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Improving Soluble Chemical Oxygen Demand Yields for Anaerobic Digester Feedstock using Leaching

A thesis presented in partial fulfilment of the requirements for the degree of

Master of Engineering

in

Environmental Engineering

By

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2012

Abstract

Waste biomass is often a liability to many municipalities. Technologies exist that can turn this biomass into energy which can then be sold. Anaerobic digestion is one of the important technologies that utilises this biomass to turn it into biogas. One of the factors that affects the rate that biogas can be produced is the speed that suitable organic compounds can be delivered to methanogenic microorganisms. These organic compounds such as sugars and amino acids are released from plant material at different rates depending on their availability. A portion of the compounds are readily soluble in water and are immediately available, some of the compounds are locked up inside the plant cells and some of the compounds such as cellulose are not soluble and need to be hydrolysed into sugars before they can be converted into methane. Hydrolysis is usually the rate limiting step in anaerobic digestion. Leaching of green waste was investigated as a form of pre-treatment to externalise the initial stages in anaerobic digestion that makes soluble organic compounds available for the consecutive mthanogenic stages of anaerobic digestion. The added benefit of leaching is it removes the complexity of solids handling from inside anaerobic digester. Many various forms of leaching technologies that are coupled to anaerobic digesters have been trialled with grass and silage, little research was found on leaching green waste and few trials had used the simplified unheated flooded tank system as tested here. Pilot and laboratory leaching trials were conducted on shredded green waste as well as grass clippings to establish the efficiency of leaching by measuring the COD yields in the leachate. Additionally, rumen contents from cattle rumen were added to grass clippings in order to investigate if the leaching efficiency from the grass could be improved. Leaching was tested at a pilot scale in an open to the air reactor tank in ambient temperature in a temperate climate. Hydraulic retention times ranging from 4 hours to 7 days were tested to establish the most effective leaching strategy. The laboratory trials were conducted with the temperature controlled at 25°C to simulate ambient environmental conditions in a temperate climate. The effect of storing feedstock was tested to see how changes in handling times affected the process. Gas production from the leachate was tested using 2 L CSTR (Continuously Stirred Tank

Reactor) anaerobic digesters to confirm the usability of the leachate as a feedstock in an anaerobic digester.

Pilot scale trials of shredded green waste and grass clippings gave maximum COD concentrations of 5.4 ± 0.5 and 47±4 g COD / L of leachate respectively. Pilot trials of shredded green waste and grass leachate reached a maximum total COD yields of 53 ± 2 and 410 ± 20 kg COD / tonne VS respectively. Laboratory scale trials of shredded green waste and grass clippings gave maximum COD concentrations of 7.0 ± 0.1 and 49 ± 2 g COD / L of leachate respectively. Laboratory trials of shredded green waste and grass leachate reached a maximum total COD yields of 132 ± 8 and 410 ± 20 kg COD / tonne VS respectively. Laboratory trials are indicative of how pilot trials will behave and differences are likely to be due to an increased bulk density in solids in pilot trials.

Shredded green waste and grass leachate gave maximum 3.7 and 7.8 g BOD / L respectively. Nutrients in the leachate were tested: nitrogen levels in shredded green waste and grass leachate reached maximum levels of 51 and 460 mg / L respectively; DRP (Dissolved Reactive Phosphorus) levels in the shredded green waste and grass leachate reached maximum levels of 6 and 85 mg / L respectively. The leaching tanks produced gas while leaching was taking place; a sample of this gas was captured and the levels of CH_4, CO_2 and H_2 were measured as 0%, 25.5% and 5.0% respectively. Gas production from anaerobic digestion of shredded green waste and grass in a CSTR at 35°C produced 0.23 ± 0.01 and 0.534 ± 0.005 m^3 biogas / kg COD respectively.

Use of grass that is fresh gives much higher yields of dissolved organic compounds in the leachate than when the grass is stored in covered area for 30 days. Leaching grass with an HRT (Hydraulic Retention Time) of 1 day gave optimal results in terms of concentration and yields of dissolved organic compounds in the leachate compared to leaching trials with an HRT of 4 hours or 7 days. Green waste gave much lower concentration and yields of COD than grass and an HRT of 7 days was the most suitable for gaining the best concentration and yield of dissolved organic compounds compared to a 4 hour or 1 day HRT.

The overall mass transfer of organic compounds when leaching freshly shredded green waste is most likely limited by a combination of hydrolysis and the rate that soluble compounds are released from within plant cells as the cell membranes degrade. In trials of fresh and stored grass and stored shredded green waste, shortening the HRT increases the total yield of dissolved organic compounds leached into the leachate; however, this is at the expense of increased concentrations of dissolved organic compounds within the leachate. The lower leachate concentrations with the shorter HRTs means that the leachate is less suitable to uses as a feedstock for an anaerobic digester.

Anaerobic digestion of grass leachate produced much more biogas / kg COD than anaerobic digestion of shredded green waste leachate, this may be a result of an inhibiting compounds such as tannins, additionally to this the material that the shredded green waste is composed of will have higher levels of lignocellulose materials that are not readily soluble. The leachate was found not to degrade when stored at 25°C in an open top container, this maybe a result of low pH inhibiting degrading micro-organisms, this has significant benefit as the leaching process can be separated from the anaerobic digestion process without degrading the quality of the leachate while it is being stored.

Acknowledgements

The inspiration for carrying out a Master of Engineering degree can be wholly attributed to my partner Milena Mitić, her support and encouragement throughout the year ensured my perseverance. Guidance provided by my supervisor Professor Andrew Shilton was of critical value. Financial support from the Palmerston North City Council made this project possible and is greatly appreciated. Dr. Nicola Powell provided outstanding support and guidance throughout the year, her never-ending patience and attention to detail provided me with a sounding board I could whole-heartedly rely on. Bruce Collins and Anthony Wade from the electronics workshop provided enormous amounts of their time in support of my project; although their work did not end up being used for this thesis the effort is greatly appreciated none the less. The engineering workshop technicians, Stan, Clive and Kerry, were most helpful, their instruction of the use of machinery added greatly in enabling me to quickly build experimental equipment. John Sykes was forever patient with my continuous questions about laboratory procedure and his assistance with showing how to use analytical equipment was critical to the outcome of the experimental results. His work in testing nutrient contents of samples was also greatly appreciated. Johanna Güttler was of value in her assistance with taking samples and mostly for the companionship she provided that kept me sane in the long days in the lab. I would finally like to thank my sister Kezia for providing her expertise in the proofreading of this document.

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1 Introduction

1.1 Background

New Zealand has vast resources of waste biomass from the forestry industry. Most of this is lignocellulose material i.e. waste wood. There is an estimated 18.3 PJ / year of energy available from this resource; however, its potential is mostly for thermal conversion processes (Hall et al., 2008). Additional to this New Zealand has 3.7 PJ / year of energy from biodegradable municipal waste including sewage sludge and 14.54 PJ / year of agricultural residues (Hall et al., 2008).

Waste biomass is often a liability to many municipalities, yet opportunity exists to harvest useful energy from this biomass in a sustainable manner. Some of the major sources of biomass that many municipalities deal with are green waste including grass clippings. All of the various kinds of green waste are a financial and energy consumption liability. Currently these are either landfilled or composted, With the exception of landfills with gas recovery systems, these methods fail to recover any of the valuable energy green waste contains. Prospects exist for the use of alternative technologies to recover energy from this waste.

Biomass can be converted to a usable form of energy utilising two pathways: thermal or biological conversion. The thermal conversion pathway has a range of options from straight combustion of the raw biomass for heat through to production of syngas and oil with gasification and pyrolysis processes. Biological processing offers the advantage of not having to dry the biomass out before processing; this prevents wasting energy in the extra processing step. Two biological processes that can be used for converting biomass to a usable form of energy are anaerobic digestion and fermentation. Anaerobic digestion produces a mixture of CO_2 and CH_4 known as biogas and fermentation for energy production produces ethanol.

A typical anaerobic digester is an airtight tank where slurry is pumped in. Often the tank is heated to provide ideal temperatures for anaerobic digestion to occur. The slurry is mixed in the tank and removed once an optimal amount of biogas has been produced or sufficient degradation of the biomass has occurred. Biogas is removed from the top of the tank and either flared, burned in a boiler for heat, or used in an internal combustion engine for heat and electricity.

Anaerobic digestion occurs by proceeding through a series of metabolic pathways including hydrolysis / fermentation, acetogenesis and methanogenesis. Hydrolysis is the rate-limiting step in almost all cases. Hydrolysis involves taking molecules of a higher molecular mass and reducing them in sizes to become smaller soluble compounds such as amino acids, monosaccharides and fatty acids. A method to evaluate the amount of a substance that has been hydrolysed is to measure its chemical oxygen demand (COD).

Hydrolysis is the rate-limiting step in anaerobic digestion. The financial viability of anaerobic digestion can be improved by either increasing the rate of hydrolysis usually by pre-treatment or shifting the hydrolysis step outside of the anaerobic digestion tank into a cheaper process.

Most pre-treatment methods used are for the hydrolysis of lignocellulose to sugar, which is then fermented to ethanol. There is potential for many of these same pre-treatments to be used as part of the anaerobic digestion process. One of these pre-treatments is leaching and can be considered as the hydrolysis stage in a two-stage anaerobic process. Because hydrolysis is taking place externally to the main anaerobic digester, the size of anaerobic digester can be reduced which decreases the capital and operating cost and reduces the parasitic energy demands for heating, mixing and pumping.

The process of leaching is a mass transfer operation which moves organic compounds from solid to the liquid phase. Additionally it is likely that microbial action is converting insoluble organic compounds into soluble organic compounds within the solid phase. Once leachate is produced in the leaching tank it can be fed into the second stage of the anaerobic digester process so acetogenesis and methanogenesis can be completed, which produces biogas. The opportunity exists to test green waste as a source of material to be leached for the production of biogas using anaerobic digestion. While grass and grass silage have been extensively tested using leaching technology to produce biogas very little evidence for testing leaching on green waste is available. To date the anaerobic digestion of green waste has been carried by attempting to digest the entire received green waste and was described as municipal solid waste which contains other materials such as waste food. Green waste is a vast and readily available feedstock that is often kept separate from other solid waste streams. The sheer volume of green waste produced means that any biogas that can be produced even with low efficiencies may end up making a significant amount of biogas.

1.2 Aims

The aims of this project include testing of both shredded branches and leaves and grass portions of green waste for their ability to produce leachate suitable for feeding to an anaerobic digester; analysing the effects of storing shredded green waste and grass before leaching; studying the effects of scaling from a laboratory scale to pilot scale; and examining the effects of HRT on leaching systems and the effects of adding cattle rumen contents to grass.

The effects of type of feedstock, feedstock storage, scale, HRT and supplementation with rumen contents will be tested. This will be achieved by establishing levels of COD concentrations and total COD yields in the leachate from the feedstocks being leached. Establishing the COD concentrations and yields will give an accurate indicator of how the changing the parameters tested will effect biogas production. Additionally nutrients levels, gas composition of gas released in the leaching tanks and gas production from laboratory scale anaerobic digesters will be tested. These measurements will test that the system actually produces biogas from the tested feedstock and the measurement will give an indication as to how well the system performs at producing biogas. Running a leaching system has implications for its environmental loading due to fugitive emissions and the release of effluent at the end of the process. These outputs will be quantified so that impact of using a leaching technology can be assessed and opportunities for using the released waste as a resource can be explored. Leaching trials will be run at both laboratory and pilot scale for the purpose of establishing the effect of scale-up. Laboratory trials will also be used to test the effects of storage of feedstocks before leaching. Effects of storage of feedstock is important to test as the feedstock does not always arrive for processing continuously and the relative importance of how storage of the feedstock effects the leaching system needs to be understood so that storage can either be used as method of improving the leaching process or if storage has a negative effect ways of mitigating the effects of storage can be investigated. Supplementation of rumen contents with grass will be tested in a laboratory scale leaching tank to establish if COD levels in the leachate are improved. Testing of rumen contents on improving anaerobic digester yields has been inconclusive in the past, however it is thought that the enzymes contained in the rumen contents may assist with hydrolysis. The rumen contents is a waste product from freezing works so if it improves yields it will help solve the waste dispose problem as well as improve the leaching process.

2 Literature Review

2.1 Biomass Energy Sources

New Zealand has substantial amounts of biomass that has potential to be converted into usable forms of energy. Table 2.1 summarises the bioenergy availability in New Zealand for 2005. Most of the energy available comes from forestry residue; however, there are still vast amounts of bioenergy available from municipal solid waste and agriculture residue, which may be more easily bioprocessed.

Biodegradable municipal solid waste in New Zealand had the energy potential for 2.8 PJ / year in 2005 (Hall et al., 2008). This waste is made up of garden waste such as grass clippings, branches and leaves, and food scraps. Only a small portion of this is composted and sold back to the public (Slack, 2010).

Table 2.1: New Zealand's bioenergy availability in 2005

Source / Type	PJ / year (2005)
Forest residue	18.3
Wood process residue	8.8
Municipal wood waste	4.4
Horticultural wood waste	0.4
Straw	9.1
Stover	3.8
Fruit and vegetable culls	1.5
Municipal biosolids	0.9
Municipal solid waste, putrescible	2.8
Farm dairy effluent	1.5
Farm piggery effluent	0.1
Farm poultry litter	0.04
Dairy industry effluent	0.5
Meat industry effluent	0.6
Waste oil	0.2
Tallow	4.5
Total	57.44
New Zealand primary energy	690.0
All biomass, as % of primary energy	8.3%

Source: (Hall et al., 2008)

2.2 Energy Conversion Technologies

Biomass can be converted to various forms of energy using different process pathways which can roughly be divided into thermal or biochemical process pathways as shown in Figure 2.1.

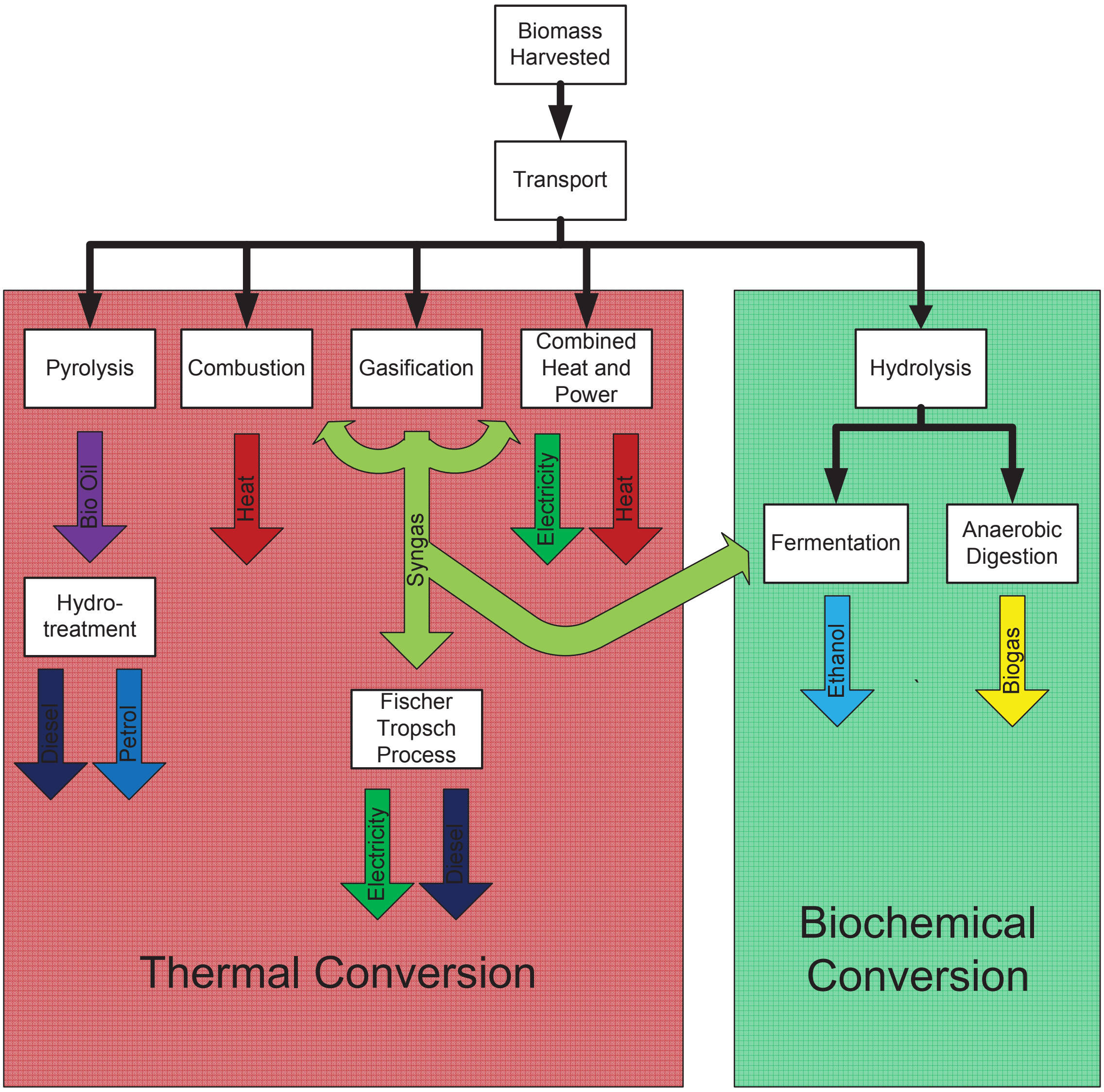

Figure 2.1: Process pathways for biomass energy conversion

Source: adapted from (Hall et al., 2008; Young, 2010)

Anaerobic digestion is of particular interest as feedstocks with high water content can be processing into useful energy without the energy-intensive drying stage.

2.3 Anaerobic digestion

2.3.1 Stages and Metabolic Pathways in Anaerobic Digestion

Methane is produced through multiple biochemical pathways utilising a diverse community of microorganisms. The ways these various pathways move through the stages of anaerobic digestion are shown in Figure 2.2.

Hydrolysis / Fermentation

Hydrolysis involves the initial transformation of organic material of high molecular mass compounds such as lipids, fats, carbohydrates, proteins and nucleic acids to soluble organic materials such as amino acids, monosaccharides and fatty acids (das Neves et al., 2009; Khanal, 2008). Hydrolysis is of great interest in the study of anaerobic digestion as it is the rate-limiting step (Choi et al., 2006). Fermentation takes the products of hydrolysis through to acetate, hydrogen and carbon dioxide. Intermediate products such as propionate, butyrate, ethanol and lactate are produced as part of this process (Khanal, 2008).

Acetogenesis

Acetogenic bacteria are divided up into two categories: hydrogen producing and homoacetogens. Homoacetogens are further divided into two categories: autotrophs and hetrotrophs. The autotrophs use hydrogen and carbon dioxide to produce acetate, while the hetrotrophs use single carbon molecules such as methanol and formate to produce acetate (Khanal, 2008).

Methanogenesis

Methanogens are classified as archaea. These microorganisms use two separate metabolic pathways to produce methane. Most methanogens can use H_2 as an electron source and approximately 28% of the methane in anaerobic digestion uses this metabolic pathway. The other 72% is produced using acetate. The end result is a mixture of carbon dioxide and methane. This mixture is referred to as biogas (das Neves et al., 2009; Khanal, 2008).

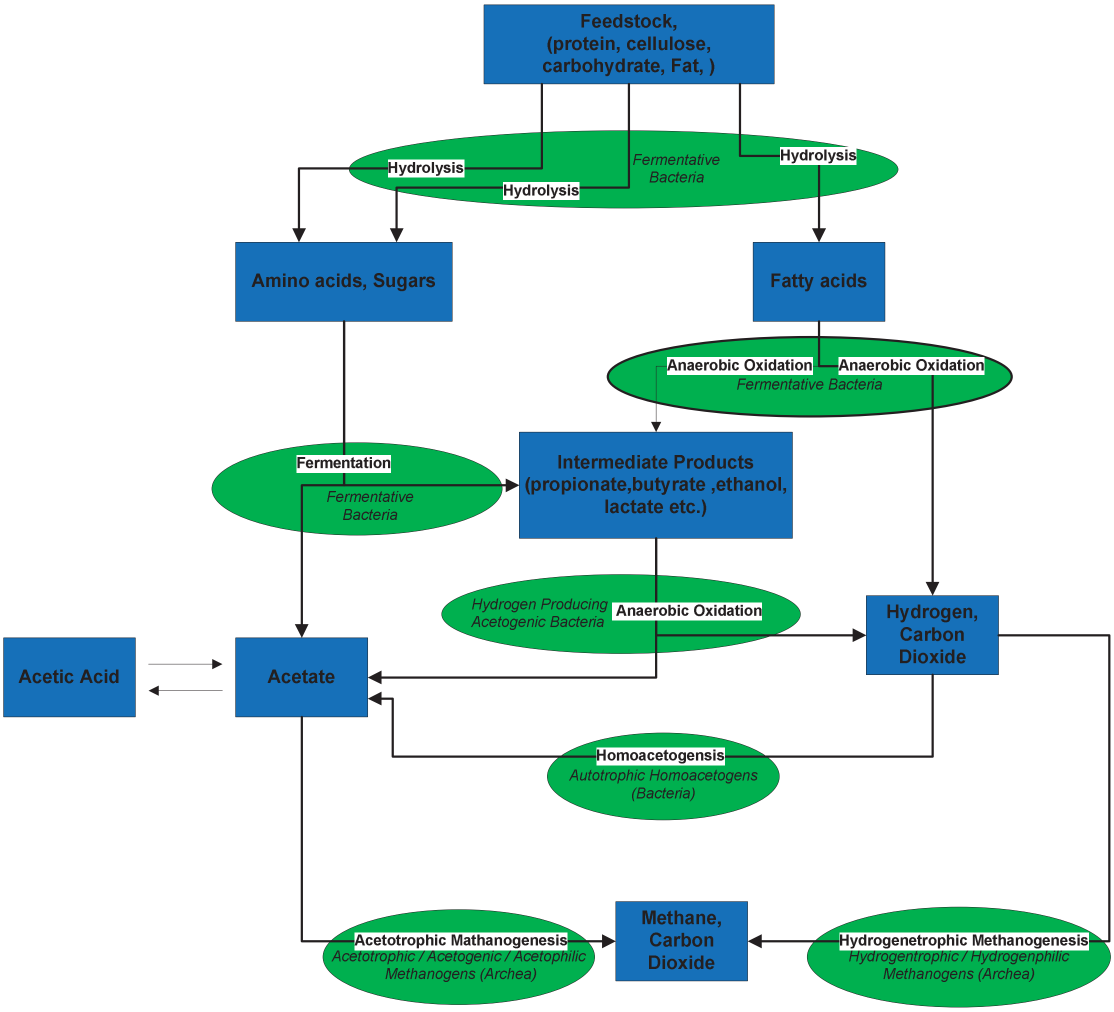

Figure 2.2: Metabolic pathways in anaerobic digestion

Adapted from: (das Neves et al., 2009; Khanal, 2008; Zehnder et al., 1981)

2.3.2 Typical Digester Design

Most high-rate reactors are continuously stirred tank reactor (CSTR) designs. To improve efficiency more advance designs have been built to treat various types of waste. Each of these has their own advantages and disadvantages along with their unique set of operating parameters.

Continuously Stirred Tank Reactor

A continuously stirred tank reactor (CSTR) is a simple tank with an inlet and outlet for the influent and effluent, a gas removal outlet and a mechanism for mixing as shown in Figure 2.3. CSTRs are operated under mesophilic or thermophilic conditions. They are used for digestion of waste with high solids contents, 1-6%, and the SRT and HRTs are directly coupled so the solids are removed at the same time as the liquids (Khanal, 2008). Typical volumetric organic loading rates are 1.0-5.0 kg COD / m^3.day and typical HRTs are 15-30 days. This equates to influent concentrations of 15-150 g COD / L (Metcalf & Eddy et al., 2003).

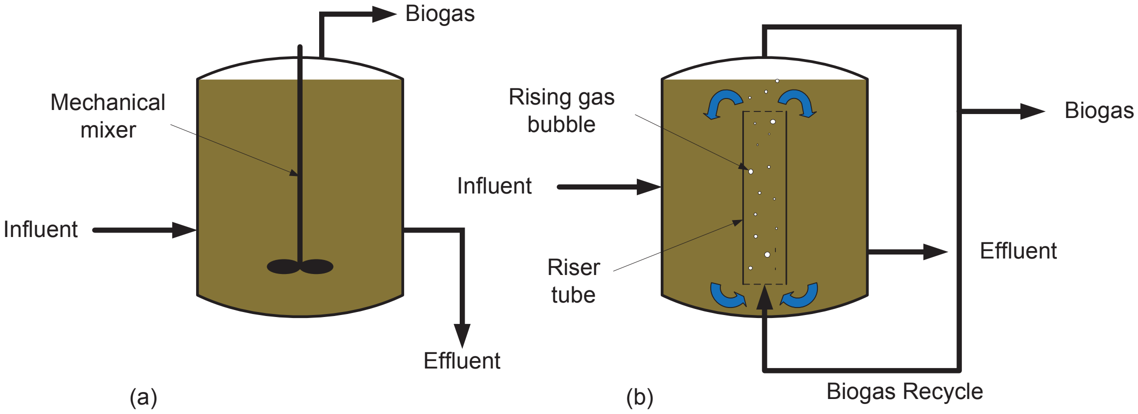

Figure 2.3: (a) Mechanically mixed CSTR (b) Gas mixed CSTR

Anaerobic Contact Process

The anaerobic contact process is shown in Figure 2.4. It is similar to the CSTR but it has an external clarifier where the effluent is decanted off the top and the heavier sludge is recycled back into the system. The sludge is degassed before entering the settling tanks to ensure that it does not float (Khanal, 2008). Typical volumetric organic loading rates are 1.0-8.0 kg COD / m^3.day and typical HRTs are 0.5-5 days. This equates to influent concentrations of 0.5-40 g COD / L (Metcalf & Eddy et al., 2003).

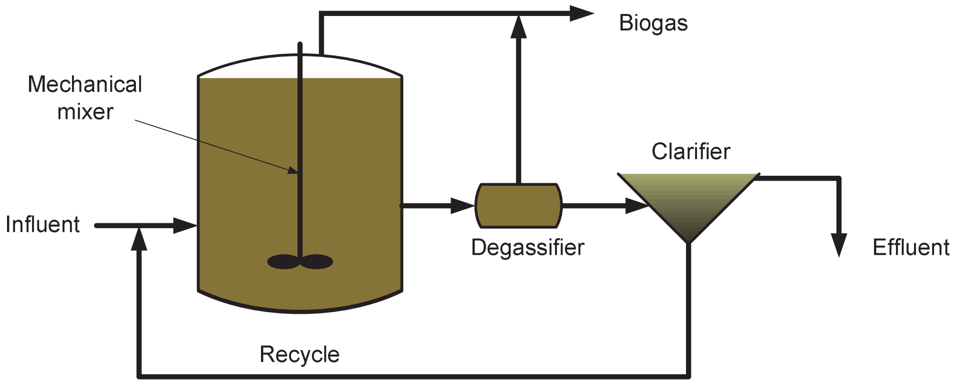

Figure 2.4: Anaerobic contact digester

Upflow Anaerobic Sludge Blanket

The upflow anaerobic sludge blanket (UASB) system is shown in Figure 2.5. It has the influent enter at the bottom. Within the reactor is a sludge blanket usually made up of granules that are formed from the growth of biomass. Most of these granules settle at the same rate as the fluid rises through the reactor. Above the blanket of granules is a series of baffles which capture the gas. Settling zones are situated above the baffles and are where the remaining granules settle back into the blanket. The effluent then exits at the top of the reactor. UASBs have the ability to effectively process high-strength soluble waste. This is because the HRT and the SRT are decoupled; the HRT can be as little as 6 hours while the SRT can be as long as 200 days (Chynoweth and Isaacson, 1987; Hobson and Wheatley, 1993; Khanal, 2008). The disadvantage of this system is that as the temperature drops the efficiency is lost. This needs to be rectified by either heating the reactor or extending the HRT (Kettunen and Rintala, 1998). Organic loading rates can vary from 2-24 kg COD / m^3.day with operating temperatures from 15°C-40°C and HRTs from 6-14 hours. This corresponds to concentrations of influent from 1-18 g COD / L (Metcalf & Eddy et al., 2003).

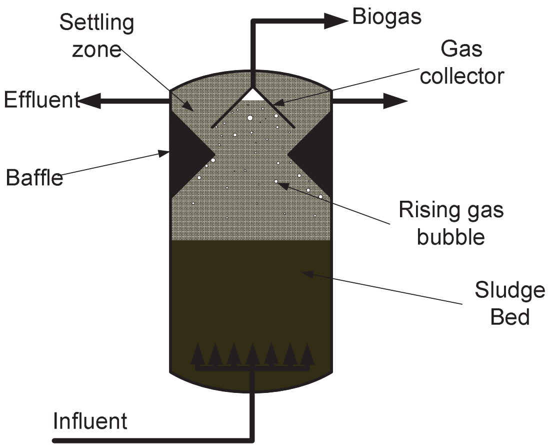

Figure 2.5: Upflow anaerobic sludge blanket reactor

Anaerobic Sequence batch reactor

An anaerobic sequence batch reactor is a simple tank with an inlet, several decanting outlets at various levels and a biogas outlet at the top. The process is shown in Figure 2.6. The waste is allowed to settle in the reactor and the effluent is then decanted off the top, leaving the sludge and biomass behind. The reactor is then refilled; mixing is then achieved by bubbling biogas up through the reactor, after which settling is allowed to occur to start the sequence once again. This system is good for high-strength waste with medium solid contents such as meat processing facilities (Chynoweth and Isaacson, 1987; Khanal, 2008). Typical volumetric organic loading rates are 1.2-2.4 kg COD / m^3.day and typical HRTs are 0.25-0.5 days. This equates to influent concentrations of 0.3-1.2 g COD / L (Metcalf & Eddy et al., 2003).

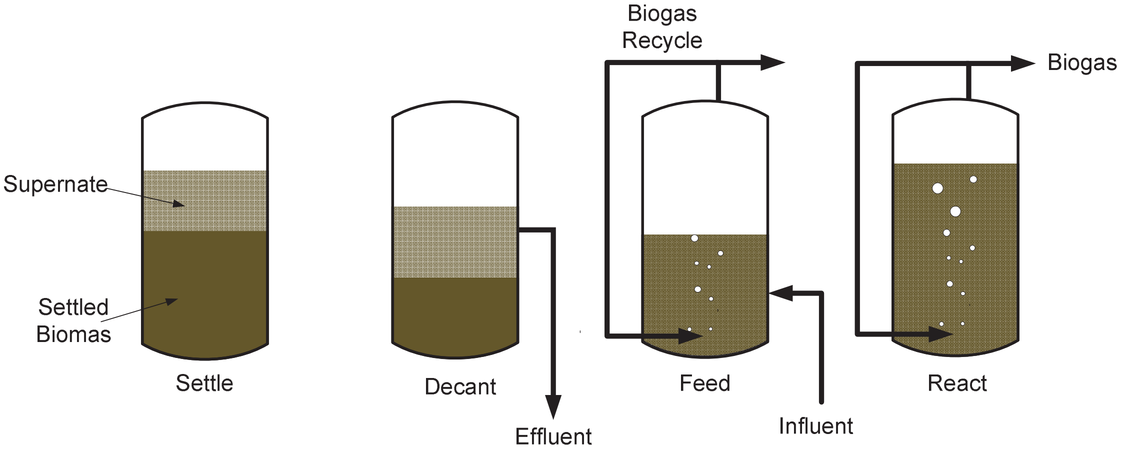

Figure 2.6: Anaerobic sequence batch reactor

Anaerobic Composter

Anaerobic composting is useful for treating high solids content wastes such as the organic fraction of municipal solid waste. A leaching or non-leaching configuration can be used as shown in Figure 2.7. The added benefit of anaerobic composting is that a compost product is produced additionally to biogas (Chynoweth et al., 2003; Molnar and Bartha, 1988). Figure 2.7 (a) shows the setup of a sequence batch reactor as described by Chynoweth et al. (2003). These tanks have trafficable hatches so earth-moving equipment can move in and out for solids handling. Leachate is recycled between the tanks to enhance inoculation and nutrients distribution. Heating of the system is required to reduce retention times. Volatile solids reduction of the organic fraction of municipal solid waste and green waste were 57% and 20% respectively (Chynoweth et al., 2003). Figure 2.7 (b) shows the system described in Molnar et al. (1988). Solid organic material is piled up on a concrete base and aerated until it reaches a temperature of 55°C. A membrane cover is then placed over the pile and sealed at the bottom with a water lock. The pile is then inoculated and then left to sit while biogas is removed from the top of the pile.

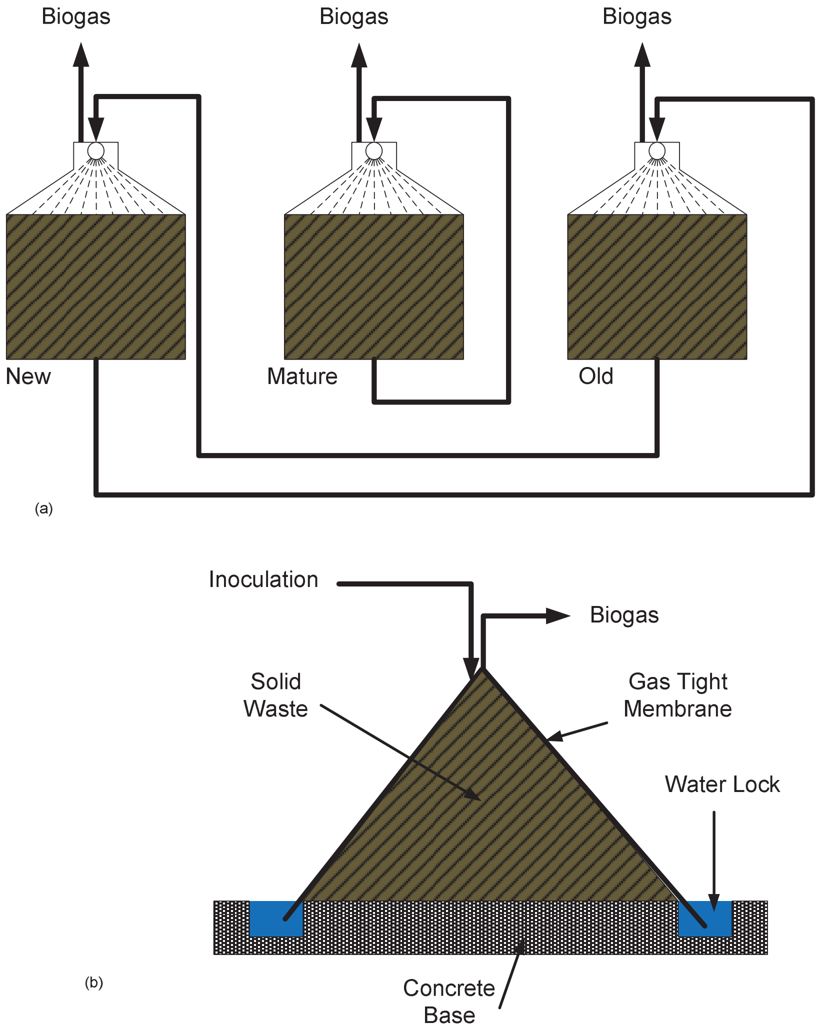

Figure 2.7: (a) Sequence batch anaerobic compost reactor (b) Compost pile anaerobic reactor

Anaerobic Filter

Media with a high surface area is packed inside the reactor on to which biofilms attach themselves. The anaerobic filter decouples the SRT from the HRT. The system can be arranged in an upflow or downflow configuration as shown in Figure 2.8. The downflow configuration is capable of handling a small amount of suspended solids whereas the upflow cannot. The downflow system is also good at treating waste streams with sulphates as the sulphate reduction occurs in the upper portion of the reactor and the methane production occurs in the bottom by a separate microbial community (Chynoweth and Isaacson, 1987; Hobson and Wheatley, 1993; Khanal, 2008). Typical volumetric organic loading rates are 0.1-15 kg COD / m^3.day and typical

HRTs are 0.5-37 days. This equates to influent concentrations of 5-20 g COD / L (Metcalf & Eddy et al., 2003).

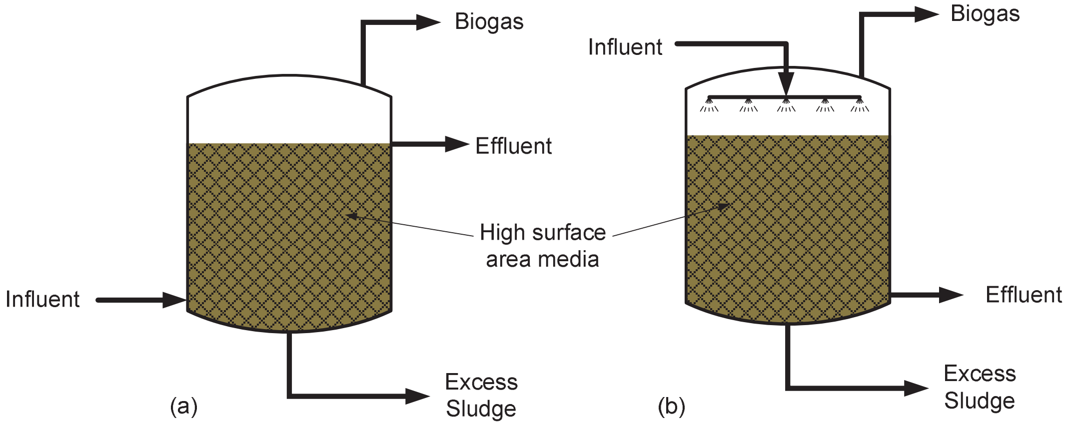

Figure 2.8: (a) Upflow anaerobic filter (b) Downflow anaerobic filter

Fluidised Bed Reactor

The concept is similar to the anaerobic filter except that the media (biocarrier) is kept suspended by the rapid upflow of the fluid as shown in Figure 2.9. This prevents problems of clogging and short-circuiting that happens in anaerobic filters (Hobson and Wheatley, 1993; Khanal, 2008). These reactors are mostly suitable for waste streams with high soluble content as solids are not well trapped. Typical volumetric organic loading rates are 3-42 kg COD / m^3.day and typical HRTs are 3-62 hours. This equates to influent concentrations of 0.3-42 g COD / L (Metcalf & Eddy et al., 2003).

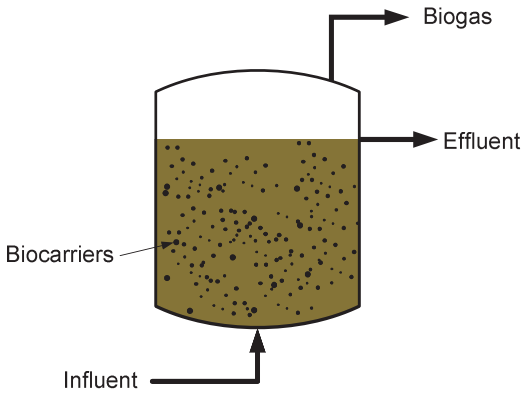

Figure 2.9: Fluidised bed reactor

Static Granular Bed Reactor

Operates in a similar principle to a UASB; however, the flow of fluid is down through the granules as shown in Figure 2.10. A disadvantage of this system is the head loss due to build-up of suspended particulates (Khanal, 2008).

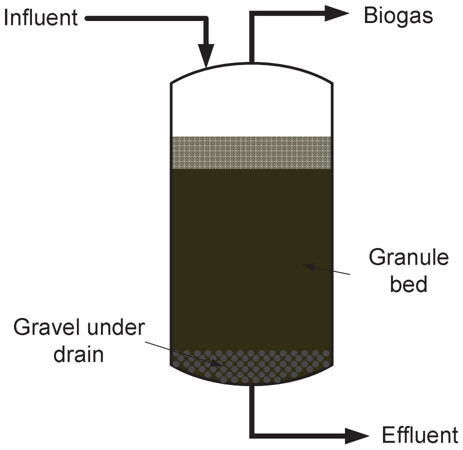

Figure 2.10: Static granular bed reactor

Anaerobic Membrane Reactor

An anaerobic membrane reactor is a CSTR that has a cross flow membrane attached either externally or immersed in the reactor. The fluid is passed through the membrane and the retentate is recycled back to the reactor and the permeate leaves as effluent as shown in Figure 2.11. This system solves the problem that CSTRs have of having the SRT coupled to the HRT. The quality of the effluent can therefore be significantly improved compared with a standard CSTR (Khanal, 2008). Typical volumetric organic loading rates are 2-22 kg COD / m^3.day typical HRTs are 0.5-15 days. This equates to influent concentrations of 1-330 g COD / L (Metcalf & Eddy et al., 2003).

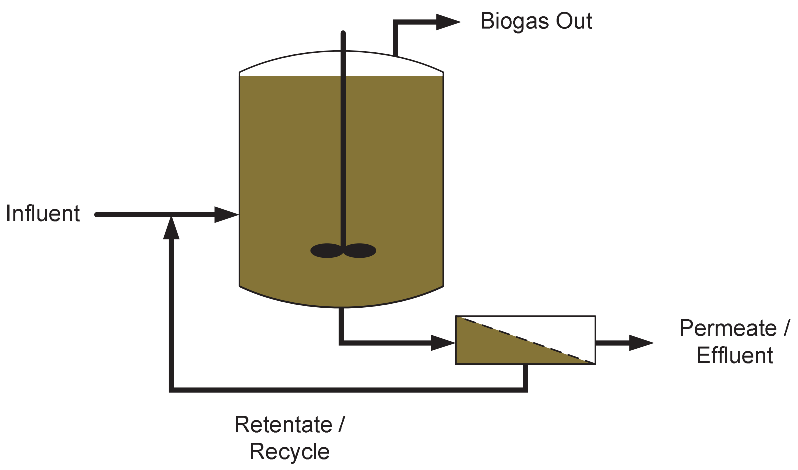

Figure 2.11: Membrane reactor

Covered Anaerobic Lagoon

A covered anaerobic lagoon is a pit in the ground usually about 10 m in depth. It is covered with a floating geomembrane that captures biogas and allows rainwater to run off. The system is not generally heated, so the temperatures range from 15-30°C. Advantages of an anaerobic lagoon are that it can handle a wide variety of waste streams including solids and oils; because of the large volumes of the lagoon they can equalise inconsistent loading. The main disadvantage is the large amount of land they require. Typical volumetric organic loading rates are 0.2-2 kg COD / m^3.day and typical HRTs are 30-50 days. This equates to influent concentrations of 6-100 g COD / L. Lower loading rates can be used and result in up to 80-90% removal of COD (Metcalf & Eddy et al., 2003).

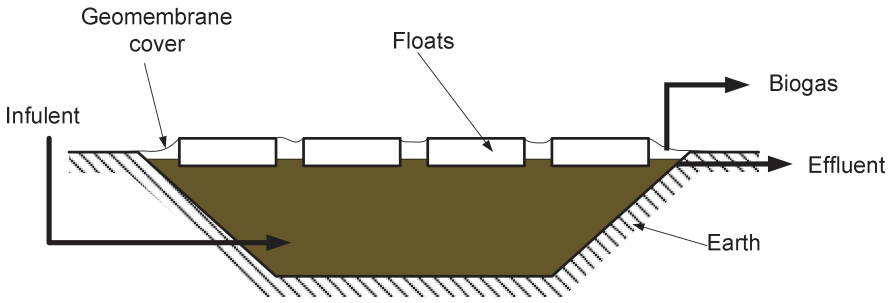

Figure 2.12: Covered anaerobic lagoon

2.3.3 Gas Production from Grass and Municipal Solid Waste

Various gas yields have been acquired from digesting grass and municipal solid waste. Table 2.2 shows the results achieved by different studies. These values have been achieved using many variations of parameters such as HRT, temperature and different types of anaerobic digesters.

It is interesting to note that the amount of biogas yielded in these studies varies significantly; this illustrates difficulty in getting consistent results from a system where the feedstock can be inconsistent despite careful characterisation. Subtle differences in an anaerobic digester reactor setup along with the very complex microbiological interactions that occur in an anaerobic digester are the main cause for these inconsistencies. Additionally to this, some studies use grass as their feedstock, others use grass silage. Turning grass into silage can be considered a form of pre-treatment and in the process of grass becoming silage some of the volatile solids are used. This skews the results in the favour of silage when $m^3{}_{biogas}$ / kg VS. To truly compare the results the original level of volatile solids in the grass before ensiling must be measured.

Some studies report their yields from anaerobic digestion as m^3 CH_4 / kg VS instead of $m^3{}_{biogas}$ / kg VS. The metric of m^3 $CH_{4/}$ kgVS provides more accurate information about useful yields from anaerobic digestion.

Table 2.2: Gas production from grass and municipal solid waste (MSW)

System Configuration	Substrate	Gas Yield*	Source
Leach bed + CSTR	Grass	0.165 $m^3{}_{biogas}$ / kg VS	(Pratt et al., 2008)
CSTR	Organic fraction MSW	0.187 – 0.430 $m^3{}_{biogas}$ / kg VS	(Nallathambi Gunaseelan, 1997)
Leach bed + Anaerobic filter	Grass	0.39 $m^3{}_{biogas}$ / kg VS	(Lehtomäki and Björnsson, 2006)
Leach bed + Anaerobic filter	Grass	0.165 $m^3{}_{biogas}$ / kg VS	(Yu et al., 2002)
Leach bed + UASB	Grass	0.36 m^3 CH_4 / kg VS	(Jagadabhi et al., 2011)
Single stage leach bed	Organic fraction MSW	0.115 – 0.384 $m^3{}_{biogas}$ / kg VS	(Huy, 2008)
Batch Digester	Grass & grass silage	0.65 – 0.85 $m^3{}_{biogas}$ / kg VS	(Mahnert et al., 2002)[a]
Leach bed + USAB	Grass silage	0.27 - 0.39 $m^3{}_{biogas}$ / kg VS	(Lehtomäki et al., 2008)
Leach bed + USAB	Grass silage	0.052 – 0.305 m^3 CH_4 / kg VS	(Nizami et al., 2011)
Sequence Batch Anaerobic Composter	Organic fraction MSW	0.3 m^3 CH_4 / kg VS	(Chynoweth et al., 2003)
Sequence Batch Anaerobic Composter	Green Waste	0.07 m^3 CH_4 / kg VS	(Chynoweth et al., 2003)

[a] value taken from table 3 in (Nizami and Murphy, 2005)

*Kg volatile solids added

2.4 Feedstock Pre-treatment

The purpose of pre-treatment is to speed up the rate-limiting step of hydrolysis. The cellulose fraction of organic waste can be hydrolysed into sugar for fermentation to ethanol or anaerobically digested. Many of the same technologies that are used for the hydrolysing of lignocellulose for producing sugar for fermentation to ethanol can also be used to improve the hydrolysing step of anaerobic digestion.

Many of the plentiful and high-solid-content feedstocks that can be used for anaerobic digestion such as primary sludge, Waste Activated Sludge, animal manure, food waste, green waste and agricultural residues are limited in their feasibility for digestion because of the rate-limiting hydrolysis step. Different approaches have been taken in the past to pre-treat the feedstocks to assist in the breakdown of the larger molecules and destroy the integrity of existing cellular structure. There are five categories of pre-treatment: chemical, physical, physico-chemical, biological and physical-biological. Some pre-treatment methods use a combination of processes.

2.4.1 Chemical

Alkali

The most common form of chemical pre-treatment is the use of alkalis on lingo-cellulosic feedstocks such as straw. Two main alkalis used are NaOH and Ammonia. Gas yields have been shown to increase by as much as 33% with addition of NaOH. Over dosage of NaOH can lead to reduced biogas yield; this may be a result of microbial toxicities from sodium. Ammonia offers the advantage of increasing the N:C ratio in low nitrogen plant residuals. The cost of chemicals is a factor to consider when using alkali pre-treatment; it is likely the cost will prevent this from becoming a viable method (Hobson and Wheatley, 1993).

Organosolv

Organosolv is when an organic solvent is used to dissolve or decompose the lignin and possibly part of the hemicellulose portion of the lignocellulose feedstock. Up to 70%

w/w of the lignin can be dissolved using this method. Various solvents such as alcohols, esters, ketones, glycols, organic acids, and phenols can be used. The treatment is carried out at elevated temperatures of 150-200°C. The solvent needs to be removed from the feedstock as it inhibits the activity of enzymes involved in further hydrolysis (Taherzadeh and Karimi, 2008).

Wet oxidation

Wet oxidation is an exothermic treatment that has been used on lignocellulose feedstocks. It uses water with air or oxygen at temperatures between 148-200°C. The reaction is self-supporting and fast reacting once started. Therefore the temperature of the reaction must be carefully controlled. Biogas production increases of 35-70% have been observed when raw and digested lignocellulose feed stocks have been treated (Taherzadeh and Karimi, 2008). Wet oxidation has also been successfully achieved using 2% H_2O_2 at temperatures of 30°C (Azzam, 1989).

Acid hydrolysis

Hydrolysis of lignocellulose feedstocks with acids has shown to be effective at improving enzymatic hydrolysis. Bagasse treated with HCl increased biogas yields by 31% and treatment of coconut fibres with HCl increased biogas output by 71% (Taherzadeh and Karimi, 2008). The treatment can be either carried out at high temperature and low concentration or low temperature and high concentration. The acid needs to be recovered for economic reasons (Jones and Semrau, 1984). The disadvantages of acid hydrolysis systems are that the feedstock needs to be neutralised before further processing and the process is very energy intensive, making it prohibitive at industrial scales (Taherzadeh and Karimi, 2008).

2.4.2 Physical

Homogenization

Homogenization is when waste activated sludge is fed through a very small nozzle (<1 mm) at high pressures of about 82,700 kPa. The jet then hits an impact ring, causing a very sudden pressure drop, which causes the cells to lyse. This method has shown to be effective at increasing biogas yields but it is very equipment intensive due the extreme pressures required (Khanal, 2008).

Ultrasonic treatment

Ultrasound is very high-frequency sound-waves, usually above 20 kHz, which is above the threshold of human hearing. The ultrasound in a liquid produces cavitation, which causes strong hydro-mechanical shear forces in the liquid phases. This force ruptures the cell walls in the activated sludge that is being treated. The localised conditions caused by the cavitation can create temperatures up to 5,000 K and 50,000 kPa. The ultrasonic wave is created by applying a high-frequency electrical current to a piezoelectric substance. It has been found that there is little benefit to installing an ultrasonic device on a primary sewage sludge line as this material is more readily degradable. Waste activated sludge has shown to have significant improvements in biogas yields with the maximum being an improvement of 75%; however, significant amount of sonication was required to achieve this (Khanal, 2008).

Milling / Size reduction

Milling is mostly applied to lignocellulose feedstocks prior to further chemical or biological treatments. It has been shown to improve biogas yields depending on feedstock treated. The two disadvantages of milling are the high energy cost (Taherzadeh and Karimi, 2008) and inability to remove lignin, which restricts the access of cellulolytic enzymes to the cellulose (Mooney et al., 1999). A study by Sharma et al., (1988) showed an increase in biogas when the particle size of Bermuda Grass was reduced, but it was found that further size reduction below 0.4 mm did not produce additional biogas.

Irradiation

Irradiation of feedstock can be done with gamma rays, electron beams or microwaves (Kumakura and Kaetsu, 1984; Mamar and Hadjadj, 1990). It has been shown that irradiation is effective at degrading cellulose into oligosaccharides and cellobiose (Kumakura and Kaetsu, 1983). Irradiation is however expensive and is difficult to manage in an industrial application (Taherzadeh and Karimi, 2008).

2.4.3 Physico-chemical

Steam explosion

Steam explosion is where the feedstock is treated with steam at high pressures and temperatures between 160-260°C for periods between 30 seconds to 20 minutes, after which the pressure is suddenly released. The process effectively removes hemicellulose, and decreases levels of other compounds such as xylose. The process leaves behind slurry which may be separated into solid and liquid fractions (Taherzadeh and Karimi, 2008). Steam explosion has been investigated for several types of feedstocks including forest residuals (Hooper and Li, 1996), activated sludge (Dereix et al., 2006), cattle manure (Mladenovska et al., 2006) and municipal solid wastes (Solheim, 2004). A 93% increase in biogas was demonstrated by Dereix et al. (2006) when used on waste activated sludge. Steam explosion is considered to be moderately energy intensive (Taherzadeh and Karimi, 2008).

Ammonia fibre explosion

Ammonia fibre explosion is a process that has been used on lignocellulose feedstocks and is similar to steam explosion, using liquid ammonia at pressures and temperatures of 90-100°C for a period of about 30 minutes, after which the pressure is suddenly released. A solid residue remains after treatment. The process modifies or reduces lignin content and leaves hemicellulose and cellulose intact (Mosier et al., 2005). The disadvantages of this method are that the feedstock needs to be washed to remove enzyme inhibitory products from the breakdown of lignin, which increases wastewater (Chundawat et al., 2007), and the ammonia needs to be recycled to reduce cost and environmental impact (Eggeman and Elander, 2005).

CO_2 explosion

Supercritical CO_2 (pressures above 7.39 bar and temperatures above 31.1°C) act as a solvent for delignification on lignocellulose feedstocks. The CO_2 can be used with co-solvents such as ethanol and water or acetic acid and water to increase lignin removal (Pasquini et al., 2005). The sudden pressure release is thought to disrupt the cellulose structure (Taherzadeh and Karimi, 2008). Hydrolytic enzymes have also shown to be reasonably stable in supercritical CO_2 and simultaneous enzymatic hydrolysis has been successfully conducted with CO_2 explosion (Zheng, 1996). Despite the advantages of CO_2 explosion it is a very expensive process due to the very high pressures which prohibits its use at an industrial scale (Taherzadeh and Karimi, 2008).

Liquid hot-water

Liquid hot-water has been tested on lignocellulose feedstocks. The treatment consists of treating the feedstock with water at temperatures of about 160-220°C. To maintain water in the liquid phase at these temperatures high pressures must also be used (23 bar for 220°C). The process removes hemicellulose and part of the lignin which gives better access to the cellulose for the hydrolytic enzymes. The advantage of this system is that fewer chemicals are needed to neutralize products at the end of the process compared with methods such as acid hydrolysis but similar results are obtained (Taherzadeh and Karimi, 2008).

Electrohydraulic discharge

Electrohydraulic discharge is the discharge of high-voltage electricity in a liquid medium. It results in shockwaves, UV, strong electric fields and production of highly reactive chemical species. All of these phenomena are thought to contribute to the breakdown of organic material (Locke et al., 2006).

MicroSludge ™

Khanal (2008) reported on a system known as MicroSludge that first treats the waste activated sludge with NaOH and then uses homogenization to further lyse the cells. This system is very comprehensive and requires considerable capital expense to install. No data is available on the how this treatment affected gas production; however, the volatile solids reduction was increased from 40-50% to 50-60% on an industrial plant in Chilliwack near Vancouver Canada.

2.4.4 Biological

Co-digestion

Often the nutrient requirements that microorganisms in anaerobic digestion need to convert the feed substrate to biogas are not present in the required ratios. If all the nutrients and trace elements were available in a perfectly balanced ratio all the substrate could theoretically be converted to biogas. If a feedstock has a nutrient imbalance then a secondary feedstock can be added to correct this imbalance. An example of this is that adding a feedstock high in carbon such as rotten potatoes to farm waste that is high in nitrogen ensures the correct C:N ratios (Hobson and Wheatley, 1993).

White Rot Fungi and Enzymes

Various types of white rot fungi have been used to pre-treat feedstocks that are high in hemicellulose and lignin such as coffee pulp and straw. White rot fungi has been found to be effective at breaking down cellulose and lignin and has the added benefit of reducing levels of caffeine and polyphenols, which have an inhibitory effect on anaerobic digestion. Based on the weight of the feedstock going into the digester biogas yields are significantly increased: the disadvantage is that the white rot fungi consumes some of the carbohydrates that would otherwise be available to produce biogas and therefore the overall biogas yield for the same initial amounts of feedstock is reduced (Hobson and Wheatley, 1993). Attempts have been made to prevent carbohydrates being consumed by white rot fungi by pre-treating the feedstocks with the same enzymes that would otherwise be produced by the white rot fungi. The time it takes for the enzyme to break down the cellulose is very substantial and the feedstock still needs some form of pre-treatment to create a large-enough surface area for the enzymes to be able to attack (Xu et al., 2009).

Rumen Fluid to Enhance Hydrolysis

Cattle have the ability to break down 50% of the volatile solids in grass in two days; however, an ordinary CSTR digester can take up to 60 days to destroy 60% of the volatile solids in grass (Nizami et al., 2009). The rumen contains a complex microorganism population that use enzymes to break down cellulose materials (Hobson and Stewart, 1997). It has been suggested by Nizami et al. (2009) that addition of rumen fluids to the leaching stage of a combined leaching / methanogenic anaerobic digester will increase biogas production. Broughton (2009) tested the addition of rumen contents from a fistulated sheep to cow manure in an anaerobic digester. No evidence was found that the rate of hydrolysis was increased. The rumen contents added included the entire sample removed from the sheep's rumen, of which a portion was partially digested grass. It has been suggested that hydrolysis of cow manure could be enhanced if the rumen contents is strained and the fluid portion is added to the cow manure. In a study by (Nair et al., 2005), rumen fluid from a fistulated sheep along with a nutrient solution was added to a grass leach bed system in a 1:4 ratio rumen fluid : nutrients solution. A 70% reduction of the organic waste was achieved within 1 week. This is a considerable increase in degradation compared with conventional anaerobic digestion, which takes 5-6 weeks to achieve a 60% reduction of organic waste.

2.4.5 Physical - Biological

Leaching

The goal of leaching is to remove the COD from the solid phase in the feedstock into a more-usable liquid phase. The system comprises of a bed of solids inside a container. Water is either sprinkled over the solids or the container is flooded to cover all the solids. The container can be either heated or left at ambient temperature. The leach bed can be sealed off and made to operate in an anaerobic environment and a small amount of biogas can be captured (Nizami et al., 2010). Leaching is simultaneously pre-treatment technology and the first stage of a two stage anaerobic process (Wang et al., 2005).

Below in Figure 2.13 is the outline of where the various pre-treatments fit in regards to producing various chemical feedstocks from biomass.

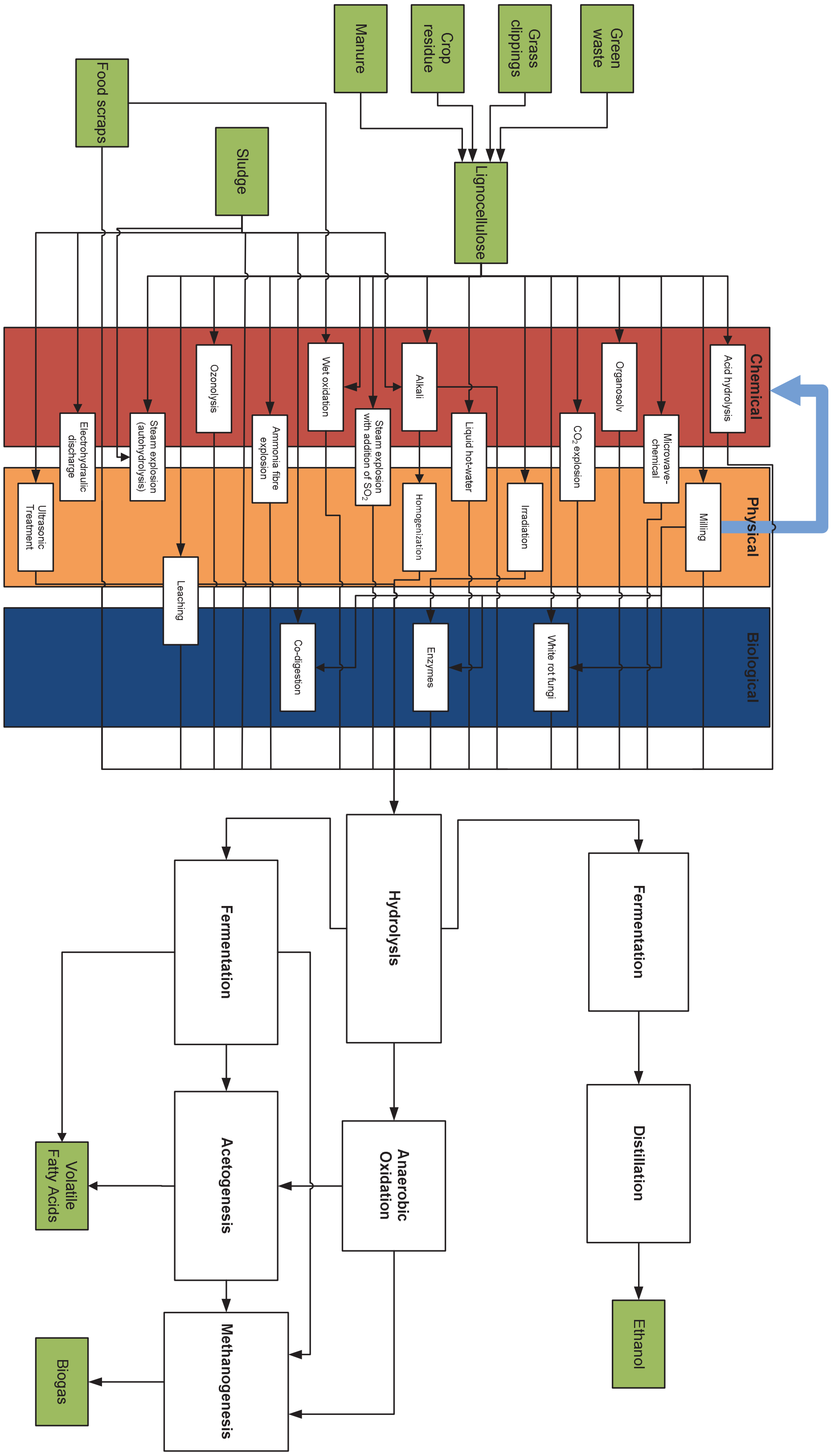

Figure 2.13: Feedstock pre-treatment options and metabolic pathways for various products

Source: adapted from (Banker, 2008; Khanal, 2008; Taherzadeh and Karimi, 2008)

2.5 Overcoming the Barriers to Anaerobic Digesting Solids

Vast amounts of waste organic materials that have the potential to be anaerobically digested are solids. Using most digester designs, pre-treatments are needed to process these materials before they can be anaerobically digested. The pre-treatments are mostly technically difficult, expensive and at times energy intensive. Traditionally there have been two ways to anaerobically digest solids. These both use a single-stage digestion system. The first types are dry batch / anaerobic compost systems; because these systems are not continuous feed, the gas production is not consistent and drops off towards the end of a cycle. The second types are wet continuous processes; the feedstock must be pre-processed into fine particles and then have water added in order to enable mixing and pumping. The disadvantage of this is the extra capital cost of the equipment and the parasitic energy losses involved in the extra processing. The extra volume from the added water also uses more energy for heating and pumping (Lehtomäki and Björnsson, 2006; Nizami and Murphy, 2005). Leaching is a technology that can be used as an alternative to the single-stage methods mentioned above.

2.6 Leaching

2.6.1 Leaching as a Process Operation

Leaching is one of the oldest process operations and is commonly used in the mining and pharmaceutical industries. Leaching is essentially the transfer of organic compounds from the solids phase into the liquid phase (Geankoplis, 2003; Treybal, 1980). The concentration of organic compounds in the leachate are represented by the concentration of the COD in the leachate (Nizami et al., 2010). This is achieved by interfacing the solid feedstock with water (Geankoplis, 2003; Treybal, 1980). In the case of anaerobic digestion the leaching system can be described as a tank that is loaded with organic solids and water with a drain situated at the bottom to release the leachate. In typical leaching operations the solids and the solvents are contacted in a multi-stage countercurrent method, known as the Shanks System. In this method the final leachate is removed from the freshest solids and the fresh solute is added to oldest solids. This method ensures that the maximum cumulative solute is leached, less solvent is used, and the concentration of solute in the solvent is higher in the final stage (Geankoplis, 2003; Treybal, 1980). In the case of leach beds employed for anaerobic digestion systems the solvent is water and the solute is organic compounds leached that can be directly used by acetogenic and methanogenic microorganisms in the anaerobic digester.

The rate that the build-up of organic compounds in the liquid phase occurs will depend on several mechanisms:

- Hydrolysis of insoluble organic compounds to soluble organic compounds
- Release of soluble organic compounds trapped inside cell structures
- Mass transfer of organic compounds from solid to the liquid phase
- Degradation of organic compounds into CH_4 and CO_2 and H_2
- Build-up of inhibitory compounds
- Saturation / equilibrium levels of organic compounds

The overall mass transfer in the leaching system is illustrated in Figure 2.14.

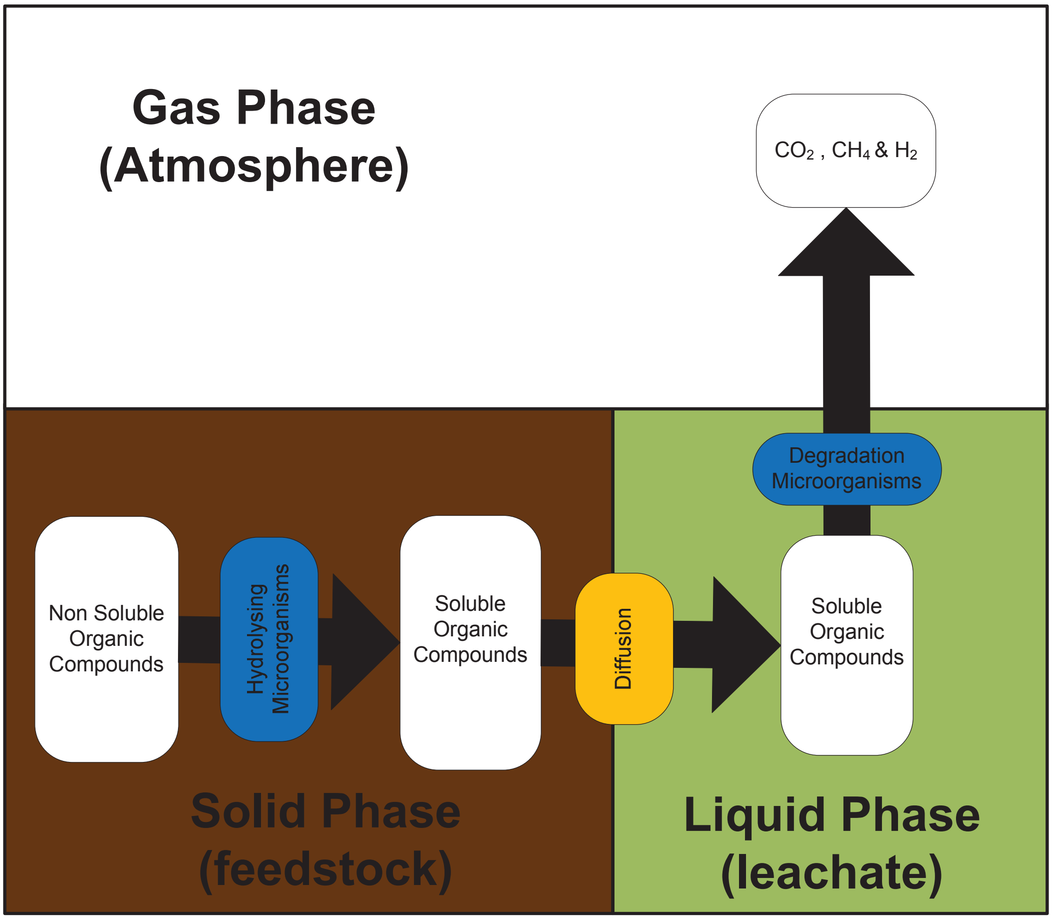

Figure 2.14: Mass transfer in a leaching system

Concentration gradients of soluble organic compounds between solid and liquid phase drives mass transfer through diffusion of the organic compounds from the solid to the liquid phase (Nopharatana et al., 2003). Increasing the concentration gradient can be achieved by either increasing the concentration of the organic compounds in the solid phase or decreasing the concentration of the organic compounds in the liquid phase. Increase of concentration of organic compounds in the solid phase can be achieved by increased hydrolytic microbial action in the solid phase. It has been pointed out by Jagadabhi et al. (2010) that nutrient deficiency and lack of inoculation may also slow down the rate of hydrolysis. The reduction in concentration of organic compounds in the liquid phase can be achieved by reducing the HRT. This happens by flushing the compounds out (Geankoplis, 2003).

Mass transfer of the dissolved soluble organic compounds through the solids to the surface is affected by the composition of the solids. Size reduction of the solids decreases the distance the compounds have to travel from the centre of the particles to the surface (Geankoplis, 2003; Treybal, 1980).

Microbiological action within the liquid phase of the leaching tank will consume the organic compounds. As these organic compounds are the feedstock for the microorganisms in the later anaerobic digestion stage, they are undesirable unless biogas is captured from the leach bed (Nizami et al., 2010).

It is thought that hydrolysing microorganisms can also be inhibited by low pH levels from organic acids and/or other metabolic compounds (Bhattacharyya et al., 2008; Lehtomäki et al., 2008).

Saturation of organic compounds in the leachate occurs when the concentration in the leachate does not increase even if the concentration in the solid phase increases. Equilibrium occurs when the concentration of organic compounds in the liquid phase is equal to the concentration in the solid phase. Once equilibrium has been achieved no more organic compounds can be moved to the liquid phase until the concentration is reduced; this is normally achieved by draining the liquid (solvent + solute) and replacing it with pure (or less concentrated) solvent. The organic compounds will continue to leach into the liquid phase until a new, lower, equilibrium is reached. In this process the higher the number of stages the more solute is leached. If saturation of solute in the solvent occurs, successive stages of leaching will give the same concentration until the available solute reaches a level below saturation within the solid phase (Treybal, 1980).

Other factors which influence concentrations of solutes in the solvents are mentioned by Geankoplis (2003), where they state that when biological products are leached for the pharmaceutical industry drying helps rupture the cell walls, which means the solvent can more readily dissolve the solute.

2.6.2 COD Solubilisation Achieved from Leaching

Various levels of COD concentrations have been achieved in studies of leaching grass silage and grass clippings. These values change over time as the leaching process proceeds. The maximum values achieved are shown in Table 2.3.

Table 2.3: Grass leaching results from literature

Feed Stock	COD Concentration (g / L)	kg COD / Tonne Volatile Solids*	Source
Grass Silage	34	510	(Jagadabhi et al., 2010)
Grass silage	55-61	-	(Lehtomäki and Björnsson, 2006)
Grass silage	12.6	890	(Nizami et al., 2010)
Fresh lawn grass	35	-	(Yu et al., 2002)

* Volatile solids added

2.6.3 Leach Bed as an Acid Phase Reactor

Overloading of an anaerobic reactor tends towards the overproduction of organic acids, which reduces the pH. The low pH inhibits the methanogenic microorganisms and hydrogen-producing microorganisms become dominant, causing the gas production to tend towards H_2 and CO_2 production (Valdez-Vazquez et al., 2005).

2.6.4 Leaching Bed Configurations

Leach bed reactors do not always operate independently and are often coupled with a methanogenic reactor such as shown in Figure 2.15 (b) and (c). UASBs are able to process waste streams at a much higher organic loading rate than an ordinary CSTR. When a UASB is coupled to a leaching bed organic loading rates of up to ten times higher can be achieved than if the solids were simply loaded into a CSTR. Effectively the size of the reactor is ten times smaller, resulting in cost savings on capital expenditure (Nizami et al., 2009).

Figure 2.15 (c) illustrates recycling of leachate from methanogenic reactors back into the leach bed; it has been shown that this increases the rate of hydrolysis (Lü et al., 2008). It is thought that the reason for this is that the dispersion of inoculums prevents nutrients deficiency. Additional advantages are recycling of heat from the methanogenic reactor and reducing water use. (Lehtomäki et al., 2008; Wang et al., 2005). When digesting vegetable and flower waste Lü et al. (2008) showed that supplementing the methanogenic effluent with the leach bed effluent for recycling into the leach bed was optimal at a ratio of 1:3 leach bed to methanogenic effluent. The recycling of too much leach bed effluent caused inhibition.

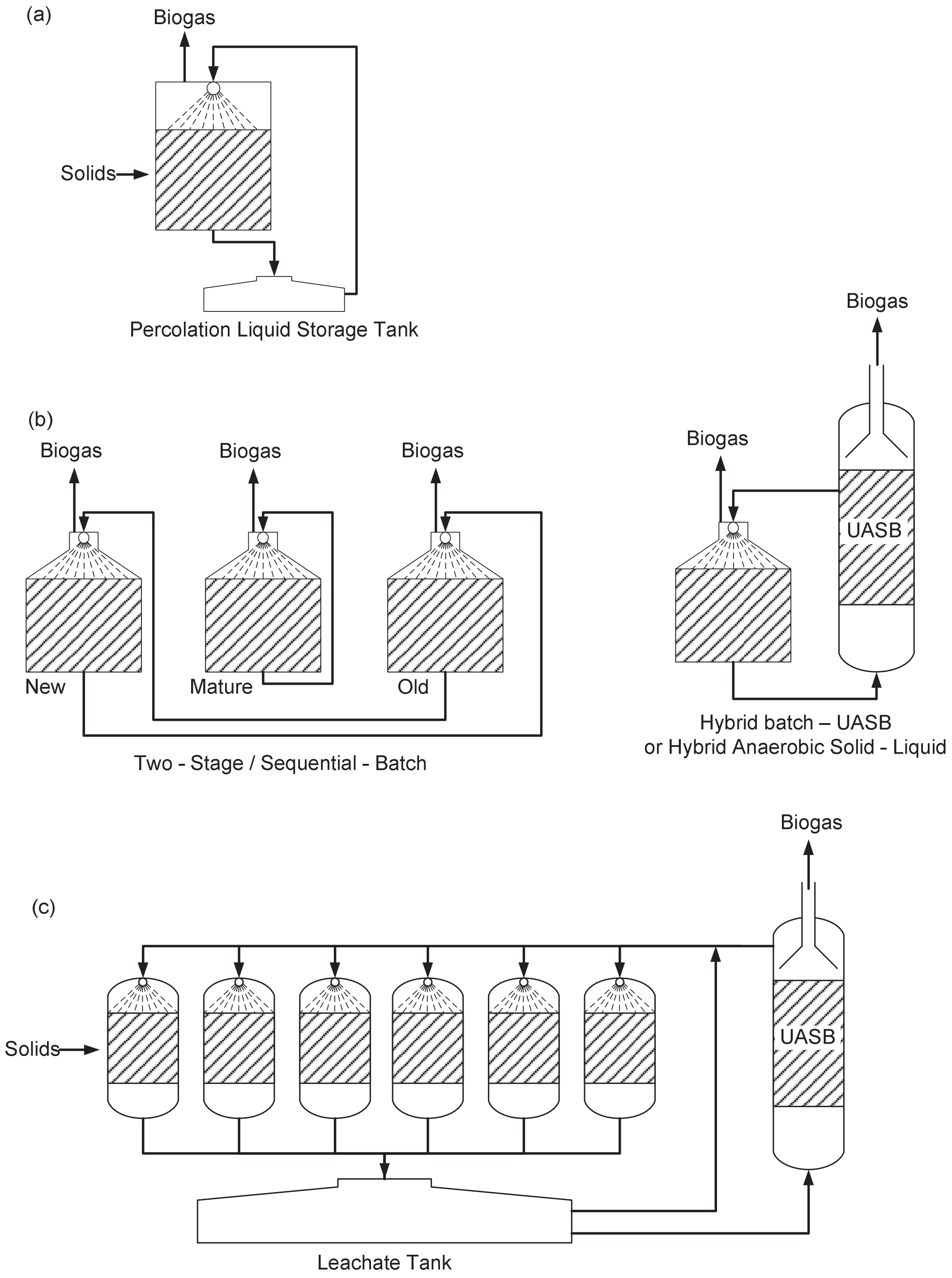

Figure 2.15: (a) One-stage batch digester (b) Two-stage batch digesters (c) Sequenced fed leach bed digesters coupled with UASB

Source: (Nizami and Murphy, 2005; Wang et al., 2005)

Single-stage vs two-stage leach bed + UASB with recycle was studied by Lehtomäki et al. (2008). It was found that the single-stage system only produced 20% of the methane potential in the grass silage whereas the two-stage system produced 66% of the methane potential. Sprinkling is a common method and is used by the following authors in their work, (Lehtomäki and Björnsson, 2006; Nizami et al., 2010; Yu et al., 2002; Zhang and Zhang, 1999). Leach bed systems often have a sprinkler nozzle attachment at the top of the tank. The liquid is contacted with the solids as it trickles down through the bed and is captured at the bottom and recirculated to the top of the bed through the sprinkler nozzle. Alternatively the leach bed can be flooded so all the solids are immersed. The leachate can also be recirculated in this configuration. Flooding is thought to be beneficial as the soluble material can be more readily solubilised since it is in contact with the material all the time. Sprinkling is also thought to be beneficial as the rapid flow of liquid over the solids theoretically increases the hydrolysis rate constant. It has also been suggested that flooding will require more energy than sprinkling as more water is required, which is a larger thermal mass to heat (Nizami et al., 2010).

The physical configuration of leaching tanks varies significantly from laboratory to commercial scale. As the leaching tanks are scaled up, loading becomes a concern; providing trafficable watertight hatches, preventing gas leaks through the large trafficable hatches and scrubbing the tanks of noxious fumes before operators enter with earth-moving equipment, are all issues that must be overcome before current laboratory systems are scaled up to commercial size (Nizami et al., 2009).

2.6.5 Leaching Temperature

Leaching has been carried out at various temperatures; often the leach bed is integrated with a methanogenic anaerobic reactor such as an anaerobic filter or USAB and the effluent is recycled back to the leach bed. In this case the temperature of the leach bed is kept at the same temperature as the reactor. Examples of various temperatures that leaching has been carried out at, with the resulting COD yields, are shown in Table 2.4.

Table 2.4: COD yields from leaching at varying temperatures

Substrate	Temperature	COD (g / kg VS)	Source
Silage	40°C	891- 318	(Nizami et al., 2010)
Grass Clippings	35°C	460 - 330	(Pratt et al., 2008)
Grass Clippings	15°C	440	(Powell, 2009)

Experimental work carried out by Powell (2009) showed that when the temperature of a leaching bed is lowered from 35°C to 15°C the COD yields is not majorly effected. It was noted that that the system could then be run in ambient conditions in a temperate climate without having parasitic energy lost for heating.

2.6.6 Aeration of Leach Beds

It is thought that external enzymes secreted by aerobic bacteria result in increased rates of hydrolysis (Hasegawa et al., 2000; Nguyen et al., 2007). Nguyen et al. (2007) found that the methanogenic reactor was also much faster in start-up if the leach bed had been aerated. Aerobic conditions in the leachate will increase the rate of loss of COD due to degradation; however, the increased rate of hydrolysis will more than make up for this (Lissens et al., 2001). In experiments carried out by Nizami (2010) flooding of the leaching tank was conducted with no attempt to seal the tank from the atmosphere, so small amounts of oxygen could have taken part in the leaching process. The tanks remained flooded at all times and the liquid was circulated using a pump. In work carried out by Powell (2009) the leaching tanks were drained completely before adding more water; this meant oxygen was likely introduced into the leach bed at higher levels.

2.7 Nutrients Requirements

Both micronutrients and macronutrients are critical to the operation of all microbiological systems; micronutrients are (K, Mg, Ca, Fe, Na, Cl, Zn, Mn and Mo), macronutrients are nitrogen and phosphorus. For optimal anaerobic digestion, the ratios of nutrients need to be correct. These ratios of COD : N : P range from 1000 : 7 : 1 to 350 : 7 : 1 (Gerardi, 2003). Additional to this, nutrients are a pollutant when discharged into waterways. Removal in a treatment process is required before disposal of any effluent from leaching processes (Metcalf & Eddy et al., 2003).

2.8 Literature Summary

There is little evidence in literature of green waste being tested as a feedstock for anaerobic digester systems. Because of the large size of the resource, and its current treatment as a liability as a waste product, it is attractive for use as a feedstock in an anaerobic digester. Considerable pre-treatment and processing is required before solids can be used in a CSTR anaerobic digester. While pre-treatment of feedstocks can reduce the time needed for anaerobic digestion, many pre-treatments are difficult to achieve on a practical and economical level. Studies made of various methods of preteatment use a narrow partial size range, highly homogenised, and characterised feedstock; realistically feedstocks arrive in a wide size range, from many sources and the exact characteristics are hard to determine due to the variety of organic matter in the feedstock. These studies admit the drawbacks of their own methods of pre-treatment in terms of scale up and financial viability.

Making use of the advantages offered by the advanced designs of anaerobic digesters such as UASBs is not possible with direct feeding of high-solid feedstocks. Leaching is a promising technology that enables both CSTRs and advanced designs of anaerobic digesters to utilise solid waste material. Pre-treatment and the first stage of a two-stage anaerobic digestion system happen simultaneously within leaching tanks preventing additional processing steps.

Leaching for anaerobic digestion systems is normally carried out in an anaerobic environment, although success has been had with intentional aeration. Testing of leaching systems with open-topped tanks has also been successfully trialled. Laboratory work carried out by Powell (2009) indicates that open-topped tanks at lower ambient temperatures perform in a similar manner to sealed and heated units. These systems make no attempt to create an anaerobic environment and offer the advantage of simplified design and ease of operation. The simple configuration of an open-topped tank solves many of the problems associated with scaling up leach bed systems. Loading and unloading will be much more simplified as no water or gas-tight hatches need to be used and noxious gases created during leaching will not have to be flushed before operators can enter the tanks.

Various leach bed configurations have been successfully tested at a laboratory scale including sprinkling and flooding. Both sprinkling and flooding have been tested with and without recirculation of the leachate through a separate methanogenic reactor. While most leach bed systems are set up with a sprinkler configuration, flooding offers opportunities to save energy by not having to operate a circulation pump. Sprinkler systems are promoted because less water is used, therefore less thermal mass needs to be heated (Nizami et al., 2010). However, if the leach bed is not heated, as suggested by Powell (2009), then full advantage of the flood systems can be made. Nizami et al. (2010) tested both sprinkling and flooding with mixed results, but because this was done at a laboratory scale only, for further evidence flood-type systems need to be tested at a pilot scale before scale-up.

A novel approach of using rumen fluid in a leach bed to increase biogas yields and enhance organic waste degradation has been tried with mixed results ranging from very profound improvements to none at all. Mixed results have been obtained with rumen contents from sheep. Nair et al. (2005) obtained profound improvements in organic waste degradation in a leach bed of grass, and Broughton (2009) conducted leaching trials with cow manure supplemented with sheep rumen contents to establish if the rate of hydrolysis would be improved; however, the results were inconclusive. Supplementing grass leach beds with rumen contents from cattle, which is a waste product from meat works, is not found in literature. Study of the effects of adding cattle paunch contents to leach beds could possibly provide an excellent improvement to the leaching process.

Nutrients will be part of the effluent released from a leach bed; these nutrients are essential and must be in the correct ratios for the optimum operation of successive anaerobic digester stages. Nutrients can be potential pollutants so any that are discharged from the leach beds will give an indication of the level of nutrients discharged from attached anaerobic digester systems.

3 Method

Experiments were designed to test the leaching of both grass and shredded green waste in open tanks in a controlled laboratory environment as well as in an outdoor pilot scale environment. The laboratory scale was done primarily to establish the effects of the following variables: HRT, different solids being leached and storing the solids in a controlled environment before leaching was carried out. A rumen contents and grass mixture was leached and tested to establish if addition of rumen contents to the mix increased COD yields of the grass. Laboratory scale CSTR methanogenic reactors were run to give an indication of gas production rates from both shredded green waste and grass leachate.

3.1 Experimental Variables

Table 3.1 shows the manipulated variables, these are variables which values are changed to cause an effect e.g. the change in COD concentration and yield. The method of control of these variables is reflected in the design and procedures for running the experiments. Table 3.2 shows the variables that are changing that cannot be controlled or are fixed. All of these variables are measured and accounted for to ensure that their effect on the results is understood.

Table 3.1: Variables that changeable and are manipulated to test response to leaching

Manipulated variables	
Variable	Method of control
Hydraulic Retention Time	Drain liquid and replace with clean water on a set schedule
Solids Retention Time	Solids remain in vessel when liquid is changed until end of experimental run
Types of Feedstock	The feedstocks will be limited to two types that will be tested independently
Storage time of feedstock	Fresh and stored feedstocks under controlled conditions will be tested

Table 3.2: Variables that were not either fixed or not manipulated

Factors		
Variable	Experimentally changeable or Fixed	Measurement and Control Methods
Position	Changeable	Took samples from top, middle and bottom of leaching vessels to obtain a representative sample
Temperature	Changeable / Fixed	Pilot scale trials monitored daily for temperature, all laboratory trials were conducted in temperature-controlled room at 25°C
Solids Moisture Content Before Leaching	Changeable	Measured before experimentation
Volatile Solids Content Before Leaching	Changeable	Measured before experimentation
Water : Solids Ratio	Changeable	Measured from weight of solids and volume of water for each trial (consequence of weight & volume)
Bulk density of feedstock	Changeable	Calculated from weight once leaching vessel is full of solids
Volume	Fixed	All vessels in field are the same size and all vessels in laboratory are same size
Weight	Changeable	Weighed all feedstock

3.2 Trial Matrix

The tables below show the trials that were carried out to achieve the aims of the project. Each laboratory and pilot scale trial has various combinations of solid and hydraulic retention times tested. As shown in Table 3.3. 4 hours, 1 day, 7 days, and 21 days were chosen as practical times to conduct measurements and were based on results from Powell (2009), as her results showed that rate of increase of concentration dropped off drastically after 7 days. Not all combinations of HRT and SRT were tried due to time and equipment restraints. HRT of 1 day for grass was run for 7 days initially and then 21 days to establish if higher total yields of COD could be obtained and what would happen to the concentration over the long term.

Trials to test gas production of CSTR anaerobic digesters at 35°C for shredded green waste and grass leachate are shown in Table 3.4.

Table 3.3: Leachate experimental runs

Trial	Type of Trial	Fresh or Stored	Feedstock	Solid Retention time	Hydraulic retention time
1L	Lab	Fresh	Green Waste	8 hours	4 Hours
2L	Lab	Fresh	Green Waste	7 Days	1 Day
3L	Lab	Fresh	Green Waste	21 Days	7 Days
4L	Lab	21 Days Stored	Green Waste	8 hours	4 Hours
5L	Lab	21 Days Stored	Green Waste	7 Days	1 Day
6L	Lab	21 Days Stored	Green Waste	21 Days	7 Days
7P	Pilot	Fresh	Green Waste	7 Days	1 Day
8L	Lab	Fresh	Grass (spring)	8 hours	4 Hours
9L	Lab	Fresh	Grass(spring)	7 Days	1 Day
10L	Lab	Fresh	Grass(summer)	21 Days	1 Day
11L	Lab	Fresh	Grass(spring)	21 Days	7 Days
12L	Lab (2 Litre)	Fresh	Grass(spring)	14 Days	1 Day
13L	Lab (2 Litre)	Fresh	Grass / Paunch Grass	14 Days	1 Day
14L	Lab (2 Litre)	Fresh	Paunch Grass	14 Days	1 Day
15L	Lab	21 Days Stored	Grass (spring)	8 hours	4 Hours
16L	Lab	21 Days Stored	Grass (spring)	7 Days	1 Day
17L	Lab	21 Days Stored	Grass (spring)	21 Days	7 Days
18P	Pilot	Fresh	Grass (summer)	21 Days	1 Day

Table 3.4: Gas production experimental runs

Feed	Type of Digester	COD concentration (g / L)	OLR (Kg COD / m^3.day)	Temperature
50 ml Shredded green waste leachate	2 L CSTR	6.9	0.17	35°C
100 ml Grass leachate	2 L CSTR	18.7	0.94	35°C

3.3 Laboratory Scale Leaching Experimental Procedure (Grass and Shredded green waste)

3.3.1 Collection of feedstocks

Feedstock was made up of highly heterogeneous green waste, which was divided into two groups: shredded green waste and grass (lawn clippings). Many factors influence the consistency of the green waste. This leads to great variability in its characteristics. Typically, members of the public and commercial garden maintenance contractors delivered green waste to site, which means there was no control over a variety of factors. These factors include, but are not limited to, where the green waste was collected, the species of the plants, maturity of the foliage, the amount of water and fertilizer provided, the time between cutting and delivery to site, and the time it was stored on site before shredding. The shredded green waste was a highly heterogeneous solid that was made up of leaves and branches from domestic gardens and public parks in the Palmerston North area. The green waste was shredded using a Willibald MZA4000 chipper (large mobile industrial shredder).

Rumen contents were acquired directly from the floor of the Feilding New Zealand AFFCO meat works floor before it was diluted with wash-down water.

3.3.2 Laboratory Experimental Set-up for Both Grass and Shredded Green Waste

The leach bed was constructed from uncoated steel drums with the dimensions 575mm diameter x 850 mm high. PVC sampling tubes are inserted into the solids as shown in Figure 3.1.

Figure 3.1: Laboratory leaching tank setup

3.3.3 Experimental Procedure

In order to gain a consistent feedstock for both fresh and stored experiments, approximately 2 m^3 of solids was placed in a pile on the laboratory floor and left for 21 days for the 'Stored' trial.

A fresh sample of the same solids was taken for testing. 3 x 200 L steel drums were filled with fresh solids—one for each treatment type i.e. 1 day, 7 days, 21 days. The mass of the solids in the drums was weighed.

PVC sampling tubes were placed into solids as shown in Figure 3.2 to collect leachate samples from the middle and bottom of the drum. The drums were filled with 25°C tap-water while measuring the volume of water.

The drums were placed in a temperature controlled room set at 25°C. Airtight bungs were placed on top of sampling tubes.

Samples were taken daily from top, middle and bottom for trials with 1 and 7 day HRTs. Sample were taken at the end of each 4 hours for the 4-hourly water changes. Temperature and pH of all sampling points were measured daily.

Leachate was drained weekly for the 7 day HRT trials, daily for the 1 day HRT trials and every 4 hours for the 4-hour HRT trials. The leachate was replaced with 25°C tap-water in all cases.

Once the ‘fresh’ trials were complete, the procedure was repeated for ‘stored’ solids.

3.4 Pilot Scale Leaching Experimental Procedure (Grass and Shredded green waste)

3.4.1 Experimental Setup

The leaching tank was constructed from an uncoated steel tank with the dimensions 1.4 m high x 1.15m x 2.m and a 50 mm ball valve attached to the bottom for drainage. PVC sampling tubes were inserted into the solids as shown in Figure 3.2. A plastic cover was secured over the top to keep out rainwater.

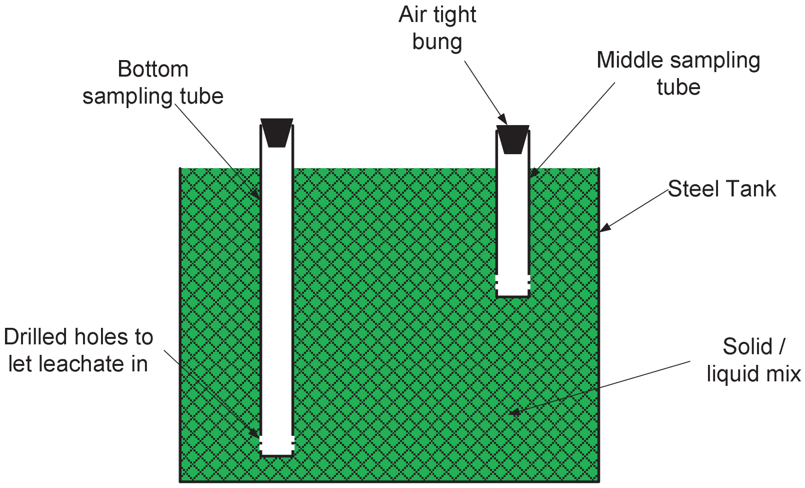

Figure 3.2: Pilot scale leaching tank set-up

3.4.2 Experimental Procedure

A 3.8 m^3 open-topped steel container was filled with grass / shredded green waste. The mass of the feedstock was weighted on a vehicle weigh-bridge. A sample of solids was taken in order to test moisture and volatile solids.

PVC sampling tubes were inserted into the solids as shown in Figure 3.2 to collect leachate samples from the middle and bottom of the container. Airtight bungs were placed on top of sampling tubes.

The container was filled with tap-water until all the solids were immersed. The volume of water was measured using a battery powered turbine flow meter made by GPI, model: 01N31GM.

Samples were taken daily from top, middle and bottom for trials with 1 day and 7 day HRTs. Sample were taken at the end of each 4 hours for the 4-hourly HRTs. Temperature and pH of all sampling points was measured daily. Leachate was drained weekly for the 7 day HRT trials and daily for the 1 day HRT trials. The leachate was replaced with tap-water in all cases.

3.5 Laboratory Grass and Paunch Grass Leaching Experimental Procedure

3.5.1 Experimental Setup

The leaching tank was constructed from acrylic columns with the dimensions 100 mm diameter x 250 mm high. A stainless steel 1x1 mm mesh was inserted into the bottom to facilitate drainage. There is a drain hole in the bottom with a valve attached to drain leachate as shown in Figure 3.3 below.

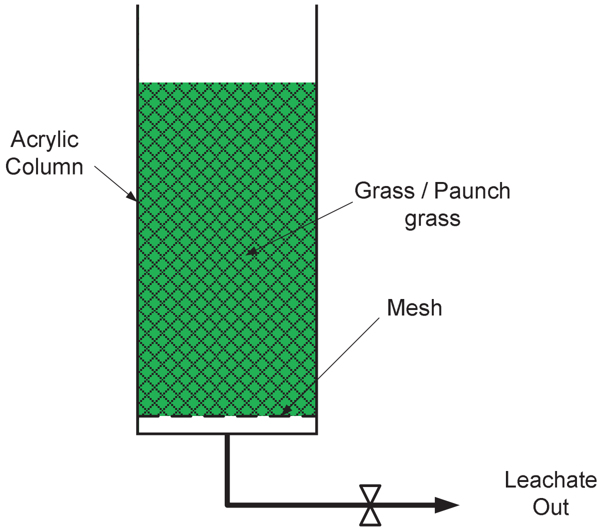

Figure 3.3: Rumen contents leaching tank set-up

3.5.2 Experimental Procedure

Approximately 400 g of fresh grass was placed in an acrylic column with dimensions 100 mm diameter x 250 mm high. A mixture of approximately 200 g fresh grass and 200 g rumen contents that had been well mixed was placed in a second column.

Approximately 400 g of rumen contents was placed in a third column. The exact amounts of material in each column was weighed. All columns were filled with water until the solids were completely immersed. Columns were placed in a controlled temperature room set at 25°C. A sample of all leachates was taken daily before replacement. The leachate was replaced with 25°C tap-water in all columns daily.

3.6 Solids Sampling (All Experimental Runs)

Solids are very heterogeneous, especially shredded green waste with its larger particle size. The characteristics will vary depending on time of year, what happens to be brought in for disposal by the public and how long it was left to sit before and after shredding. In an attempt to be consistent the shredded green waste samples were taken within a couple of hours after shredding of green waste that had been delivered within 24 hours. Solid sampling from shredded green waste and grass was taken by taking ten grab samples at random.

3.7 Leaching Tank Gas Composition Testing (Lab Trials in 200L Tanks)

It was observed that gas was being produced in the leaching tanks. Testing was carried out to establish the composition of the gas. A funnel with a gas sampling port attached to the stem was placed upside down on top of the grass leach bed in laboratory as shown in Figure 3.4. The funnel was pushed into the leach bed so an airtight seal was formed against the liquid. All air was purged from the funnel by drawing it out with a syringe and needle until the funnel was completely filled with water. A rod was used to disturb the grass, causing gas to bubble up and be caught under the funnel. A sample of the gas was taken with the syringe and needle through the gas sampling port.

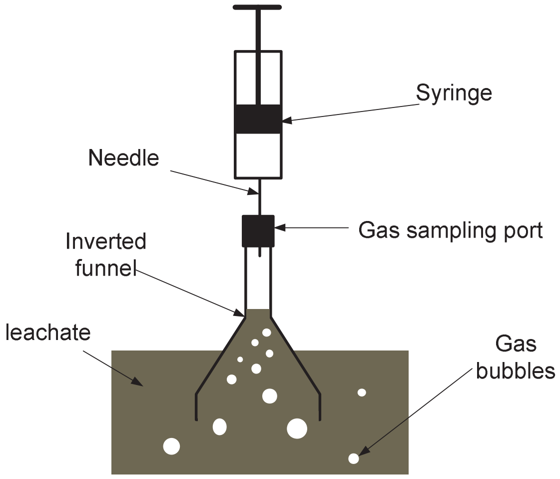

Figure 3.4: Gas collection apparatus

3.8 Leachate Stability - Testing Procedure

In order to test how stable the leachate was and if any degradation was happening during leaching trials, 20 L of grass leachate was placed in a plastic 20 L open-topped container. The container and leachate were left in the 25°C room for 7 days. Samples were collected and tested for COD daily.

3.9 Biogas Production in an Anaerobic Digester – Testing Procedure

3.9.1 Experimental Setup

Gas production from leachate was tested in a 2 L CSTR to simulate a typical mesophilic anaerobic digester and establish if biogas will be produced and, if so, give an indication on the amount produced. Leachate was placed in a 2.5 L reactor with a working volume of 2 L. The set-up consisted of a glass conical flask with a magnetic stirrer with a rubber bung and a tube running to a tipping bucket gas meter, as shown in Figure 3.5. The reactor was mixed via the magnetic stirring bar.

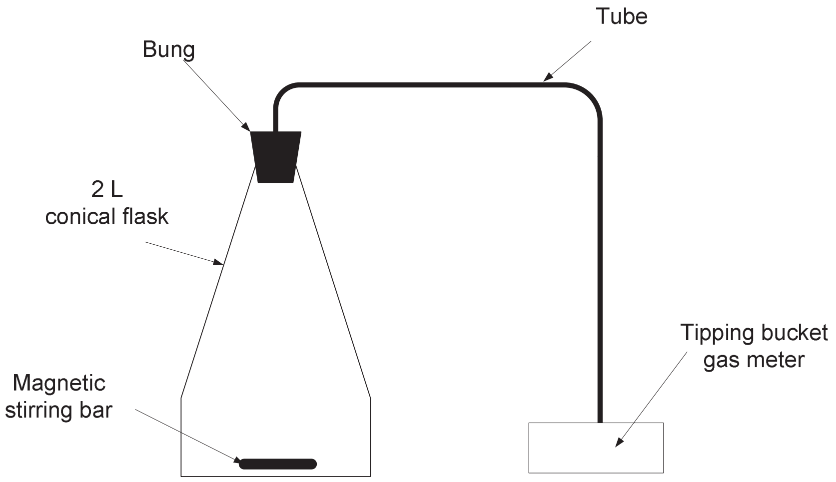

Figure 3.5: Mesophilic CSTR gas production setup

3.9.2 Experimental Procedure

The set-up was run in a controlled temperature room set at 35°C. The reactor was started with digestate from the Palmerston North City Council Waste Water Treatment Plant anaerobic digesters. 2 L of digestate was placed in the set-up described above and left without feeding until gas production ceased.

Shredded green waste leachate was tested by running 2 reactors simultaneously. 50 ml of digestate was withdrawn from each reactor and replaced with 50 ml of shredded green waste leachate with a COD of 6.9 g / L daily. Gas production and pH of digestate was measured daily.

Grass leachate was tested by running a single reactor. 100 ml of digestate was withdrawn from the reactor and replaced with 100 ml of grass leachate with a COD of 18.7 g / L daily. Gas production and pH of digestate was measured daily.

3.10 Analytical Test Matrix

Table 3.5: Leachate analytical testing matrix

Substrate	Test						
	COD	Bomb Calorimeter	Moisture / Total solids	Volatile Solids	Temperature	pH	Nutrients
Pilot scale leachate	✓				✓	✓	✓
Lab scale leachate	✓				✓	✓	✓
Pilot scale fresh solids	✓	✓	✓	✓	✓		
Pilot scale leached solids	✓	✓	✓	✓	✓		
Lab fresh solids	✓	✓	✓	✓	✓		
Lab leached solids	✓	✓	✓	✓	✓		
Lab stored solids	✓	✓	✓	✓	✓		
Lab stored leached solids	✓	✓	✓	✓	✓		

3.11 Analytical Tests

3.11.1 COD

Purpose: COD is a direct measure of the amount of oxygen required to oxidise organic compounds. The test establishes the amount of organic compounds available in a substrate that can theoretically be converted into biogas.

Analytical Method: COD was tested using the standard method 5220 D. 'Closed reflux colorimetric method' as laid out in (Clesceri et al., 1998). All samples were tested in triplicate. Each batch was checked for accuracy by digesting and testing a COD standard. Calibration curves were set using a COD standard as described in 5220 B of Clesceri et al. (1998). In studies carried out by Powell (2009) it was established that SCOD (Soluble Chemical Oxygen Demand) in leachate is the same as total COD in leachate; therefore, there is no need to conduct extra analytical procedural steps to establish the SCOD, as it is the same as the total COD.

3.11.2 COD of Solids

Purpose: Solids were tested for their COD to gain an understanding of the characteristics of the solid feedstock and to establish the amount of COD available in total that had the potential to be leached.

Analytical Method: COD of solids were tested in triplicate by taking 0.25g of dried and ground powder and adding it to 1 L of water. This was well mixed then tested using the standard method 5220 D. 'Closed reflux colorimetric method' as laid out in (Clesceri et al., 1998). All samples were tested in triplicate. Each batch was checked for accuracy by digesting and testing a COD standard. Calibration curves were set using a COD standard as described in 5220 B of Clesceri et al. (1998).

3.11.3 BOD

Purpose: BOD was tested to establish how readily biodegradable the COD leached is. This is to give an indication of the amount of biogas that can be made from the COD in the leachate.

Analytical Method: BOD was tested using the HACH respirometric standard method with the BODTrak™ apparatus laid out in (HACH, 2008). A seed was prepared by taking 2L of water from the Massey University Vet Duck Pond and aerating it for two weeks using an aquarium air stone and air pump. The pond water was fed 1 teaspoon of lactose and 1 teaspoon of milk powder twice weekly during these two weeks. All samples were tested in triplicate.

3.11.4 Energy Content - Bomb Calorimeter

Purpose: Bomb Calorimeter gives an indication of the energy content in the solid feedstocks being leached, this allows an understanding of the total available energy in the feedstock.

Analytical Method: Energy values of dried solids were tested using the method of ‘Gross Energy: Bomb calorimetry’ by the Nutrition Laboratory, Institute of Food, Nutrition & Human Health, Massey University, Palmerston North.

3.11.5 Solids Total Solids (Moisture Content)

Purpose: Moisture content is tested in order to calculate the total solids content. Total solids can then be used as a constant parameter in the feedstock to compare COD yields against each other. The feedstocks all vary in their moisture content, and moisture content is not a parameter that can be controlled.

Analytical Method: Total solids were tested in triplicate using the standard method 2540 B. ‘Total solids dried at 103-105’ method as laid out in (Clesceri et al., 1998). The test were carried out in triplicate.

3.11.6 Volatile Solids

Purpose: Volatile solids give an indication of the energy content in a solid. This is useful in characterising solids. It can also be used as a base-line to compare COD yields against.

Analytical Method: Dried solids from each triplicate were separately ground with a coffee grinder until all particles could be sieved through a 1 x 1 mm mesh.
Each of the triplicates of the dried solids were then further tested in triplicate, making a total of 9 samples to be tested. Testing was carried out using the standard method 2540 E. 'Fixed and volatile solids ignited at 550°C' method as laid out in Clesceri et al. (1998).

3.11.7 Temperature

Purpose: Temperature is an environmental factor that was monitored to see if it has an effect and to ensure that it remains constant in controlled environments.

Analytical Method: Temperature was tested at all sample points using a Eutech DO+6 probe.

3.11.8 pH

Purpose: pH is a response that is measured in order to create a better understanding about what is happening within the system; lowering of pH gives an indication that the system is becoming an acidogenic reactor and organic acids are being produced.

Analytical Method: pH of leachate samples was tested using a Eutech pH-510 meter and probe.

3.11.9 Nutrients

Purpose: Nutrients are tested as a way of characterising the leachate, which gives an indicator of any further uses or treatment that will be needed from the effluent of a leaching bed system.

Analytical Methods:

Total nitrogen and total phosphorus were tested in samples taken at day 7, 14 and 21 of the fresh shredded green waste laboratory trial and from the fresh grass laboratory trial that had an HRT of 7 days. All shredded green waste leachate was tested in triplicate while all grass was tested only once due to lack of sample volume. Nutrients testing was undertaken by John Sykes in the Environmental Laboratory, School of Engineering and Advanced Technology, Massey University.

Total Nitrogen - Total nitrogen was established by testing for and summing the values of:

- Total Kjeldahl Nitrogen
- Nitrate
- Nitrite

Total Kjeldahl Nitrogen was tested in triplicate using the standard method 4500-N_{org} B. 'Macro-Kjeldahl method' in Clesceri et al. (1998).

Nitrate and Nitrite were tested using the standard method in the Dionex ICS-2000 Ion chromatography system fitted with a onPac® AS11-HC analytical column, a IonPac® AG11-HC guard, a ASRS 300 4 mm self-regenerating suppressor and using potassium hydroxide as an eluent.

Total Phosphorus - Total phosphorus was established using the standard method 4500-P B. ‘Sulfuric acid-Nitric acid digestion’ for sample preparation and the standard method 4500-P E. ‘Ascorbic acid method’ in Clesceri et al. (1998) for analysis.

3.11.10 Gas Composition from Leaching Beds

Purpose: Leach bed gas composition was tested to establish if any useful or harmful gas is being released from the leach beds. It also gives an indicator of the type of anaerobic microbiology that is happening in the leaching tank i.e. to establish if the microbial population is causing the leach bed to act as an acid phase reactor by producing hydrogen or a methanogenic reactor by producing methane.

Analytical Method: Gas was tested for CH_4, CO_2 and H_2 using Shimadzu GC-2014 Gas chromatographer fitted with a TDC-L thermal conductivity detector operated at 45°C and an Alltech® CTR I packed column 1.8 m long 6 mm inner diameter operated at 35°C using nitrogen as a carrier gas.

4 Results and Discussion

4.1 Feedstock Characteristics

Some general characteristics of the feedstock were measured to establish an idea of the material being tested. These are shown in Table 4.1. Laboratory trials of shredded green waste have bulk densities of 123-188 kg / m^3 whereas the pilot trials have bulk densities of 605 kg / m^3. The less-dense laboratory trials required more water per tonne of solids in order for the solids to be completely covered in water. The densities directly affected the solids to liquid ratios in the leaching tanks to achieve flooding.

Shredded green waste lost moisture when it was stored inside in the laboratory for 21 days. The same shredded green waste left in large piles outside stayed moist and decomposed, which was evident by the heat and water vapour given off when the piles were moved. The smaller pile, which was left inside, was less compact and allowed good airflow. The moisture content of the shredded green waste that was stored inside changed from 49.4% to 41% over 21 days, as shown in Table 4.1.

Variation in VS contents of shredded green waste can be seen where samples of fresh shredded green waste were taken weeks apart. The shredded green waste for the laboratory trials contains 0.92 g VS / g dry solids whereas shredded green waste for the pilot trial showed much lower volatile solids at 0.66 g VS / g dry solids.

Energy content that was measured using a bomb calorimeter the values between samples ranged from 19 – 21.8 kJ/ g VS. replicates were not taken on these samples so the natural variation is unknown. The values measured are however helpful in characterising the feedstocks for further comparisons.

Grass showed much more consistency in all characteristics, with the only major departure being stored grass. When grass was stored inside it tended towards aerobic degradation and reached temperatures of 44°C in 4 days in ambient temperatures no higher than 15°C. The effect of aerobic degradation can be seen with the increase in moisture content, the loss of volatile solids and the increase in bulk density, as seen in Table 4.1 below.

Table 4.1: Laboratory trials - leaching solids characteristics

Feedstock	Bulk Density (kg/m^3)	Moisture content (%)	Volatile Solids (g VS / g dry solids)	Energy Content (kJ/g VS)	COD (mg/ g VS)
Fresh Green Waste	188	49.4±0.6	0.926±0.004	19.0	1200±200
Stored Green Waste	123	41±2	0.862±0.002	19.6	990±30
Green Waste Pilot Trial	605	52.2±0.5	0.66±0.02	-	1000±100
Fresh Grass (spring)	308	76±1	0.833±0.001	20.6	1220±60
Stored Grass (spring)	450	82±3	0.74±0.06	21.4	1200±100
Grass(summer) Lab Trial	352	64±1	0.848±0.006	20.5	1230±50
Grass(summer) Pilot Trial	375	64±1	0.848±0.006	20.5	1230±50
Paunch Grass (summer)	974	87.9±4	0.865±0.004	21.8	1460±50

NB: Errors show a 95% confidence interval based on replicated analysis of the same sample

4.2 Establishing COD Levels in Leachate, Establishing Degradability of Leachate and Measuring Gas Production from Anaerobic Digestion of Leachate

4.2.1 Leaching Using a Hydraulic Retention Time of 4 Hours (trials 8L, 15L, 1L and 4L)

Leaching of green waste was carried out in the laboratory using an HRT of 4 hours to establish the amount of COD leached into water over a short time period. All previous attempts at leaching in literature were carried out over a period of days, this was to establish if there was any benefit from leaching feedstocks with much shorter HRTs and to establish the bounds of reasonable HRTs. The tank took 2 hours to fill and 2 hours to empty. Samples were taken when the tanks were full. Figure 4.1 shows the concentration of COD in the leachate of grass and shredded green waste. Fresh grass produced the highest concentrations of COD in the leachate initially, with a value of 15.1 ± 0.7 g COD / L, which dropped to 4.4 ± 0.4 g COD / L after 4 hours during the second soaking. Stored grass initially produced 5.7 ± 0.6 g COD / L and dropped down to 3.4 ± 0.4 g COD / L during the second soaking. Fresh shredded green waste produced concentrations of 0.3 ± 0.5 g COD / L during the first soaking and 0.50 ± 0.06 g COD / L 4 hours later during the second soaking. Stored shredded green waste produced concentrations of 1.3 ± 0.2 g COD / L during the first soaking and 1.0 ± 0.1 g COD / L during the second soaking.

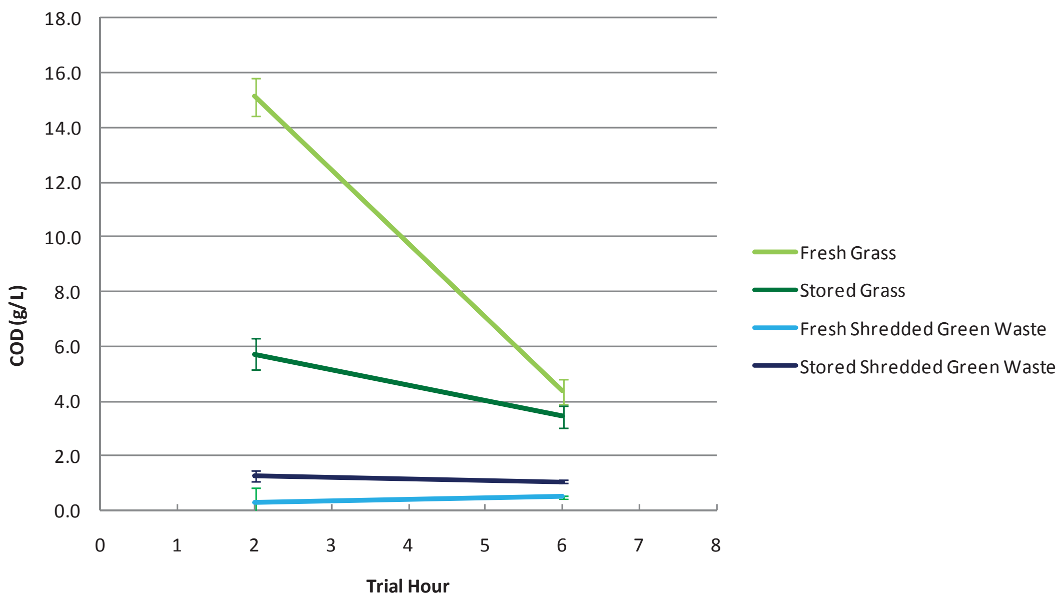

Figure 4.1: Concentrations of COD in leachate from grass and shredded green waste in laboratory trials when using a 4-hour HRT (trials 8L, 15L, 1L and 4L), error bars show a 95% confidence interval based on replicated analysis of the same sample

Figure 4.2 shows the total yield of COD leached from the feedstock over the trial. Fresh grass reached 149 ± 9 kg COD / tonne VS followed by stored grass which reached 80 ± 14 kg COD / tonne VS. Shredded green waste produced far lower total yields, with fresh shredded green waste producing 6 ± 4 kg COD / tonne VS and stored green waste producing 18 ± 14 kg COD / tonne VS.

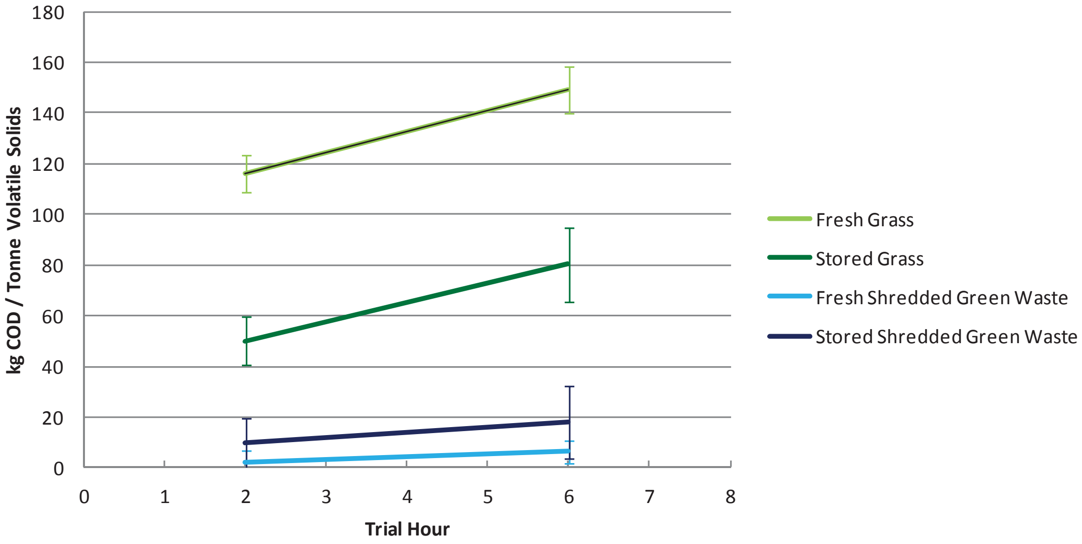

Figure 4.2: Total COD yield in leachate from grass and shredded green waste in laboratory trials when using a 4-hour HRT (trials 8L, 15L, 1L and 4L), error bars show a 95% confidence interval based on replicated analysis of the same sample

Fresh grass produces significantly more COD for any given mass of feedstocks than stored grass and shredded green waste; fresh grass also achieved higher concentrations, which is desirable for reducing water usage and reactor sizes. The initial concentrations of fresh grass was high compared to the second soaking; this indicates that there are high levels of soluble compounds in fresh grass, of which significant portions are washed out after the first flush. Additionally, the stored grass did not exhibit the same level of readily soluble compounds, which suggests they are degraded during storage.

4.2.2 Leaching Using a Hydraulic Retention Time of 1 Day (trials 9L, 16L, 2L and 5L)

Leaching was carried out using an HRT of 1 day over a 7 day period to establish the longer-term trends of leaching of grass and shredded green waste. Figure 4.3 shows the concentrations of COD in the leachate for grass and shredded green waste. Fresh grass started with an initial value of 13 ± 1 g COD / L in the leachate and peaked after one day at 22 ± 2 g COD / L and remained steady until day 5, after which the concentration rapidly decreased. Stored grass leachate had lower concentrations of

COD in the leachate with initial values at 5 ± 2 g COD / L, which peaked at day 1 with a concentration of 12 ± 1 g COD / L and then decreased in concentration until day 4.

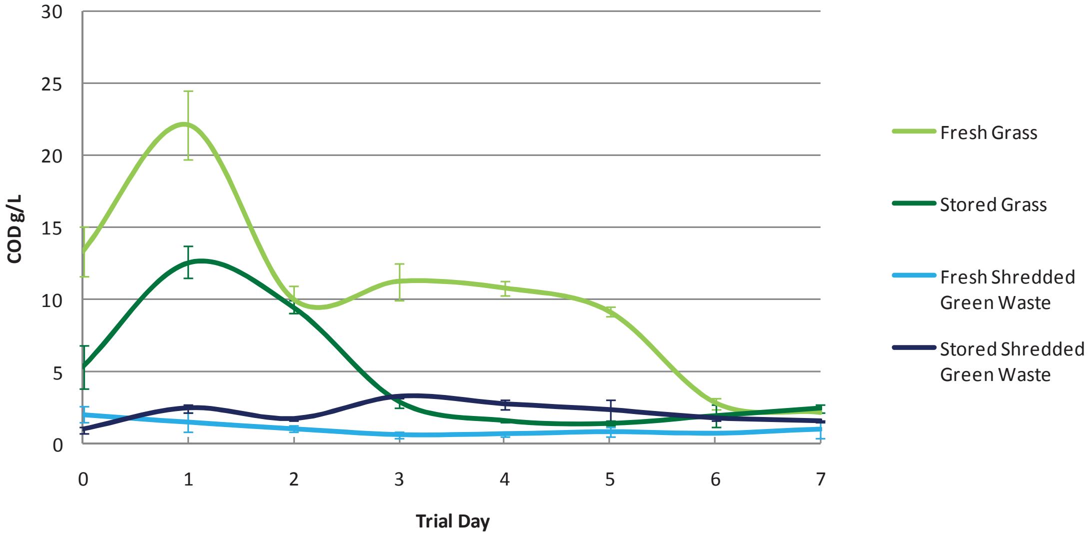

Figure 4.3: Concentrations of COD in leachate from grass and shredded green waste in laboratory trials when using a 1 day HRT (trials 9L, 16L, 2L and 5L), error bars show a 95% confidence interval based on replicated analysis of the same sample

Figure 4.4 shows the total yield of COD leached from the feedstock over the 1 day HRT trials. Fresh grass achieved a total COD yield of 410 ± 20 kg COD / tonne VS after 7 days whereas stored grass achieved only a maximum of 200 ± 40 kg COD / tonne VS after 7 days. Fresh shredded green waste produced the least total amount of COD, with a value of 70 ± 9 kg COD / tonne VS after 7 days. Stored shredded green waste produced significantly more COD than fresh shredded green waste, with the total amount rising to 132 ± 8 kg COD / tonne VS.

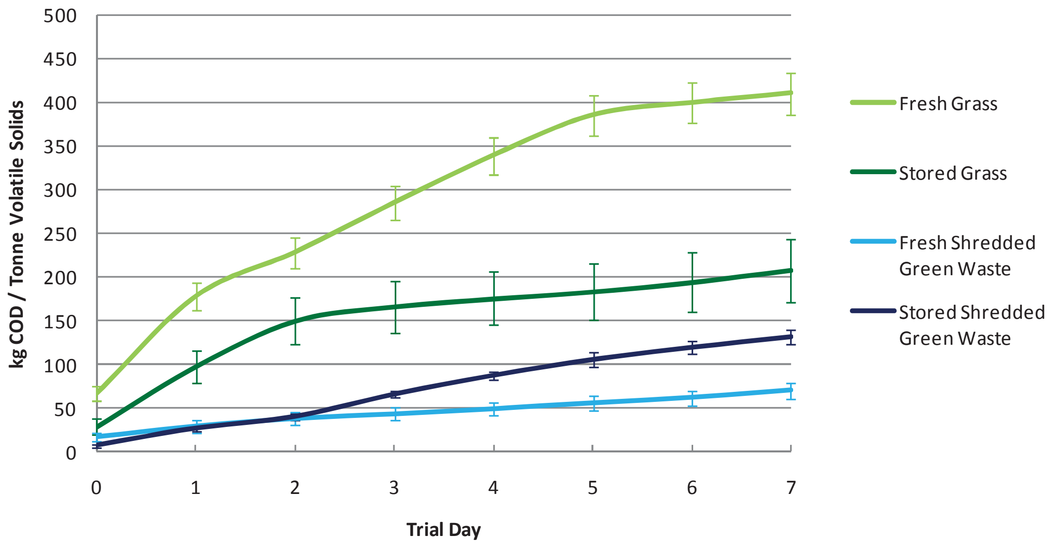

Figure 4.4: Total COD yield in leachate from grass and shredded green waste in laboratory trials when using a 1 day HRT (trials 9L, 16L, 2L and 5L), error bars show a 95% confidence interval based on replicated analysis of the same sample

The 1 day HRT trials further reinforce the findings from the 4-hour HRT trials, with fresh grass leaching the highest amount of organic compounds, followed by stored grass. Ensuring that the grass is processed as fresh as possible is paramount to maximising the amount of organic compounds leached therefore the amount of bio gas produced to make maximum use of available feedstock and processing equipment. Storing of shredded green waste enabled more organic compounds to be leached than if the shredded green waste was leached immediately. When the shredded green waste was stored it lost moisture content; while the storage conditions were not the same as an industrial drying process, the shredded green waste did tend to dry out. Geankoplis (2003) has pointed out that many substances in the pharmaceutical industry are intentionally dried to increase the amount of organic compounds that are leached.

Figure 4.5 shows the concentration of COD leached in 1 day HRT pilot trials for both fresh grass and fresh shredded green waste (trials 18P and 7P). Fresh grass shows high initial concentrations after 1 day of 47 ± 4 g COD / L. It drops sharply on day 2 down to 13 ± 1, then steadily decreases to 1.0 ± 0.1 g COD / L on day 15 where it remains relatively stable until day 21. Fresh shredded green waste produced much lower concentrations with the peak happening on day 1 with a value of 5.4 ± 0.5 g COD / L. The concentrations steadily decreased to 2.4 g COD / L on day 7, after which the trial was terminated.

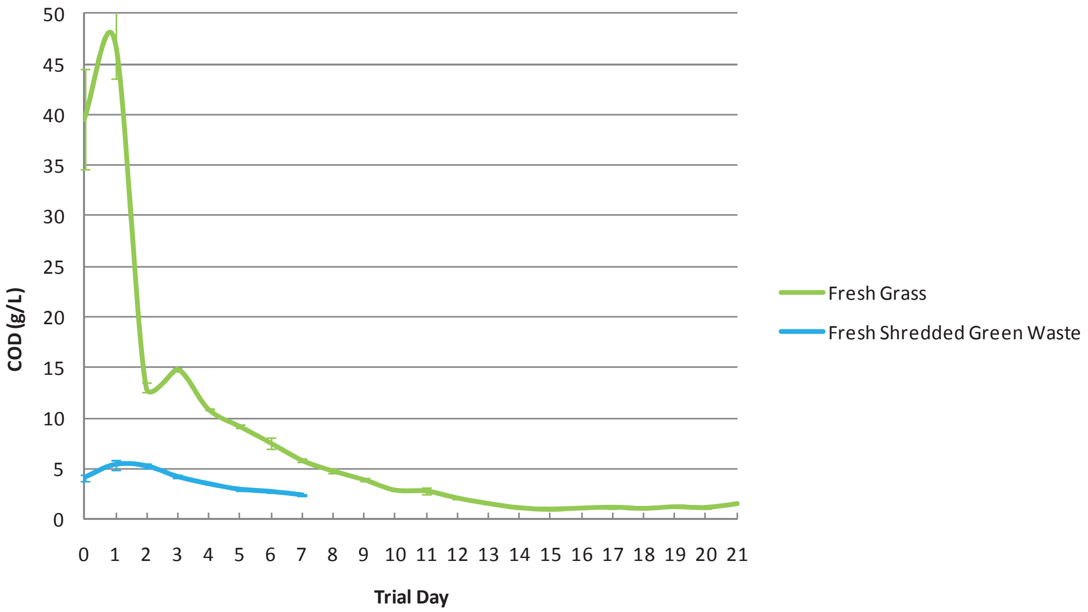

Figure 4.5: Concentrations of COD in leachate from grass and shredded green waste in pilot trials when using a 1 day HRT (trials 18P and 7P), error bars show a 95% confidence interval based on replicated analysis of the same sample

Figure 4.6 shows the total COD yield from the 1 day HRT pilot trial of fresh grass and fresh shredded green waste. Fresh grass gained a total of 410 ± 30 kg COD / tonne VS after 21 days and 360 ± 20 kg COD / tonne VS after 7 days. Fresh shredded green waste gained a total of 53 ± 2 kg COD / tonne VS after 7 days.

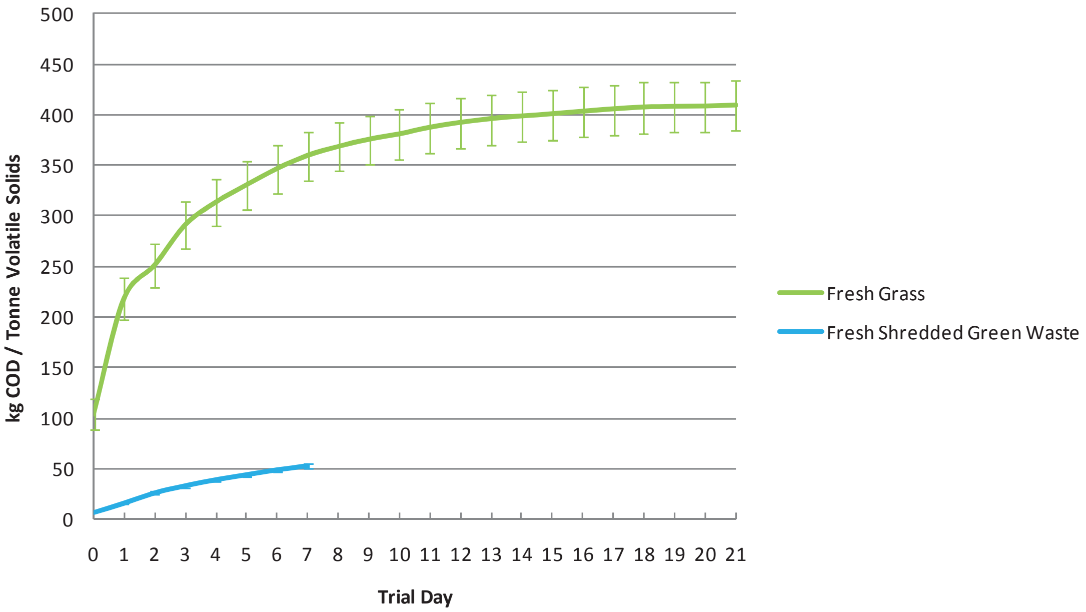

Figure 4.6: Total COD yield in leachate from grass and shredded green waste in pilot trials when using a 1 day HRT (trials 18P and 7P), error bars show a 95% confidence interval based on replicated analysis of the same sample

The concentration of organic compounds in the leachate and the total amount of organic compounds leached are similar to laboratory trials as shown in Figure 4.3 and Figure 4.4. Differences that are seen can be attributed to factors such as the bulk density on the material, which affects how much water is required to completely immerse feedstock. The amount of water used will in turn affect the concentration of organic compounds in the leachate; the concentration is the driving force for mass transfer of soluble compounds. The bulk densities of the pilot trials are higher, which means less water per tonne is used and the concentrations of organic compounds in the leachate are higher. This reduces the amount of soluble compounds that are transferred from the solid to liquid phase, which explains why the total yields are lower in the pilot trials.

4.2.3 Leaching Using a Hydraulic Retention Time of 7 Days (trials 11L, 17L, 3L and 6L)

An extended laboratory trial of 21 days with an HRT of 7 days was conducted with both fresh and stored grass and fresh and stored shredded green waste. Figure 4.7 shows the concentration of COD in the leachate for all 7 day HRT trials. Fresh grass initially showed the highest level of COD with a level of 20.7 ± 0.8 g COD / L in the leachate but dropped to similar levels as stored grass after 12 days. Fresh shredded green waste leachate reached a maximum COD concentration of 6.9 ± 0.6 g / L after 7 days. Stored shredded green waste showed lower levels of COD in the green waste with maximum levels reaching 5.1 ± 0.3 g / L. In all cases, the concentration dropped after each successive flushing of the leach bed, which can be seen at day 7 and day 14.

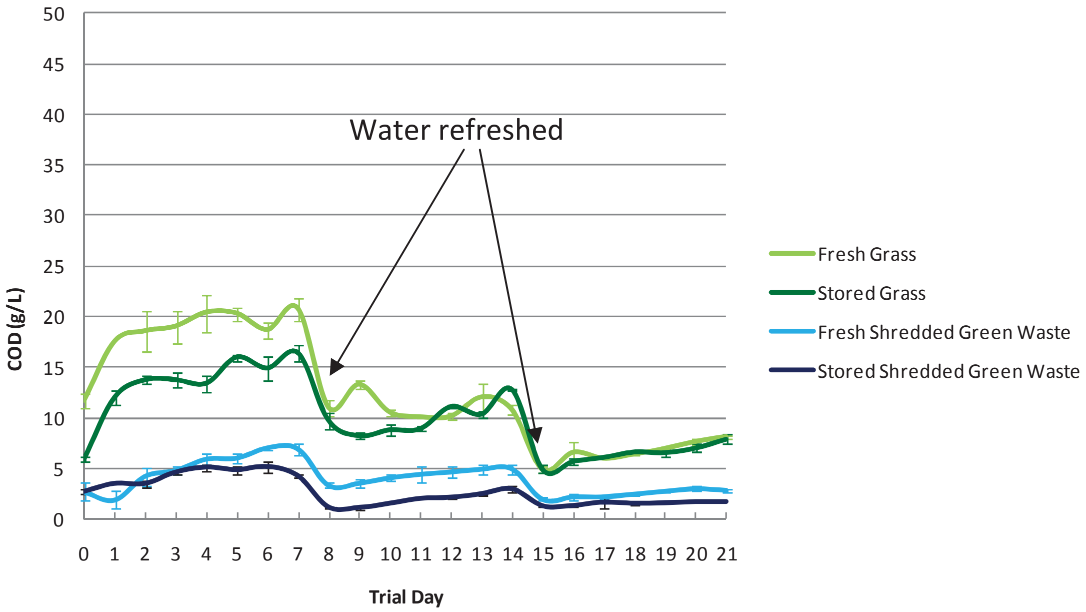

Figure 4.7: Concentrations of COD in leachate from grass and shredded green waste in laboratory trials when using a 1 day HRT (trials 11L, 17L, 3L and 6L), error bars show a 95% confidence interval based on replicated analysis of the same sample

The stored shredded green waste leachate COD concentration was lower than the fresh green waste COD concentration in the 7 day HRT. This is a deviation from the 4-hour HRT and 1 day HRT trials; the reason for this deviation is not clear.

Figure 4.8 shows the total COD concentration in the leachate for the duration of the 7 day HRT laboratory trial. Fresh grass reached a maximum 200 ± 20 kg COD / tonne VS after 21 days and stored grass reached a maximum concentration of 180 ± 30 kg COD / tonne VS after 21 days. The differences between stored and fresh grass are not significant in the 7 day HRT trial. Fresh shredded green waste reached a maximum of 106 ± 20 kg COD / tonne VS and stored green waste reached a maximum of 90 ± 10 kg COD / tonne VS after 21 days.

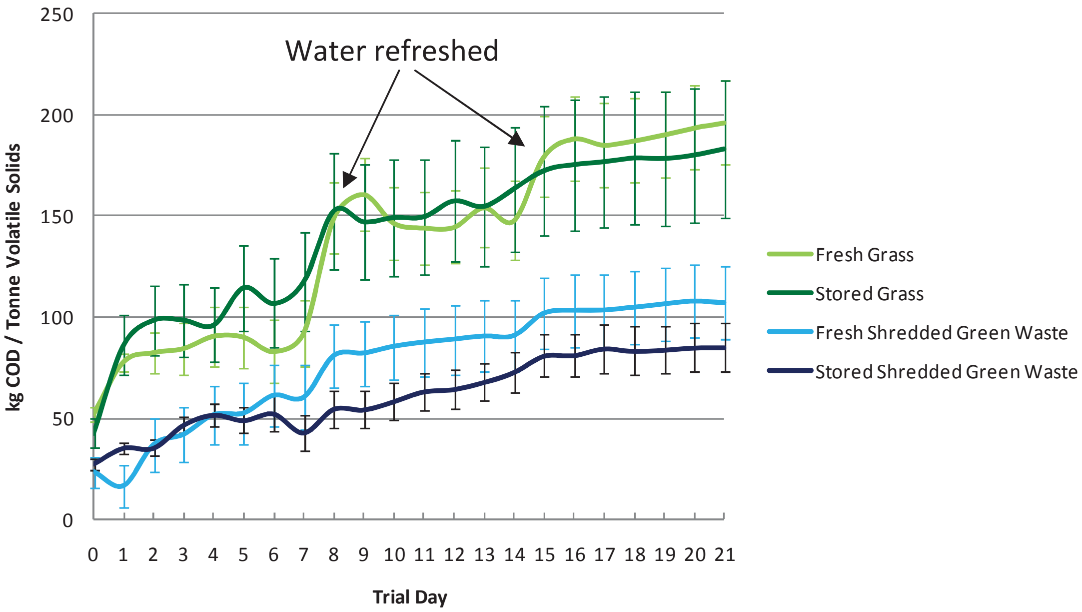

Figure 4.8: Total COD yield in leachate from grass and shredded green waste in laboratory trials when using a 7 day HRT (trials 11L, 17L, 3L and 6L), error bars show a 95% confidence interval based on replicated analysis of the same sample

The sharpest increases on total organic compounds yielded into the leachate occur on days 7 and 14 when the leachate is drained out and replaced with fresh water. This would suggest that running a shorter HRT would give higher total COD concentrations.

4.2.4 Leaching of Grass Supplemented with Rumen Contents (trial 12L, 13L and 14L)

Figure 4.9 shows the steady increase of total COD yield leached over the 7 days the experiment was run. The slope of the line decreases as the concentration of COD in the leachate drops due to the daily water changes. The lower blue line shows the total COD yield from the grass control whereas the higher red line shows the COD leached from the grass only in the rumen contents / grass mixture trial. To differentiate which fraction of the COD was attributed to the grass and which fraction was attributed to the rumen contents, calculations based on leaching trials of rumen contents only and a mixture of rumen contents and grass were carried out. The COD that was not attributed to grass in the mixed trial was then subtracted from the total COD yield in the mixed trial. See appendix 7.6 for details of a sample calculation.

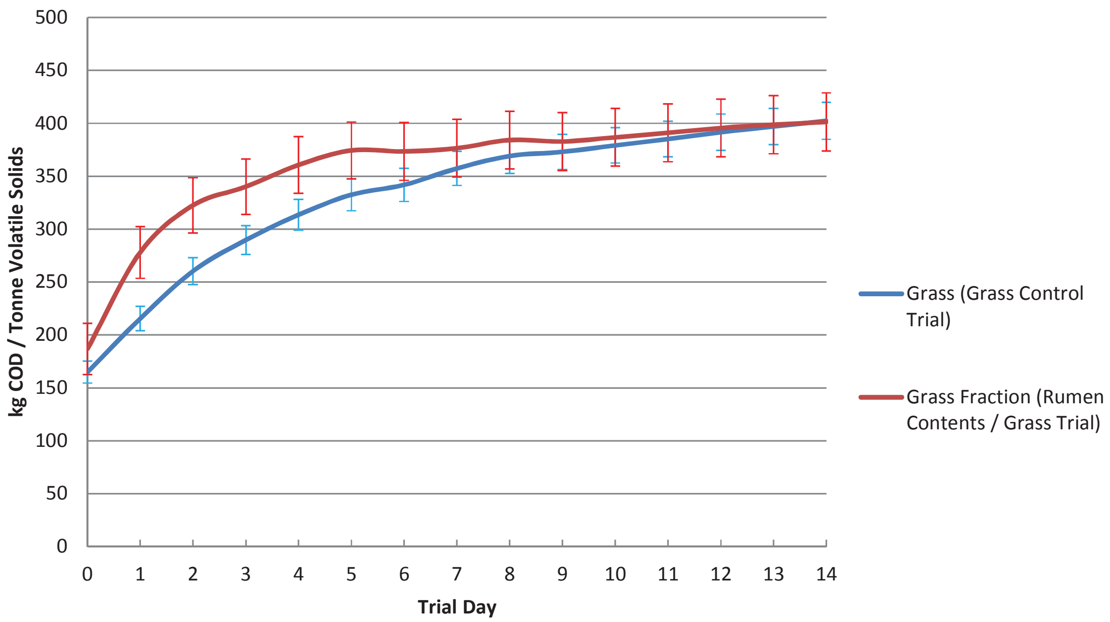

Figure 4.9: COD from grass in grass and paunch / grass leaching trial (trial 12L, 13L and 14L), error bars show a 95% confidence interval based on replicated analysis of the same sample NB: the red line has been adjusted to remove all COD associated with the actual rumen contents as described in appendix 7.6.

Addition of rumen contents to the fresh grass clippings raises the amount of COD released from grass initially but over a 7 day period the total COD yield leached attributed to grass from a rumen contents / grass mixture is the same as seen in Figure 4.9. Rumen contents was a thick sticky fibrous sludge material that did not leach well as water tended to sit on top of the solids and not drain through. Better results may be obtained if rumen contents is dewatered using a centrifuge or belt press and the liquid fraction is used with the water fed into the leaching tank.

4.2.5 Leachate BOD as a Measure of Degradability

BOD gives an indication of how readily biodegradable the leachate is. BOD is an aerobic degradation measurement whereas the ultimate use for the leachate will be degradation in an anaerobic digester to make biogas; the metabolic pathways and preferred compounds for microorganisms to feed on are going to be different. As shown in Table 4.2 the BOD : COD ratio is roughly 0.5-0.4 except for stored grass, which was much less degradable, with a ratio of 0.28 ± 0.08. This indicates that stored grass leachate may not be as suitable to feed into an anaerobic digester.

Table 4.2: BOD : COD ratios for leachate, errors show a 95% confidence interval based on replicated analysis of the same sample

Leachate tested	**COD**	**BOD**	**BOD : COD Ratio**
Fresh Shredded Green Waste	7.0 ± 0.1	3.7 ± 0.7	0.53 ± 0.02
Stored Shredded Green Waste	5.1 ± 0.6	2.1 ± 0.4	0.4 ± 0.1
Fresh Grass	18.7 ± 0.8	7.8 ± 1.2	0.41 ± 0.05
Stored Grass	14.9 ± 1.2	4.1 ± 0.8	0.28 ± 0.08

4.2.6 Anaerobic Digestion of Leachate for Gas Production

Figure 4.10 shows the biogas production from both grass and shredded green waste leachate using 2 L CSTR reactors. The plots are taken from the CSTRs once the gas production and pHs had stabilised. Higher HRTs were tried initially but they caused the system to drop in pH and gas production. The HRTs for the anaerobic digestion were adjusted by changing the volume of digestate replaced with leachate on a daily bases.

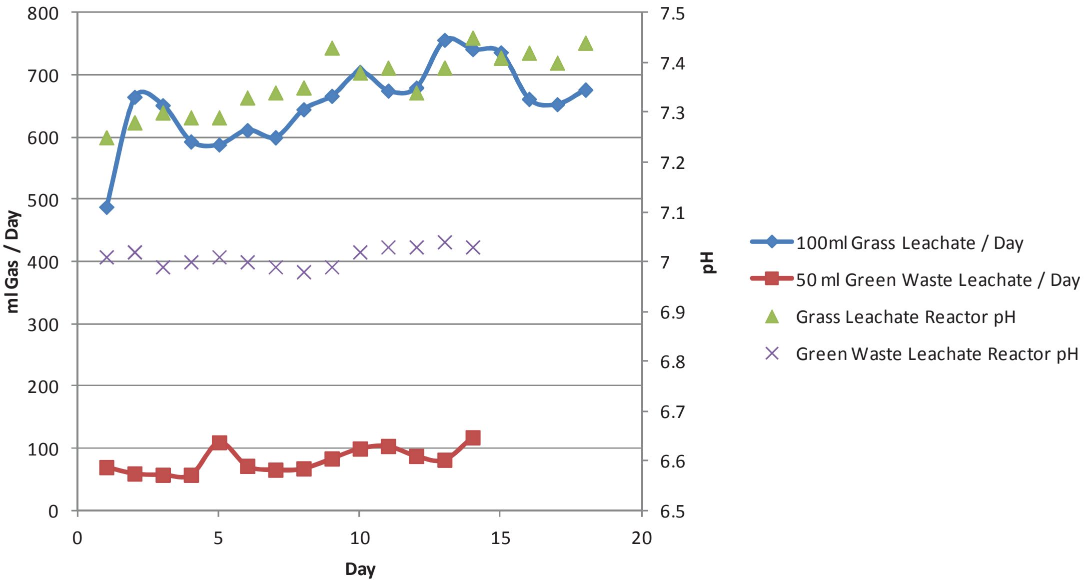

Figure 4.10: Gas production and pH from 35°C anaerobic digester CSTRs

The plot above is useful as an indication of gas output in relation to reactor volume and HRT. The leachate COD concentrations for grass and shredded green waste are different.

Figure 4.11 shows the gas production based on amount of COD feed to the reactor, this gives an indication of the efficiency conversion of COD of Biogas.

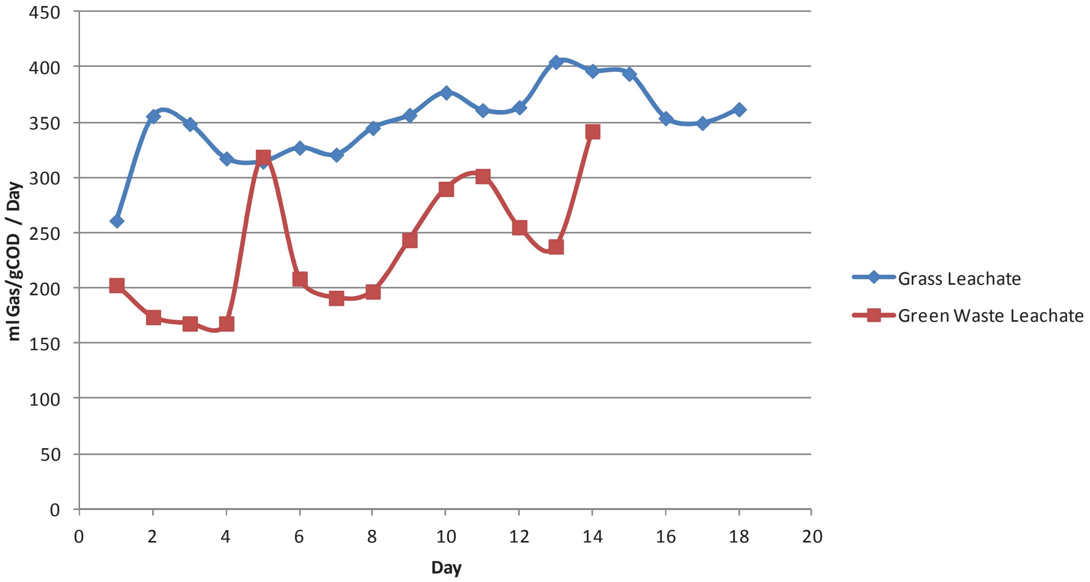

Figure 4.11: Gas production per g of COD

Using only COD as the measure of efficiency in the conversion of COD to biogas to can be seen that the grass leachate is more efficient this is reflected in Table 4.3 below. Gas production as a function of organic loading rate has been shown in. The production of gas in the CSTR digester showed that digesting shredded green waste leachate produced 42% of the theoretical gas possible from the COD fed to the reactor, and the digester with grass leachate produced 66% of the theoretical yield.

Table 4.3: Gas production results, errors show a 95% confidence interval based on replicated analysis of the same sample

Feed	Type of Digester	OLR (Kg COD / m^3.day)	m^3 gas / kg VS	m^3 gas / kg COD	% Biogas of Theoretical Yield from COD [c]
50 ml Shredded Green Waste Leachate / day	2 L CSTR @ 35°C	0.17	0.025 ± 0.005 [a]	0.24 ± 0.01	44%
100 ml Grass Leachate / day	2 L CSTR @ 35°C	0.94	0.146 ± 0.008 [b]	0.356 ± 0.004	66%

[a] assuming 0.107 kg COD / kg VS based on Figure 4.4
[b] assuming 0.402 kg COD / kg VS based on Figure 4.4
[c] assuming 65% of the biogas is methane
[c] 1 kg COD produces 0.35 m^3 CH_4 (von Sperling and de Lemos Chernicharo, 2005) cited in (Nizami et al., 2010)

In both green waste and grass leachate the amounts of gas produced were within the ranges reported in literature as shown in Table 2.2; however, the results are in the lower ranges. Testing of gas production was carried out to test if the leachate did produce biogas. Testing composition or optimising the amounts of gas produced in any given configuration was not within the scope of the study. However, during the trial it was found that a 40 day HRT for the shredded green waste leachate reactor was the most stable. The grass leachate reactor was stable with a 20 day HRT. Field et.al. (1988) demonstrated that tannins found in bark are toxic to methanogenic microorganisms. It was observed that shredded green waste has a lot of bark in it. So the leaching of tannins from the bark would explain why the yields of biogas were lower for green waste than grass.

4.2.7 COD, Nitrogen and Phosphorous Ratios

The correct ratio of COD : N : P in an anaerobic digester is important for the production of biogas. The ideal range or ratios for COD : N : P lies between 350 : 7 : 1 and 1000 : 7 : 1 (Gerardi, 2003). Table 4.4 shows the COD : N : P ratios in the leachate from laboratory leaching trials of fresh shredded green waste and grass.

Table 4.4: COD : N : P ratios in leachate

Fresh Shredded Green Waste

HRT	COD : N : P Ratio Normalised for N
7 Days	882 : 7 : 4.2 - 1182 : 7 : 2.4
1 Day	265 : 7 : 3.4 - 1656 : 7 : 12
4 Hours	90 : 7 : 3.9 - 292 : 7 : 41

Fresh Grass

HRT	COD : N : P Ratio Normalised for N
7 Days	227 : 7 : 4 - 315 : 7 : 3.2
1 Day	35 : 7 : 0.4 - 525 : 7 : 4
4 Hours	316 : 7 : 18 - 323 : 7 : 4.8

The ratios are not ideal in most cases for both the grass and shredded green waste trials. The amount of phosphorous is high compared with COD and nitrogen and in many cases the nitrogen is low compared against the COD. These imbalances in nutrient ratios may explain why gas production rates are at the lower end of the values reported by literature.

4.2.8 Variability of Experimental Trials (trials 9L and 10L)

Figure 4.12 shows the variability between two trials of grass leaching carried out in the in the lab using an HRT of 1 day. All experimental conditions were kept the same; however, the summer trial was conducted over a longer period of time. Grass that was leached during the summer showed higher concentrations of COD on day 1, with maximum concentrations of 49 ± 2 g COD / L, than grass leached in the spring, which had maximum concentrations of 24.5 ± 0.7 g COD / L. Both experiments exhibited similar concentrations from day 2 to 7.

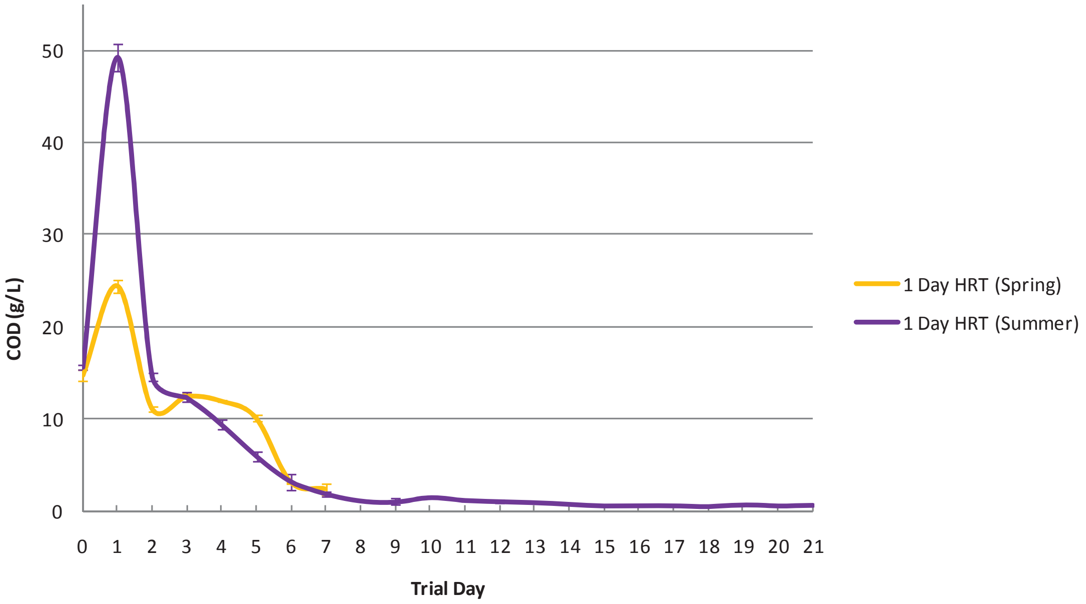

Figure 4.12: Comparison of COD concentrations between two trials run at different times of the year under the same conditions (9L and 10L), error bars show a 95% confidence interval based on replicated analysis of the same sample

Figure 4.13 shows the total COD leached in each trial on a basis of volatile solids. The spring trial leached a maximum of 410 ± 20 kg COD / tonne VS after 7 days whereas the summer trial leached a maximum of 290 ± 20 kg COD / tonne VS.

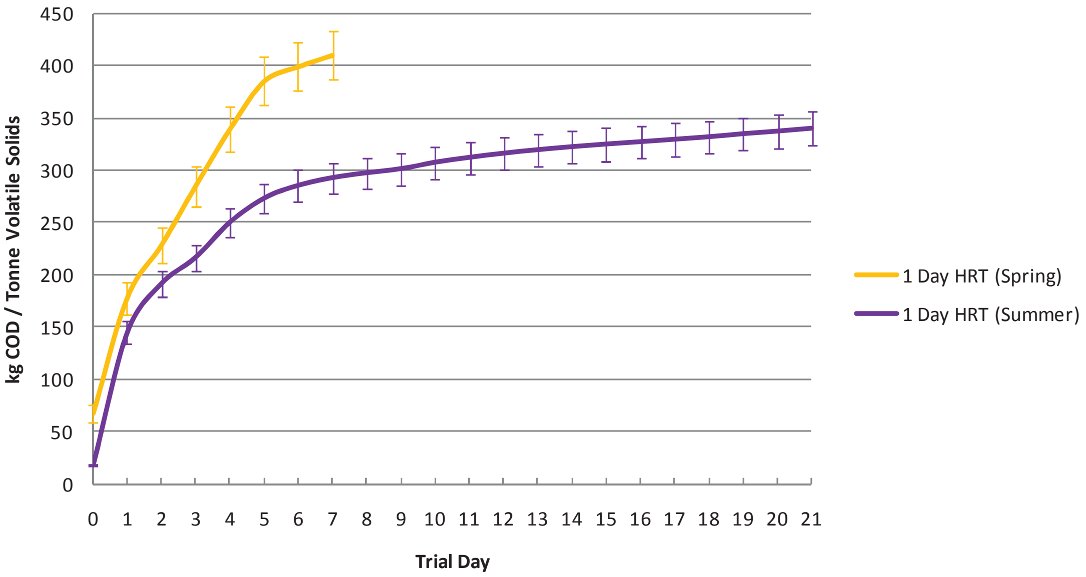

Figure 4.13: Comparison of total COD between two trials run at different times of the year under the same conditions (trials 9L and 10L), error bars show a 95% confidence interval based on replicated analysis of the same sample

It was not possible to maintain control of the characteristics of the feedstock before it was delivered to site. This can account for variability seen between trials run at different times using grass clippings as the feedstock. Many factors can influence how much organic material is leached. These include but are not limited to season, time of day grass was cut, time stored before leaching, species of grass, fertilizer applied to grass while growing, amount grass was watered, moisture content of cut grass, and length of clippings.

4.3 Establishing Rate-limiting Mechanisms Involved in Leaching

4.3.1 Establishing if the transfer of soluble compounds between the solid and the liquid phase is limited by the concentration gradient between the solid and liquid phase or the rate that soluble compounds are produced in the solid phase. (trial 2L and 3L)

The plant material will contain organic compounds that are insoluble such as cellulose these compounds need to be converted to soluble compounds such as sugars and amino acids by hydrolysis before moving from the plant material (solid phase) into the leachate (liquid phase). Additionally the plant material will contain soluble organic compounds which when soaked in water will readily transfer to the liquid phase to turn the water into leachate, this explains the higher initial concentrations in first flushes in all trials. Other mechanisms of cell break down of the plant need to be considered such as soluble compounds that are not able to be release into the liquid phase as they are trapped within a cell membrane, as this membrane degrades any soluble compounds will then diffuse into the liquid phase and increase the concentration of the leachate. The rate of movement of organic compounds from the solid to the liquid phase in shredded fresh green waste is independent of concentrations of organic compounds in the leachate. This was tested by comparing the HRTs of 1 and 7 days. The concentrations of COD—thus the dissolved organic compounds—are lower in the 1 day HRT trial than in the 7 day HRT trial. The rate at which compounds dissolve is dependent on the mass transfer constant, which is dependent on the velocity of the liquid over the solid (Nizami et al., 2010) and the concentration of the organic compounds already dissolved in the liquid phase. The velocity of the liquid was small, and similar in all experiments, as the tanks were flooded and left to sit in still conditions. The concentrations of organic compounds in the liquid phase are different when different HRTs are used, as seen in Figure 4.14. Short HRTs give lower concentrations and the longer HRT of 7 days gives a higher concentration. The overall movement of organic compounds from the solid to the liquid phases in fresh shredded green waste is the same in both trials, as seen in Figure 4.15. Even though the concentrations are different, this indicates that rate soluble material being made avalivible for diffusion across to the liquid phase is likely to be the same in both trials and is the rate-limiting step.

Figure 4.14 shows the change in concentration of COD in the leachate from fresh shredded green waste over time. This represents the change in concentration of organic compounds in the leachate. The blue line shows the concentration of the leachate that has an HRT of 7 days; the concentration increases up to the 7th day at which point the leachate is removed and replaced with fresh tap-water. The replacement of the leachate with water every 7 days causes the concentration to drop suddenly on the 7th and 14th days. The red line shows the concentration of the leachate with a 1 day HRT. This shows a steadily decreasing concentration until the 3rd day, where the concentration stabilises.

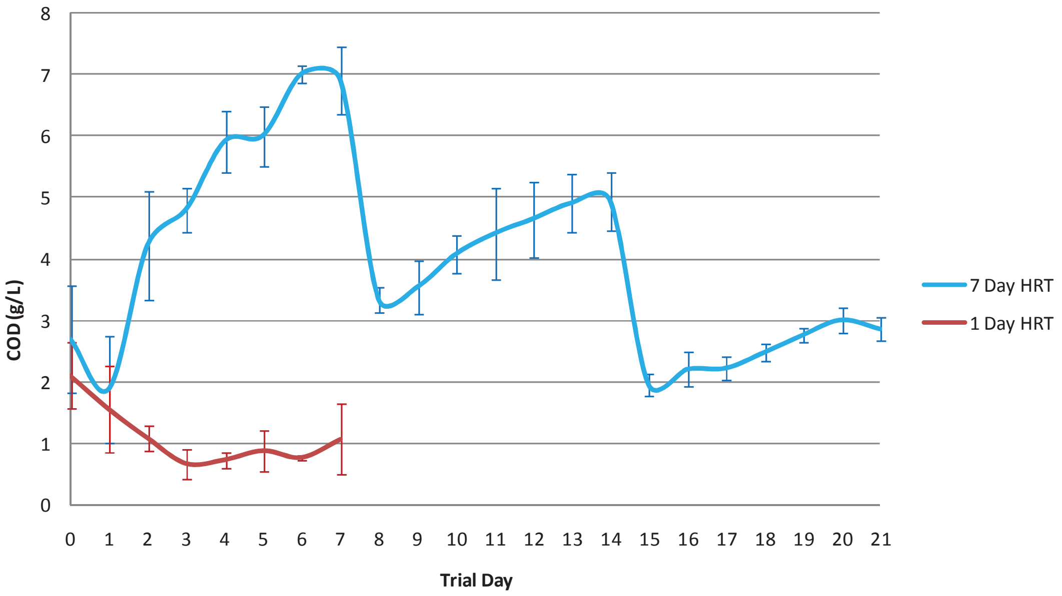

Figure 4.14: Change of COD concentration in leachate over time from the laboratory trials of fresh shredded green waste (trials 2L and 3L), error bars show a 95% confidence interval based on replicated analysis of the same sample

Concentrations of COD in fresh shredded green waste leachate remain low in all cases. When an HRT of 7 days is used, the maximum concentration of 7.0 ± 0.1 g / L was obtained at day 6 and was reduced to 2.9 ± 0.2 g / L at 21 days (blue line Figure 4.14). The 7 day HRT trial showed decreasing returns after each leachate replacement. The concentration after 7 days is within the range used with commercial USAB digesters, as suggested by Metcalf & Eddy et al. (2003). 1 day HRT shows decreasing concentrations of COD from 2.1 ± 0.5 with each leachate replacement until it remains steady from day 3 at approximately 1 g COD / L (red line Figure 4.14).

Figure 4.15 shows the total cumulative COD that was leached into the liquid phase over time for fresh shredded green waste in both 1 and 7 day HRT laboratory trials. Both 1 and 7 day HRT trials increase the total COD yield at a steady state until the 7th day. The blue line representing the 7 day HRT increases slightly. As on the 8th and 15th days, this is where the leachate is replaced with water. The rate of increase for the total COD yield decreases in the second and third set of 7 days for the 7 day HRT trial, as indicated by the decreasing slope of the blue line.

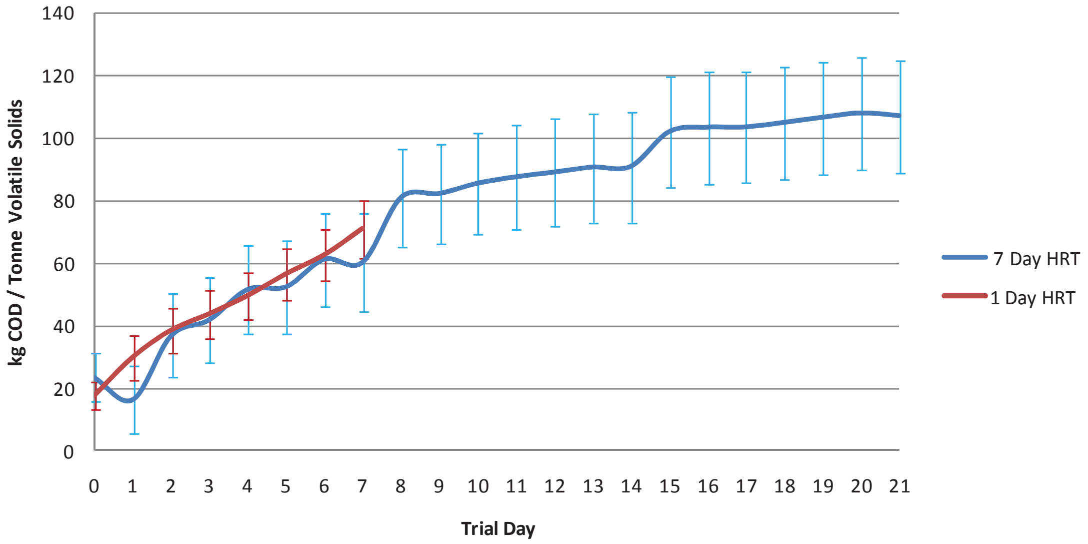

Figure 4.15: Comparison of total COD yield for fresh shredded green waste between 1 and 7 day HRTs (trials 2L and 3L), error bars show a 95% confidence interval based on replicated analysis of the same sample

The comparison between HRTs of fresh shredded green waste leachate in Figure 4.15 shows that HRT has little effect on total amount of COD leached.

The rate in which soluble material is made available for diffusion/ dissolving from either hydrolysis or the breakdown of cell membranes containing soluble material is likely to be the rate-limiting step with the leaching of fresh shredded green waste. This is shown by the fact that increasing the concentration gradient between the solid and the liquid phases by decreasing the HRT did not result in an increase of total COD yield in the liquid phase; an increase in concentration gradient will increase COD yield only if there is available SCOD in the solid phase to leach.

4.3.2 How the Storing of Shredded Green Waste Affects Release of Soluble Compounds (trials 5L and 6L)

Geankoplis (2003) suggests that drying of organic feedstocks causes the cell membranes to rupture, which makes their soluble contents available to be dissolved on leaching. The shredded green waste was stored inside and dried slightly from a moisture content of 49.4% to 41%, as shown in Table 4.1. The drying was most evident as the leaves turned from a soft green texture and colour to a hard brown. When the shredded green waste was stored in dry conditions and then leached, it appears hydrolysis is not the rate-limiting step and soluble organic compounds are readily available in the solid phase.

Figure 4.16 shows the change in concentration of COD in the leachate from stored shredded green waste over time. The blue line shows the concentration of the leachate that has an HRT of 7 days; the concentration of the leachate increases until the 4th day where it stabilises at approximately 5 g COD / L until the leachate is refreshed with tap-water on the 7th day. The red line shows the concentration of the leachate with a 1 day HRT. This shows the concentration of the leachate peaking at day 3, after which it steadily decreases to approximately 1.5 g COD / L.

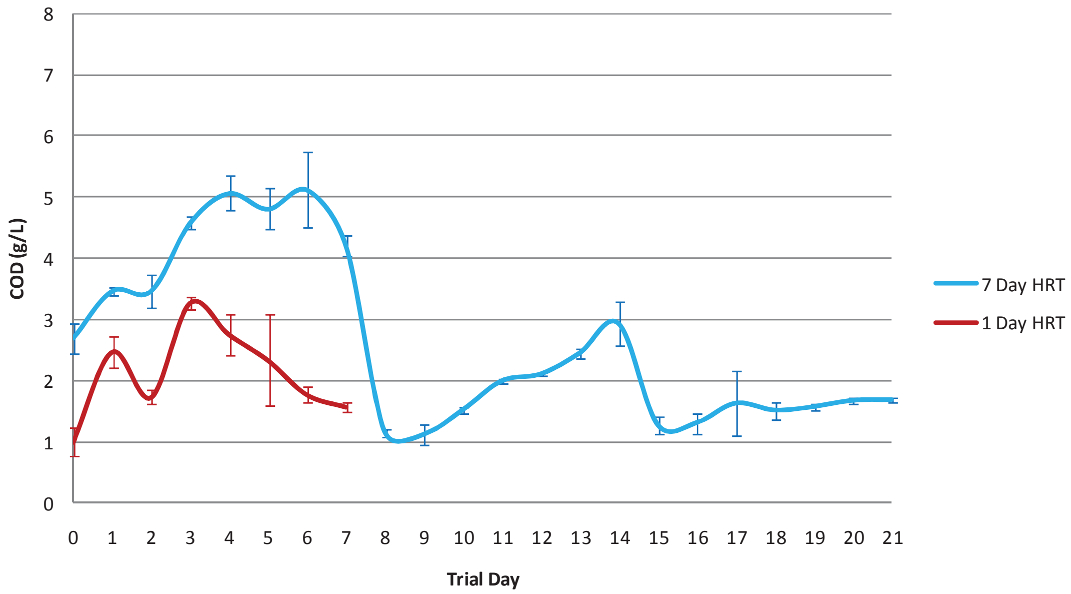

Figure 4.16: Change of COD concentration in leachate over time from the laboratory trials of stored shredded green waste (trials 5L and 6L), error bars show a 95% confidence interval based on replicated analysis of the same sample

COD in stored shredded green waste leachate with a HRT of 7 days reached a maximum concentration of 5.1 ± 0.6 g / L at day 6 and was reduced to 1.7 ± 0.1 g / L at 21 days (blue line above). The concentration of COD appears to reach equilibrium at day 4, which indicates that all the organic compounds that can diffuse across for a concentration of 5 g COD / L have done so within the first 4 days. The 7 day HRT trial showed decreasing returns after each leachate replacement; this indicates that the levels of readily available soluble compounds in the solid phase are being reduced with each flushing. The concentration of the 1 day HRT trial of stored shredded green waste peaked at 3.3 ± 0.1 and then decreased to 1.6 ±0.1 g COD / L on day 7 (red line above).

Figure 4.17 shows the total cumulative COD that was leached into the liquid phase over time for stored shredded green waste in both 1 and 7 day HRT laboratory trials. The 7 day HRT trial (blue line) increased the total COD yield at a steady state until the 14th day, after which there was a slight decline in the rate of leaching. The 1 day HRT trial (red line) shows a steep increase in the total COD yield leached in the 7 days the trial was run.

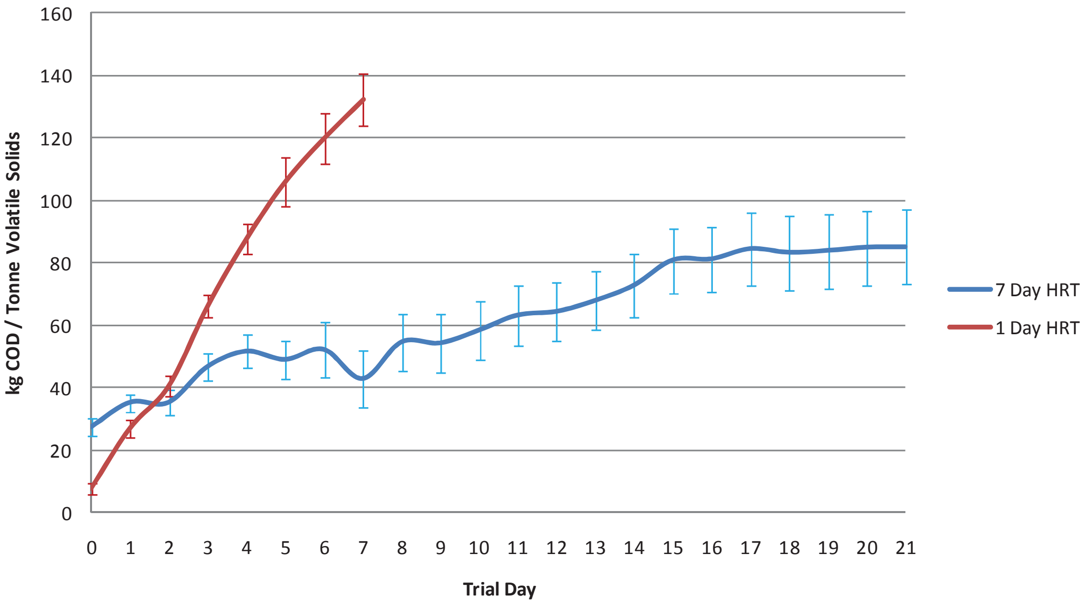

Figure 4.17: Comparison of total COD yield between 1 and 7 day HRTs for stored shredded green waste (trials 5L and 6L), error bars show a 95% confidence interval based on replicated analysis of the same sample

A 1 day HRT trial achieved a total yield of 132 ± 8 kg COD / tonne VS after 7 days whereas the 7 day HRT trial achieved a total COD yield of 52 ± 6 kg COD / tonne VS after 7 days. A comparison between HRTs of stored shredded green waste shows a marked increase of total COD yield in the leachate when the HRT is reduced to 1 day.

Concentration gradients between the solid and the liquid phases make the largest contribution to the rate of transfer of dissolved organic compounds into the leachate. An increase in concentration gradient of COD between solids and liquid phases as a result of a decrease in HRT made a significant impact on the amount of COD leached. The process of drying appears to make compounds that are more soluble readily available in the solids to be leached into the liquid phase. This is likely to be a result of the drying action assisting in the rupture of cell walls, as described in (Geankoplis, 2003; Treybal, 1980). While the overall drying of the shredded green waste was from moisture content only 49.4%-41%, it is likely that the leafy portion underwent much more significant drying than the wood stems of the plants. These leafy green portions are likely to be contributing the most soluble compounds to the leachate. The gains to be made by drying the shredded green waste and running batches at a short HRT are not likely to be practical as drying of shredded green waste is prohibitively difficult at large scale, since it immediately starts to aerobically degrade once shredded, especially if it becomes damp from inclement conditions. However, understanding how green waste behaves for a treatment of leaching once it has been stored conditions that cause it to dry could be useful in some locations.

A study of how green waste behaves when it is stored in conditions the same as it is stored in reality would provide useful information as to whether improvements COD yields and concentration can be made by simply dumping the shredded green waste in unprotected piles on the ground. Testing the effects of storing green waste in similar condition to how it is stored in large piles on site in a controlled manner will take significant resources such as a temperature controlled shed and earth moving equipment. The operators who drive the earth moving equipment that handle all the green waste at Palmerston North City Councils green waste dumping site observed that climatic conditions have a significant effect on how the green waste degrades. They observed that when it gets a small amount of moisture from rain the green waste becomes very hot from composting action. No heat generation was observed in the smaller pile that was stored indoors in the lab.

4.3.3 How Storing of Grass Affects COD Concentration and Yield in Leachate

Figure 4.18 shows the concentrations of COD in leachate of grass that had been stored for 21 days. The light-blue line presents the 7 day HRT trial results. The concentration only slowly increases over a period where the leachate is not changed and rapidly drops on day 7 and 14 when the leachate is replaced with water. The concentration remains above 10 g COD / L until the 14th day. The red line presents the 1 day HRT trial results: the concentration remains above 10 g COD / L for the 1st and 2nd day before quickly decreasing to approximately 1 g COD / L.

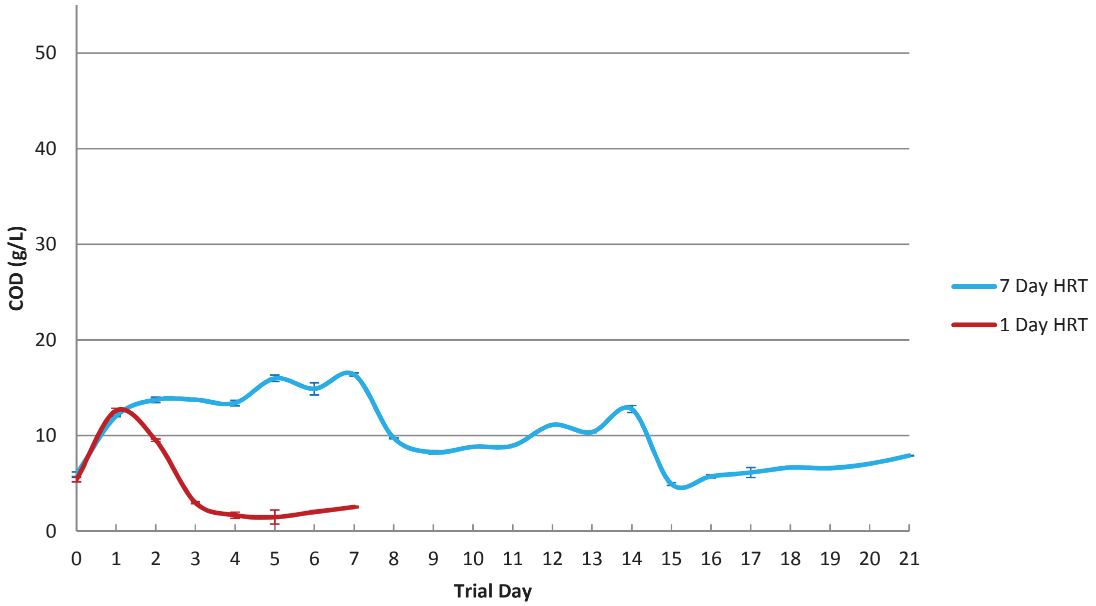

Figure 4.18: Change of COD concentration in leachate over time from the laboratory trials of fresh grass, error bars show a 95% confidence interval based on replicated analysis of the same sample

Stored grass shows a similar behaviour of steady increase in concentration when the leachate is not being replaced, suggesting a similar rate of hydrolysis to fresh grass; however, the initial concentrations are much lower. The 1 day HRT trial stabilises at approximately 1 g COD / L within 4 days (red line above), opposed to 8 days for fresh grass. This suggest that the total readily available soluble compounds are not as high as they are in fresh grass. This is further supported by lower volatile solids in the stored grass as shown in Table 4.1. Aerobic degradation of the grass while it was being stored is likely to be the reason for lower availability of VS and readily soluble compounds

Figure 4.19 shows the comparison of cumulative total yields of COD from all trials of leaching stored shredded green waste in the lab. The graph shows that leaching with an HRT of 1 day (red line) yields a higher amount of COD than leaching with an HRT of 7 days (blue line) over a 7 day period.

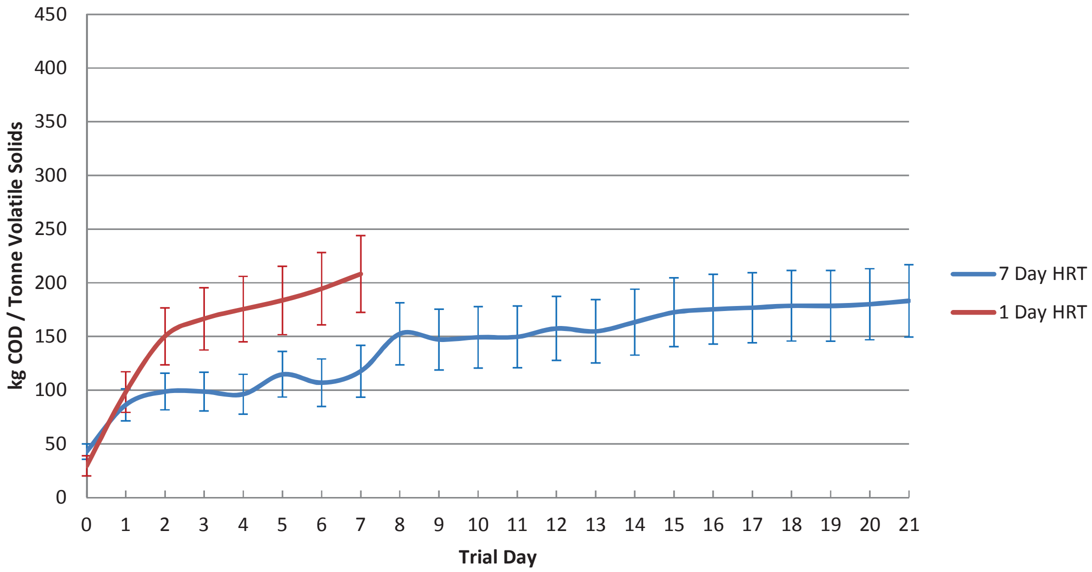

Figure 4.19: Comparison of total COD yield for stored shredded green waste between 1 and 7 day HRTs error bars show a 95% confidence interval based on replicated analysis of the same sample

The 1 day HRT trial reached a total yield of approximately 200 kg COD / tonne VS in 7 days (red line Figure 4.19) whereas the 7 day HRT only achieved approximately 120 kg COD / tonne VS in 7 days (blue line Figure 4.19).

4.3.4 How pH Affects Gas Composition from Leaching Tanks

It was observed that gas was being produced in the leaching tanks while the grass and shredded green waste was being leached. Gas samples taken from the fresh grass 1 day HRT laboratory trial contained 5% hydrogen, 25.5% carbon dioxide and 0% Methane. The fact that any gas was being produced is evidence that the leaching is not just a purely mass transfer operation; microbiological action is also taking part in the process. This supports findings by H. Wang et al. (2010) which demonstrated a dynamic population of microorganism in a grass leaching bed. Lack of methane indicates that methanogenesis is being inhibited, which also corresponds to the low pHs consistently found in the leachate (see appendix 7.4). H_2 production instead of CH_4 production indicates that the leaching tank is operating as an acid phase reactor as described by (Valdez-Vazquez et al., 2005).

4.4 Effects of Scale-up

4.4.1 Bulk Density Affect on Concentration and Yields of Shredded Green Waste Leachate

The major difference between the pilot and laboratory trials of shredded green waste is the bulk density of the feedstock in the leaching tanks. Laboratory trials are useful as an indicator of how a larger-scale system will perform; however, differences in COD concentrations and yields that do exist are most likely to be a result of differences in bulk density.

Figure 4.20 shows a comparison of concentrations of COD in the leachate between trials of fresh shredded green waste, stored shredded green waste, and the pilot trial, all at an HRT of 1 day.

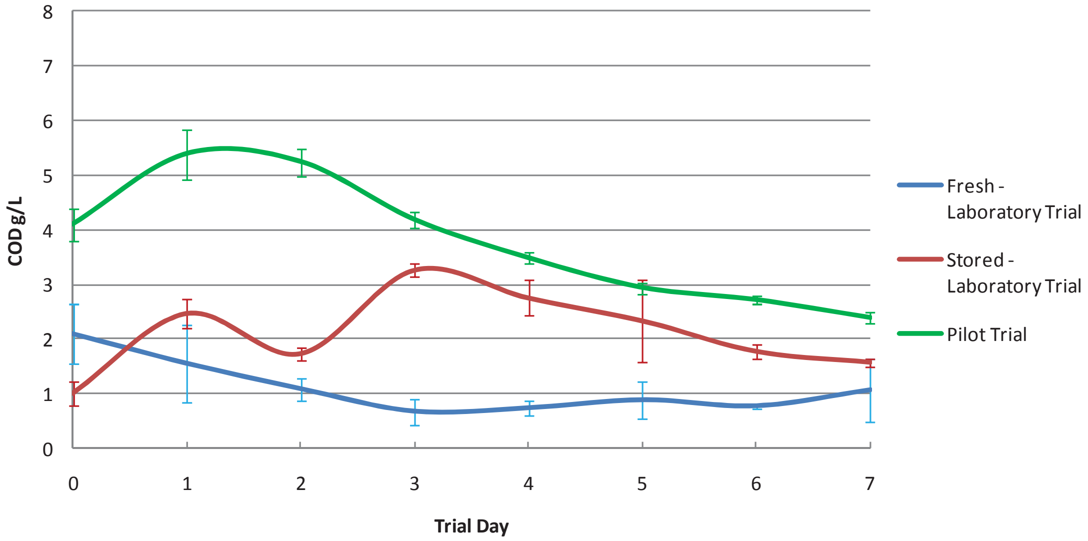

Figure 4.20: Comparison of concentrations of COD in leachate for trials with an HRT of 1 day between fresh shredded green waste laboratory trial, stored shredded green waste laboratory trial and the pilot trial, error bars show a 95% confidence interval based on replicated analysis of the same sample

Pilot trials of shredded green waste with an HRT of 1 day resulted in overall concentrations higher than both fresh and stored shredded green waste trials in the lab. Less water is used in the pilot trials to flood the same amount of solids due to the higher bulk density; this is a likely cause for the higher concentration in the pilot trial, as it is not as diluted as the laboratory trials.

Figure 4.21 shows the total COD yield for 1 day HRT trials of shredded green waste. The stored shredded green waste shows an improvement overall in the amount of COD leached while the fresh shredded green waste laboratory and pilot trials have very similar yields.

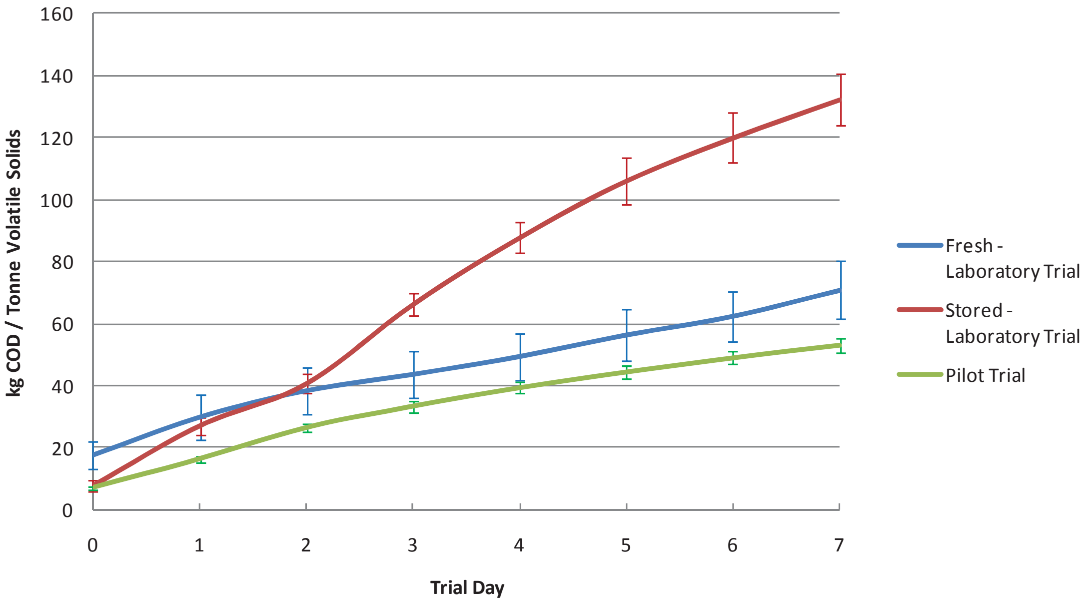

Figure 4.21: Comparison of total COD yield between fresh and stored laboratory trials and the pilot trial for shredded green waste—1 day HRT, error bars show a 95% confidence interval based on replicated analysis of the same sample

Despite the higher concentrations of COD in the pilot trial, using less water per tonne of solids results in lower total COD leaching yield, as shown in Figure 4.21. The water to solids ratio in the pilot trial is 8 times lower to achieve flooding of the shredded green waste. This is because the solids are more compacted by their own weight and the earth-moving equipment when they are loaded into the leaching tanks. This increased bulk density means less water is required to cover solids when flooding the tank. The reduction in the amount of water used in the pilot trial is profound and is desirable from a practical engineering point of view as there is less waste fluid to dispose of.

4.4.2 Laboratory Sale as an Indicator of Pilot Scale Performance

Figure 4.22 gives a comparison 1 day HRT results for grass leaching. The pilot trial of grass cut in the summer (green line) shows a slightly higher yield than the laboratory trial of grass cut in summer (blue line). The trial of fresh grass cut in the spring (orange line) shows higher COD yields than the trial of fresh grass cut in the summer (blue line) over the first 7 days. The stored grass trial (red line) shows low total COD yields compared to all other 1 day HRT trials.

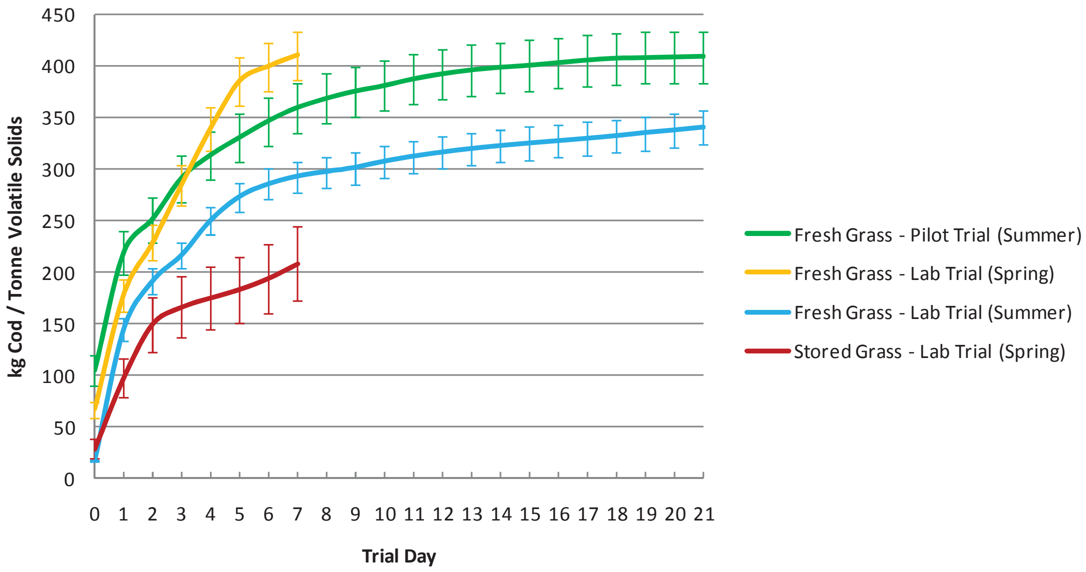

Figure 4.22: Comparison of COD yield for all fresh grass trials with a 1 day HRT, error bars show a 95% confidence interval based on replicated analysis of the same sample

The variation between laboratory and pilot trials can be attributed to differences in environmental factors that could not be controlled in the pilot scale trial. These factors include temperature, degree of decomposition before tanks are flooded (large piles of grass appear to start degrading very rapidly compared to small piles) and solids to liquids ratio. The high yield from the spring trial indicates that more soluble COD is initially available to be leached. The difference in the spring and summer trials gives an indication of the variability that can be expected throughout the seasons.

The pilot trial continued to show results that are comparable to the laboratory trials despite the significant scale-up. This indicates the system will work successfully if it is further scaled up to a full-size system.

4.5 Implications of Results on Process Design

4.5.1 Stability of Leachate for Storage

Grass leachate did not significantly degrade when left in a drum at 25°C. The leachate was tested at a concentration of 24 g COD / L for 7 days with no measurable drop in concentration. Signs of degradation were present, as fungi grew on the surface of the leachate and small amounts of gas bubbles were formed under the fungi layer. This indicates that low levels of COD degradation were taking place in the leaching tanks; however, the degradation is below levels that could be accurately measured.

In leaching trials the pH dropped and stabilised within the first two days to values between 5 and 6 in all cases except spring grass trials, which had higher pHs. The low pH is likely to inhibit further degradation from methanogenesis (Bhattacharyya et al., 2008). This is desirable as degradation during leaching will make the process less efficient, and environmentally polluting biogas is released from open-topped tanks into the atmosphere. Stability of the leachate gives operators more flexibility as they can choose to store it before it is fed into a methanogenic reactor without worrying about loss of productivity.

4.5.2 Nutrient Discharge

Total nitrogen and total phosphorous were measured. No significant correlation could be found between COD concentration and nutrients concentration. As shown in Table 4.5 grass yields have much higher concentrations than shredded green waste. Details of results are shown in Appendix 7.2. The DRP (Dissolved Reactive Phosphorus) level allowed to be discharged into waterways is site dependent and is controlled by government bodies with a consent. Typically, the total loading of nutrients into a system is controlled to achieve nutrient levels below a certain concentration in a body of water. e.g. in the Manawatu region of New Zealand the target concentration for DRP is less that 0.006 - 0.015 g/m^3 (Horizons, 2010), the actual concentration targeted is site specific. This means that during high flow periods more nutrients are allowed to be discharged into waterways.

Table 4.5: Nutrient concentration in leachate, errors show a 95% confidence interval based on replicated analysis of the same sample

Leachate	Total Nitrogen (mg / L)	Total Phosphorus (mg / L)	DRP (mg / L)
Fresh Shredded green waste	51 ± 7 - 7.0 ± 0.2	26 ± 20 - 6 ± 2	6.0 ± 0.6 - 0.08 ± 0.03
Fresh Grass	460 - 75	215 - 30	85 - 1

It is possible to reuse the leachate as a nutrient solution for a hydroponics style setup once the leachate is well aerated and diluted down to the correct concentrations. This was successfully tried informally in the lab, herbs and vegetables grew well to full size. The growing of plants was not conducted in a scientific manner nor was it within the scope of the project; it was done on mere curiosity to see if it would work.

Because of the dilute nature of the nutrients in the leachate it is not likely feasible to transport to use as a fertiliser at different locations.

4.5.3 Tank Sizing and Solid Retention Times

Increasing solid retention times increases the total yield of COD i.e. increasing the total time one unit of solids is kept in the tank regardless of how many times it is flushed with water increases total COD yield. However, there is a trade-off as the rate that COD production drops off as time goes on. The majority soluble compounds from grass and shredded green waste are leached within the first 7 days. The compounds that are leached in this time can be mostly attributed to readily soluble compounds in the feedstock that do not need to be hydrolysed. If efficient use of capital equipment is to be optimised then shorter solid retention times with HRTs of 1 day will yield the most biogas. If optimising the amount of soluble compounds / biogas from a set amount of feedstock SRT and HRTs will need to be extended to maintain concentrations of COD in the leachate to high-enough levels for effective operation of the second stage of the anaerobic digester.

4.5.4 Matching Digester type with Solid Retention Time, Hydraulic Retention Time and Feedstock

Low overall concentrations of COD in the leachate from shredded green waste means that a methanogenic reactor with the SRT and HRTs decoupled will have to be used in order to maintain high-enough organic loading rate for normal working conditions. Suitable methanogenic reactors would be anaerobic contact, UASB or anaerobic filters, as these systems have been operated commercially with influent COD concentrations as low as 0.3, 1 and 5 g COD / L respectively (Metcalf & Eddy et al., 2003).

Figure 4.23 shows the change in concentration of COD in leachate from leaching of fresh grass in the lab. The blue line represents the COD concentration in the leachate of the 7 day HRT trial. The concentration stabilised at approximately 20 g COD / L after the second day, it dropped at the 7th and 14th day when the leachate is replaced with water, and the concentration of COD remained above 10 g / L until the 14th day. The orange line represents the concentration of COD in the leachate of the 1 day HRT trial that was run using grass cut in the spring. This trial was run for a total of 7 days. The concentration of COD remained above 10 g / L until the 5th day. The purple line represents the concentration of COD in the leachate of the 1 day HRT trial that was run using grass cut in the summer. The concentration after day 1 was approximately 50 g COD / L. After this it steadily declined to approximately 1 g COD / L at day 8, where it remained stable.

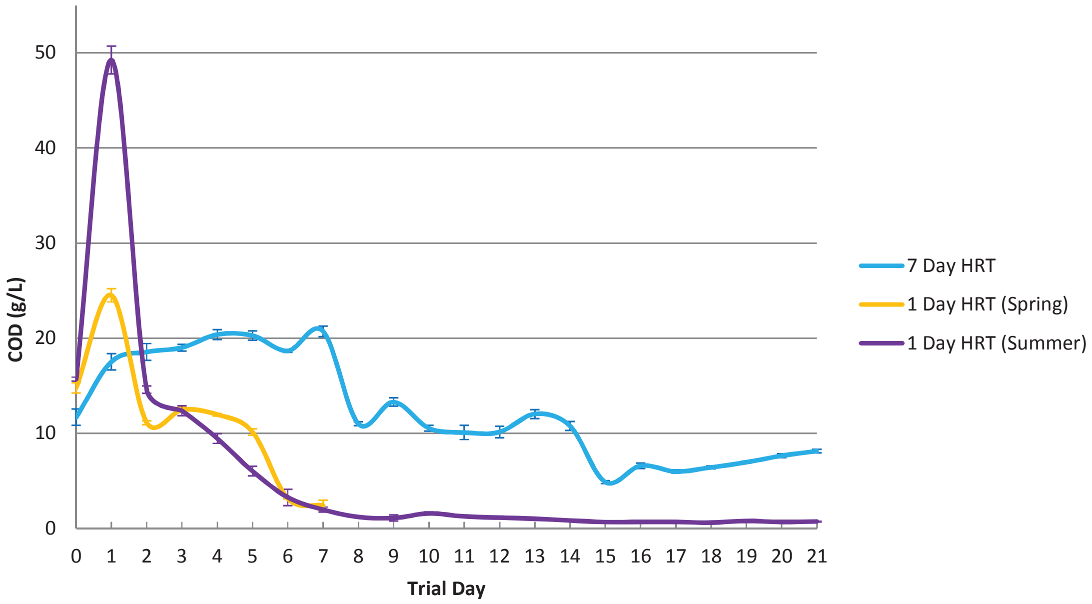

Figure 4.23: Change of COD concentration in leachate over time from the laboratory trials of fresh grass, error bars show a 95% confidence interval based on replicated analysis of the same sample

The 7 day HRT trial indicates that an equilibrium between the solid and the liquid phase is likely being achieved, as the concentration does not rapidly increase. Small levels of increasing concentration are likely due to more SCOD being made available in the solid phase as a result of hydrolysis and or plant cell degradation. Equilibrium is likely to be achieved in less than 1 day since there is no significant change in concentration after 1 day in the 7 day HRT trial. This shows that in the case of leaching fresh grass there are few gains to be made from leaving it to soak more than one day.

The initial concentrations of COD in the leachate is likely to be high in all cases as a result of compounds in the grass that are readily soluble and the rate of their transfer into the liquid is only limited by the rate of diffusion from the solid to the liquid phase. COD cannot be all moved out in one stage. As illustrated by all trials in Figure 4.23 , the concentrations fall only gradually after each leachate replacement. The reason the entire COD in the solid phase does not move to the liquid phase in a single flush is likely a combination of residual leachate left in the leaching tank after the tank is drained and the fact that COD in the leachate can reach its equilibrium concentration only in relation to the concentration of SCOD in the solids. This phenomenon is well documented by Treybal (1980) and the best way to overcome this issue is to allow complete drainage before replacing the liquids, along with running a multi-stage countercurrent leaching system.

4.5.5 Quantity of Water, Hydraulic Retention Time and Feedstock

When grass is leached initially, the readily soluble COD is transferred from the solid to the liquid phase. The progressive reduction in concentration after each flushing of the leachate demonstrates that the available COD in the solid phase is reduced until the concentration is in equilibrium with the rate of hydrolysis and plant cell degradation. In the initial stages the maximum yield of COD can be obtained while maintaining a high COD concentration by running a multi-stage countercurrent system, described by Geankoplis (2003) and Treybal (1980). Once the readily available soluble COD has been released from the solids, and the rate of leaching drops to the rate of hydrolysis and plant cell degradation, the HRTs can be extended to a point where a stable desired concentration is maintained, e.g. a hydrolysis rate that corresponds to 1g COD / L.day (shown by the purple line in Figure 4.23) would make a leachate with a concentration of 10 g COD / L with an HRT of 10 days.

The main disadvantage of extending the HRT mid-run is maintaining a balanced fluid volume in the second stage of the anaerobic digester. This would have to be carefully balanced by running multiple leaching tanks in sequence. In practice this would mean more equipment to gain higher yields of biogas. As the HRTs are extended, the gains diminish to a point where they will no longer be economically feasible

If water use is not an issue then more dilute leachate can be at run at high rates through UASB type reactors and possibly recycled back through the leach beds, as suggested by Nizami et al. (2005). If water use and disposal is expensive, then longer HRTs will increase the concentration of the leachate, reduce the amount of water used, and make the leachate of a suitable strength for digesting in a CSTR-type anaerobic digester.

4.6 Outputs from Grass and Shredded Green Waste Leaching System

From all the data acquired, it is possible to make estimates on how a system would perform overall when scaled up. Figure 4.24 and Figure 4.25 show the expected output from a leach bed + anaerobic digester system from shredded green waste and grass. The inputs are based on 1 tonne of wet solids as they are delivered to site.

Shredded green waste utilises less volume per tonne than grass; however, the SRT is much longer so the amount processed per standard-size tank will be less. Shredded green waste produces about 5 times less biogas per tonne of wet material. Nutrient levels are much less in shredded green waste effluent than grass effluent. This is most likely to be a result of lower levels of leaching.

The COD yields are calculated using the results from the 7 day HRT / 21 day SRT laboratory trial of fresh shredded green waste and the 1 day HRT / 21 day SRT pilot trial of fresh-cut spring grass, as these gave the best results in terms of concentration and yield. Biogas yields are based on results shown in

Table 4.3, which were obtained from running laboratory 2 L scale CSTR reactors at 35°C. Nutrients discharged are based on average concentrations of nutrients discharged from laboratory trials (7 day HRT for shredded green waste shown in Figure 7.5 and 1 day HRT for grass shown in Figure 7.9).

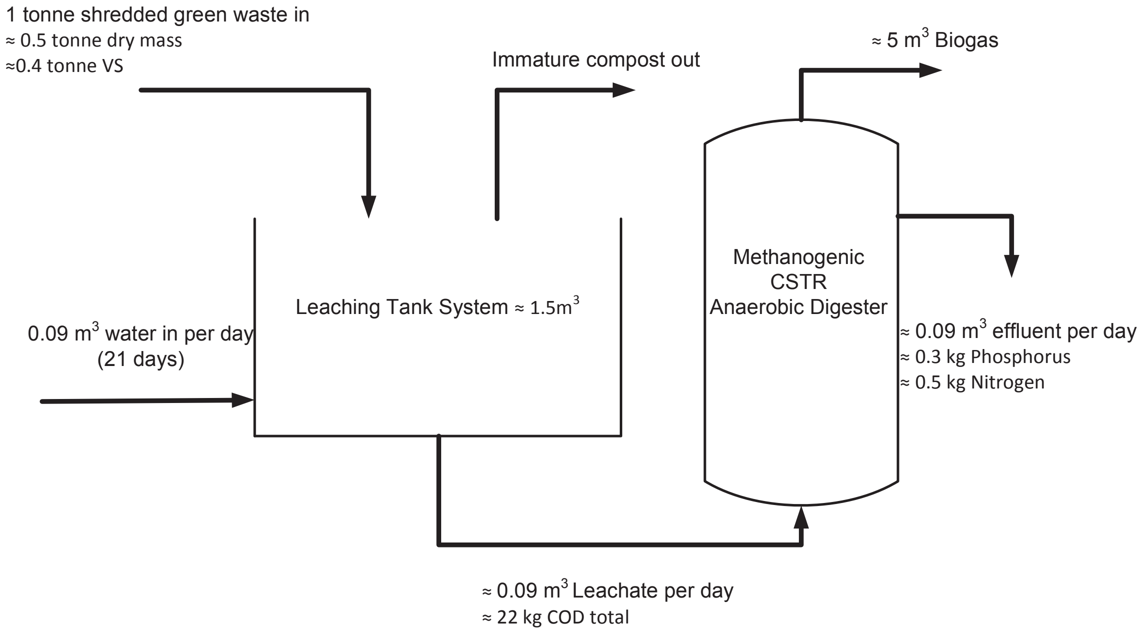

Figure 4.24: Material inputs and outputs from a shredded green waste system based on a 7 day HRT and 21-SRT

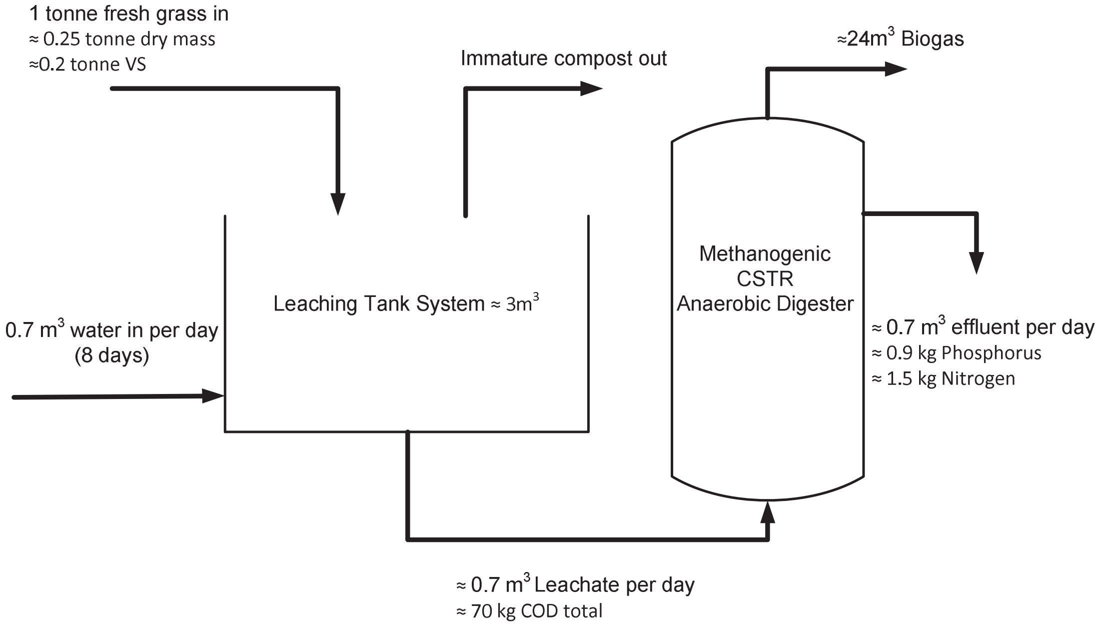

Figure 4.25: Material inputs and outputs from a grass system based on a 1 day HRT and 8 day SRT

Using Palmerston North City Council as an example and the figures provided by Slack (2010), 6000 tonnes of green waste are delivered every year. With an estimate of 10% grass, 5400 tonnes of green waste could produce approximately 27,000 m^3 of biogas. An additionally 14,400 m^3 could be produced from the grass.

The total leaching tank size required to process the shredded green waste would be 466 m^3 and the methanogenic reactor would be 1100 m^3. These calculations are based on the numbers in Figure 4.24, a 7 day HRT in the leaching tank, a 21 day SRT in the leaching tank and a 40 day HRT in a CSTR anaerobic digester, as demonstrated in laboratory trials.

The total leaching tank size required to process the grass would be 39 m^3 and the methanogenic reactor would be 182 m^3. These calculations are based on the numbers in Figure 4.25, a 1 day HRT in the leaching tank, a 21 day SRT in the leaching tank and a 20 day HRT in a CSTR anaerobic digester. Using an anaerobic digester that decouples the HRT from the SRT could significantly reduce the size of the anaerobic digester, as suggested by Nizami et al. (2010).

5 Conclusions

Leaching of grass and shredded green waste produces a leachate that can be used as a feedstock solution that produces biogas that is simpler to handle than solids in an anaerobic digester. Testing of how COD concentrations in leachate responded grass and green waste being stored before leached showed that storing grass before leaching reduces the amount of readily soluble organic compounds that can be leached.

When comparing between HRT's of leaching trials of grass that had been leached fresh and grass and green waste that had been stored before leaching, in both cases, the trials with the shorter HRT of 1 day, compared to the longer HRT of 7 days, increases the total COD leached for a given mass of volatile solids; however, this is at the expense of COD concentration in the leachate.

Laboratory trials of green waste are indicative of how the system is going to perform in the pilot trial; differences are a result of higher bulk densities and lower uncontrolled temperatures in the pilot trials and inability to control how much the green waste aerobically degraded while it was being processed and handled. When a consistent bulk density in grass is obtained between laboratory and pilot trials the concentration and cumulative COD yields are similar. Therefore, the laboratory results can be used as a good indicator of pilot leaching results if the bulk density is kept the same.

Pilot trials of shredded green waste tended towards higher concentrations of COD in the leachate (2.4-5.4 g COD / L) than laboratory trials (0.7 – 2.1 g COD/ L); however, the increased concentration found in the pilot trial was at the compromise of the total COD yields obtainable when compared to laboratory trials. The pilot trials yielded 53 ± 2 kg COD / tonne VS whereas the laboratory trials yielded 132 ± 8 kg COD / tonne VS when both were tested with a 1 day HRT for a period of 7 days. The increased concentration found in pilot trials is likely to be a result of the higher bulk density.

Drying of shredded green waste enables more readily soluble compounds to be released into the leachate, which enables shorter leaching HRTs to be used to gain higher total COD yields. This indicates that drying of shredded green waste before leaching makes the mass transfer of soluble compounds between solid and liquid phases the rate-limiting step. The high availability of soluble compounds in the solids phase is likely to be a result of cell walls in the plant material being ruptured as a result of the drying.

Leaching of grass with a 1 day HRT increases the yield compared with a 7 day HRT without major decreases in the COD concentration. A yield of 410 ± 20 kg COD / tonne VS was achieved. An HRT of 1 day with fresh grass gives concentrations above 10 g COD / L for the first 4 days which makes it an excellent candidate for using in an anaerobic digester.

The amount of organic compounds leached into the water decreases with each successive flushing until only the soluble COD produced as a result of the rate that soluble compounds are made available through hydrolysis and other plant cell break down mechanisms. As the concentration of dissolved organic compounds decreases with each successive flushing so does the usefulness of the leachate as a feedstock for an anaerobic digester. The lower concentrations mean that larger anaerobic digesters will be needed to make the same amount of biogas as digesters feed with a higher concentration leachate.

Trials in which rumen contents was mixed in with grass that was leached were inconclusive. Addition of rumen contents to grass when leaching with a 1 day HRT showed a slight initial increase of COD yielded by the grass fraction; however, after 5 days of leaching there is no significant difference in yields of COD between grass with and without rumen contents mixed in.

Testing of BOD_5 to use as a metric to compare COD yields against and to give an indication of the biodegradability of the dissolved organic compounds showed that

BOD_5 was approximately 50% or less of COD in all cases. The BOD test is aerobic so the COD may degrade slightly differently in anaerobic conditions, however it is a much faster, more simple and more reliable test than running small scale anaerobic digesters to test biodegradability of leachate.

Testing of leachate in laboratory scale CSTR anaerobic digesters showed that the leachate was able to be converted to biogas and the reactor could maintain stable operation within the trial with both grass and shredded green waste leachate as the only feedstock. The trials of shredded green waste and grass leachate using a laboratory scale CSTR at 35°C showed gas production levels of 0.23 ± 0.01 and 0.534±0.005 m^3 / kg COD respectively, which is 42% and 66% of theoretical yields obtainable.

Signs of degradation of feedstock in the leaching tanks were occurring with observations of gas bubbles rising. Gas captured from the fresh grass leaching tank in the laboratory on the second day of the 1 day HRT trial contained 5% Hydrogen, 25.5% carbon dioxide and 0% Methane. This is confirmation that microbiological action is taking part in the leaching process and that methanogenesis is being inhibited. This has important implications for designing of the process equipment, as it shows that tanks do not need to be covered to capture fugitive emissions of methane. An open tank is much easier and cheaper to construct and operate.

Storing of leachate may be required to smoothly operate a leaching / anaerobic digester system. It was demonstrated that the concentration of grass leachate was stable at a concentration of 24 g COD / L over a 7 day period at 25°C.

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7 Appendices

7.1 Glossary

BOD – Biological Oxygen Demand
COD – Chemical Oxygen Demand
CSTR – Continuously Stirred Tank Reactor
DRP– Dissolved Reactive Phosphorus
HRT– Hydraulic Retention Time
SRT – Sludge Retention Time
UASB – Upflow Anaerobic Sludge Blanket
SCOD – Soluble Chemical Oxygen Demand
VS – Volatile Solid(s)

7.2 Characterisation of Feedstocks

Figure 7.1 shows the general consistency of the green waste after shredding.

Figure 7.1: Shredded green waste before leaching

Figure 7.2 shows the shredded green waste before leaching laid out on a 10 x 10 mm grid. The variability in the characteristics of shredded green waste can be seen by the difference between Figure 7.1 and Figure 7.2. Figure 7.1 shows fine shredded green foliage whereas Figure 7.2 shows broken woody material and black clumps.

Figure 7.2: Shredded green waste on 10 x 10 mm grid

Figure 7.3 gives an indication of the particle sizes of the grass clippings when they are laid out on a 10 x 10 mm grid.

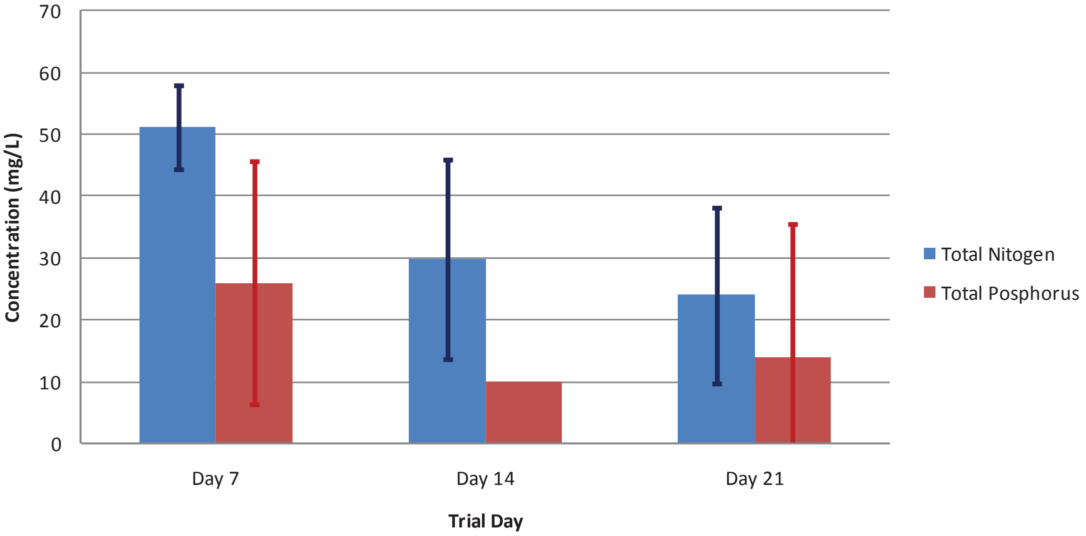
Figure 7.3: Fresh grass on a 10 x 10 mm grid

Rumen contents had the consistency of a thick fibrous sticky sludge that did not lend itself well to leaching as there were few open voids. Figure 7.4 below shows the appearance of the rumen contents (the picture is approximately 200 mm across)

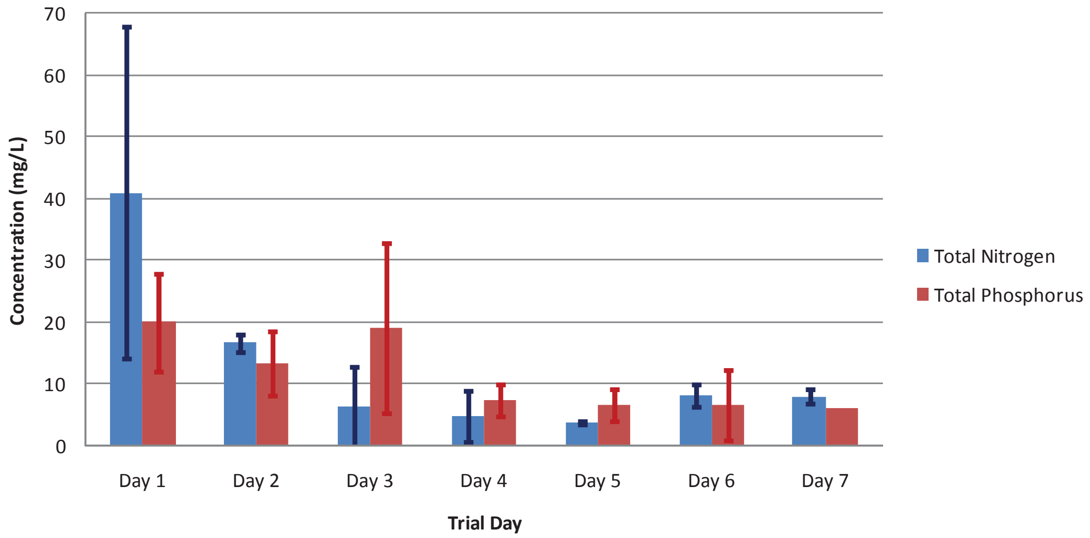

Figure 7.4: Rumen contents before leaching

7.3 Nutrients from Leachate

Total nitrogen and total phosphorous were measured by John Sykes.

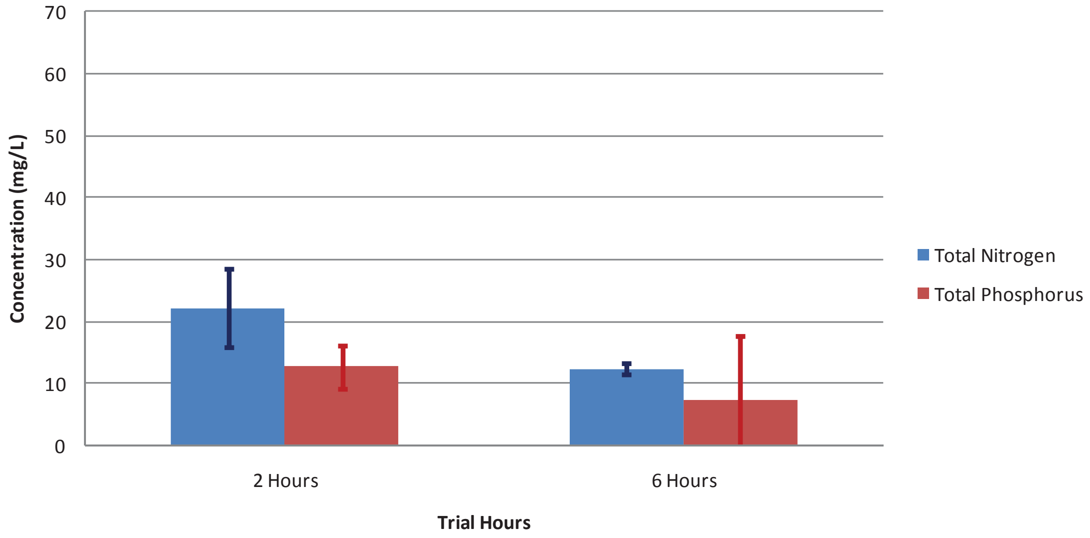


NB: Error bars show a 95% confidence interval based on replicated analysis of the same sample from the top, middle and bottom.
Figure 7.5: Nutrients discharged from leaching fresh shredded green waste—7 day HRT



NB: Error bars show a 95% confidence interval based on replicated analysis of the same sample from the top, middle and bottom.

Figure 7.6: Nutrients discharged from leaching fresh shredded green waste—1 day HRT



NB: Error bars show a 95% confidence interval based on replicated analysis of the same sample from the top, middle and bottom.

Figure 7.7: Nutrients discharged from leaching fresh shredded green waste—4-hour HRT

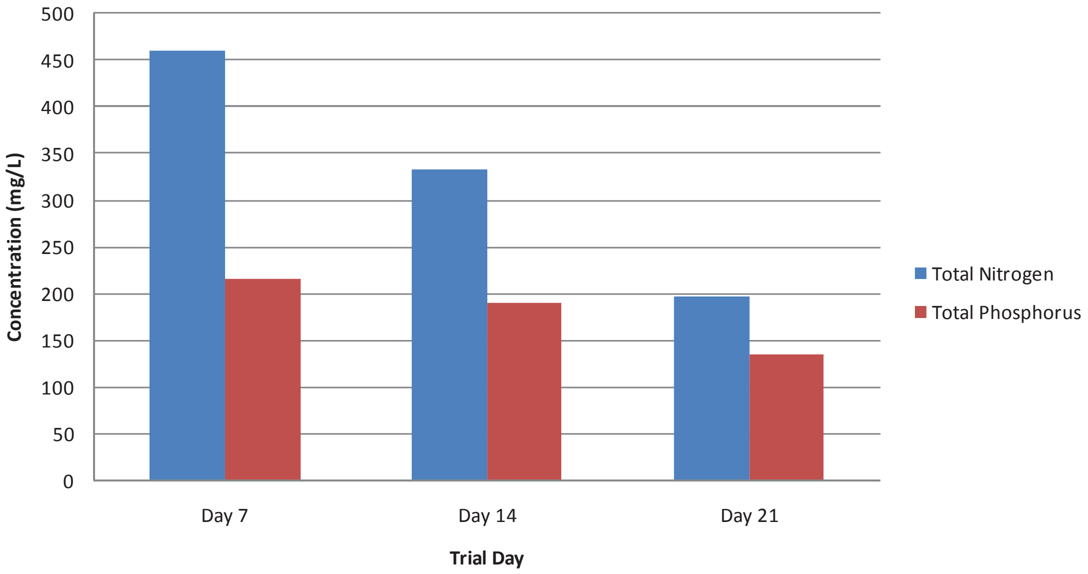


Figure 7.8: Nutrients discharged from leaching fresh grass—7 day HRT

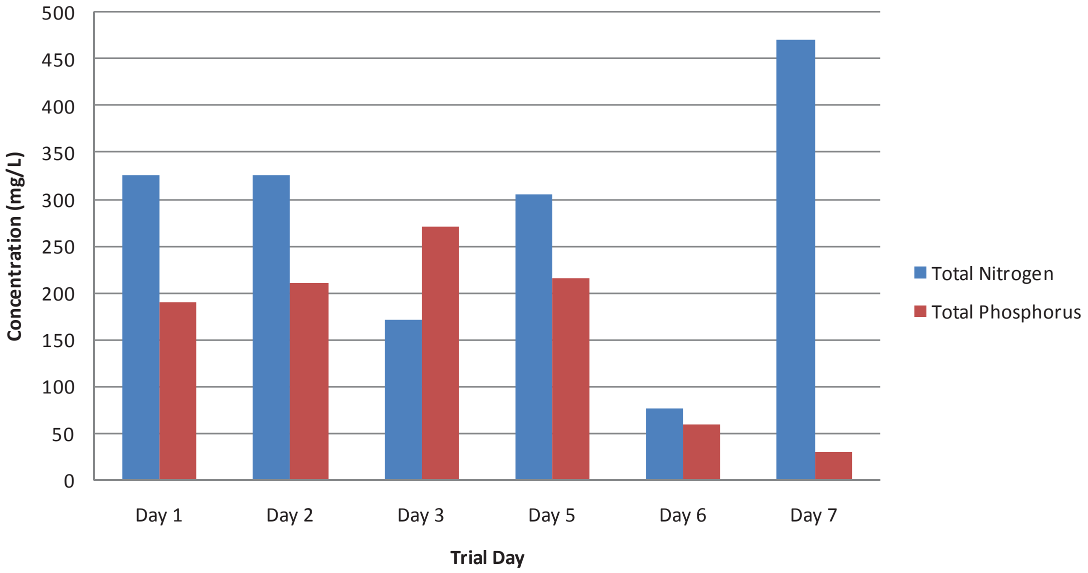


Figure 7.9: Nutrients discharged from leaching fresh grass—1 day HRT

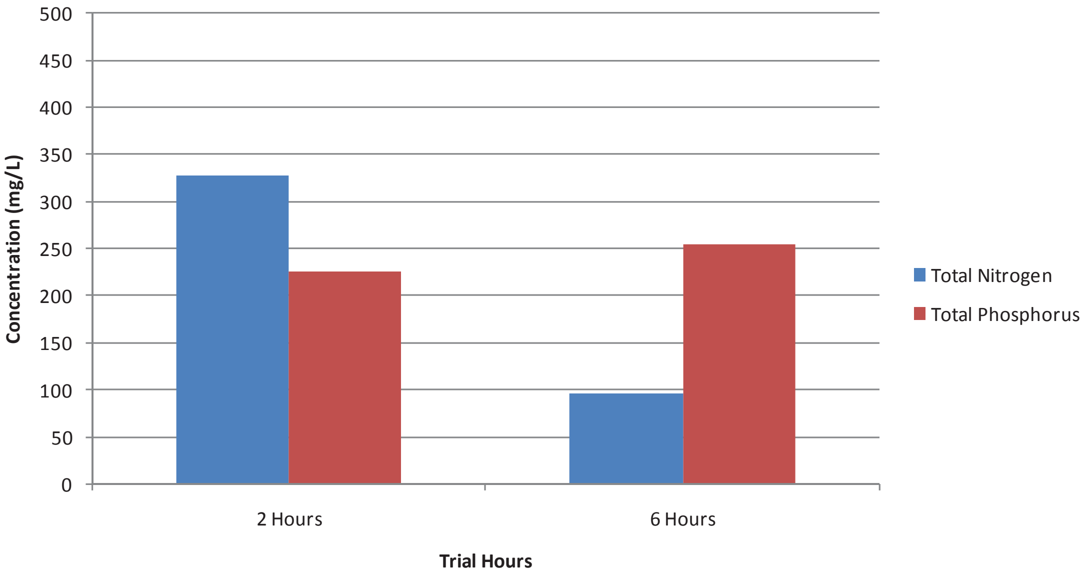


Figure 7.10: Nutrients discharged from leaching fresh grass—4-hour HRT

7.4 pH of Leachate for all Trials

Table 7.1: pH of Leachate for all trials

Type of Trial	Fresh or Stored	Feedstock	SRT	HRT	Average pH
Lab	Fresh	Shredded green waste	8 hours	4 Hours	6.5±0.2
Lab	Fresh	Shredded green waste	7 Days	1 Day	5.7±0.3
Lab	Fresh	Shredded green waste	21 Days	7 Days	5.0±0.1
Lab	Stored	Shredded green waste	8 hours	4 Hours	6.7±0.1
Lab	Stored	Shredded green waste	7 Days	1 Day	5.8±0.2
Lab	Stored	Shredded green waste	21 Days	7 Days	5.18±0.09
Pilot	Fresh	Shredded green waste	7 Days	1 Day	6.2±0.1
Lab	Fresh	Grass (spring)	8 hours	4 Hours	5.1±0.4
Lab	Fresh	Grass (spring)	7 Days	1 Day	4.9±0.2
Lab	Fresh	Grass (summer)	21 Days	1 Day	5.12±0.09
Lab	Fresh	Grass (spring)	21 Days	7 Days	4.97±0.09
Lab	Fresh	Grass / Rumen contents	14 Days	1 Day	5.16±0.05
Lab	Fresh	Rumen contents	14 Days	1 Day	6.7±0.1
Lab	Stored	Grass (spring)	8 hours	4 Hours	7.9±0.2
Lab	Stored	Grass (spring)	7 Days	1 Day	6.9±0.5
Lab	Stored	Grass (spring)	21 Days	7 Days	6.8±0.2
Pilot	Fresh	Grass (summer)	21 Days	1 Day	5.1±0.1
Pilot	Fresh	Grass (autumn)	21 Days	7 Days	5.97±0.09

NB: Errors show a 95% confidence interval based on replicated analysis of the same sample

7.5 Temperature of Trials

Table 7.2: Temperature of trials

Type of Trial	Fresh or Stored	Feedstock	SRT	HRT	Average Temperature (°C)
Lab	Fresh	Shredded green waste	8 hours	4 Hours	22± 1
Lab	Fresh	Shredded green waste	7 Days	1 Day	22±2
Lab	Fresh	Shredded green waste	21 Days	7 Days	22.6±0.7
Lab	Stored	Shredded green waste	8 hours	4 Hours	22.8±0.8
Lab	Stored	Shredded green waste	7 Days	1 Day	23.70±0.05
Lab	Stored	Shredded green waste	21 Days	7 Days	22.9±0.1
Pilot	Fresh	Shredded green waste	7 Days	1 Day	20±3
Lab	Fresh	Grass (spring)	8 hours	4 Hours	25.1±0.3
Lab	Fresh	Grass (spring)	7 Days	1 Day	24±1
Lab	Fresh	Grass (summer)	21 Days	1 Day	24.7±0.4
Lab	Fresh	Grass (spring)	21 Days	7 Days	23.8±0.5
Lab	Stored	Grass (spring)	8 hours	4 Hours	22±2
Lab	Stored	Grass (spring)	7 Days	1 Day	22.7±0.5
Lab	Stored	Grass (spring)	21 Days	7 Days	22.5±0.3
Pilot	Fresh	Grass (summer)	21 Days	1 Day	25±2
Pilot	Fresh	Grass (autumn)	21 Days	7 Days	17±3

NB: Errors show a 95% confidence interval based on replicated analysis of the same sample

7.6 Sample Calculations for Gas Production

Calculate the ml of gas per gram of COD for the first point in the GW leachate data.

Concentration of COD in leachate = 6.9 gCOD / L
Gas produced = 70 ml
Leachate added = 50 ml

COD per ml = 6.9 g COD / 1000 ml
= 0.0069 g COD / ml
Total COD added = 50 ml x 0.0069 g COD / ml
= 0.345 g COD
Gas produced per gram of COD = 70 ml / 0.345 g COD
= 202.90 ml/ g COD
= 0.2029 m^3 / kg COD

Average gas production per day = 235 ± 14 ml gas / g COD / day
= 0.24 ± 0.01 m^3 gas / kg COD / day

Using 0.107 kg COD / kg VS

Gas production based on VS = 0.107 kg COD / kg VS x 0.24 m^3 gas / kg COD
= 0.025 m^3 gas / kg VS

Assume methane content of gas at 65% = 0.15 m^3 CH_4 / kg COD
Theoretical methane production = 0.35 m^3 CH_4 / kg COD

Yield = 0.15/0.35x100 = 44%

7.7 Sample Calculations for Rumen Contents Trials

The rumen contents-only trial is used as an indicator for how much COD can be attributed to rumen contents in the grass and rumen contents trial.
Paunch control trial yielded 56.6 kg COD / tonne VS in day 1

⇒ 56.6 g COD / kg VS

Total VS of paunch in grass mixed trial = 0.021 kg VS

Total COD attributed to rumen contents in mixed trial:
$=56.6 \text{ g COD / kg VS} \times 0.021 \text{ kg VS}$
$=1.2 \text{ g COD}$

The total amount of COD produced in the mixed trial is calculated

Concentration of COD in mixed trial:
$=12.8 \text{ g COD / L}$

Total Litres drained in day 1 = 1.12 L

Total COD in day 1 from mixed trial:
$=12.8 \text{ g COD / L} \times 1.12 \text{ L}$
$=14.28 \text{ g COD}$

The amount of COD attributed to grass can then be calculated from the total COD and the rumen contents COD

Total COD in day 1 attributed to grass:
$=14.28 \text{ g COD} - 1.2 \text{ g COD}$
$=13.07 \text{ g COD}$

The total solids in the system from grass is = 228g

The total volatile solids in the system from grass:
$= 228\text{g} \times 0.308 \text{ g VS /g}$
$=70 \text{ g VS}$
$= 0.07 \text{ kg VS}$

COD yield:
$= 13.07 \text{ g COD / } 0.07 \text{ kg VS}$
$=186.76 \text{ g COD / kg VS}$

7.8 Sample Calculations of Outputs of Green waste Leaching system

1. **Calculate mass of volatile solids into the tank based on 1 tonne of dry solids**

   From Table 4.1 pilot scale green waste moisture content is 52.2 ± 0.5% ~ 50%

   ∴ 1 tonne of green waste = 0.5 tonnes of dry mass

   From Table 4.1 average fresh green waste VS content is 0.793 g VS / g dry mass ~ 0.8 g VS / g dry solids

   ∴ 0.5 tonnes of dry mass × 0.8 tonnes of VS / tonne dry mass = 0.4 tonnes of VS

2. **Calculate the volume of the tank**

   From Table 4.1 the bulk density of green waste is 605 kg/ m^3 ~ 600 kg/m^3

   ∴ 1000 kg / 600 kg/m^3 = 1.66 m^3 ~ 1.7 m^3

3. **Calculate the water use per day**

   On average the water used to fill the tank above the solids was 0.59 m^3/tonne of solids.

   ∴ 0.63 m^3 / 7 days (HRT of 7 days) = 0.09 m^3/day

4. **Calculate the total COD leached over 21 days**

   The total COD leached is 55 kg/tonne as shown in Figure 4.21

   ∴ 0.4 tonne VS × 55 kg COD / tonne VS = 22 kg COD

5. **Calculate the total amount of biogas produced per tonne of dry feedstock**

   From Table 4.3 0.24 m^3 gas / kg COD is produced from green waste leachate in the lab scale CSTR anaerobic digester.

   ∴ 22 kg COD × 0.24 m^3 gas / kg COD = 5.28 m^3 gas ~ 5 m Biogas

6. **Calculate the total prosperous released per tonne of dry feed stock**

   From Table 4.5 26 - 6 mg P/L leachate; average = 16 mg/l = 16g/m^3

   ∴1.89 m^3 leachate × 16 = 30 g =0.03 kg Phosphorus

7. **Calculate the total nitrogen released per tonne of dry feedstock**

   From Table 4.5 51-7 mg N/L leachate; average = 29 mg/L

   ∴ 1.89 m^3 leachate × 29 mg/L = 54.8 g = 0.05 kg Nitrogen