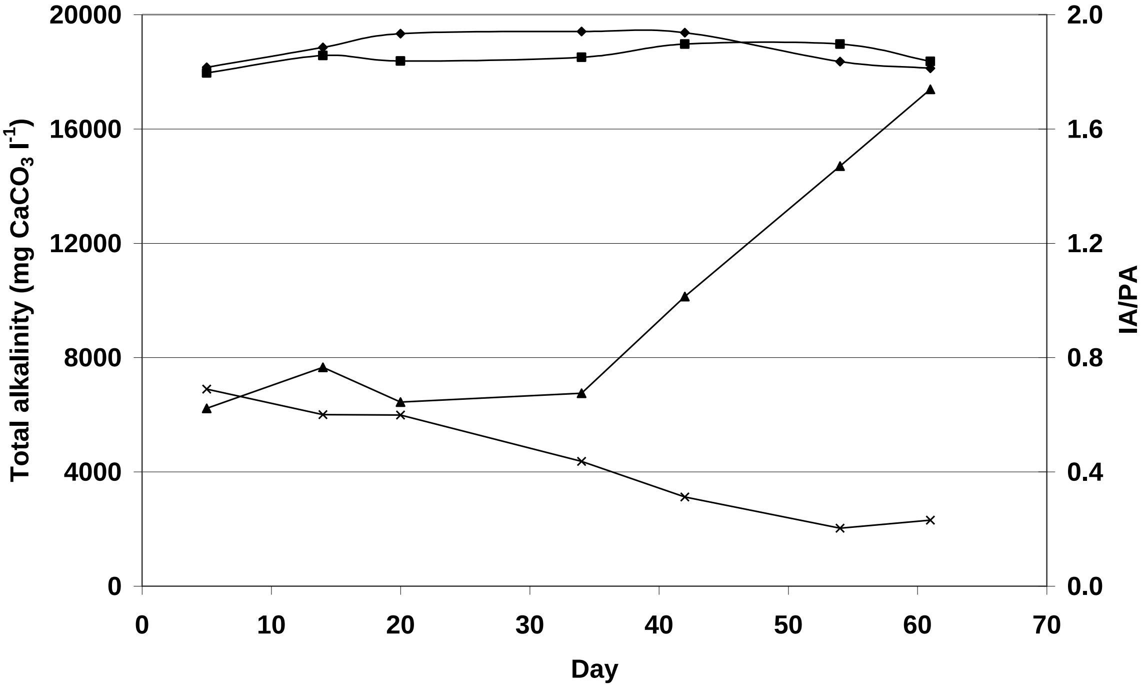


Figure 9.6: Average total alkalinity of each digester pair at different points during the digestion trial: (solids (♦) and liquid (■) recirculation) and the IA:PA (solids (▲) and liquid (X)

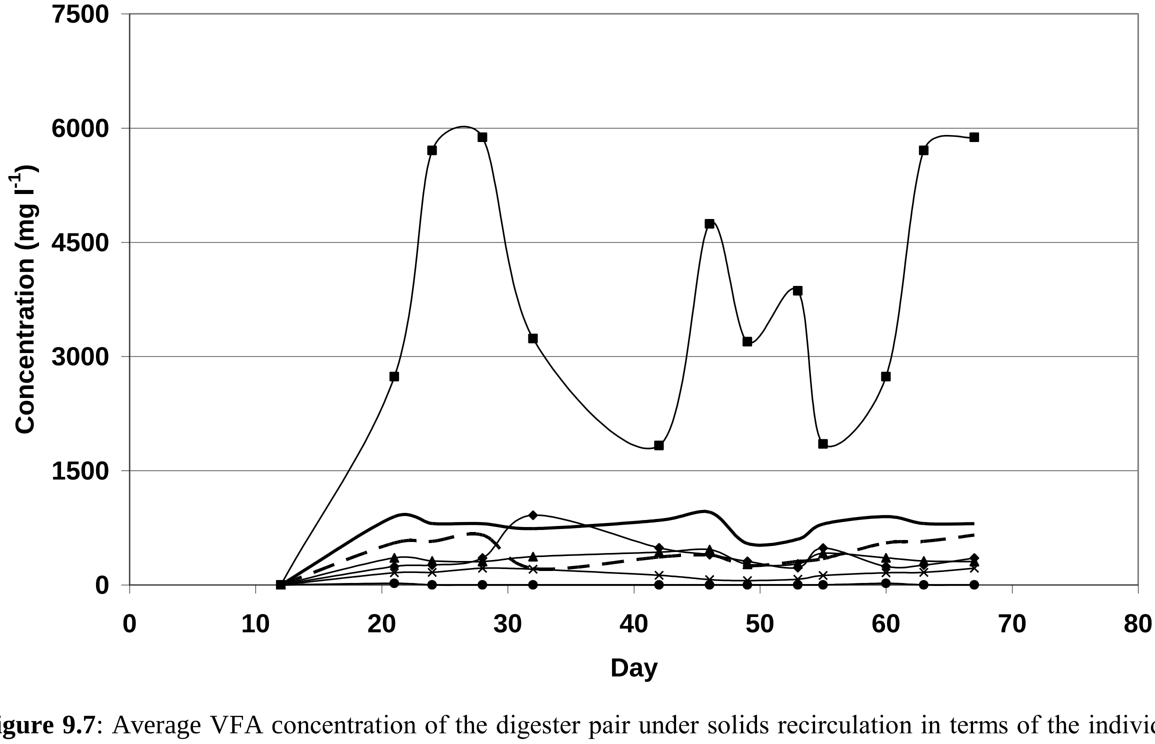


Figure 9.7: Average VFA concentration of the digester pair under solids recirculation in terms of the individual VFA's present at different points during the digestion trial: acetic (♦), propionic (■), iso-butyric (▲), n-butyric (X), iso-valeric (—), valeric (---), hexanoic (+) and heptanoic (●)

The results presented in Table 9.6 show that the different recirculation regimes produced similar ammonia and TKN concentrations with solids recirculation giving slightly higher ammonia. The ammonia concentration of the digestates with both liquid and solids recirculation was higher than in the raw cattle slurry at 2.2 and 2.7 g l^{-1} respectively compared to 1.8 g l^{-1}. A slight reduction in TKN concentration was observed in both digestates, at 5.1 g l^{-1} compared to 5.2 g l^{-1}.

Table 9.6: Daily nitrogen mass balance using the average TKN and ammonia concentration of the feedstock and the average of each digester pair from the final 20 days at all loads.

Recirculation	Daily digestate removal	Nitrogen (g)		Difference	
	l	Input	Output	g	%
Solids	0.15	0.77	0.74	-0.04	-4.8
Liquid	0.14	0.77	0.72	-0.05	-6.9

The decline in the methane yield produced by solids recirculation was reflected by the pH and the IA:PA of the digestate, as shown by Figure 9.5 and Figure 9.6. The pH fell throughout the digestion period, from a pH of 7.5 at day 20 to the final value of 6.7. The total alkalinity remained constant but the intermediate and partial alkalinity changed, resulting in an increase in the IA:PA up to the maximum ratio of 1.74. Figure 9.7 shows the VFA profile, with total VFA concentrations reaching 8000 mg l^{-1}. In contrast, the methane production from liquid recirculation showed more stability during the trial and this was mirrored in the digestate characteristics. A stable pH of 7.7 was achieved while the total alkalinity remained constant at 18.8 g l^{-1}, with a IA:PA ratio of around 0.2 and total VFA concentrations below 350 mg l^{-1}.

The concentration of the heavy metals within the solids and liquid recirculation digesters are shown in Table 9.5 and it is clear that the liquid recirculation led to a greater accumulation of heavy metals than the solid recirculation. For both regimes the concentration of the chromium and nickel is greater then the PAS110 upper limits while the zinc under liquid recirculation exceed the limits.

9.4 Discussion

The objective of this trial was to compare the effect of recirculating the solid and liquid fractions; and to see if this provided any insight into the decline in performance with solids recirculation seen in Chapter 8.

The solids recirculation results repeated those in Chapter 8, with a similar decline in performance shown. The liquid recirculation, in contrast gave stable performance for the duration of the trial, indicating that this could be a viable option for co-digestion of cattle slurry and maize. The success and failure of the two operating modes could be due to a number of factors. Retention of moisture has been identified as one benefit of introducing cattle slurry to the digestion of a high solids material, as the presence of liquid can improve the distribution of elements vital to the digestion process, such as bacteria and associated enzymes (Braun and Wellinger, 2002). In digestion trial 4 it was suggested that solids recirculation could have shifted the balance between the hydrolysis and the methanogenesis. Recirculation of the liquid does not appear to influence the anaerobic digestion process in the same way as the accumulation of VFA's was not shown to occur. This could be due to the lower accumulation of organic material under liquid recirculation reducing VFA production to a level that allows survival and growth of the methanogens. The role of liquid recirculation in the digestion of alfalfa silage was shown by Nordberg *et al.*, (2007) where it led to increased growth of *Methanosarcina* spp.

An omission from this trial was a co-digestion digester with the same batch of cattle slurry but without recirculation. The absence of this makes it difficult to determine whether liquid recirculation could actually improve the digestion performance. In trial 3 in Chapter 7 it was shown that maize and cattle slurry could be successfully digested in equal proportions on a VS basis at a loading rate of 5 g VS l^{-1} d^{-1}, with the actual methane yield equal to the calculated value. The current trial used a different batch of cattle slurry and thus a different retention time, so a direct comparison of results is not possible, but it seems reasonable to assume that the actual and calculated yields would also be equal in this case. In this digestion trial the actual and calculated methane yield were equal indicating that liquid recirculation prevents a decline in performance but does not improve it.

It is clear from this trial and digestion trials 4 and 5 that solid recirculation is not a viable option for the co-digestion process; the reasons behind this is not clear from the analysis undertaken in the research. This result conflicts with previous research where retaining the solids is shown to be beneficial. A speculative explanation for the difference in the operating modes was the impact that recirculation had on the bacterial community; this opens up for further research.

10 Summary

The aim of this summary is to bring together the results obtained by all of the trials undertaken in this research reflecting how the aim and objectives, given in Chapter 1, have been fulfilled.

10.1 Mono-digestion of cattle slurry

The mono-digestion of cattle slurry was not an individual objective of this research but an outcome of the first five objectives. Table 10.1 summarises the volumetric and specific methane yield of the different batches of cattle slurry digested under semi-continuous mono-digestion conditions.

Table 10.1: Volumetric and specific methane yields produced from the mono-digestion of the cattle slurry used in this research .

Batch	Trial (chapter)	OLR g VS l^{-1} d^{-1}	Retention time d	Methane production l l^{-1} d^{-1}	Methane production l g^{-1} VS $_{added}$
1	1 (5)	2	33	0.35	0.13
2	2 (6)	4	19	0.28	0.07
3	2 (6)	4	19	0.69	0.18
4	3 (7)	1.5	29	0.21	0.14
4	3 (7)	2.0	22	0.25	0.13
4	3 (7)	2.5	18	0.30	0.12
4	3 (7)	3.0	15	0.36	0.12
5	5 (8)	2.5	26	0.43	0.17

The range in the specific methane yields, from 0.07 to 0.18 l g^{-1} VS $_{added}$ was expected as literature has shown that digestion of cattle slurry can vary between batches (Figure 2.1, Chapter 2). The impact of the operational conditions has been shown by previous research where it has been highlighted that an increase in the loading rate can result in an increase in the volumetric methane yield (Karim *et al*., 2007) and this holds true for the cattle slurry tested in this research. With the exception of this relationship, there is no clear link between the range of OLRs and retention times tested with the methane yields produced by the cattle slurry. The difference in the methane production could have resulted from a number of differences between the batches, including the concentration of nutrients, the quality of the slurry as an inoculum or the presence of inhibitors, as with batch 2 (winter cattle slurry, Chapter 2). Alternatively, a difference in the TS and VS content, which can influence the retention time, could be influencing the methane recovery.

The summary of the different cattle slurries clearly shows that the second batch was inhibited with the specific methane yield being 61% lower than the highest methane yield achieved. From the measurements made in this research it was the VFA concentration that showed the only difference between the batches; this concentration was 70-85% greater than the four other batches of cattle slurry. Accumulation of acids within the slurry appears to suggest that the fermentation process occurring inside the rumen of the cattle was inhibited somehow. In previous research, inhibition to the digestion of cattle slurry was reported by Misi *et al.*, (2007) where a methane yield of 0.057 l g^{-1} VS was produced, the only suggested explanation for this being ammonia inhibition. For the cattle slurries digested here this explanation seems less likely as the highest ammonia concentration was 2.28 g l^{-1} (batch 3, summer), 22% greater than that reported by Misi *et al.*, (2007). An alternative explanation for the poor digestion performance may be provided by the fact that the second batch of cattle slurry was the only one collected when the cattle were housed indoors Moving the cattle indoors resulted in a change in the diet: to maize/grass silage, rather than fresh grass, with an increase in the concentration of feed supplement. The influence of changing the diet was shown by Amon *et al*., (2001) where a decline in the methane yield was observed when the cattle's diet changed from summer grass to winter hay.

Research into the mono-digestion of cattle slurry has previously been undertaken and a number of these studies investigated the variation that has been shown to occur (Amon *et al.*, 2007, Amon *et al.*, 2001 and Moller *et al.*, 2004). The presence of lignin was put forward as an explanation for the differences: an increase in the amount of lignin in the diet will increase the amount excreted and this was shown to affect the specific methane yield. Unfortunately, lignin has not been measured in the research reported here so this impact is unknown. It was stated by both, Amon *et al.*,(2007) and Moller *et al.*,(2004) that a more balance diet leads to a greater methane yield so a speculative explanation for the poor performance by the winter cattle slurry could be that at the time of collection the cattle diet was not balanced.

10.2 Impact of the addition of maize (Objectives 2-5, 8)

Biogas production

The addition of maize to the digestion of cattle slurry appeared to have a significant impact on the volumetric methane yield where the addition of a small quantity of maize caused the volumetric methane yield to increase by over 200% (Table 7.7). The addition of maize was also shown to be important when the digesters were fed with poor quality cattle slurry, as shown in Chapter 2 in the case of the winter cattle slurry. The difference between the batches of cattle slurry, shown in Table 10.1 makes it difficult to compare the different working conditions tested but the summary in Table 10.2 gives an approximate idea to which conditions would provide the farmer/digester operator with the greatest volumetric methane yield.

Table 10.2: Comparison of the average volumetric and specific methane yield from each co-digestion trial tested in this research following no recirculation. Additionally, the improvement to the volumetric methane yield when compared to the corresponding control is shown. The **bold** values represent the greatest values while the ***bold italic*** values represent the lowest values.

Trial	OLR g VS l^{-1} d^{-1}	Retention time d	Cattle slurry %	Methane yield l l^{-1} d^{-1}	Methane yield l g^{-1} VS d^{-1}	Improvement compared to cattle slurry alone l l^{-1} d^{-1} (%)
1	2	33	100	0.35	0.13	
1	3	30	67.7	0.76	0.21	0.42 (120)
1	4	28	50	1.20	0.26	0.85 (246)
1	5	26	40	**1.46**	0.26	1.11 (320)
2-winter	4	19	100	0.28	0.07	
2-winter	4	24	75	***0.66***	***0.17***	0.38 (137)
2-winter	4	26	65	0.80	0.20	0.52 (185)
2-winter	4	44	25	1.27	0.32	0.99 (355)
2-summer	4	19	100	0.69	0.18	
2-summer	4	24	75	0.97	0.24	0.28 (40)
2-summer	4	26	65	1.14	0.28	0.45 (65)
2-summer	4	44	25	1.34	**0.34**	0.65 (94)
3	3	29	50	0.67	0.23	0.46 (219)
3	4	22	50	0.90	0.23	0.65 (260)
3	5	18	50	1.09	0.22	0.79 (263)
3	6	15	50	1.26	0.21	0.90 (250)

It was highlighted in Chapter 7 that the introduction of cattle slurry increased the level of ammonia and therefore the alkalinity of the system. This appeared to allow maize to be digested at higher loading rates and shorter retention times without a clear decline in the specific methane yield. The importance of the buffering capacity of the cattle slurry was suggested by Angelidaki and Ellegaard (2003) and was shown in the digestion of food waste (Alvarez and Lindén, 2008). In addition, this benefit was highlighted when the stability of the digestion of OFMSW was improved during the initial stages of the process (Capela *et al.*, 2007). This strong support does suggest that the main contribution of cattle slurry to the digestion of energy crop was the buffering capacity. The addition of maize to the cattle slurry was also shown to have a positive influence on the digestion process and this was clearly shown in Trial 2 (Chapter 6). This trial suggested that the addition of maize to cattle slurry played an important role when the anaerobic digester was fed with cattle slurry with low digestibility. This 'dilution' impact was highlighted in Chapter 6 and supports research that looked at dilution as a means of improving the digestion of cattle slurry (Vedrenne *et al.*, 2008). This highlights that both co-substrates can bring benefits to the system and the benefits do not necessarily all come from the introduction of cattle slurry.

Increasing the proportion of energy crops in the co-digestion process appears to produce contradictory results. The research by Nordberg *et al.*, (2005) demonstrated no clear difference in the specific methane yield as the amount of energy crops increased from 45 to 72% while Lehtomäki *et al.*, (2006) indicated that increasing energy crops from 30% to 40% resulted in a decline in the specific methane yield. Explanations for the decline after 30% were not given and from the performance data no clear difference can be observed. The trend shown in the initial two digestion trials of this current research was that of an increase in the volumetric methane yield with an increase in the proportion of energy crops. This supports the previous research but unlike Lehtomäki *et al*., (2006) it was possible for the maize proportion to increase to 75% without a significant decline in the specific methane yield.

The benefit of increasing the ammonia concentration and alkalinity was shown when comparing the digestion of maize alone and with cattle slurry (Chapter 7). These parameters could be responsible for the difference in the energy crop proportion achieved by this research and Lehtomäki *et al*., (2006). In Lehtomäki *et al*., (2006) the digestion of grass and cattle slurry at a 40:60 ratio had a ammonia concentration of 0.5 g l^{-1} while the digestion of maize and cattle slurry at a 75:25 ratio had a concentration between 2 and 2.5 g l^{-1}. The one piece of research that did touch upon the impact of increasing the proportion of maize when co-digested with cattle slurry was Mähnert *et al.*, (2006) and this can be directly compared to digestion trial 2 (Chapter 6) as both followed a similar process. In trial 2 a loading rate of 4 g VS l^{-1} d^{-1} was tested with a three different proportions, ranging from 25 to 75% for both batches of cattle slurries. As the maize proportion increased the specific and volumetric methane yields both showed an increase, supporting the trend shown by Mähnert *et al.,* (2006).

In the literature reviewed in this research, the majority of the co-digestion trials focused on loading rates ranging from 1 to 4 g VS l^{-1} d^{-1} with only Nordberg and Edström (1997) testing a co-digestion mixture of 6 g VS l^{-1} d^{-1}. The impact of increasing the loading rate was tested in Chapter 7 and it was shown that the loading rate could increase to 6 g VS l^{-1} d^{-1} with no clear decline of methane yield during the trial. Application to the Hill model (Husain., 1998) suggested that the maximum load for the co-digestion process, with co-substrates at equal proportions, was 6 g VS l^{-1} d^{-1}; this is 4 g VS l^{-1} d^{-1} lower than the suggested maximum loading rate for dairy cattle slurry (Figure 2.2). The literature review highlighted the fact that minimal research has been undertaken on the impact of increasing the loading rate on a fixed proportion of co-substrate. This gap in the research was addressed by the trials reported in Chapter 7 which provided a detailed study on the impact that increasing the load had on both the mono-digestion of the substrates and when they were co-digested in equal proportions. Both Lehtomäki *et al*. (2006) and Mähnert *et al*. (2007) highlighted that increasing the loading rate resulted in a decline in the specific biogas yield. The specific methane yields given in Chapter 7 were only shown to decline by 0.02 l g^{-1} VS in comparison to an increase in the volumetric methane of 0.59 l l^{-1} d^{-1} suggesting that, unlike the work by Lehtimäki *et al.,* (2006), increasing the load past 3 g VS l^{-1} d^{-1} can be beneficial in terms of the methane output.

Digestate

In addition to the production of biogas, the impact that co-digestion had on the characteristics of the digestate was also investigated as this has often been ignored or forgotten in previous co-digestion research. Section 2.5 of the literature review focused on the application of the digestate and it highlighted that a number of characteristics changed upon digestion including the reduction in methane emitted after application (Amon *et al.,* 2006a, Clemens *et al*., 2006, Weiske *et al.,* 2006). This was supported by the residual methane yield trials undertaken on the digestate produced by the mono-digestion trials in Chapter 7; a decline of 24% and 36% was shown by the cattle slurry and maize respectively. The impact that co-digestion, with no recirculation, had on the residual methane yield was not tested but the impact that solids and liquid recirculation had was investigated in Chapter 9. In both cases the post-digestion methane production was lower than that produced during digestion, 50% and 32%. The impact that the addition of maize had on the residual methane yield was not touched upon in this research but the impact of the addition of a co-substrate was highlighted by Clemens *et al*., (2006) where the addition of potato starch to cattle slurry was shown to lower post-digestion emissions.

In addition to the release of methane the application of cattle slurry to the land has been associated with the emission of ammonia. Clemens *et al.,* (2006) showed that emissions of ammonia related to an increase of ammonia that occurred upon digestion. An increase in ammonia was shown in all trials when the cattle slurry was digested but the addition of maize resulted in a reduction in concentration suggesting that the addition of maize could be having a positive influence on the emissions.

An important characteristic highlighted by the literature review was the dry matter content and the positive influence that digestion had by reducing this content (Johnson *et al.,*2005, Smith *et al*., 2001a, Thompson and Meisinger.,2002, Misselbrook *et al.*,2005). This was repeated in all the trials tested which also highlighted that the addition of maize reversed this, with an increase in dry matter content as the quantity of maize increased. The negative impact of digesting cattle slurry was the increase in the pH which, as shown by Sommer *et al.,* (1993), can result in an increase in the loss of ammonia during storage. The impact of the addition of maize was to reduce the pH but only by one unit in the first two trials. The range of impacts that the addition of maize has on the digestate, both positive (ph, ammonia, VFA content) and negative (dry matter), could be counterbalancing each other. For example, the increase in the dry matter may lead to an increase in emissions and a reduction of nutrients reaching the crops but the decline in pH and ammonia may be contributing to a reduction of ammonia emissions. The actual impact that the addition of maize can have on associated emissions is not known but opens up to interesting future work.

In an attempt to determine how the different scenarios effect the total emissions produced by the farm a GHG emissions calculator (Salter, pers comm 2010) was applied and the results are presented in Table 10.3. This uses the case study of a large dairy farm with the following constraints:

- 192.5 hectare total area
    - 162.5 hectares for grazing (*based on a stock density of 2 livestock units per hectare)*
    - 22 hectares for maize silage (fodder for cattle)
- 325 Cattle herd
    - 150 followers (such as bulls, calves)
    - 175 dairy
- Cattle are housed indoors for 50% of the year
- Farm has an on-site CHP unit

The model assumes that the farm remained as a dairy farm with the herd size and supporting land remaining constant; it was therefore assumed that the farmer would rent or buy additional land for the maize required by the digester. Table 10.3 gives the associated GHG emissions produced and saved by different working conditions; these conditions relate to those tested in this research, as summarised by Table 10.1 and Table 10.2

Table 10.3: GHG emissions

OLR	HRT	Cattle slurry	Digester size	Land required for maize	Emissions from fossil fuels required	Emissions saved by exported energy	Total emissions
kg m^{-3}	d	%	m^3	ha		Tonnes ($CO_{2\,eq}$)	
2	37	100	172	0	341	40	301
3	33	67.5	166	5	344	87	257
4	30	50	163	10	348	133	215
5	27	40	165	15	352	183	169
4	19	100	86	0	341	42	299
4	22	75	110	3	343	65	278
4	25	65	126	5	344	88	256
4	43	25	318	29	362	314	48
3	40	50	221	10	348	136	212
5	24	50	133	10	348	136	212
6	20	50	111	10	348	136	212

NB: Assumes a methane potential of 0.18 and 0.35 l g^{-1} VS for cattle slurry and maize respectively

The GHG emissions considered here include the emissions produced from the fuel required by the farm and the emissions saved by exporting the energy produced from the digester, in terms of carbon dioxide equivalents ($CO_{2\,eq}$). The emission balance of the farm, in the absence of a digester, was calculated to be 341 tonnes $CO_{2\,eq}$; comparing this value with the emission balance produced by introducing a digester indicates an emission savings at all scenarios. The emissions from the energy required by the farm did increase as the maize proportion increased however; this was shown to be counterbalanced by the increase in the emissions saved by exporting the energy produced by the digester. It was the 25% cattle slurry proportion that produced the greatest emissions saved resulting in the total emissions being just 48 tonnes $CO_{2\,eq}$., 208 tonnes CO_2 eq lower than that of a equivalent loading rate but with a cattle slurry proportion of 65%.

VFAs and phenols are the main contributors odour and these have been shown to be reduced during digestion (Powers *et al.*, 1999) When compared to cattle slurry, which is commonly applied directly to land, it was shown in all the trials the concentration of VFA's declined suggesting a potential decline in odour. Upon the addition of maize, no significant difference was shown with the exception of the trial testing the winter cattle slurry (Chapter 6) where the addition of maize resulted in a decline in VFA's suggesting a beneficial impact on the odour.

The heavy metal contents of the digestates produced in digestion trial 2 (Chapter 6: winter cattle slurry) and digestion trial 3 (Chapter 7) were tested and compared to the upper limits specified in PAS110 (Table 2.3). From the comparison it was shown that chromium, nickel and zinc all exceeded the upper limits indicating that application of the digestate would result in non-compliance (British Standards Institute, 2008). The PAS 110 limits are expressed in terms of mg kg^{-1} DM so compliance of the digestate is less likely to be achieved as digestion reduces the DM content, increasing the concentration. A more suitable approach would be to determine the quantity of heavy metals applied to a field from the raw cattle slurry and the digestate; this is shown in Table 10.4. This comparison is based on the application of the slurry/digestate to a 22 hectare field growing maize with a soil nitrogen supply index of 1. The quantity of slurry/digestate applied was calculated based on recommended fertiliser inputs of 80, 85 and 205 kg ha^{-1} N, P_2O_5 and K_2O (Defra, 2000). The data used for the raw cattle slurry was the average of the five batches used in this research.

Table 10.4: Quantity of selected heavy metals to a 28 hectare field growing maize assuming limits of 80, 60 and 250 kg^{-1} for nitrogen, phosphorous and potassium. The digestates relate to that produced in digestion trial 2 (winter) and in digestion trial 3 (co-digestion trial).

OLR	**Cattle slurry**	**Digestate required (based on limit for P_2O**		**Cadmium**	**Chromium**	**Copper**	**Nickel**	**Zinc**
kg m^{-3}	**%**	**t (ww)**	**t (DM)**		**kg**			
4	100	622	53	0	19	4	12	14
4	75	676	57	0	9	3	5	15
4	65	679	60	0	12	3	7	13
4	25	589	61	0	28	3	13	10
3	50	601	45	0	9	2	5	8
4	50	610	48	0	12	2	4	9
5	50	594	49	0	25	2	11	7
6	50	611	51	0	12	3	5	8
Raw Cattle slurry		**598**	**63**	**0**	**36**	**3**	**17**	**14**

Despite the concentrations showing non-compliance with the upper limit, chromium, nickel and zinc all showed lower or equal quantities to that applied from the raw cattle slurry. This indicates that applying limits in terms of the dry matter content to the use of digestate as a fertiliser may not be sensible and may not give an accurate picture of the actual amount of metals applied to the field.

10.3 Synergy (Objective 5)

Literature on co-digestion has resulted in a number of studies suggesting that synergy between the substrates may occur (Machmuller *et al.,* 2007, Lehtimäki *et al.,* 2006) However research by Mähnert *et al.,* (2006) suggests that it is possible to calculate the biogas yield of a co-digested mix by the sum of the individual substrates. In the first long term trial undertaken in this research there was evidence of potential synergy but subsequent trials suggested that this could have been due to the inaccuracy of measuring the predicted methane yield and/or the impact of washout. Research by a number of different authors highlighted the difference between digesting substrates under batch and long term trials (Callaghan *etal.,* (1998,1999)) suggesting that quoting the presence of synergy based on comparison of batch and long term trials could be brought into doubt (Lehtimäki *et al.,* 2006, Chapter 5, this research). One strength of this research is that it attempted to increase the accuracy in the calculation of the predicted yield by comparing trials that followed the same operational conditions. The comparison between the mono and co-digestion trials in Chapter 7 provided support for the statement given by Mähnert *et al.,* (2006) as the calculated combination of the maize and cattle slurry methane yields, determined by long term mono-digestion trials, gave a yield that was more or less equal to that produced by co-digestion of the two substrates.

10.4 Impact of recirculation (Objective 6-7)

The purpose of introducing recirculation to the system was to see if the co-digestion process could be improved by increasing the methane yield produced. For the solids recirculation instead of improving the digestion performance, a decline in biogas production was shown indicating inhibition. Liquid recirculation did not show failure but it was suggested in Chapter 9 that an improvement to the process was not achieved questioning the benefit of the introducing liquid recirculation. This held true for both the co-digestion process and mono-digestion process.

There is no published work on the impact of solids and liquids recirculation on cattle slurry and maize and from the data measured in this report it is difficult to determine the explanation behind the failure of recirculating the solids. Alkalinity and ammonia concentration have been shown to be important parameters for the digestion process both in the literature (refs/chap reference) and in this research, however, when comparing the digesters following no recirculation and solids recirculation no clear difference in these parameters was observed suggesting that solids recirculation was not affecting these parameters. The literature review highlighted the benefits that have been identified from the use of cattle slurry, outlined by the three statements from Angelidaki and Ellegaard (2003) listed in section 2.3.1. By recirculating the solids the benefit of a high percentage of liquid within the system is reduced. This potential impact was highlighted in Chapter 8 and the negative impact of solids content has been shown in previous research (Callaghan *et al*., 1999, Forster-Carneiro *et al.*, 2008). This is only speculative as it is not known how the increase in the solids content is influencing the co-digestion process and as mentioned in the final discussions of the trials, further research will be required to determine what is creating the inhibition or what is being removed in the liquid fraction.

10.5 Identifying the optimal working conditions

The overall aim of this research was to identify the optimal working conditions that allowed for the maximum methane production to occur from the combination of cattle slurry and maize. The working conditions tested by this research were: the loading rate, the proportion of cattle slurry and recirculation. Specific recommendations for the full scale digestion of cattle slurry and maize are difficult to quote due to differences shown by the batches of cattle slurry tested in this research. However, by fulfilling the objectives, optimal conditions can be suggested to be in the range of 4 to 5 g VS l^{-1} d^{-1} for the loading rate and a cattle slurry proportion of 25 to 50%. It is recommended that no type of recirculation should be included as this research has not shown any benefit of introducing recirculation, liquid or solid.

While meeting the aim of the research, the impact that increasing the co-substrate had on the digestate characteristics was considered as this has often been overlooked in co-digestion studies. It was highlighted by all trials that increasing the quantity of maize may result in an increase in the methane yield but, at the same time have a negative impact on the digestate (e.g. increase in total solids). This suggests that when choosing from the optimal ranges it is important to consider the potential impact that it can have on the second output of anaerobic digestion: the digestate.

11 Conclusions and future work

11.1 Conclusions

The aim of this research was to identify the optimal working conditions that allowed the maximum methane production to occur from the combination of cattle slurry and maize while ensuring that the full potential of both substrates was achieved. Additionally, the influence that the combination of cattle slurry and maize had on the properties of the digestate was presented.

The following conclusions can be drawn from this research:

- Introducing maize to the digestion of cattle slurry had a pronounced effect on the volumetric methane yield with improvements up to 355% when compared to the mono-digestion of cattle slurry. In the case of the kinetics trial the loading rate of the cattle slurry could be doubled by the addition of an equal quantity of maize, on a VS basis, with the volumetric methane yield increasing by over 200% without a great loss of the methane potential of the maize

- The co-digestion of cattle slurry and maize was successful at loads ranging from 3 to 6 g VS l^{-1} d^{-1} and at cattle slurry proportions from 25 to 100%. This included successful digestion at retention times as low as 15 days. Increasing the quantity of maize led to the volumetric methane yield increasing at all conditions tested with the specific methane yield increasing or remaining approximately constant.

- The greatest volumetric methane yield of 1.46 l l^{-1} d^{-1} was produced at the 5 g VS l^{-1} d^{-1} loading rate with a 40% cattle slurry proportion while it was the 4 g VS l^{-1} d^{-1} load with 25% cattle slurry that gave the greatest specific methane yield of 0.34 l g^{-1} VS d^{-1}.

- It was shown that different batches of cattle slurry produced a range of specific methane yields, from 0.07 to 0.18 l g^{-1} VS d^{-1}; the impact of this on the co-digestion process was shown by the replacement of the winter cattle slurry with a summer collected batch. The winter cattle slurry had the lowest methane yield of all batches but the digestion process was still possible, with the addition of maize at a 1 g VS l^{-1} d^{-1} load producing an increase in the volumetric methane yield by 141%. This improvement in the yield indicates that the addition of maize could be vital during times of poor quality cattle slurry. An additional conclusion that can be drawn from the change in batch of cattle slurry is that the process can recover rapidly after times of poor quality cattle slurry: introducing the summer cattle slurry led to an increase in the methane yield within 23 days.

- Previous literature has suggested that synergy can occur during the co-digestion process and this appeared to be supported by the first two digestion trials. This was brought into doubt by the kinetics trial where an improved method of calculating the predicted yield was tested and no increase over the predicted value was shown. This does not necessarily invalidate the concept of synergy but it can be suggested that the improved performance shown in this research was the result of an inaccurate or inappropriate determination of the predicted yield. In the case of the winter cattle slurry (Chapter 6), the improved performance was likely to be the result of diluting the cattle slurry with maize.

- Solids recirculation was tested in this trial, which was a new approach in the co-digestion of cattle slurry and maize; however, this was shown not to be viable due to the decline in methane performance. This was also the case for the mono-digestion of the two substrates as both produced unstable conditions indicating that the failure of the co-digestion trial was not the result of just one substrate failing. In contrast liquid recirculation was shown to be a viable option but this did not lead to improved methane yield when compared to that predicted

- In terms of the digestate, the addition of maize led to an increase in the solids content and a decline in the ammonia concentration but in the majority of the digestates the solids content remained lower than the raw cattle slurry while the ammonia remained greater. The change caused by the addition of the maize could prove to be a disadvantage as it could affect the level of nutrients reaching the plants and could lead to an increase in the emissions related to field application.

- The digestate indicated non-compliance with specification given for digestate with the concentration of chromium, nickel and zinc exceeding the upper limits. Despite this, evidence was given that the application of digestate could lead to an equal or lesser quantity of heavy metals than the application of raw cattle slurry.

11.2 Future work

Quality of digestate

This research has indicated that the addition of maize does influence the characteristics of the digestate in terms of the solids content and the form of nitrogen but only provides superficial understanding of the influence that the addition of maize has on the digestate. The real implications, such as the impact on crop yield and associated emissions have not been tested leading to uncertainty into whether the addition of maize has a significant influence on the quality of the digestate. Understanding of this can be important in determining how much maize should be digested with the cattle slurry. Further work into the heavy metal content of the digestate may also prove to be beneficial as this research has indicated that this could be a problematic area in terms of meeting the limits set for heavy metals.

Further investigation into solids and liquid recirculation

Recirculating the solids was tested in this research as a means to increase the retention time of the slowly degrading fraction of the cattle slurry and maize however, this was shown to be detrimental to the process. Recirculating the liquid recirculation was successful but no improvement to the methane yield was shown. Speculative suggestions were put forward about the influence that the different recirculation regimes had on the bacteria community within the systems. Research aimed at identifying the source behind the solids recirculation failure but the success of the liquid recirculating could provide further insight of the co-digestion process and could aid future attempts at improving the volumetric methane yield.

In-depth study of the overall energy balance

The AD tool was used and applied to each working condition tested to determine how the different regimes influenced the energy balance of the system; this was only applied to one scenario to get an idea how the conditions could differ. Applying the AD tool to several different scenarios, such as reducing the cattle herd to allow maize to be grown in a fixed area, can provide more information for prospective farmers giving a wider picture of how introducing a digester to their farm could boost the energy balance

Economic study

The addition of maize clearly had positive benefits to the volumetric methane yield and therefore the overall energy balance but corresponding to this was an increase in the area of land required. To get a true picture of a full scale digester fed on cattle slurry and maize a full economic study should be applied to determine if the increase in the energy output offsets the cost of purchasing/renting land. This would provide an improved picture of how the different working conditions influence the system as a whole.

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