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Biomethane production from food waste and organic residues

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Thesis submitted for the degree of Doctor of Philosophy to University College Cork, Ireland

Supervisor: Prof. Jerry Murphy

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July 2013

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Declaration

I hereby declare that this thesis is my own work and that it has not been submitted for another degree, either at University College Cork or elsewhere. Where other sources of information have been used, they have been acknowledged.

Signature: 

Date: 4th July 2013

Dedication

I dedicate this thesis to my amazing wife Kasia and wonderful daughter Emma. For the love and happiness they give to me.

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Abstract

Anaerobic digestion (AD) of biodegradable waste is an environmentally and economically sustainable solution which incorporates waste treatment and energy recovery. The organic fraction of municipal solid waste (OFMSW), which comprises mostly of food waste, is highly degradable under anaerobic conditions. Biogas produced from OFMSW, when upgraded to biomethane, is recognised as one of the most sustainable renewable biofuels and can also be one of the cheapest sources of biomethane if a gate fee is associated with the substrate. OFMSW is a complex and heterogeneous material which may have widely different characteristics depending on the source of origin and collection system used. The research presented in this thesis investigates the potential energy resource from a wide range of organic waste streams through field and laboratory research on real world samples. OFMSW samples collected from a range of sources generated methane yields ranging from 75 to 160 m^3 per tonne. Higher methane yields are associated with source segregated food waste from commercial catering premises as opposed to domestic sources. The inclusion of garden waste reduces the specific methane yield from household organic waste. In continuous AD trials it was found that a conventional continuously stirred tank reactor (CSTR) gave the highest specific methane yields at a moderate organic loading rate of 2 kg volatile solids (VS) m^{-3} digester day^{-1} and a hydraulic retention time of 30 days. The average specific methane yield obtained at this loading rate in continuous digestion was 560 ± 29 L CH_4 kg^{-1} VS which exceeded the biomethane potential test result by 5%. The low carbon to nitrogen ratio (C: N <14:1) associated with canteen food waste lead to increasing concentrations of volatile fatty acids in line with high concentrations of ammonia nitrogen at higher organic loading rates. At an organic loading rate of 4 kg VS $m^{-3}day^{-1}$ the SMY dropped considerably (381 L CH_4 kg^{-1} VS), the pH rose to 8.1 and free ammonia (NH_3) concentrations reached toxicity levels towards the end of the trial (ca. 950 mg N L^{-1}). A novel two phase AD reactor configuration consisting of a series of sequentially fed leach bed reactors connected to an upflow anaerobic sludge blanket (UASB) demonstrated a high rate of organic matter decay but resulted in lower specific methane yields (384 L CH_4 kg^{-1} VS) than the conventional CSTR system.

Thesis output

Chapters which have been published or currently under review in peer reviewed international journals:

Chapter 3: Browne, J., Nizami, A.S., Thamsiriroj, T., Murphy, J.D. (2011) Assessing the cost of biofuel production with increasing penetration of the transport fuel market: a case study of gaseous biomethane in Ireland, Renewable and Sustainable Reviews, 15 (9): 4537 – 4547

Chapter 4: Browne, J., Murphy, J.D., (2013) Assessment of the resource associated with biomethane from food waste, Applied Energy, 104: 170–177

Chapter 5: Browne, J., Allen, E, Murphy, J.D. (2013) Evaluation of biomethane potential from multiple waste streams for a proposed community scale anaerobic digester. Environmental Technology, 34 (13-14): 2027-2038

Chapter 6: Browne, J., Allen E., Murphy, J.D. (2013) Improving hydrolysis in multiphase digestion of food waste, Waste Management, 33 (11): 2470-2477

Chapter 7: Browne, J., Murphy, J.D. (2013). The impact of increasing organic loading in two phase digestion of food waste, Renewable Energy, in review

Chapter 8: Browne, J., Allen E., Murphy, J.D. (2013). Assessing biomethane production from the organic fraction of municipal solid waste in batch and continuous operation, Applied Energy, in review

Other co-authorship peer reviewed publications

Appendix A: Allen, E., Browne, J., Murphy, J.D. (2013). Evaluation of the biomethane yield from anaerobic co-digestion of nitrogenous substrates, Environmental Technology, 34 (13-14): 2059-2068

Murphy, J.D., Browne, J., Allen, E., Gallagher, C. (2013) The resource of biomethane, produced via biological, thermal and electrical routes, as a renewable transport fuel, Renewable Energy, 55: 474-479

Allen, E., Browne, J., Hynes, S., Murphy, J.D. (2013) The potential of algae blooms to produce renewable gaseous fuel. Waste Management, 33 (11): 2425-2433

Peer Reviewed Conference Papers

Browne, J., Allen E., Murphy, J.D. (2012) Improving hydrolysis in multiphase digestion of food waste, Fourth International Symposium on Energy from Biomass and Waste, Venice 2012

Allen, E., Browne, J., Hynes, S., Murphy, J.D. (2012) The potential of algae blooms to produce renewable gaseous fuel, Fourth International Symposium on Energy from Biomass and Waste, Venice 2012

Murphy, J.D., Browne, J., Allen, E, Gallagher, C. (2012) Assessment of the bioresource of biomethane. World Renewable Energy Conference, May 2012, Denver, Colorado, USA

Contribution to the papers

Chapter 3: I was the main author of the paper and was responsible for gathering data and the majority of the writing and analysis.

Chapter 4: I was the main author of the paper and was responsible for planning and experimental design of the study. I performed the laboratory studies and analysed the data.

Chapter 5: I was the main author of the paper and was responsible for planning the study and overall experimental design. I made a significant contribution to the sampling of organic materials and subsequent laboratory studies with assistance from colleagues named as co-authors in the paper. I conducted the majority of the data analysis.

Chapter 6: I was the main author and was responsible for the planning and experimental design of the study. I performed the majority of AD trials and data analysis.

Chapter 7: I was the main author of the paper and was responsible for the planning and experimental design of the study. I performed the laboratory based AD trials and data analysis.

Chapter 8: I was the main author of the paper and was responsible for the planning and experimental design of the study. I made a significant contribution to the sampling of organic materials and subsequent laboratory AD trials with assistance from colleagues named as co-authors on the paper. I conducted the statistical analysis and the majority of the writing.

Nomenclature

ABP:	animal by-product regulations
AD	anaerobic digestion
BI	biodegradability index
BMP	biochemical methane potential
BMW	biodegradable municipal waste
CAD	centralised anaerobic digester
CH_4	methane gas
CHP	combined heat and power
CNG	compressed natural gas
CO_2	carbon dioxide gas
COD	chemical oxygen demand
CSTR	continuously stirred tank reactor
DM	dry matter (equivalent to total solids in this thesis)
DS	dry solids (equivalent to total solids in this thesis)
EU	European Union
FW:	food waste
H_2	hydrogen gas
H_2S	hydrogen sulphide gas
HHV	higher heating value
HRT	hydraulic retention time
LBR	leach bed reactor
MBT:	mechanical biological treatment
MSW	municipal solid waste
NG	natural gas
NH_3	free ammonia
NH_3-N	ammonia nitrogen (equivalent to TAN in this thesis)
OFMSW	organic fraction of municipal solid waste
OLR	organic loading rate
pH	power of hydrogen
RES-T:	renewable energy supply in transport
SHW	slaughter house waste
SLBR	sequencing leach bed reactors

SMY:	specific methane yield
SSFW:	source segregated food waste
t/a	tonnes per annum
TA	total alkalinity
TAN	total ammonia nitrogen
TS	total solids
UASB	upflow anaerobic sludge blanket
UCC:	University College Cork
VAT	value added tax
VFA	volatile fatty acids
VS	volatile solids
ww	wet weight

1 Introduction

1.1 Introduction and background of thesis

Effective management and treatment of biodegradable waste is a topic of increasing importance for municipalities across the globe. A significant portion of municipal biodegradable waste is dominated by food waste from domestic and commercial activities and is often referred to as the organic fraction of municipal solid waste (OFMSW). In 2010, approximately 2 million tonnes of biodegradable municipal waste was produced in Ireland of which 820,000 t was classified as OFMSW. By 2016, it is estimated that 950,000 tonnes of OFMSW will be produced annually in Ireland of which a minimum of 530,000 t will require biological treatment under the terms of the European Union (EU) Landfill Directive 1999, which has set out significant targets for reducing biodegradable waste going to landfill.

As EU countries seek to find more sustainable waste treatment solutions that incorporate energy and materials recovery, the concept of utilising anaerobic digestion (AD) as a waste treatment technology that incorporates energy and nutrient recovery is gaining favour across Europe (Figure 1.1). The AD process produces a biogas which is typically 55-65% methane (CH_4) 35-45% carbon dioxide (CO_2) with traces of other gases such as hydrogen (H_2) and hydrogen sulphide (H_2S). By removing the non calorific gases such as CO_2 and H_2S a high calorific gas referred to as biomethane can be achieved. Biomethane has the equivalent energy content of natural gas and can be utilised in the same manner for the production of heat, electricity and transport fuel as compressed natural gas (CNG). In addition to the production of biogas the AD process also produces a nitrogen rich digestate which may be used in agricultural applications, offsetting the cost of artificial fertiliser.

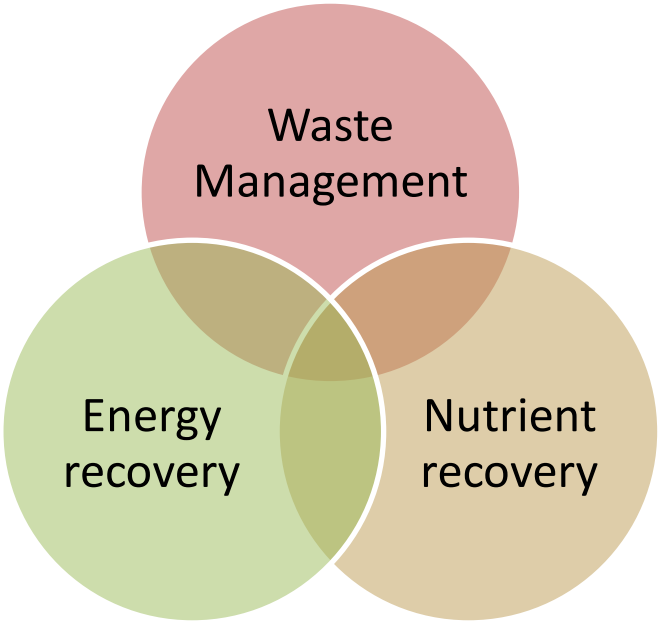


Figure 1.1 The three main goals of anaerobic digestion of organic wastes

Although AD is not a new technology it is widely reported that most anaerobic digesters are not optimised for energy production. Current and future research in anaerobic technology is focused on bioprocess control, high solids bioreactor design, effective pretreatment processes and digestate processing. This thesis examines the biomethane potential and bioprocess operation of different bioreactor designs using municipal organic waste as substrate. The optimum type of bioreactor and most favourable operational conditions for methane production is sought. Continuous AD trials were carried out on two main reactor configurations; (a) a novel two phase system which incorporates a series of leach bed reactors connected to an upflow anaerobic sludge blanket (SLBR-UASB) and (b) a conventional continuously stirred tank reactor (CSTR). In addition to the continuous digestion trials, the role of food waste as a co-substrate when digested with other organic wastes such as abattoir waste and cheese processing waste was also examined.

1.2 Thesis aims and objectives

The aims and objectives of the thesis were as follows:

- To estimate the cost of producing biomethane as a transport fuel using organic wastes and residues

- To investigate the factors which affect the biochemical methane potential (BMP) test of food waste such as source of inoculum and acclimatisation to substrate.
- To outline a scientific methodology for the assessment and selection of organic waste streams which are most suitable for the production of biogas and biomethane based on a real world case study
- To examine the impact of increasing the portion of food waste in a co-digestion process treating three common organic waste streams
- To examine the process performance of a novel two phase AD system which comprised of a series of leach bed reactors (first phase) connected to a second stage upflow anaerobic sludge blanket under increasing organic loading rates
- To compare the AD process performance of a conventional continuously stirrer tank reactor and a novel two phase AD system designed for high solids substrates using the same organic waste
- To statistically assess the level of variation in biomethane potential between major organic municipal waste streams

1.3 Thesis outline and link between chapters

This thesis is composed of 9 chapters and 1 appendix with the common theme of biogas/biomethane production *via* anaerobic digestion of food waste and organic residues. Chapter 2 is a literature review of previously published research on anaerobic digestion of food waste and organic residues. It includes an extensive review of progress in the field of AD since the late 1920s up to the current state of the art. Chapters 3 to 8 of this thesis represent the majority of the work carried out during the course of the research programme. This thesis follows the so called "paper model" whereby the chapters are written with the view of publication as academic journal papers. Therefore each chapter is designed with the dual capability of being read in isolation while also forming a block of knowledge for the theme of the thesis. Chapters 3 to 8 are the original manuscripts of journal papers, each with its own sections for introduction, materials and methods, results and discussions and conclusions. Chapters 3, 4, 5 and 6 have been published in international peer reviewed scientific journals while Chapters 7 and 8 are currently under review. A summary of chapters 3 to 8 including the link between chapters is given as follows:

Chapter 3: Assessing the cost of biofuel production with increasing penetration of the transport fuel market: A case study of gaseous biomethane in Ireland.

The aim of chapter 3 is to put forward the case for biogas to be upgraded to biomethane and used as a renewable transport fuel. This chapter highlights the diversity of anaerobic digestion as a technology which can provide sustainable waste management and a renewable gaseous biofuel which can be utilised to provide renewable heat, electricity or transport fuel. In particular, the potential of biomethane as a possible source of renewable transport energy is discussed. This study was written in the context of Ireland's national renewable energy targets for 2020 which stipulates that 10% of transport energy should come from renewable sources. Biomethane *via* anaerobic digestion was largely ignored in government policy documents with regards to renewable energy in transport, even though the majority of the renewable energy in transport target was predicted to come from "biofuels". At the time of writing this target appeared to be extremely ambitious given the very low base of biofuels in the transport market. The cost of producing biomethane from readily available organic wastes and residues, based on published data, is presented and compared against the current cost of current petrol and diesel prices for context. The findings of this paper concluded that biomethane produced from organic wastes and residues could be cheaper than conventional fossil fuels assuming a modest gate fee income and continuation of the exemption on excise duty for compressed gas transport fuel. While this chapter is essentially a desk top study of existing data, it highlights the potential of biomethane from organic wastes and residues to make a significant impact in the renewable energy sector. The organic fraction of municipal solid waste was identified as a high methane yielding substrate and presented favourable economics due to the current cost of waste disposal, thus providing the context to pursue laboratory trials on the anaerobic digestion of OFMSW in the following chapters.

Chapter 4: Assessment of the resource associated with biomethane from food waste

This chapter is a basic research paper which examines the biochemical methane potential (BMP) of canteen food waste and the factors which affect the results from

this test. The research was carried out in the context of national waste management legislation which stipulates that all commercial premises producing more than 50kg of food waste per week must separate food waste from other waste at source. Limited data on the methane potential from source separated canteen food waste in Ireland was available. Therefore this paper seeks to estimate the methane potential from this waste stream using food waste from the main restaurant in University College Cork as a case study. Another objective of the paper was to assess the effects of important parameters such as the source of inoculum and the type of apparatus used on results of BMP from the same substrate. BMP tests were carried out at different scales (5L and 0.5L) with acclimatised and non-acclimatised inoculum for both fresh matter and dried substrate samples. The upper bound BMP results for source segregated canteen food waste gave specific methane yields of between 467-529 L CH_4 per kg volatile solids added. The higher results were associated with acclimatised inoculum and fresh matter samples of food waste. First order kinetic modelling was used to examine the differences in kinetic behaviour between different sources of inoculum using the same substrate. This paper confirms the high methane potential from source separated food waste and sets the scene for further research into continuous AD processes which are presented in later chapters (6, 7 & 8).

Chapter 5: Evaluation of the biomethane potential from multiple waste streams for a proposed community scale anaerobic digester

Chapter 5 is the first part of a two paper series which examines the biomethane potential from 5 major organic waste streams for a real world proposed community scale anaerobic digester in a rural town in Ireland. The biomethane potential test was used to assess the suitability of waste streams for biomethane production and to examine the variation in biomethane potential between waste sub streams. A methodology for accurately estimating the biomethane potential from multiple heterogeneous organic waste substrates was developed to help identify which wastes were most suited for biogas production. Five main waste streams were identified as possible substrates for biogas production, namely: Abattoir waste, (consisting of paunch content and dewatered activated sludge); cheese waste effluent; commercial and domestic food waste; pig slurry; and waste water treatment sludge. Using the

results from elemental analysis of the substrates, the theoretical maximum methane yield was calculated using the Buswell equation. A series of BMP tests were carried out to determine the upper limit of biological methane production and the biodegradability of the substrates. Based on these findings and availability of substrate a short list of most suitable substrates for biomethane production was made. The findings of this study were published in the journal of Environmental Technology. A follow on paper, "Evaluation of the biomethane yield from anaerobic co-digestion of nitrogenous substrates" is based on the suggested substrates from the chapter 5. Two semi-continuous AD trials were carried out (in duplicate) for 26 weeks to assess the long term specific methane yields and bioprocess stability using different co-digestion ratios of abattoir waste, food waste and cheese processing waste. The optimum process conditions such as organic loading rate and hydraulic retention time for maximum methane yields were sought. The specific methane yields were compared to BMP results to assess biodegradability and process performance. It was found that increasing the portion of food waste in the co-digestion mix led to higher specific methane yields. This paper was also published in the journal of Environmental Technology and is shown in appendix A for further reading.

Chapter 6: Improving hydrolysis of food waste in a leach bed reactor

This chapter reports on basic research which investigates the rate of degradation of food waste in a leach bed reactor by imposing four different operating conditions. The studies done in this chapter are focused on improving the hydrolysis and acidification of food waste in a leach bed reactor which forms the first phase in a two phase AD system (the background of two phase AD is discussed in more detail in chapter 2, sections 2.2.2. and 2.2.3). In this trial the effects of leachate recirculation at a low and high flow rates were examined with and without connection to an upflow anaerobic sludge blanket (UASB). Two dilution rates of the effective volume of the leach bed reactors were investigated: 1 and 6 dilutions per LBR per day. The aim of this paper was to find the optimum process conditions for conversion of organic solids to chemical oxygen demand (COD) in the liquid phase and increase the efficiency of the leach bed reactors which form the first phase in the two phase system.

Chapter 7: The impact of increasing organic loading in two phase digestion of food waste

This Chapter is a follow on paper from Chapter 6 and examines the impact of increasing organic loading in a two phase digestion system treating commercial food waste. The aim of this paper was to assess the optimum organic loading rate for the two phase system. The trial ran for 192 days and included 4 distinct periods of operation which corresponded to increments in organic loading. The system operated well at moderate organic loading rates; however accumulation of chemical oxygen demand (COD) in the liquid phase led to increased volumetric loading rates and reduced specific methane yields. The increased concentration of ammonia nitrogen over time coupled with a high pH led to inhibition of the methanogenesis phase with significant reduction of methane yields towards the end of the trial.

Chapter 8: Assessing biomethane production from the organic fraction of municipal solid waste in batch and continuous operation

In this paper the variability in biomethane potential from OFMSW depending on source of origin. In total 8 organic waste streams were examined for biochemical methane potential (BMP). Commercial waste samples were found to give significantly higher methane yields than household samples. Higher methane yields were generated from household streams that did not include garden waste. A semi continuous trial on commercial food waste produced the highest average methane potential of the bioreactors tested, at a moderate organic loading rate (OLR) of 2 kg VS m^{-3} day^{-1} with a hydraulic retention time (HRT) of 30 days. However at higher OLRs and reduced HRTs a reduction in specific methane yield was observed. Evidence of process instability due to increasing concentrations of total ammonia nitrogen (TAN) was observed towards the end of the trial. The low carbon to nitrogen (C: N) ratio of commercial food waste is a concern for long term process stability as an extremely large accumulation of TAN (>7000 mg N L^{-1}) was observed toward the end of the trial.

2 Review of anaerobic digestion of food waste and residues

2.1 Early research on anaerobic digestion of organic waste

The potential for organic waste stabilisation and energy recovery *via* anaerobic digestion (AD) has been under investigation for many years. One of the most significant advantages of an anaerobic treatment system is that it can produce more energy than is required for operation in the form of methane gas. One of the earliest comprehensive scientific studies on the anaerobic digestion of municipal sewage sludge was carried out by Buswell and Neave [1]. By this time most medium to large sewage treatment works in the USA were separating suspended solids *via* sedimentation and transferring these solids to anaerobic digesters for stabilisation and production of "combustible gases". Although the use of anaerobic digestion was widespread in sewage sludge stabilisation, the biochemical pathways and mechanisms were not widely understood. The aim of the work carried out by Buswell and Neave [1] was to develop, "a true understanding of the complicated phenomena involved" in the digestion of complex organic matter by stepwise "artificial experiments upon simpler materials, in which the varying factors can be controlled, and which can be repeated at will by independent observers." To this effect Buswell and Neave made considerable contributions to the understanding of the biochemical changes in nitrogenous and carbonaceous matter under anaerobic conditions [1]. A further study on, "The anaerobic oxidation of fatty acids" by Neave and Buswell [2] demonstrated that anaerobic bacteria, capable of decomposing fatty acids, gave approximate stoicheometric yields of methane and carbon dioxide. They also demonstrated that water acts as an oxidising agent in the degradation of organic acids and that a simple relationship exists between the number of carbon atoms in the acid and the number of participating water molecules. A study carried out by Symons and Buswell [3] demonstrated that biogas quality and quantity could be predicted (with 90-95% accuracy) using an empirically derived equation based on the stoicheometry of the organic substrate. Buswell and Mueller [4] further expanded on the mechanisms of methane fermentation and concluded that the empirical equation holds for a range of possible biochemistry pathways producing methane. This empirical equation would later be become known as the Buswell equation and is still used to estimate methane potential of organic substrates.

Further research into the biochemistry of AD was carried out over the next few decades to better understand the complexity of the process. McCarty [5] conducted a

number of trials on salt toxicity in anaerobic digestion and showed that calcium and magnesium are the least inhibitory cations to acetic acid utilisation while ammonium was shown to be the most toxic to acetoclastic methanogens. Ammonium concentration at higher pH resulted in greater toxicity to acetic utilising methanogens which is thought to be as a result of the greater concentration of free ammonia. For many years AD has been utilised in the waste water treatment industry to stabilise and reduce the volume of primary and secondary sludge. A series of articles by McCarty [6] on anaerobic waste treatment summarised many of the important biochemistry pathways, process monitoring parameters and waste composition for anaerobic digestion of municipal and industrial waste sludge. McCarty outlined many of the important characteristics for successful anaerobic treatment of organic sludges including the quantity of biodegradable organic matter in the waste stream, the alkalinity of the digester, the inorganic nutrient content, the process temperature and the presence of potentially inhibitory substances. Further research on the nutrient requirements for stabile AD was carried out by Speece and McCarty [7] and showed the importance of the correct balance of nitrogen to phosphorus for successful digestion of sludge. By the late 1960s much research had been undertaken to understand the biochemistry and biomechanics behind methane fermentation; however the topic was still very much rooted in the field of waste water treatment and sludge stabilisation.

2.2 Advances in AD technology

2.2.1 The expansion of AD research

In the 1970s AD became more a more popular research topic due to growing concerns over energy security (largely due to the international oil crises from1973-1974). It was recognised that there was a significantly large energy potential from organic wastes and residues to merit further investigation into improving AD bioprocess control and efficiency. Ghosh et al. [8] estimated that, “in a city of 1 million people, 0.28 to 0.56 million m^3/day of substitute natural gas (sng) may be obtained by digesting municipal refuse alone. This quantity of sng may satisfy 5 to 9 per cent of the community's gas demand and would be a welcome relief from the impending shortage of natural gas”. As research into the array of potential sources of

biomass for biogas production was expanded Owen et al. [9] developed a methodology for accessing the biochemical methane potential (BMP) and potentially inhibitory substances of any organic material using readily available lab ware. The anaerobic bioassay techniques described are relatively rapid and accurate methods for assessing methane potential and toxicity. Several variables can be investigated simultaneously and the more promising conditions screened for more detailed studies. In an article on, "Anaerobic biotechnology of waste water treatment" by Speece [10] the advantages of AD are presented along with the difference digester configurations, and the range of organic substrates which had been tested at the time.

2.2.2 Development of two phase AD

Research by Ghosh et al. [8] demonstrated that the AD process can be optimised by separating the acidification and the methanation phases resulting in greatly reduced retention times and improved gas yields. The concept behind 2 phase digestion recognises, "the substantial difference in the metabolic characteristics of the acid and the methane formers. By providing phase separation of the two major microbial groups and culturing in isolated environments, optimum environments could then be provided for both groups of organisms, and the substrate loading rates to each group could be controlled, thereby enhancing process efficiency and reliability". Other benefits of two phase over single phase AD cited by Ghosh and colleagues [8] include a substantial reduction in total reactor volume and the consequent savings in capital and operating costs.

The benefits of two phase AD were also highlighted by Cohen, et al. [11] in a study on, "Anaerobic digestion of glucose with separated acid production and methane formation". In a two phase anaerobic digestion system a 1% glucose solution was almost completely converted into biomass and gases. The acid reactor was operated at 30°C and pH 6.0, with a retention time of 10 hr. Main products of the acid-forming phase were hydrogen, carbon dioxide, butyrate and acetate. On a molar base, these products represented over 96% of all products formed. On average, 12% of the COD content of the influent was evolved as hydrogen. The effluent of the first reactor was pumped to the methane reactor after passing through a storage vessel. The methane reactor was operated at 30°C, pH 7.8, and a retention time of 100 hr

was given. Approximately 98% of the organic substances fed to this reactor were converted to methane, carbon dioxide and biomass. About 11% of the glucose fed to the digesting system was converted to bacterial mass.

In the following two decades the concept of two phase anaerobic digestion continued to gain greater attention from researchers seeking to improve digester stability, improve gas yields and reduce retention times. Ghosh et al. [12] carried out studies on "Methane production from industrial wastes by two-phase anaerobic digestion". In this paper Ghosh and colleagues highlighted the large potential source of renewable energy from anaerobic digestion of industrial liquid waste. The paper presents data illustrating the limitations and vulnerability of the conventional digestion process in digestion of high concentrations of volatile organic matter, and discusses the application and advantages of two-phase digestion design.

Ghosh [13] reported on the successful operation of a pilot scale two phase anaerobic digestion process was developed to stabilize concentrated (7-5%) activated sludge at a 12-day SRT and a loading rate of 5 kg VS m^{-3} day^{-1}. The pilot system exhibited a VS reduction of 73% and a methane yield of 0.3 m^3 kg VS^{-1} added. Optimum acidogenic fermentation producing 9500 mg L^{-1} of organic acids was achieved at an HRT of 3 days and a loading rate of 16 kg VS m^{-3} day^{-1}. The acidification phase eliminated digester foaming which had previously been a problem in single phase digestion. There was no inhibition of acetogens or methanogens at ammonia-N concentration of 2500 mg L^{-1} and pH 7.7.

2.2.3 High rate anaerobic digesters - Upflow Anaerobic Sludge Blanket

One of the main reasons cited for digester inefficiency is the inevitable washout of active anaerobic sludge from conventional CSTRs under higher loading conditions. However, the development of the Upflow Anaerobic Sludge Blanket (UASB) in the Netherlands in the late 1970s led to great improvements in high rate anaerobic digestion for waste treatment processes. Lettinga and colleagues [14] [15] reported on a number of trials evaluating the effectiveness of the UASB process with a variety

of wastes, using reactors varying in size from 1L to 200 m^3. The UASB process was shown to be feasible for handling a large variety of industrial wastes at exceptionally high organic loading and hydraulic loading rates. Sugar beet and potato processing wastes have been applied with organic loading rates up to 30 and 45 kg COD m^{-3} day^{-1} respectively at 27-35 °C and liquid retention times of 4-8 hrs [16]. In addition to the treatment of industrial wastes the UASB process was investigated for its feasibility in treating domestic sewage. Results obtained in 1 m high UASB-reactors indicate that anaerobic pretreatment of domestic sewage may represent an attractive proposition [17]. Inoculum sludge grown from sugar beet waste demonstrated excellent settleability and was shown to be superior to digested sewage sludge as seed material for an anaerobic treatment process. In the UASB experiments sludge loads up to 0.6 kg COD kg VSS^{-1} day^{-1} could be accommodated within 1 week, so that within this period a space load could be handled as high as 20 kg COD m^{-3} day^{-1}, simply by supplying the reactor with approximately 30 kg VSS sludge m^{-3} averaged over the total reactor volume [18].

2.2.4 Dry anaerobic digestion

The use of dry anaerobic digestion sometimes referred to as anaerobic composting has been used for substrates with higher solids generally greater than 20% TS. The organic fraction of MSW has a total solids content of between 20-30% and has been treated in patented dry AD systems such as Bekon©, Bioferm© and DRANCO©. Such systems generally achieve greater than 60% volatile solids (VS) reduction but usually require a post composting process to meet waste stabilisation standards. Some of the main advantages of dry AD systems are reduced operational costs for heating and mixing. Previous research on dry fermentation by Wujcik and Jewell [19] indicate that substrates with an initial concentration of 40% TS or less, the degradation of solids to gas will be as complete as for liquid reactors given sufficient time. A pilot scale batch reactor filled with 25% TS substrate of wheat straw, seeded with effluent from a daily manure anaerobic digester, produced methane for over 6 months.

The concept of dry fermentation was incorporated into a two phase AD system by Ghosh [20] whereby MSW would be placed in a static pile with leachate

recirculation to increase hydrolysis and acidification of organic solids. Once the leachate contained sufficient soluble nutrients it was then conveyed to a secondary methane reactor for biogas production. The effluent from the methane reactor was then aerated and recirculated over the static pile to increase solubilisation of the substrate. The results of this study showed that gasification and stabilisation of a refuse bed can be achieved by two phase solid bed digestion involving acid phase leachate production and methanation of the leachate in an external methanogenic digester. During batch operation gas production was initially suppressed in the leach bed owing to the low pH and low alkalinity conditions. Hydrolysis and volatile acid (VA) production were the major reactions in the leach bed. These reactions and gasification were accelerated substantially by recirculation of an acidogenic culture and by total internal recycling of nutrients from the methane digester to the refuse bed. The bulk density of the digested refuse was 770 kg m^{-3} compared with 268 kg m^{-3} for raw refuse, showing substantial volume reduction occurring during the solid phase digestion process. The methane phase digester operated well on leachate with VA and COD concentrations up to 9000 mg L^{-1} and 18,000 mg L^{-1}, respectively. COD and VA conversions up to 81 percent, methane content up to 79 %, and a methane production rate up to 7 m^3 CH_4 m^{-3} day^{-1} were obtained with the methane reactor. The overall system resulted in specific methane yield of 0.21 m^3 kg VS^{-1} added after three months of digestion which corresponded to about 81% of the biodegradable organic matter.

Cho et al. [21] also incorporated a solid bed reactor for acid fermentation connected to an upflow blanket filter (methane reactor) for the digestion of food waste. Cho and colleagues found that VFA were produced rapidly at the initial stage of fermentation and need to be controlled using a two phase digestion method. Clear phase separation was obtained when the total VFA levels exceeded 6 g L^{-1} and pH < 6 in the leachate. After the VFA levels fell below 5-6 g L^{-1} and pH > 6 separated acidogenic and methanogenic fermentation could not be maintained. It was found that the rate of degradation of solids in the leach bed depended on recycle flow rate and the methane digester hydraulic retention time.

2.3 State of the art in anaerobic digestion of OFMSW

2.3.1 From landfill to AD

Looking at the period from 1970 to 2013 it is noticeable that the number of publications on anaerobic digestion of food waste has dramatically increased since the mid 1990s (figures based on a search of the Scopus database for scientific publications). During the mid 1990s more evidence became available on the negative environmental impacts from the landfilling of OFMSW [22]. These harmful effects were primarily due to gas and leachate formation from the breakdown of organic matter. Besides potential health hazards, landfills posed serious environmental risks such as fires and explosions, vegetation damage, unpleasant odours, landfill settlement, ground water pollution, air pollution and uncontrolled emissions of greenhouse gases [22]. Methane has a global warming potential (GWP) of 23 times that of carbon dioxide over a 100 year time horizon [23] and is thought to be a significant contributor to climate change. In an effort to move away from landfilling of biodegradable the EU Landfill Directive (1999) [24] has set significant targets for reducing biodegradable waste going to landfill up to the year 2020. The increased research effort into AD of OFMSW and food waste in particular, has been simulated by the need for more sustainable waste management, energy recovery and nutrient recycling.

2.3.2 Improvements in modelling of the AD bioprocess

There are many challenges in the modelling of the anaerobic digestion of OFMSW as there are many biochemical reactions, many types of micro organisms involved and the substrate is complex and may vary depending of source and collection system. Many of the models reported in the literature discuss the kinetics of soluble substances and so only consider the fermentative, acetogenic and methanogenic steps [25]. However there is an increasing body of research based on modelling complex materials such as OFMSW and primary sewage sludge [26]. In certain circumstances the hydrolysis of complex polymeric substances may be the rate limiting step depending of the composition and source of the material [27, 28]. Arguably one of the most comprehensive publications on modelling of the AD process was the

Anaerobic Digestion Model 1 (ADM1) published by the International Water Association (IWA) in 2002 [29]. In the ADM1 model the applicability of different kinetics to the hydrolysis of particulate organic material in anaerobic digestion is discussed in detail [30].

2.3.3 The current state of the art in food waste AD

Biogas production *via* anaerobic digestion of organic wastes, residues and certain energy crops is now seen as one of the most environmentally sustainable and available technologies for renewable energy production from biomass [31]. By 2010 there was an installed capacity of about 6 million tonnes per year for the anaerobic digestion of OFMSW divided over 200 plants in 17 European countries [32]. However for anaerobic digestion to release its full potential as a renewable energy technology, improvements in process efficiency, monitoring and control are necessary. According to Weiland [33], only a fraction of the microbes in an anaerobic digester have been identified and there is a need for further research into the effects of microbial community structure on process stability and biogas yield. Recent research results have demonstrated that strong variations in the community structures occur during the ongoing fermentation process which influences the process efficiency. Other topics such as pretreatment of substrates and the addition of micronutrients have also shown promise for increasing biogas yields. Better bioprocess control is also necessary for future improvements as there are currently only a few sensors available that are sufficiently robust to monitor online. Some sources of OFMSW such as canteen food waste are high in protein which breaks down to ammonia nitrogen during anaerobic digestion. High concentrations of ammonia nitrogen coupled with a high pH (~8) lead to higher levels of free ammonia which has been linked to process inhibition. In food waste digestion the control of ammonia within the digester is necessary for stabile AD. Final digestate quality is also an important aspect to an efficient AD process and may have a large role in agricultural based anaerobic digesters [31].

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3 Assessing the cost of biofuel production with increasing penetration of the transport fuel market: A case study of gaseous biomethane in Ireland

Assessing the cost of biofuel production with increasing penetration of the transport fuel market: A case study of gaseous biomethane in Ireland

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Abstract

Biomethane is an indigenously produced gaseous sustainable transport fuel that uses organic feedstock. Allowing for a realistic collection of organic residues and grass silage from 2.5% of pasture land would allow Ireland to generate 17% renewable energy supply in transport (RES-T) and surpass its 10% target for renewable transport energy by 2020. This would significantly lessen Ireland's dependence on imported fossil fuels, allow compliance with the EU Landfill Directive, and reduce pollution of waterways. Biomethane generated from the organic fraction of municipal solid waste (OFMSW) is the cheapest biomethane (€ 0.36/L diesel equivalent including for value added tax (VAT) of 21%). This is the least expensive fuel because of the associated gate fee of € 70/t. If no gate fee were available the cost would be 1.35/L diesel equivalent including VAT: this underlines the importance of gate fee to what is primarily a waste treatment system. Biomethane from slaughter house waste (SHW) is estimated at € 0.65/L diesel equivalent while biomethane produced from grass and slurry is more costly to produce (€ 1.40/L diesel equivalent). This is still in the cost range of petroleum derived transport fuels at the service station (diesel and petrol prices ranging from € 1.38 to 1.45/L in February 2011). OFMSW and SHW can between them provide 1.4% RES-T at a minimum cost of € 0.52 /L. To achieve 10% RES-T biomethane will cost a minimum of € 1.28/L diesel equivalent. Gaseous fuel can be more competitive by considering a blend of biomethane and natural gas (BioCNG) e.g. 20% biomethane mixed with 80% natural gas. If natural gas at approximately € 0.7/L diesel equivalent is considered, BioCNG will cost € 0.82/L at the 10% RES-T target.

Keywords: Biofuel; biogas; biomethane; OFMSW; grass silage.

3.1 Introduction

3.1.1 Transport Energy in Ireland

In the period 1990-2009 Ireland experienced substantial expansion of the transport sector with an increase in final energy consumption of approximately 150% over the period [1]. Since 2008 there has been a decrease in transport growth which is related to the downturn in the Irish economy; however transport continues to consume over a third of primary energy and accounts for 41.4% of total final consumption [1]. Imported petroleum products account for approximately 98% of transport energy, while biofuel penetration has increased somewhat to 1.8% of petrol and diesel sales in 2009. To accelerate the growth of renewable energy in transport, the Irish Government recently changed the support mechanism from excise relief on biofuel producers, to a biofuels obligation on transport fuel suppliers. The initial biofuels obligation is set at 4% by volume of biofuel as a proportion of road fuel sold [2] and aims to increase the biofuels proportion to a level that will comply with the 10% renewable energy in transport (RES-T) target for 2020. The Irish government also has a target of 10% electric vehicles (EV's) by 2020; however this is expected to meet only 1% RES-T, therefore biofuels will account for the outstanding 9% RES-T [3].

3.1.2 Biofuel Concerns

Ireland's arable land (9% of total agricultural land) is already fully utilised for food and beverage production and the conversion of permanent pastureland to arable required by most energy crops (such as sugar beet and rape seed) is restricted by EU agricultural policy. As a result the majority of ethanol and biodiesel is imported. Questions pertain as to how Ireland can fulfil its biofuels target and meet the criteria for sustainable biofuels as set out in the EU Renewable Energy Directive [4]. An additional obstacle in developing an indigenous biofuels industry in Ireland relates to the fact that Ireland imports approximately 66% of its transport fuel from the UK [5]. This imported fuel already contains 4% biofuels in accordance with the UK's Renewable Transport Fuel Obligation [6] and by default also fulfils 2.64% of the 4% Irish biofuels obligation. As the UK imports the majority of its biofuel (e.g. 80% bioethanol from Brazil and 38% biodiesel from the USA) [7], there is some concern

about the sustainability associated with this practise and the reported negative environmental effects on sensitive eco-systems [8]. As the EU Renewable Energy Directive stipulates that biofuels must not harm sensitive eco-systems it is suggested that national government policy should re-focus attention on the development of sustainable indigenous biofuels.

3.1.3 Energy Forecasts for Ireland

Ireland's energy forecasts for 2020 have been revised a number of times since 2008 [3, 9] to incorporate the effects of sharp economic decline but also to allow for energy savings associated with Ireland's National Energy Efficiency Action Plan (NEEAP) and the implementation of the National Renewable Energy Action Plan (NREAP). In the most recent Energy Forecasts for Ireland to 2020 the baseline scenario for total final energy in transport is 187 PJ, while the NEEAP/NREAP scenario is 178 PJ [3]. The latter assumes Ireland will meet its overall target of renewable energy supply (RES) of 16% and also the renewable energy supply in Transport (RES-T) of 10%. This projection (178 PJ) will be assumed in the analysis below.

3.1.4 Greenhouse gas emissions and related EU Policy

In 2008 Ireland's major contributor to green house gas (GHG) emissions was agriculture (27.3% of GHG emissions) followed by industry and transport (21.8%, 21.1% respectively) [10]. The European commission (EC) has proposed new emission targets for 2020 which will replace Kyoto when it expires in 2012 [11]. The target set for Ireland is 20% less emissions by 2020 relative to 2005. This is a significant target as can be evidenced by Ireland's difficulty in meeting its targets under the Kyoto protocol. Ireland's GHG emissions are 26% above the 1990 level [10], while the committed target allows for only a 13.5% increase in GHG emissions. The EU Renewable Energy Directive [4] has highlighted the sustainability of biofuel production and set GHG savings targets compared to conventional fuels such as petrol and diesel. Article 17 states that "The GHG emission saving from the use of biofuels and bioliquids …shall be at least 35% … from 2017 GHG emission savings shall be at least 50%". According to the same directive biomethane produced from wastes and residues readily meet the

requirement through GHG savings of 75-85% which may not be said for many first generation indigenous liquid biofuels. As a result many European countries are assessing biofuel systems that will satisfy the required GHG savings and fulfil the sustainability criteria set out in the directive. Ireland's waste disposal problem is increasing with time and according to the EU Landfill Directive [12] alternative waste management options other than landfill must be implemented for over 1 million tonnes of biodegradable waste by 2016. The diversion of municipal, industrial and agricultural waste towards the production of biofuel will help Ireland to meet the RES-T targets, satisfy the Landfill Directive, reduce pollution and eutrophication and reduce dependence on expensive imported fossil fuels.

3.1.5 Biogas, a source of biofuel

Biogas is the major energy output from anaerobic digestion (AD), where organic waste and wet biomass (e.g. energy crops) are converted to a gaseous biofuel. Various organic wastes can be used as feedstock, such as the organic fraction of municipal solid waste (OFMSW), slaughter house waste (SHW), agricultural slurries and wet biomass such as ensiled energy crops [13]. Besides the production of energy (in the form of biogas), AD also produces an organic fertiliser with lower pollution potential and significantly better availability of nutrients when compared to slurries [14]. By using the digestate as fertilizer, the goal of a sustainable cropping system can be achieved [15, 16]. Traditionally biogas has been used in on-site combined heat and power plants (CHP); heat and electricity may be used on-site or electricity may be exported to the grid and the heat exported via a district heating system. In 2010 the renewable energy feed-in tariff (REFIT) for electricity offered 15 c/kWh for biogas facilities producing less than 500kW_e and 13 c/kWh for larger facilities. It has been suggested that the present feed in tariff structure is not economically attractive for investors as it does not take into consideration the cost of producing energy crops such as grass silage [5]. Small scale biogas CHP plants (less than 500 kW_e) offer efficiencies of 30-40% electricity and 35-45% heat [17]. It is argued that on site CHP generation is not the most efficient use of biogas unless a market can be found for the heat produced [5]. It has been demonstrated in countries such as Germany, Sweden, and Switzerland that a more efficient use of biogas can be achieved through upgrading biogas to biomethane. Biomethane can then be injected

into the gas grid or used as a transport fuel in compressed natural gas (CNG) vehicles. Gases such as CO_2 and H_2S are eliminated and as a result the CH_4 content is raised to ca. 97% .The end product is practically identical to natural gas and can be blended as BioNG or sold separately [18]. The existing natural gas infrastructure allows for an efficient distribution system with the possibility to sell the biomethane anywhere on the gas grid.

3.1.6 Bio-resources suitable for Biomethane Production in Ireland

As 91% of Ireland's agricultural land is under grass it has been shown that grass silage has the most potential as an indigenous feedstock to meet Ireland's renewable heat and transport obligations for 2020 [19]. Approximately 1% of the EU population live in Ireland; however the country is home to 8% of the total EU cattle herd. The quantity of agricultural slurry which is land spread is in excess of 40 million tonnes annually. This slurry is a major source of eutrophication, air pollution and toxicity in rivers, streams and lakes in the country. Nevertheless, current agricultural practice allows for slurry and slaughter waste to be spread over pasture and tillage land respectively. A study of Ireland's bioresources by Singh and co-workers suggests that there is potential to generate 15PJ/a biomethane from animal slurries, the organic fraction of municipal solid waste (OFMSW), slaughterhouse waste (SHW) and surplus grass. It is estimated that 5.3 Mt/annum of grass (i.e. 2.5% of pastureland) and 3.87 Mt/annum of slurry (which corresponds to 12% of projected slurry production) would be readily available for AD by 2020. Other feedstocks such as OFMSW and SHW also present a great opportunity for biogas. Additionally, they attract a gate-fee and have relatively high biogas yields, thus improving the economics and efficiency of the system. It is conservatively predicted that 25% of the organic fraction of municipal solid waste and 50% of slaughter house waste will be available for biogas production by 2020 [13]. Assuming the latest energy projections for transport in 2020 [3], 10% RES-T will equate to 17.8 PJ, biomethane can supply 8.4% of energy in transport. By allowing for the double credit weighting of biofuels from wastes and lignocellulosic material under the Renewable Energy Directive [4] biomethane can readily provide 17% RES-T without impinging on food supply, therefore exceeding the RES-T 10% target for 2020 as shown in Table 3.1.

Table 3.1 Energy potential of biomethane in Ireland to meet RES-T 2020 target

Feedstock	Practical energy potential in 2020 (PJ)	Including RES-T factor (x2) (PJ)	Percentage of Final Energy in Transport
OFMSW	0.57	1.14	0.64%
Slaughter waste	0.68	1.36	0.76%
Agricultural Slurry	1.88	3.76	2.12%
Grass Silage	11.90	23.79	13.36%
Total	15.03	30.05	17%

3.1.7 Focus of the paper

The objective of this paper is to assess the economics of producing biomethane for use as a transport fuel from various bioresources while also assessing the relationship between increased penetration of biomethane in the transport sector and production cost. The cost of biomethane production to meet the 10% RES-T target for 2020 is sought. This paper builds upon two previous papers: one which assessed the bioresource for biomethane production in Ireland [13]; the second evaluated the cost of mono-digestion of grass silage at farm scale [20].

3.2 Background & Methodology

3.2.1 Methodology

Much of the cost analysis is based on existing biomethane facilities in Europe, data taken from scientific literature, discussions with industry and case studies. The case studies are not named as facilities are commercially sensitive. A simple economic analysis is carried out which assesses the total cost of producing a unit of biomethane based on a minimum breakeven price yielding a return on investment of 6% per annum over 15 years. The cost of producing biomethane for sale as a transport fuel can be divided into three major process steps; biogas production, biogas upgrading to biomethane and distribution of biomethane. Each step of the process will be discussed in detail.

3.2.2 Functional unit

For biomethane systems, the major output is biomethane and therefore the functional unit of annual production is measured in m_n^3 biomethane per annum (where n stands for normalised gas volume at standard temperature and pressure). However, the capacity of the upgrading facility is usually measured in m_n^3/h of raw biogas. The economic analysis uses the functional unit of €/kWh and €/m^3 product gas (i.e. biomethane at 97% CH_4) for comparing the operating costs of the system; 1 m_n^3 biomethane has an energy value of 36.6 MJ or 10.2 kWh. Typically 1m_n^3 of biomethane equates to 1 L of diesel.

3.2.3 A biogas/biomethane strategy for Ireland

In order to benefit from economies of scale, the centralised anaerobic digester (CAD) model has been proposed. The CAD model usually employs biogas plants in the range of 20,000 – 80,000 tonnes per annum of feedstock [21]. A minimum size of a CAD is assessed here as suggested by Singh et al. (2010) at 50,000 t/a biomass feedstock [13]; however the optimum size of a biogas facility is very much dependant on the substrate properties and its availability within the surrounding area of the biogas plant [17]. The following three scenarios will be investigated to demonstrate the large variation in cost associated with biomethane from different feedstocks; Scenario 1: Examines biomethane from agriculture: Grass Silage and Animal Slurry. Scenario 2: Biomethane from meat rendering residues – Slaughter House Waste (SHW). Scenario 3: Biomethane from domestic and commercial food waste - the organic fraction of municipal solid waste (OFMSW).

3.2.4 AD Plant- Biogas Production Technologies

The type of technology used to convert organic substrate to biogas is of critical importance to the efficiency of the process [22, 23]. Substrates with a low total solids content (i.e. less than 15% DS) such as agricultural slurries and SHW are suited to a wet technology such as a continuously stirred tank reactor (CSTR), this can be a one or two stage process. Feedstocks with higher TS content may also incorporated by diluting with water or a low solids co-substrate [23, 24]. OFMSW with TS of approximately 30% may be better suited to a dry technology such as the dry continuous or batch process. In the dry batch process a series of batch chambers are

sequentially loaded to give a relatively constant rate of biogas output. The dry continuous process usually involves higher technical specifications than the batch, with greater automation. In countries with well established biogas expertise (e.g. Germany) biogas technology providers supply standardised units which have been optimised for biogas production for a range of substrates (e.g. maize silage) [25]. In the analysis of each scenario, a particular AD technology is suggested for the relevant substrate.

3.2.5 Biogas Upgrading Technology

The major difference between biogas and natural gas is in relation to CO_2 content. Biogas usually contains 30-40% CO_2 and 55-70% CH_4, while natural gas consists primarily of methane with small proportions of propane and butane depending on the blend and standards. Biogas also contains small quantities of water vapour, hydrogen sulphide, nitrogen, oxygen, ammonia, siloxanes and particles. The feedstock determines the concentration of the impurities and gases in the biogas. For efficient operation, for protection of mechanical equipment from corrosion, and to maximise the volumetric energy density, contaminants and gases with no energy value need to be removed [24].

For most upgrading systems removal of hydrogen sulphide prior to upgrading is necessary. This is usually achieved by addition of iron hydroxide to the digester; if larger quantities of hydrogen sulphide are present in the biogas (i.e. greater than 2000 ppm) the use of a H_2S bio-scrubber may be necessary before CO_2 removal (depending on upgrading technology). There are various techniques and methods for CO_2 removal which involve cooling, compression, precipitation, absorption or adsorption to upgrade the biogas The three most commercially available upgrading techniques are high pressure water scrubbing (HPWS), pressure swing adsorption (PSA) and chemical (amine) scrubbing. To avoid the contamination of the end product, standards have been set in a number of European countries (e.g. Germany, Sweden, and Switzerland) with limits on certain components such as oxygen, water dew point, particles and sulphur. According to Persson et al., (2006) it is possible to achieve these standards by using existing upgrading processes [26]. HPWS and PSA systems are currently the dominant upgrading systems in the biomethane industry.

HPWS systems were identified as being the least complex in operation and therefore are currently the most economically attractive and most employed systems in Europe [27]. Therefore HPWS is assumed as the upgrading technology in this analysis as plants are commercially available from several suppliers in a broad range of capacities [24]. HPWS does not require heat input to the process, operates on approximately 0.25 kWh_e/m^3 of raw biogas input and can also remove H_2S. Methane losses are reported as being approximately 1.5% [24, 25] .

The fundamental operating principle of the HPWS system is that carbon dioxide has a higher solubility in water than methane, particularly at lower temperatures and will therefore be dissolved to a higher extent. In the scrubber column, carbon dioxide is dissolved in the water and thus the methane concentration in the gas phase increases. The water leaving the absorption column is transferred to a flash tank where the dissolved gas, which contains mostly carbon dioxide but also some small amount of methane (~ 1.5%), is combusted to mitigate any possible methane release to the atmosphere. If higher amounts of methane are present in the exhaust gas (i.e. greater than 1.5%) it is transferred back to the raw gas inlet. The water is cooled down to achieve the large difference in solubility between methane and carbon dioxide before it is recycled back to the absorption column. The extracted heat can be used by the biogas plant to help meet thermal demand.

3.2.6 Scenario 1: Grass & Slurry

Grass yields in Ireland are relatively high in comparison to central European countries due the cool temperature oceanic climate [5]. Perennial rye grass, which is the dominant grass type in Irish pastureland, has an average yield of 12 tonnes of dry matter (DM) per hectare per annum [28] and is usually preserved in a horizontal silo commonly known as a silage pit, such grass silage has a total solids content of approximately 22%, of which 90% are volatile [29]. In this analysis a methane yield of 300 m^3 CH_4 /tVS added (at 55% methane content) is assumed (i.e. 108 m^3 biogas/t) [28]. It should be noted that higher methane yields have been reported in literature e.g. Thamsiriroj and Murphy [29] reported 440 m^3 CH_4 /tVS using perennial rye grass in a wet continuous two stage process with a solid retention time of 60 days. Asam and co-workers reported methane potential of 361 m^3 CH_4 /tVS for grass silage from a laboratory batch test [30], while Nizami and co-workers reported

a methane yield of 305 m^3 CH_4 /tVS from a sequencing leach bed reactor coupled with an upflow anaerobic sludge blanket [31]. Grass has specific characteristics such as its long fibrous nature and its tendency to float which can lead to inhibition of the biological process [32]. In continental Europe grass is usually co-digested with a larger proportion of maize or animal slurry, however maize requires tillage land to grow and is better suited to a continental climate. Therefore, based on the practical collectable quantities of grass and slurry at national level, as outlined above, it is suggested that an agricultural based biogas plant would co-digest grass and slurry at a ratio of 3: 2.

The composition and concentration of animal slurries can vary considerably depending on livestock, type of animal feed, farming methods, age and storage of slurry. Cattle slurry is freely available in vast quantities with total solids content ranging from 6 – 12% TS. While pig slurry is more dilute generally 3 – 9% TS. In Ireland cattle are generally housed only for winter months (maximum 20 weeks) while pigs are generally kept indoors throughout the year. Taking this into consideration it may be more feasible to use pig slurry to ensure a constant supply of feedstock. Pig slurry has an average methane yield of approximately 0.32 m^3 CH_4/kg VS_{added}, however due to the dilute nature of slurry it has a low volumetric biogas yield per tonne feedstock (i.e. 22 m^3/t slurry) [30, 33]. Slurry lends itself to co-digestion process utilising a wet technology such as a one or two stage CSTR. From a technical and economic viewpoint the use of a co-substrate with high biogas yields per tonne (e.g. grass silage or OFMSW) is necessary to increase biogas production rates. However, from an environmental protection viewpoint, the use of animal slurry in biogas plants should be encouraged as a waste treatment process for the large quantities produced in agriculture. In addition, the use of fresh animal slurry is an ideal co-substrate for grass silage due to the presence of digestive tract bacteria and enzymes in the slurry [14]. The energy yield from the co-digestion of 30,000 t grass silage and 20,000 t of slurry is mostly influenced by the grass portion as shown in Table 3.2 (87% of energy comes from grass).

Table 3.2 Energy Yields from Grass Silage & Slurry

Total Feedstock	**50,000**	**t/a**	
Grass Silage			
Annual Grass Feedstock	30,000	t/a	1.5 : 1 Ratio of Grass Silage to Slurry
Total yield of TS	6,600	tTS/a	22% TS average for pit silage [a]
Total yield of VS	5,940	tVS/a	90% VS in grass silage [a]
Yield of Grass Silage	12	tTS/ha	Average grass yields in Ireland [a]
Total area under grass	550	Ha	Land required for grass
Gross yield of CH_4	1,782,000	m^3/a	300 m^3 CH_4/tVS [a]
Gross Biogas yield	3,240,000	m^3/a	55% CH_4 [a]
Gross Energy from grass	67,324	GJ	37.78 MJ/m^3 [a]
Pig Slurry			
Annual Slurry Feedstock	20,000	t/a	
Total yield of TS	1,200	tTS/a	6% TS in pig slurry [b]
Total yield of VS	900	tVS/a	75% VS [b]
Gross yield of CH_4	288,000	m^3/a	320 m^3CH_4/tVS [b]
Gross Biogas yield	443,077	m^3/a	65 % CH_4 [b]
Gross Energy from slurry	10,881	GJ	
Grass Silage & Pig Slurry			
Total Gross Biogas Yield	3,683,077	m^3/a	
Average rate of Biogas production	460	m^3/h	8,000 hrs/annum [a]
Total CH_4 Yield	2,070,000	m^3/a	
Losses in Upgrading	31,050	m^3/a	1.5%
Net CH_4 Yield	2,038,950	m^3/a	
Total biomethane yield	2,102,010	m^3/a	97% CH_4 [a]
Total Energy Yield	77,032	GJ/a	37.78 MJ/m^3 [a]
Percentage Energy from grass silage	87	%	

[a] values for grass silage taken from Smyth et al. [28]

[b] values for pig slurry taken from Murphy and McCarthy [33]

3.2.7 Scenario 2: Slaughter House Waste (SHW)

The total number of livestock (i.e. cattle, pigs and sheep) slaughtered in Ireland is estimated to be about 9 million annually [34]. The energy potential from the waste products associated with the meat rendering process is outlined in detail by Thamsiriroj and Murphy [34]. Due to the importance of the agricultural and food sector to the Irish economy, the Department of Agriculture, Food and Forestry

(DAFF) has published a strict list of permitted feedstocks [35], which fall under the animal by-products (ABP) regulations, [36] for use in biogas plants. With regards to SHW, DAFF allow digestive tract content separated from the digestive tract to be used in biogas plants. Such paunch content, often referred to as belly grass, is highly amenable to AD and biogas production. Paunch content is assumed to have a TS of 11% and VS of 80%, with 85% VS destruction [34]. Thus a relatively high methane yield of 440 m^3 CH_4/tVS (i.e. 75m^3 biogas/t/a) is used in calculating the biogas yields from SHW (energy yields are calculated similar to method shown in Table 3.2). A similar biogas plant treating SHW in Sweden reported biogas yields of approximately 105m^3 biogas/t; therefore the biogas yields assumed in this analysis can be viewed as conservative. Other SHW wastes such as offal and process water are also amenable to biogas production and may be treated on site subject to DAFF approval. The use of processed animal protein and fats (i.e. tallow) are also allowed under the ABP but these already have markets in bio-diesel production [18] and are not considered for biogas production.

3.2.8 Scenario 3: The organic fraction of municipal solid waste (OFMSW)

OFMSW refers to all domestic and commercial food and garden waste [37]. At present the collection and treatment of OFMSW is a topic of much debate in Europe with some member states encouraging source segregation and recycling of waste material (e.g. Germany and Spain) while other countries (such as France and UK) are more in favour of centralised waste separation. With regards to using OFMSW as a substrate for biogas production such concerns can have a profound effect on the type of system required and the costs involved. Pre-treatment steps depend on the level of contamination and whether the feedstock has been source separated or not. Separating mixed waste streams requires intensive processing and results in much larger costs. Basic pre-treatment for source segregated OFMSW includes removal of inert contaminants and partial size reduction.

There is a wide range of biogas yields reported from OFMSW depending on the source of the feedstock, how it was collected and the type of AD process employed. For dry batch digestion, biogas yields of between 80-125 m^3 biogas/t OFMSW with an average methane content of 60% are quoted by technology providers. Source

separated OFMSW is reported as having higher methane yields [38, 39] and the resulting digestate is of a higher quality and may have a market value as a soil conditioner. Due to the diverse and changing nature of the OFMSW it is vital to monitor the properties and characteristics of the feedstock. Large quantities of garden waste containing lignin (found in woody material) is not best suited for AD, thus maintaining a feedstock high in water soluble carbohydrates and volatile solids (i.e. VS content of greater than 60%) is important to ensure good biogas yields. The analysis of biomethane from OFMSW is based on a dry batch process similar to that employed by many waste management companies across Europe. A typical facility which processes 50,000 t/a of source segregated OFMSW with a biogas yield of 110 m^3/t feedstock is conservatively assumed in this analysis [40].

3.3 Analysis – Production Cost of Biomethane

3.3.1 Biogas Plant - Capital Costs

The capital investment of a biogas plant is a function of feedstock, plant size and technology. The cost of a biogas plant per unit energy output generally decreases with increasing plant size, however in the case of biogas plants producing electricity from CHP, once plant size reaches 1 MW_{el} (1 MW_{el} is equivalent to 2 million m^3 biomethane/a [41])few cost benefits are gained through an increase in plant size [17]. The biogas yields per tonne of substrate also have a significant effect on the size of digester needed to produce the target energy output. Smyth and co-workers (2010) reported that a grass silage digester in Austria costs in the region of €100/t/a (excluding the cost of silage storage pits) using a wet two stage CSTR system [28]. In a German case study, Urban and co-workers (2008) examined the cost of agricultural based biogas plants in Germany at a range of sizes [25]. A typical biogas plant digesting 90% maize silage and 10% slurry was examined in detail; investment costs per tonne feedstock tend to decrease with increasing plant size, as shown in Figure 3.1. Capital costs included for structural works, maize silage storage pits, mechanical and electrical installations, miscellaneous items and decommissioning at end of life.

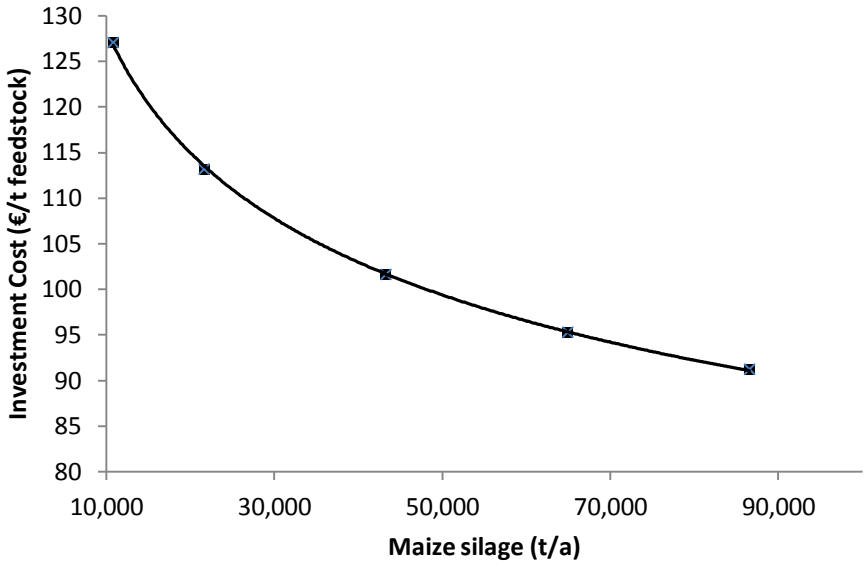


Figure 3.1 Investment costs per tonne maize silage with increasing digester size (data from Urban et al. [25])

Biogas plants treating ABP substrates generally necessitate greater capital investment to satisfy the criteria outlined in the ABP regulations [36]. As OFMSW and SWH fall under category 3 of the ABP a particle size reduction of less than 12mm followed by a pasteurization step (70°C for a minimum of 60 minutes) is required. A comparison of capital costs for different substrates and AD technologies is shown in Table 3.3.

Table 2.3 Comparison of investment costs for biogas plants in Europe

Feedstock	AD Technology	Quantity	Cost of AD Plant
Maize	Wet Continuous (Germany)	30,000 t/a	€108/t/a
SHW	Wet Continuous (Sweden)	54,000 t/a	€140/t/a
OFMSW	Dry Batch (Germany)	25,000 t/a	€220/t/a
OFMSW	Dry Batch (Ireland)	50,000 t/a	€280/t/a
OFMSW	Dry Continuous (Belgium)	50,000 t/a	€380/t/a

The capital cost of the biogas plant for scenario 1 is estimated at €110/t/a for grass silage and slurry [28]. An additional investment cost of €30/t/a silage for storage pits is also included. The capital investment for the biogas plant in scenario 2 is estimated at €140/t/a. This is in the cost range of a similar biogas facility treating

SHW visited by the authors in Sweden. The cost of a dry batch plant for scenario 3 is estimated at €280/t/a which is more expensive than existing facilities in other EU states. The additional cost includes for higher specifications required by Irish environmental authorities for such waste treatment processes (e.g. batch digesters treating OFMSW must be contained in hermetically sealed buildings).
The cost of purchasing a site for the biogas plant is not included for in this analysis as it is assumed that interested parties such as local authorities, food processing plants, abattoirs, waste collectors, farm co-operatives and others will already possess the land. Typically biogas plants utilising wastes and residues are built near former landfill sites, waste water treatment plants or industrial estates where land prices are relatively low, while biogas plants using energy crops and animal slurry would be located on farms owned by the farmer or farmer co-op. A summary of investment capital costs for the biomethane system in shown in Table 3.4.

Table 3.4 Summary of Capital Investment for Biomethane System

Capital Costs (€)	**Grass & Slurry**	**SHW**	**OFMSW**
Biogas Plant	5,500,000	7,000,000	14,000,000
Silage pit	900,000	-	-
Biogas Upgrading Plant	1,450,000	1,450,000	1,700,000
Gas Grid connection	300,000	300,000	300,000
CNG Service Station	500,000	500,000	500,000
Total Capital Cost	8,650,000	9,250,000	16,500,000

3.3.2 Biogas Operating Costs

3.3.2.1 Maintenance, Overheads and Depreciation

The operational costs associated with biogas production vary from source to source [25, 28]. Values in the range of 10 to 16% of capital are quoted for an agricultural based biogas plant [28]. From discussions with industry the cost of maintenance and overheads for an agricultural biogas plant are in the region of €5/t feedstock (scenario 1). The operation of a SHW digester is expected to require more man-hours than an agricultural plant with additional health and safety requirements such as pasteurisation of feedstock. The additional processing requirements will inevitably

lead to higher maintenance costs therefore €10/t is assumed to cover maintenance and overheads for scenario 2. The costs associated with operating an OFMSW digester are expected to be greater than scenario 1 & 2 due to the additional pre-treatment requirements such as waste screening, removal of contaminants and frequent operation of front loading machinery associated with loading and unloading batch digesters, therefore a cost of €25/t is assumed to cover maintenance and overheads for scenario 3. The higher cost of wages in scenario 3 is offset by the lower parasitic demands of the batch system and relatively less maintenance due to the simplicity of design and lack of moving parts. The cost of capital is calculated at a rate of 6% per annum over 15 years. However over the course of the life of the facility some mechanical and electrical elements (boilers, mixers, compressors etc.) may need replacing. It is conservatively estimated that mechanical and electrical installations account for up to 50% of the total cost of a biogas plant. For this reason a depreciation fund is used to cover 50% of biogas capital costs. Depreciation of capital is calculated using the straight line method. A summary of AD operating costs for the three scenarios is outlined in Table 3.5.

Table 3.5 Total Annual Costs of Biogas Production

Annual Costs - Biogas Plant (€/a)	**Scenario 1 Grass + Slurry**	**Scenario 2 SHW**	**Scenario 3 OFMSW**
Maintenance and overheads	250,000	500,000	1,250,000
Electrical demand of biogas plant	75,000	75,000	45,000
Thermal demand of biogas plant	50,001	126,424	99,435
Plant Operations	375,001	701,424	1,394,435
Substrate cost (€17/t grass silage)	510,000	0	0
Digestate disposal	0	0	200,000
Cost of Capital	658,962	720,739	1,441,479
Depreciation fund for M & E	183,055	233,450	466,900
Total Annual Costs	1,727,388	1,422,163	3,502,813
Income from gate fee	0	1,000,000	3,500,000
Annual Cost of Biogas Production	1,727,388	422,163	2,813
Cost of Biogas production (€/m^3) biomethane	0.82	0.20	0.001

3.3.2.2 Parasitic demand

Parasitic demand is most significantly influenced by the type of AD technology, substrate properties, operating temperature range of the system (i.e. mesophilic 30-40 °C or thermophilic 50-60°C) and whether or not the substrate needs to be pasteurised. As the aim of the biomethane system is to produce a valuable commodity with enhanced market value, the parasitic energy requirements should be met by other energy sources. This is an important consideration when examining the lifecycle analysis of the system. In countries where biogas technology is well established it is not uncommon for smaller biogas facilities to supply larger upgrading plants with heat and electricity, thus ensuring low GHG emissions from the system. In this analysis it is assumed that electricity is purchased from a renewable electricity supplier and a low carbon heat source is utilised (e.g. Wood

Chip Boiler). In the cost analysis for the three scenarios the cost of woodchips is taken as €0.04/ $kW_{th}h$ [28] while the cost of electricity is taken as €0.15/ kW_eh . There is a substantial difference in parasitic demand between wet continuous and dry batch AD plants [42]. In the case of wet continuous two stage systems, it is estimated that electrical demand is approximately 10 kW_eh/t biomass [33]. This includes for pre-treatment such as maceration of feedstock, mixing and pumping. The electrical demand is significantly lower in the dry batch system because of the simplicity of the batch process (technology providers quote 6 kW_eh/t). Higher parasitic thermal energy is required for pasteurising ABP feedstocks (as shown in Table 3.6), this can lead to large energy demands for substrates with low TS e.g. SHW and slurry.

Table 3.6 Cost of parasitic thermal demand for scenario 2 – SHW

Parameters	Value	Units
SHC Water	4.184	kJ/kg/°C
Moisture content of Feedstock	89%	
Initial temp	15	°C
Pasteurisation temp	70	°C
Temp rise	55	°C
Thermal Demand of feedstock	0.205	GJ/t
Boiler Efficiency	90%	
Thermal Demand	0.228	GJ/t
Total annual thermal energy	11,378	GJ/a
Annual thermal demand	3,160,599	$kW_{th}h/a$
Cost of wood chips (bulk)	0.04	€/$kW_{th}h$
Thermal Cost	126,424	€/a
Parasitic thermal demand (as % of total energy)	14.8%	

3.3.2.3 Cost of Feedstock – Energy Crop Vs Waste

As shown in Table 3.5 the feedstock has a large impact on the overall cost of biogas production. Grass silage is a crop that requires good management and cultivation with an associated cost of production attached. A production cost of €17/t of silage is estimated by the Irish Agricultural Institute (Teagasc) [28]. As SHW and OFMSW are regarded as waste products a gate fee for accepting such material can be charged. Discussions with abattoir operators in Ireland indicate the cost of SHW treatment is approximately 20-30€/t therefore a gate fee of €20/t is assumed for SHW.

The gate fee which OFMSW brings is hugely significant and is linked with the cost of landfill and competition from alternative waste treatment processes. In 2010 the Irish government introduced a landfill levy of €30/t which is part of a strategy to comply with the EU Landfill Directive by encouraging other forms of waste management, such as recycling and mechanical and biological treatment (MBT). Landfill levies are set to rise in the coming years (€50 per tonne in 2011 and €75 in 2012) to accelerate the diversion of biodegradable waste from landfill. The landfill levy (which is essentially a tax) is in addition to the operating costs of the landfill bringing the total cost of landfill to around €150/t (as of 2010). While landfill fees vary from site to site, discussions with the industry indicate €100/t is a competitive price for waste disposal at present; however, it is reasonable to assume that these gate fees will not remain constant over a period of 15-20 years. Competition from the composting industry, from other biogas plants as the industry expands, uncertainty in the national waste management strategy and economic recession all add uncertainty to the long term price associated with organic wastes and residues. Therefore a gate fee of €70/t for source segregated OFMSW is chosen as a conservative estimate.

3.3.2.4 Digestate

Digestate is a significant issue for many biogas plants. The ABP Regulations [36] as interpreted by the State is of huge significance. Digestate from scenario 1 (grass silage and slurry) should be applicable to land (pastureland and tillage). Typically the fertiliser value of the digestate will displace between 35 and 45% of mineral fertiliser [43]. If slurry (prior to AD) is compared with digestate (post AD) the availability of nutrients is doubled in the digestate. There is potentially a significant financial asset associated with digestate; however in this analysis, it is conservatively assumed that the transport and spreading costs of the digestate are covered by the displaced fossil fuel fertiliser requirement. This is also true for paunch content in scenario 2 (SHW). However the same is not true for digestate from OFMSW from a centralised Materials Recovery Facility (MRF). Digestate derived from such a process cannot be applied to agricultural land. The dry fraction must be post composted and is usually used as landfill cover as digestate derived from a MRF process is generally higher in contaminants and toxins and achieving compost of

commercial quality is difficult. Digestate from source segregated OFMSW can be used on tillage land as a soil improver (after pasteurisation) or made into garden compost. For the purpose of this paper OFMSW is assumed to be source segregated and the digestate made into garden compost at a small cost of €200,000/a (i.e. €4/t of starting material).

3.3.3 Biogas Upgrading Costs

A range of costs (€0.11-0.25/m^3 biomethane) have been quoted in literature for upgrading systems treating from 100-1000 m^3/h raw biogas [19, 24, 28]. The cost of HPWS upgrading systems can vary between technology providers; however as shown in Figure 3.2 the cost is most significantly influenced by the size of the upgrading plant. A significant decrease in cost can be seen from 250m^3/h to 1,000m^3/h, however there is little cost benefit in increasing plant size beyond 1500 m^3/h. Electricity usage which is required for compression, cooling and pumping, accounts for the largest portion of operating costs in a HPWS system. Technology providers indicate electrical use is between 0.25-0.33kW_eh /m^3 raw biogas input. Capital investment costs for HPWS upgrading systems range from €1.35 – €2 million for capacities of between 250-1000 m^3/hr [25, 26].

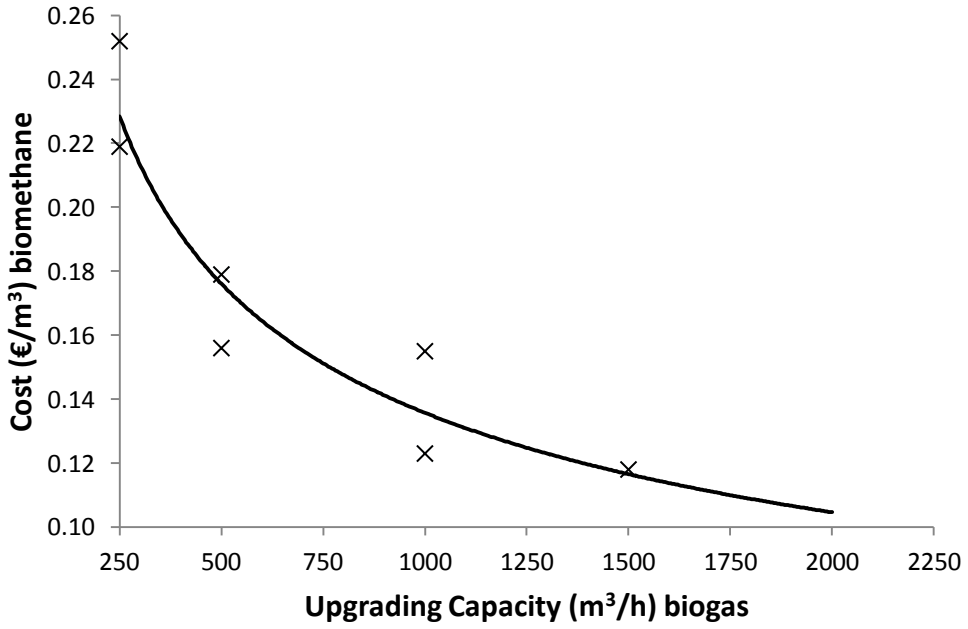


Figure 3.2 Estimated unit costs of HWPS upgrading systems, data from [25].

It is important to note that the upgrading costs per m^3 biomethane shown in Figure 3.2 are based on optimum operating conditions (i.e. max biogas throughput for given plant capacity and upgrading time efficiency of approximately 90%). To ensure economical upgrading efficiency, biogas production rates should match the upgrading capacity of the plant and any down time periods should be kept to a minimum as the cost per unit rises sharply with decreasing time efficiency. Costs shown in Figure 3.2 include the cost of capital and operational costs such as electricity, water, thermal gas treatment and plant maintenance. For scenario 1 & 2 a 500 m^3/h HPWS plant is employed, while a capacity of 750 m^3/h plant is chosen for scenario 3 to cater for the higher biogas yields. To account for different biogas production rates in each scenario, the upgrading capacity used is also considered as shown in Table 3.7 Typically upgrading plants have some inbuilt flexibility to cater for increased biogas loads (e.g. a 500m^3/h upgrading plant has some additional capacity to treat up to 600m^3/h). The formula shown in Figure 3.2 is used to estimate the cost of HPWS upgrading systems.

Table 3.7 Cost of upgrading for three scenarios

Scenario	**1** **Grass & Slurry**	**2** **SHW**	**3** **OFMSW**
Biogas production (m^3/h)	460	468	688
Upgrading capacity (m^3/h)	500	500	750
Estimated cost of upgrading (€/m^3)	0.176	0.176	0.151
Upgrading capacity used (%)	92%	94%	92%
Total cost of upgrading (€/m^3)	0.19	0.19	0.16

3.3.4 Compression and Distribution

Once the biogas has been upgraded to biomethane it must be transported or stored for later use. There are two main avenues, the biomethane can be compressed to approximately 250 bar, stored on-site and later transported to a service station or alternatively the biomethane can be injected into the gas grid and transported to an off-site compression and service station. The gas distribution grid operates at approximately 4.2 bar so no additional compression is needed for injection to the distribution grid as HPWS upgrading plants typically pressurise biomethane up to 7-9 bar [28]. In some European states such as Sweden on-site compression, storage

and distribution via pressurised containers is chosen out of necessity as the natural gas grid is limited to the west of the country. As shown in Figure 3.3, Ireland has an extensive natural gas network; injection of biomethane into the natural gas grid could be a more advantageous supply route with respect to energy efficiency and associated environmental benefits [28].



Figure 3.3 Map of Ireland's Natural Gas Grid (Bord Gáis Eireann)

At present a full pricing scheme for grid injection is not available in Ireland and the finer details of accounting for biomethane (with respect to meeting RES targets) once in the grid have yet to be finalised. However, there are a number of European states (e.g. Germany and Holland) which are successfully injecting biomethane into the national grid, leading to a sharp rise in the development of biogas upgrading plants since the introduction of grid injection. Gas grid injection is chosen as the mode of distribution to suppliers in this analysis to allow for greater energy efficiency and flexibility (e.g. gas transport via pressurised pipeline is considerably more energy efficient than electrical transport via high voltage cables).

Connection to the gas grid would allow for the blending of biomethane with natural gas to produce BioCNG. From discussions with the industry, the cost of connection to the gas grid can vary widely and depends on distance to the network, ground conditions and the type of pipe etc. It is therefore assumed in this analyses that the biomethane plants are located within 0.5 km of the distribution gas network to keep connection costs at a minimum. Smyth and co-workers [28] estimated the capital cost of grid connection at €200,000 while Urban et al., 2008 [25] estimated a higher cost of connection of approximately €300,000 including a 50% investment subsidy for network connection which biomethane suppliers are entitled to under German regulations (GasNZV) [25]. The latter is assumed as the capital cost of grid connection.

The cost of building a biomethane/BioCNG service station is estimated at €500,000 [41]. Biomethane used as a transport fuel needs to be compressed to approximately 250 bar prior to fuelling. Therefore, the cost of compression to 250 bar is included for in the analysis to allow for comparison with other fuels (i.e. petrol and diesel). A compression cost of €0.11/m_n^3 biomethane is taken in the analysis; this includes the cost of electricity used in compression, annual cost of capital, maintenance and overheads. Compression of biomethane to 250 bar also requires significant electrical input, a value of 0.35kW_eh/m^3 biomethane is taken in this analysis [19]. A summary of total production costs for each scenario is shown in Table 3.8.

Table 3.8 Summary of biomethane production costs for three scenarios

Total Production Cost in €/m^3 biomethane	**Grass & Slurry**	**SHW**	**OFMSW**
Biogas production	0.822	0.202	0.001
Biogas Upgrading	0.191	0.188	0.165
Compression & Distribution	0.149	0.149	0.135
Cost of Biomethane Production(€/m^3)	1.162	0.540	0.300
VAT @ 21%	0.244	0.113	0.063
Cost of Biomethane Production including VAT (€/m^3)	1.406	0.653	0.363

3.3.5 Cost Sensitivity

It is clear that for each scenario the cost of biomethane is based on a number of key assumptions. Having reviewed the literature and liaised with the organic waste industry, the assumptions in this study which are most likely to fluctuate are thought to be the biogas yields per tonne of feedstock and the gate fees associated with ABP substrates. Changes in these assumptions were shown to have a significant effect on the cost of biomethane. Table 3.9 shows the effects of cost sensitivity to these parameters for the 3 scenarios. The cost of biomethane production in scenario 3 is largely reliant on the gate fee which is associated with OFMSW. The baseline case assumes €70/t giving and overall production cost of €0.30/m^3. If the gate fee is decreased by 10% to €63/t the overall cost of production increases by 33%. If no gate-fee is received, the cost of production jumps to €1.35/m^3 which is 4.5 times the baseline cost. This underlines the importance of gate-fees to waste treatment systems. The cost of grass silage also has a significant impact on biogas production; according to the Irish agricultural institute (Teagasc) there is a range of costs associated with grass silage production. In the baseline scenario a cost of €17/t was chosen, however it is possible that production costs could be up to 50% more depending on soil type, farming practises etc. therefore a cost of €25/t is taken as the upper bound cost in the sensitivity analysis. This has the effect of increasing the cost of biomethane from grass and slurry by 10%. The biogas yield of the substrate also has a significant effect on the overall production cost of biomethane; this is especially important for scenario 1, by increasing the methane yield of grass silage by 10% (i.e. from 300 to 330 m^3CH_4/tVS) the cost of biomethane can be reduced by almost 8%. Increasing the cost of biogas upgrading has relatively less impact; however as discussed earlier maintaining biogas throughput to match operational capacity is necessary to maintain cost efficiency.

Table 3.9 Impact of parameter changes on production costs

Cost of Biomethane Production (€/m^3)	Scenario 1	Scenario 2	Scenario 3
Baseline Costs	1.16	0.54	0.30
Gate-fee -10%	-	0.59	0.40
Silage Production Costs €25/t	1.28	-	-
Upgrading Costs+10%	1.18	0.56	0.32
Methane Yields +10%	1.07	0.50	0.28

3.4 Discussion of results

3.4.1 Discussion of Production Costs

As shown in Table 3.8 there is a significant difference in the cost of biomethane from the three scenarios. Biomethane from scenario 3 (OFMSW) is the cheapest to produce at a cost of approximately €0.30/m^3. This is highly profitable but is largely based on income from gate fees which may change over time. A production cost of €0.54/m^3 for scenario 2 (SHW) also shows great potential for profit as a transport fuel while the cost of biomethane production from scenario 1 (grass and slurry) at €1.16/m^3 (excluding tax) is also competitive compared with current transport fuel prices. Smyth and co-workers [28] reported the cost of producing biomethane from grass silage was €1.02-1.21/m^3 depending on operational costs. As shown in Figure 3.4 biomethane from SHW & OFMSW (scenario 2 & 3) can only satisfy a relatively small percentage of final transport energy demand due to the limited resources available. Grass and slurry on the other hand are ubiquitous and have the potential to meet and even exceed Ireland's RES-T 10% targets by 2020 because of the large quantities available. If the 10% RES-T target is to be met with biomethane, agricultural feedstocks will play a significant role. Of the 10% RES-T target OFMSW accounts for only 6.4%, SHW 7.6%, while grass and slurry will fulfil the remaining 86%, therefore the weighted cost of biomethane production to meet the 10% target is dominated by the cost of biomethane from grass and slurry (scenario 1). The production cost of biomethane to meet the 10% target is estimated at €1.06/m^3 biomethane excluding taxes (€1.28/m^3 including taxes). However as EV's and liquid biofuels are expected to meet some of the RES-T requirement,

biomethane may not have to meet the full 10% the RES-T target. Figure 3.5 shows the cost of biomethane production at increasing shares of RES-T.

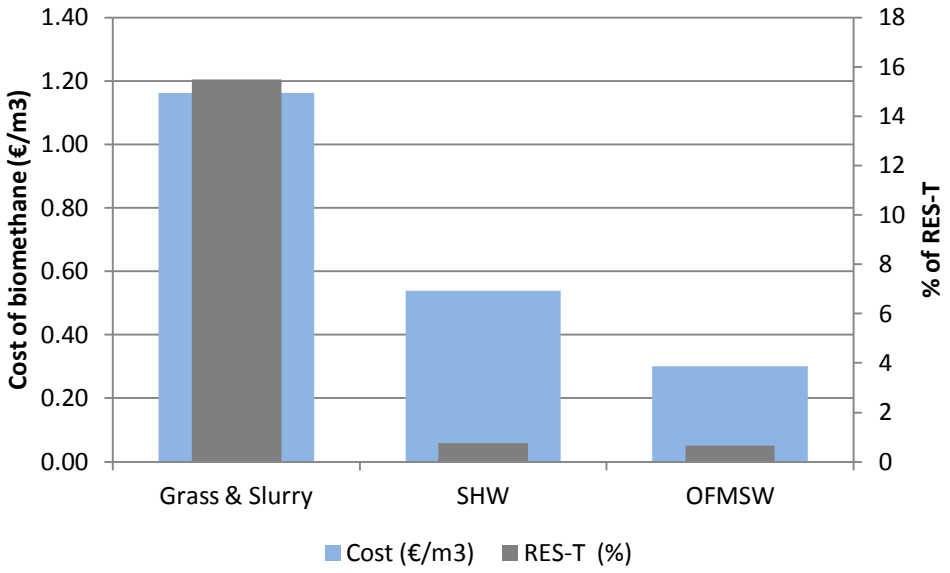


Figure 3.4 Cost of biomethane (ex. taxes) from three scenarios and potential for RES-T

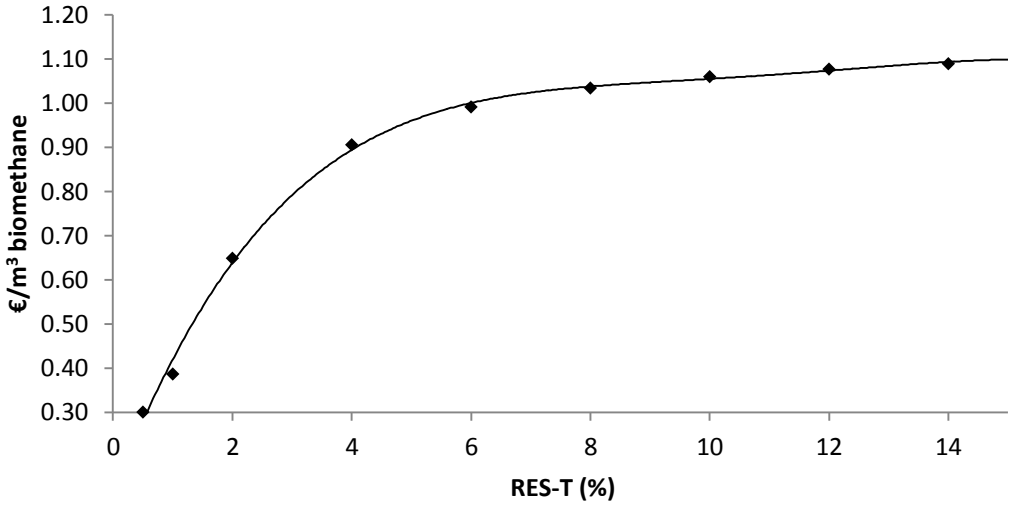


Figure 3.5 Weighted cost of biomethane production (ex. taxes) with corresponding RES-T share

Gas used as a transport fuel is currently exempt from excise duty in Ireland, however value added tax (VAT) for transport fuel is charged at the rate of 21%. The total cost of biomethane including VAT at increasing RES-T is shown in Table 3.10. The EU

Renewable Directive [4] suggests that biogas from OFMSW and slurries as a compressed natural gas effects 75 - 81% reduction in emissions of the whole life cycle analysis of the fuel it displaces. Therefore assuming that biomethane displaces 75% of CO_2 per litre of diesel equivalent and that diesel producves 2.69 kg CO2/L [34], a CO_2 saving of 2.02 kg CO_2/L diesel is achieved. Carbon tax is set at €25/t CO_2 in Ireland as of January 2011, this equates to a saving of €0.05/l diesel equivalent.

Table 3.10 Weighted cost of biomethane including taxes at increasing RES-T penetration

RES-T (%)	Cost of Production (€/m^3)	VAT @ 21%	Total Cost including VAT (€/m^3)
2	0.65	0.14	0.78
4	0.91	0.19	1.10
6	0.99	0.21	1.20
8	1.03	0.22	1.25
10	1.06	0.22	1.28
12	1.08	0.23	1.30
14	1.09	0.23	1.32
16	1.10	0.23	1.33

3.4.2 Developing a Biomethane market for RES-T

According to Howley and co-workers [1] public vehicles accounted for 4.9% of total road transport energy in 2009. By meeting public transport energy with biomethane from wastes and lignocellulosic material and allowing for the associated double credit, 9.8% RES-T could be meet, thus allowing Ireland meet its 2020 target. The argument for using CNG vehicles in cities to reduce particulate matter pollution from diesel engines and thus improve air quality is already providing a stimulus for conversion of public transport vehicles to CNG in many countries; therefore, by using BioCNG a cleaner, more environmentally friendly, more competitive transport fuel can be achieved.

Based on the price of CNG in the UK (€0.71/m^3) and the cost of biomethane (including VAT) at 10% RES-T (€1.28/m^3), a Bio-CNG blend of 20% biomethane and 80% NG would cost €0.82/m^3. This presents a significant cost saving over current transport fuel prices (average prices in February 2011 accord to AA Ireland [44]: petrol 144.5c/l, diesel 138.5c/l). Biomethane and especially BioCNG blends are competitive on a cost per unit energy bases as shown in Figure 3.6. Thus the renewable energy potential from grass and slurry can be realised along with environmental and security of supply benefits while the consumer has the chioice of a competitive transport fuel.

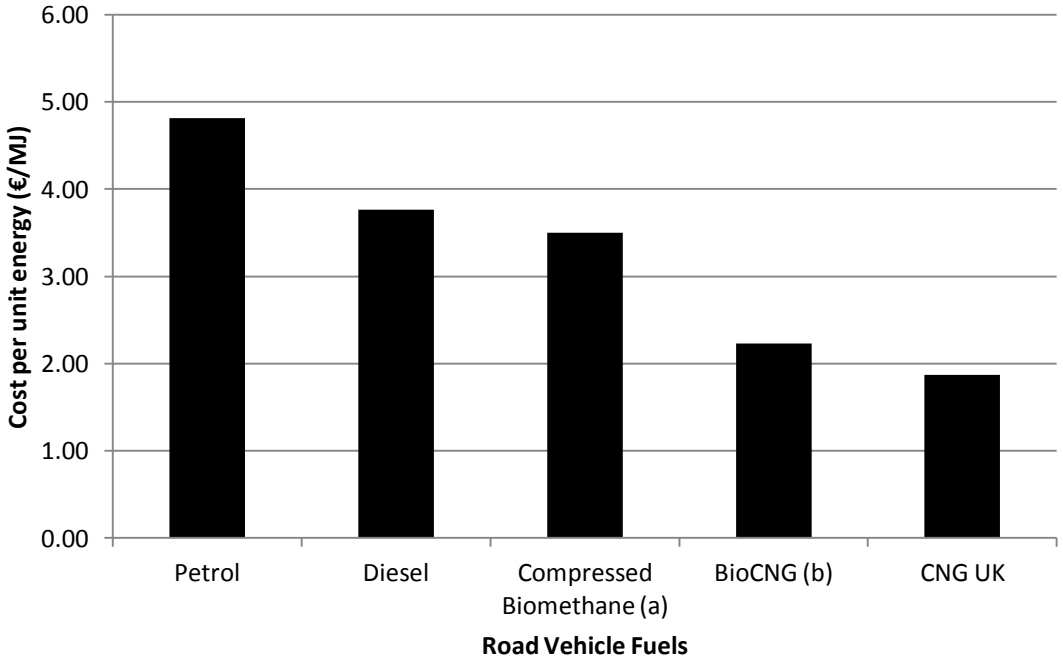


Figure 3.6. Cost comparison of vehicle fuels per unit energy

[a] Cost of biomethane production including VAT meeting the 10% RES-T target.

[b] BioCNG = 80% CNG and 20% BioCNG

The obvious flaw in developing a biomethane transport industry in Ireland is the lack of CNG vehicles and service stations. In order for a biomethane industry to develop in Ireland a captive fleet of CNG vehicles and biomethane/CNG service stations would be required. In this regard government policy to encourage the use of CNG vehicles in replacing existing vehicles in the public bus fleet would provide a stimulus for market development. A market for a competitive transport fuel in the

form of BioCNG is quite promising in bringing environmental, economical and employment benefits to the country. There are now over 12 million CNG vehicles worldwide; this is set to rise due to cost efficiency and improved air quality. The use of compressed biomethane and blended BioCNG is also increasing, e.g. in Sweden there is approximately 17,000 CNG vehicles utilising a BioCNG fuel that contains more than 55% biomethane. The proportion of biomethane used in the gaseous fuel has increased over time and is set to further increase in the future. Ireland has approximately 2 million road vehicles, the potential number of vehicles which could be fuelled by 15 PJ/a biomethane (Table 3.1) would equate to 390,000 cars/a (i.e. fuel used by a petrol car travelling 18,000 km/a at a fuel efficiency of 7km/L. This equates to 19.5% of the national vehicle fleet.

The development of a biomethane market in Ireland needs stimulus and should be lead by targeted Government policy. Incentives must be associated with public service vehicles such as buses, taxis and local authority vehicles. Subsidies must be provided to allow the ratio of vehicles to CNG service stations reach a ratio that allows financial sustainability. This can be achieved through subsidy of CNG service stations, CNG powered vehicles and/or the mandating of gaseous transport fuel. Technical standards, regulations and specifications are required for biomethane injection. At the moment, Ireland has no clear road map to meet its commitment of 10% RES-T in 2020. The benefit of a biomethane industry is an indigenous transport fuel that will help Ireland to meet the RES-T targets, significantly lessen Ireland's dependence on imported fossil fuels, allow compliance with the Landfill Directive, and reduce air pollution. Indigenous biofuel production also improves security of energy supply and reduces dependence on imported fossil fuels. The natural gas grid will provide an efficient cheap means of transporting biomethane to fuel stations. The gas grid in Ireland is connected to over 40% of homes; this may allow for a home-fill system for CNG vehicles.

3.5 Conclusions

As petrol and diesel prices at the pumps continue to rise, biomethane and BioCNG present an opportunity for a sustainable, economical transport fuel that can realistically meet Ireland's RES-T targets and provide a much needed stimulus for an

ailing economy. The cost of biomethane produced from grass and slurry is highest but is also the most reliable and plentiful resource (€1.41/L diesel equivalent allowing for 21% VAT) and should be encouraged by government policy. The weighted cost of biomethane to meet 10% RES-t is €1.28/L diesel equivalent; this is almost 8% cheaper than the price of diesel in February 2011. Biomethane has an advantage over liquid fuels as gas is not presently subject to excise duty. Biomethane from organic wastes and lignocellulosic material can save approximately 75% CO_2 of diesel emissions and therefore should be exempt from carbon tax. The cost of biomethane produced from organic wastes such as OFMSW and SHW is very competitive at 36c/L and 65c/L diesel equivalent respectively. However OFMSW is limited to approximately 0.64% of total final energy in transport while SHW can provide an additional 0.76%; thus at a scale of 1.4% RES-T biomethane will cost a minimum of 52c/L diesel equivalent. To achieve 10% RES-T, biomethane will cost a minimum of €1.28/L diesel equivalent. Gaseous fuel can be made cheaper by considering BioCNG (e.g. 20% biomethane with 80% Natural Gas at €0.82/L diesel equivalent) with the cheaper fossil fuel subsidising the more expensive biomethane. Biomethane from organic wastes which earn additional income through gate fees may present the cheapest option for initial RES-T penetration (up to 1.4% RES-T), however for long term stability and increased RES-T share, investment in biomethane from grass silage and slurry should be encouraged.

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4 Assessment of the resource associated with biomethane from food waste

Assessment of the resource associated with biomethane from food waste

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Abstract:

This paper assesses the resource of biomethane produced from food waste at a state level in the EU. The resource is dependent on the quantity of food waste available for anaerobic digestion and the specific methane yield from food waste. The specific method of undertaking biomethane potential (BMP) tests was shown to be crucial. BMP tests were carried out at different scales (5L and 0.5L) with different sources of inoculum, for both wet and dried substrate samples. The upper bound BMP results for source segregated canteen food waste gave specific methane yields of between 467-529 L CH_4 per kg volatile solids added. The higher results were associated with acclimatised inoculum and wet samples of food waste. The potential renewable resource of biomethane from food waste is shown to be equivalent to 2.8% of energy in transport in Ireland; this is significant as it surpasses the resource associated with electrifying 10% of the private car fleet in Ireland, which is currently the preferred option for renewable energy in transport in the country. However for this resource to be realised within the EU, source segregation of food waste must be effected. According to the Animal By-Products Regulations, digestate from source segregated food waste may be applied to agricultural land post anaerobic digestion. Digestate from food waste derived from a mixed waste source may not be applied to agricultural land. Thus biomethane from food waste is predicated on source segregation of food waste.

Keywords: Municipal Solid Waste; Food Waste; Biogas; Biomethane Potential Assay.

4.1 Introduction

4.1.1 Landfilling of biodegradable municipal waste

Effective management and treatment of biodegradable waste is a topic of increasing importance for municipalities across the globe. The organic fraction of municipal solid waste (OFMSW) which is dominated by food waste is problematic as it is putrescible; it contaminates recyclable material in combined waste collection systems and releases methane to the atmosphere when deposited in landfill sites. Methane has a global warming potential (GWP) over a 100 year time horizon of 23 times that of carbon dioxide [1] and is a significant contributor to climate change. The Landfill Directive 1999 [2] has set significant targets for reducing biodegradable waste going to landfill, while the Waste Framework Directive 2008 [3] has introduced more demanding waste recycling and energy recovery targets. Many EU countries have introduced landfill levies. Some countries including Germany have placed an outright ban on dumping untreated OFMSW.

4.1.2 Quantities of food waste generated

This paper uses Ireland, an EU state with a population 4.6 million [4] to exemplify the bioresource analysis. Approximately three million tonnes of municipal solid waste (MSW) is generated annually (652 kg/person/annum), two thirds of which is considered to be biodegradable [5]. Food waste makes up about 25% of domestic household waste and 42% of commercial waste [6]. It is estimated that approximately 820,000 t/annum, (178 kg/person/annum) of food waste is generated in Ireland. Ireland landfilled 860,000 t of biodegradable municipal waste (BMW) in 2010. The Landfill Directive [2] permits landfill of a maximum of 420,000 t/annum of BMW by 2016 (based on 35% of 1995 quantities). Alternative waste treatment methods are required for approximately 530,000 t/annum of BMW by 2016 (Table 4.1). The Waste Management (Food Waste) Regulations 2009 [7] has mandated source segregation of food waste from commercial premises in designated organic waste bins (brown bins). The catering sector alone produces over 100,000 tonnes per annum of food waste [8].

Table 4.1 Biodegradable Municipal Waste (BMW) disposed to Landfill in Ireland

Target Year	Allowable (kt)	Actual (kt)	Requiring stabilisation (kt)
2010	900	860[a]	-
2013	600	882[b]	282
2016	420	950[b]	530

kt kilotonne

[a] Reported BMW sent to landfill in 2010 [5](McCoole et al., 2012)

[b] Estimated BMW quantities based on economic growth rate of 2.5% from 2012 onwards

4.1.3 The requirement for source segregation of food waste

It has been widely acknowledged in many EU states and in other developed countries that in order to maximise diversion of food waste from landfill, effective source separation is required [9]. This may be effected through use of a three bin collection system which incorporates a specific bin for food waste. Department of Agriculture Regulations in EU countries only allow compost or liquid fertiliser (digestate) from food waste which is source segregated (as opposed to co-mingled food waste with other waste from a materials recovery facility) to be used in agricultural applications [10, 11]. Food waste accounts for the majority of the organic fraction of municipal solid waste (OFMSW). If not source segregated food waste may be separated from mixed waste through mechanical biological treatment (MBT). Mechanically derived OFMSW has been shown to have very stable anaerobic digestion characteristics with a carbon to nitrogen ratio of about 25:1 which is in the recommended range for stable digestion (20-30:1). However mechanically derived OFMSW contains higher concentrations of potentially toxic elements and lower nutrient content than source segregated food waste (SSFW) [12]. It is important to note that digestate from MBT derived OFMSW may not be applied to agricultural land due to potential for contamination of the food chain [10].

4.1.4 Significance of BMP assays in assessing biomethane potential from food waste

The biochemical methane potential (BMP) test is a widely used method to assess the maximum upper range of methane production from an organic substrate. There have been many papers published on the BMP yield of various organic substrates used for biogas production. However, despite a mass of data having been gathered,

comparison of biomethane potential data in literature can prove difficult as different methods and protocols have been followed. Parameters such as substrate preparation, inoculum to substrate ratio, liquid and headspace volumes, pH of substrate and inoculum, headspace pressure and the gas flow measurement system employed can all differ from one test to another [13, 14]. To assess the BMP of SSFW samples, both large and small scale BMP tests were carried out. Nizami and co-workers [14] showed that micro BMP assays using dried substrate samples gave lower BMP yields than larger BMP assays using wet weight samples. They also stressed the importance of acclimatising the inoculum to the substrate.

4.1.5 Sustainability and applications of OFMSW biomethane

Anaerobic digestion (AD) is an economical and environmentally effective waste treatment solution with the added benefit of energy recovery in the form of biogas (ca. 60% methane) [15]. The EU Renewable Energy Directive 2009 [16] indicates that biomethane from OFMSW has a nominal green house gas saving of 80% of the displaced fossil fuel when used as a compressed gaseous biofuel. This saving is well in advance of other first generation liquid biofuels [17]. Although AD technology is widely available, research in the field is still ongoing due to the complexity of the biochemical process, the wide variety of substrates which can be utilised and reported problems in applications of certain substrates. These include low C:N ratios (associated with SSFW and other biowaste streams) leading to increased levels of NH_3-N which can result in reduced biogas yields [18, 19]; Problems associated with the long term mono-digestion of food waste have been linked to a lack of essential trace elements (such as molybdenum and cobalt) which can lead to the failure of the AD process [20]. However considering the poor energy balance associated with many first generation liquid biofuels (such as rape seed biodiesel) and increasing public concern towards biofuels displacing food production, the concept of utilising biomethane from biowaste as a biofuel is very attractive [15,16, 17].

4.1.6 Objectives of the paper

The principal objective of this paper is to assess the biomethane resource from food waste, using Ireland as a case study. In undertaking this task, the importance of the scientific methodology for conducting biomethane potential assays was realised.

This paper will highlight the variance in BMP yields for food waste, taken from the same sample, depending on the BMP methodology employed. In addition, this paper seeks to highlight the impact which EU waste management policy and its implementation has on the quantity of food waste which could be utilised to generate biomethane.

4.2 Materials and Methods

4.2.1 Preparation of Food Waste

As food waste is a heterogeneous substrate that can change depending on the season and region it is difficult to model for lab scale experimental work. The food waste which was used in the experiments was collected from the main university campus canteen in University College Cork (UCC), Ireland. The canteen serves approximately 1,000 students per day and produces approximately 2,500 kg of food waste per week during the academic year (Sept-June). The canteen food waste consisted of mixed cooked and uncooked food such as pasta, rice, meat, fruit and vegetable peelings. It has been previously shown that source segregated food waste gives higher methane yields than co-mingled MSW [12, 20]. SSFW from the university canteen was chosen as the substrate to be used in the BMP tests. It was decided to take a large bulk quantity of food waste in an effort to get a representative sample. Approximately 200 kg of SSFW was collected from the main campus restaurant. The SSFW was manually screened for non biodegradable contaminants such as plastic bags and cutlery. The SSFW was first manually chopped and screened so that particle size was less than 12mm and mixed thoroughly which is required by the Department of Agriculture, Food and Fisheries (DAFF) in Ireland, under the Animal By-Products Regulations [10]. The well mixed bulk material was then passed through a Buffalo 850W food mincer (Figure 4.1), weighed and stored in 8kg bags at -20°C until required for the experiments. The bags were then defrosted at room temperature for 24 hours prior to experimental use. The characteristics of the canteen food waste are as indicated in Figure 4.2 and Table 4.2.



(a) **(b)** **(c)**

Figure 4.1 Source Separated Food Waste from UCC canteen (a) food waste collection (b) maceration process (c) homogenised substrate

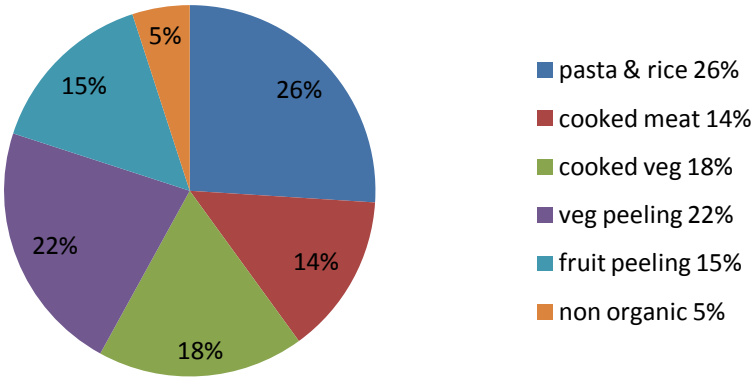


Figure 4.2 Composition of UCC Food Waste

Table 4.2 Characteristics of UCC canteen food waste

Parameters	**Food waste**
pH	4.1
Total Solids (%)	29.4
Total Volatile Solids (% DS)	95.3
Proteins (% DS)	18.1
Carbohydrates (% DS)	59.0
Lipids (fats) (% DS)	19.0
Carbon (% DS)	49.58
Hydrogen (% DS)	7.32
Oxygen (% DS)	34.88
Nitrogen (% DS)	3.53
Ash (% DS)	4.7
C:N ratio	14.2

4.2.2 Preparation of Inoculum

The inoculum used in the first round of BPM trials was obtained from an existing 300L lab scale CSTR which was previously fed with grass silage. In the second round of large BMP tests and first round of small BMP tests, the inoculum was taken from an existing farm scale digester which digests about 80% cattle slurry and 20% grease trap waste on a wet weight basis. The inoculum was passed through a 2mm sieve to remove any large particles or grit and then incubated at 37°C for a week to allow for any residual carbon source to be depleted (de-gassed) prior to feeding with new substrate. The inoculum was then analysed for dry solids (DS) and volatile solids (VS) using standard methods. Table 4.3 shows total and volatile solids for each round of BMP trials. An inoculum to substrate ratio of 3:1 (on a VS basis) was chosen to reduce the impact of any inhibitory effects such as accumulation of volatile fatty acids (VFA). It has been demonstrated that with lower inoculum to substrate ratios (i.e. less than 2) a greater build-up of VFAs can be experienced during the digestion process [23].

Table 4.3 Characteristics of inoculum used in BMP assays

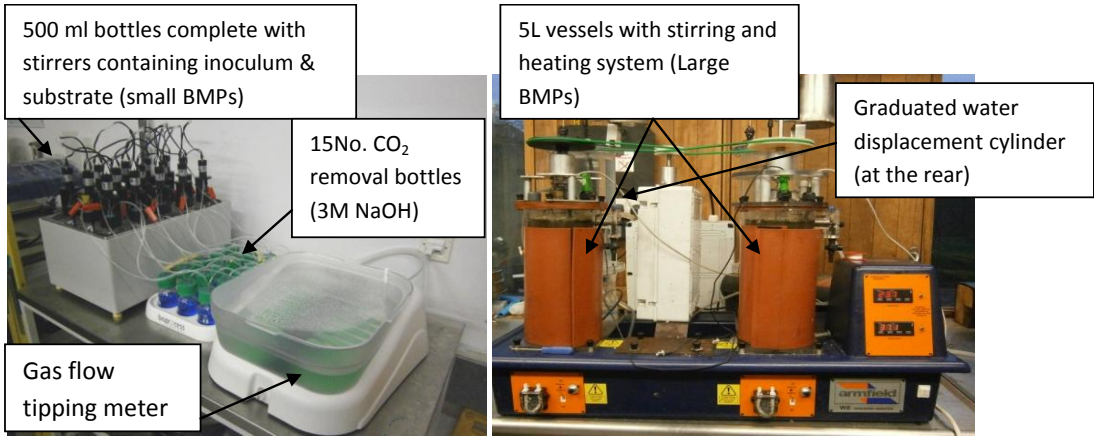
Source of inoculum	Round	BMP test	Total solids (gTS/L)	Volatile Solids (gVS/L)
Lab scale grass digester	1	Large	30.3	17.4
Farm Scale Digester	2	Large & small	30.2	20.7
Acclimatised to food waste	3	Large & small	24.6	16.6

4.2.3 Experimental set-up

The large BMP tests were carried out in an anaerobic digester which consists of two continuously stirred reactors (Figure 4.3b) with a working volume of 5L (approximately 500ml head space). Each reactor was connected to a 3.3L graduated cylinder which was used to record the volumes of biogas by water displacement. A constant temperature of 37°C was maintained in both reactors by means of a temperature sensor and controller unit. The heat was supplied by an outer heating blanket complete with an outer thick layer of insulation to ensure minimal heat loss. The stirring mechanism consisted of a vertical shaft with a propeller at the end. The

shaft was turned by a motorised pulley system. Each round of large BMP tests was carried out in duplicate.

For the small BMP tests the automatic methane potential test system (AMPTS II) supplied by Bioprocess Control was used. The AMPTS II instrument consists of three main units (Figure 4.3a), a water bath incubation unit which accommodates up to 15No 500 ml glass bottles containing the test sample and anaerobic inoculum which are incubated at the desired temperature. The media in each bottle is mixed by a slow rotating mixing rod complete with individual electric motor. 80ml vials containing a 3 molar solution of sodium hydroxide (NaOH) absorbs non-methane gases such as carbon dioxide and hydrogen sulphide. The biomethane is then passed through a tipping mechanism which measures the volume of methane gas released for each vessel. The measuring device works according to the principles of liquid displacement and buoyancy. A digital pulse is generated when a pre-defined volume of gas flows through the device. An integrated data acquisition system is used to record the results. Each sample tested in the small BMP tests was carried out in triplicate. Some samples were dried (105 °C for 24 hours) prior to the BMP test to assess the difference between the BMP of dried substrate and wet (or "as is") substrate. Three blanks were also tested in each round to determine the gas yield from the inoculum itself.



(a) **(b)**

Figure 4.3 BMP apparatus (a) Small BMP set-up (b) Large BMP set-up

4.2.4 Analytical methods

The total solids (TS) and volatile solids (VS) were measured according to Standard Methods 2540 G [24]. The pH was determined using a pH meter (Jenway 3510) calibrated with buffers at pH 4.0, 7.0 and 10.0. Elemental composition (C, H, N, S, O) of the food waste was attained by ultimate analysis using element analyzer (CE 440 Model) and was carried out at the Chemistry Department in UCC. Carbohydrates, proteins and fats were analysed by a laboratory (Southern Scientific Services Ltd.). The protein content was measured by the Kjeldahl method, the fat content was measured using Soxhlet method and the carbohydrates were calculated as the remaining fraction of volatile matter. The sample was also tested for sulphur, however it was not detected. Biogas composition in the large BMP trials was analysed using a portable gas detector (Type PGD3-IR Biogas) supplied by Status Scientific Controls Ltd. All biomethane yields are reported at standard temperature and pressure.

4.2.5 Experimental Overview

The experimental scheme is summarised in Table 4.4. Round 1 used inoculum from a grass silage lab CSTR for the large BMP system. This was carried out in duplicate as there are two available 5L digesters (Figure 4.3b). Round 2 utilised inoculum from an active, stable farm scale digester. The experiments were carried out in duplicate for the large BMP and in triplicate for the small BMP system (Figure 4.3a). For the small BMP system the food waste samples were tested on a wet and dry basis. Wet weight samples or "as is" were used for R2.1 and oven dried samples were used for R2.2 (oven dried at 105^{o}C for 24 hours). Round 3 used the inoculum from the previous BMP tests on food waste (i.e. the inoculum was acclimatised to food waste). In round 3 the small BMP system used only wet weight or "as is" samples of food waste. The ratio of inoculum to substrate was 3:1 for all runs. The mean biomethane yields are presented for both small and large BMP runs.

Table 4.4 Experimental scheme and details of inoculum used in BMP tests

Run	Large BMP	Small BMP
R1	Grass silage inoculum. Carried out in duplicate	
R2	Farm inoculum. Carried out in duplicate	
R2.1		Farm inoculum. Carried out in triplicate. "As is" sample.
R2.2		Farm inoculum. Carried out in triplicate. Sample dried at 105^{o}C for 24 hours
R3	Acclimatised inoculum. Carried out in duplicate	
R3.1		Acclimatised inoculum. Carried out in triplicate. "As is" sample.

4.2.6 Estimation of theoretical biomethane potential

One of the key considerations for designers and operators of anaerobic digestion facilities is assessing the expected methane yield from a given feedstock [25]. The predicted specific biomethane yield and percentage of methane in the biogas will affect the design of the digester and also the energy recovery units such as combined heat and power (CHP) plants or biogas upgrading systems. It is important to gather as much information as possible on the physical and biochemical nature of the substrate which is to be used in the digestion process [13, 21, 22]. The proximate and ultimate analysis of the food waste used in these trials allows the derivation of the Stoichiometric equation of the substrate ($C_{16.4}H_{29}O_{9.8}N$); from this the energy value of the feedstock can be estimated by using the modified Dulong formula (Table 4.5a). Using the Buswell equation [26] a methane content of approximately 57% in the biogas and a biomethane potential of approximately 550 L CH_4 kg VS^{-1} food waste added is predicted (Table 4.5b). These two values are in close agreement. Theoretical methane potential can also be estimated by nutrient composition (fat, protein and carbohydrate) [21].

Table 4.5 Theoretical biomethane potential from UCC canteen food waste

(a): Theoretical biomethane potential based on the Modified Dulong Formula[1]

$E°=337C +1419(H-1/8O) +93S+23.26N$

$E°=337(49.58) +1419(7.32 - 1/8(34.88)) +93(0)+23.26(3.53)$

$E°=20.15$ MJ/kg Energy Content of food waste on a dry solids (DS) basis

$E°=21.14$ MJ/kg VS (VS=95.3% of DS)

Considering that methane has an energy value of 37.78 MJ/m^3 the Modified Dulong Formula suggests the theoretical maximum methane yield is 0.560 m^3 CH_4/kg VS added

[1] Modified Dulong formula taken form Nizami, A.-S., N.E. Korres, and J.D. Murphy, Review of the Integrated Process for the Production of Grass Biomethane. Environmental science & technology, 2009. 43(22): p. 8496-8508

(b) Theoretical biomethane potential based on the Buswell Equation

$C_{16.4}$ H_{29} $O_{9.8}$ N		+	4.23	H_2O	→	9.38	CH_4	+	7.02	CO_2
383.0		+	76.13		→	150.01		+	309.10	
				459.1	→	459.1				
294	kg DS	+	58.44	kg H_2O	→	115.16	kg CH_4	+	237.29	kg CO_2
280	kg VS	+	55.70	kg H_2O	→	109.74	kg CH_4	+	226.13	kg CO_2
					→	153.72	m^3 CH_4	+	115.18	m^3 CO_2
						57.17	% CH_4	+	42.83	% CO_2
Density of CH_4		0.71	kg/m^3							
Density of CO_2		1.96	kg/m^3							
Theoretical Biomethane Potential						0.549	m^3 CH_4/ kg VS_{added}			

4.3 Results & Discussion

4.3.1 Large BMP results

The first round of large BMP tests gave a lower specific methane yield than expected (Table 4.6). The cumulative average specific methane yield was 314 L CH_4 kg VS^{-1} added. This is approximately 57% of the theoretical biomethane potential according to the Buswell equation (Table 4.5b). The lower than expected SMP in round 1 can be attributed to the inoculum used in the large BMP test which was taken from a lab scale CSTR previously fed with grass silage in continuous AD trials. It is clear from the S shaped cumulative curves from round 1 (Figure 4.4b) that there is inhibition to biomethane production in round 1. The inoculum which was used in round 1 was sourced from a laboratory based CSTR which operated for over a year on mono-

digestion of grass silage. During that trial the organic loading rate was increased to biological failure. Thamsiriroj and co-workers [27] hypothesised and modelled that the route of failure was due to inhibition of acetogenic bacteria caused by lack of trace elements. This hypothesis is in agreement with the viewpoint of Zhang and co-workers [18] on long term mono digestion of food waste. It is plausible that the inoculum used in round 1 (from previous digestion of grass silage) was deficient in acetogenic microbes. Typically 2/3rds of the total methane is formed via the acetogenic route and 1/3 via the hyrogenotrophic route [19]. For accurate BMP assessment the inoculum should be sourced from a stable AD process and preferably acclimatised to the new substrate [13].

Table 4.6 Comparison of methane BMP tests on food waste

Specific Methane Yield ($L\ CH_4\ kg\ VS^{-1}_{added}$)	Large BMP			Small BMP		
	R1	R2	R3	R2.1 fw-wt	R2.2 fw-dr	R3.1 fw-wt
Experimental BMP	314	358	467	433	396	529
Theoretical BMP (Energy Basis)	560					
Theoretical BMP (Buswell equation)	549					

fw-wt = food waste wet; fw-dr = food waste dry

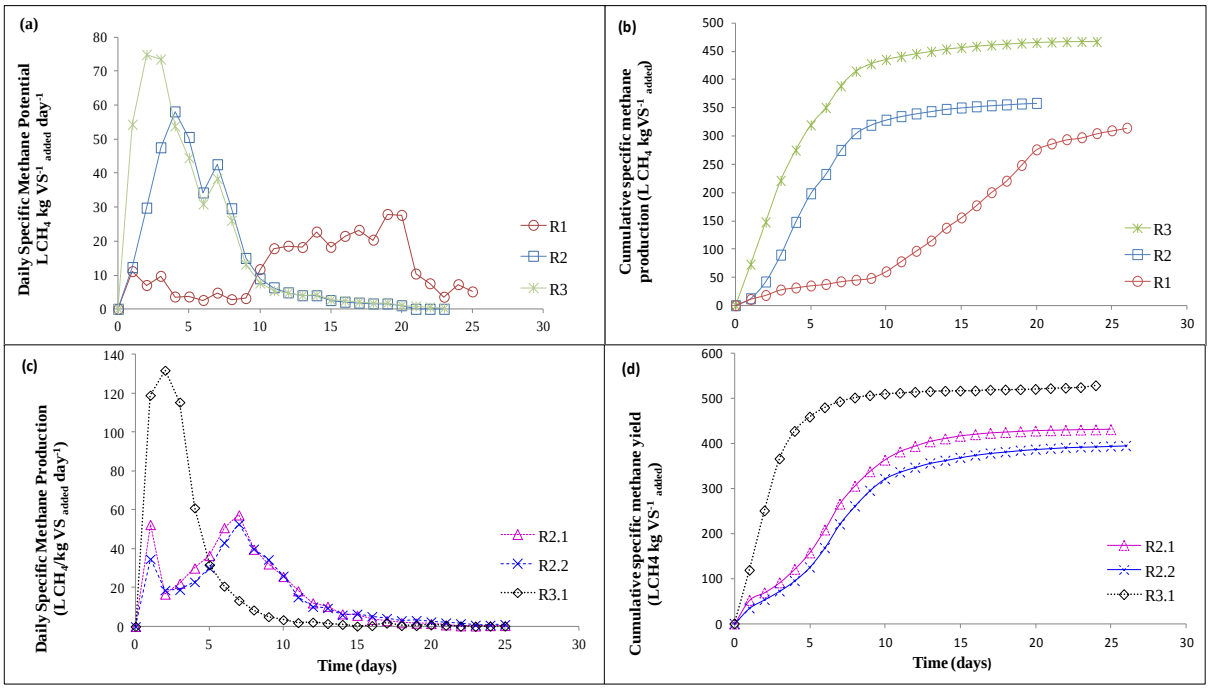


Figure 4.4 Daily and cumulative specific methane production from large BMPs (a) & (b) and small BMPs (c) & (d)

The second round of large BMP tests resulted in a cumulative specific methane yield of 358 L CH_4 kg VS^{-1} added using inoculum from the farm scale digester (Table 4.6). As seen from the daily and cumulative specific methane yield shown in Figure 4.4, the cumulative methane curve follows a normal (un-inhibited) methane production rate as expected for BMP assays [21, 23]. The ultimate specific methane yield from round 2 of the large BMP tests is approximately 65% of the theoretical methane production (Table 4.6), which again was lower than expected.
In the third round of large BMP tests using inoculum that had been acclimatised to food waste from the previous BMP test, ultimate specific methane yield of 467 L CH_4 kg VS^{-1} added was achieved. This was an increase of 16% in SMP from the previous round 2 result. This increase in methane yield can be attributed to the acclimatisation of the inoculum to the feedstock. The ultimate specific methane yield from round 3 large BMP tests was approximately 82% of the theoretical methane production and was deemed to be satisfactory. As the same substrate, apparatus and inoculum to substrate ratio were used in all large BMP trials, it is clear that the increase in SMP yield is as a result of using inoculum from a stable AD process and also acclimatising that inoculum to the substrate.

4.3.2 Small BMP results

In round 2 of BMP tests (first round with small BMP tests) two sets of small BMP tests were carried out in triplicate for samples of food waste on a wet (as is) and dry basis. The wet and dry samples gave an average ultimate specific methane yield of 433 and 396 L CH_4 kg VS^{-1} added respectively (Table 4.6). The wet samples yielded approximately 9% more biomethane than the dried sample. This can be attributed to the organic acids which are present in the wet sample but are lost during the drying process (105 °C for 24 hours). In the third round of BMP tests using inoculum which was acclimatised to food waste, the ultimate specific methane yield was 529 L CH_4 kg VS^{-1} added. This was almost a 22% increase in BMP than the previous result (on a wet basis) indicating once again that the acclimatisation of the inoculum had a beneficial effect on BMP results.

It was found that the small BMP results gave higher specific methane production yields than the large scale BMP results. The higher BMP results achieved by the small BMP trials may be due to scale; the smaller system may have a better mixing regime across the smaller volume (0.5L) as compared to the larger 5L volume. It may also be explained by the greater accuracy inbuilt in the bioprocess BMP apparatus which continuously records biomethane volumetric flow via a sensitive tipping meter system connected to an online data logger. This is in contrast to the large BMP apparatus which employed a water displacement gas flow measurement system, which required frequent refilling and the possible introduction of error in gas measurement. Walker and colleagues [28] highlighted the potential for errors in biogas flow measurements when using a water displacement gas collection system. The average cumulative SMP for the large BMP tests with acclimatised inoculum was 467 L CH_4 kg VS^{-1} added. This is approximately 85% of the theoretical BMP based on the Buswell equation. The small BMP tests (on a wet weight basis) with acclimatised inoculum gave an average cumulative SMP of 529 L CH_4 kg VS^{-1} added, which is approximately 95% of theoretical max BMP (Table 4.6). It is clear from the increase in BMP from round 2-3 that acclimatising the inoculum to the substrate is an important step for accurate BMP testing.

4.3.3 The effect of inoculum on methane yields

Specific methane production can be modelled using the commonly cited first-order decay predictor equation [12] (Equation 4.1);

$$Y=Y_m*(1 - \exp(-kt) \quad (4.1)$$

Where Y = Cumulative specific methane yield for a given time t; Y_m= Ultimate specific methane yield; k = first order decay constant.

Using the statistics toolbox in MATLAB (MATLAB and Statistics Toolbox Release 2012b, The MathWorks, Inc., Natick, Massachusetts, United States.) the cumulative methane data points from each round of both large and small BMPs were plotted and regression curves were generated using equation 4.1. It can clearly be seen from Figure 4.5 that equation 4.1 gives a good fit for small BMP R3.1(R-squared value =

0.98) and large BMP R3(R-squared value = 0.99) i.e. when using the acclimatised inoculum. For these two cases the ultimate methane yield is reached in approximately 10 days, demonstrating that under favourable conditions, food waste is a quickly degradable substrate. Good AD inoculum possesses the desirable consortium of anaerobic microbes which facilitate hydrolysis, acidogenesis, acetogenesis and finally methanogenesis of the substrate without inhibition. The full list of R-squared values for each round, are shown in Table 4.7. The first order decay constants ranged from k = 0.056 for R1, the low BMP yield from large BMP round 1, to k =0.364 for R3.1, which was the high BMP yield from small BMP round 3 using acclimatised inoculum. Table 4.7 indicates that for the same food waste, the different sources of inoculum used in the three rounds of BMP trials had a notable effect on the kinetic decay constant k.

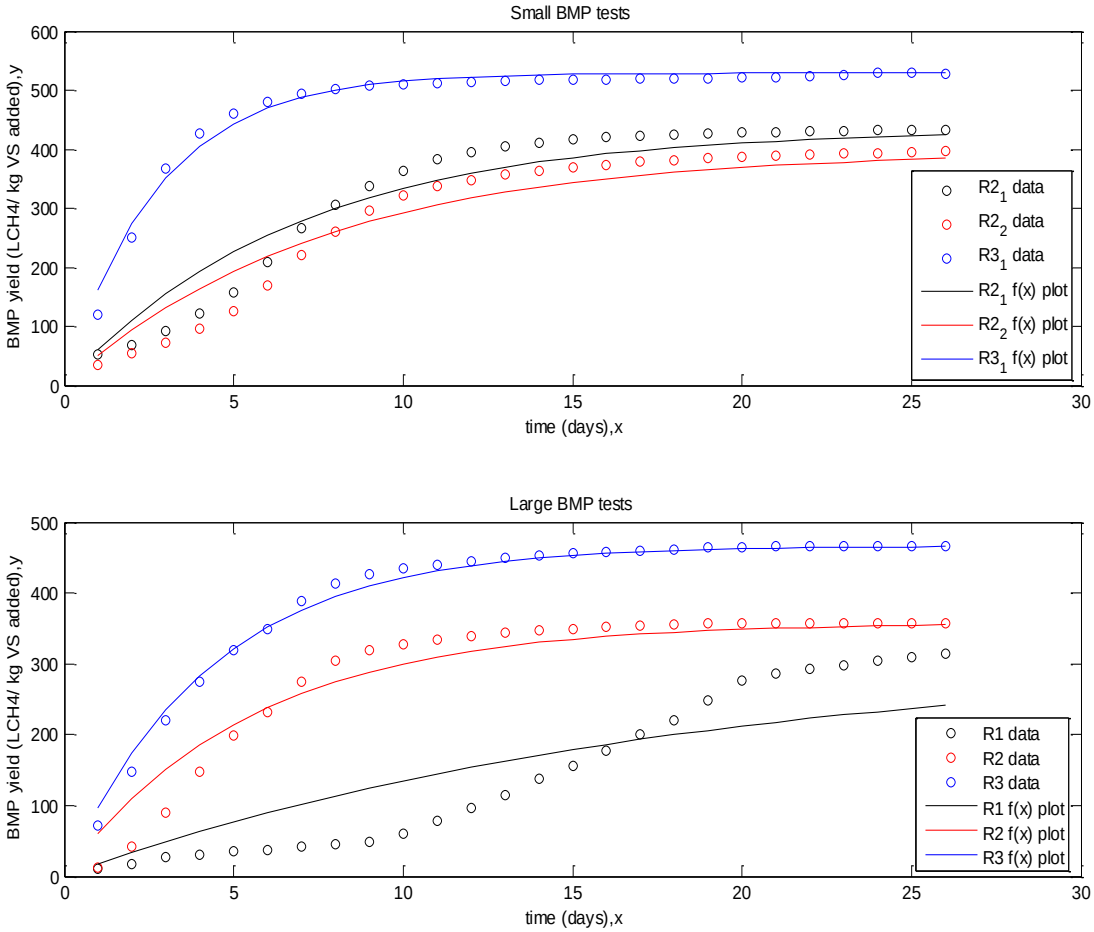


Figure 4.5 Cumulative specific methane yields from small and large BMP trials (including regression curve fitting)

Table 4.7 Kinetic constants and coefficients of determination for BMP tests

BMP Trial	Inoculum	Ultimate Methane Yield (Y_m) L CH_4 kg VS^{-1}	Kinetic decay constant (k)	Coefficient of Determination (R^2 Value)
R2.1 (small)	Healthy	433.14	0.148	0.968
R2.2 (small)	Healthy	396.39	0.134	0.970
R3.1 (small)	Healthy & acclimatised	529.22	0.364	0.984
R1 (large)	Unhealthy	314.09	0.056	0.866
R2 (large)	Healthy	357.96	0.182	0.976
R3 (large)	Healthy & acclimatised	466.51	0.234	0.995

4.3.4 Comparison of results with other published BMPs of food waste

These BMP results are somewhat large in comparison to other reported results for food waste (Table 4.8). The samples tested in this study were of source segregated canteen food waste which was collected within 24 hours of disposal and should be seen as the upper range of biomethane yields from OFMSW. On a larger regional scale, domestic food waste would contain more cellulosic material such as peelings from fruit and vegetables and would most likely be contaminated with 10- 15% other house hold streams such as paper, cardboard and textiles which are much higher in lingo-cellulosic material. Lignin is essentially non biodegradable under anaerobic conditions. Also due to waste collection logistics, OFMSW may not be collected for up to two weeks, disintegration and respiration may already be well underway (hence the foul odour associated with OFMSW). High methane yields from SSFW have also been reported by other authors, Banks and co-workers [12, 20] found that SSFW had higher methane yields than mechanically derived OFMSW; this is also in agreement with work done by Cecchi et al. [29]. However a detailed study by Davidsson and co-workers [30] showed similar biomethane yields from a large number of OFMSW samples which had all been through different pre-treatment processes (300-400 L CH_4 kg VS^{-1} added). These findings indicated that the biomethane yield was independent of the type of pre-treatment and source of OFMSW. Reported biomethane yields from food waste can vary due to the heterogeneous nature of the material and differences in food types between regions.

Also operating temperatures, bioreactor design and loading rate can significantly affect the results.

Table 4.8 Biomethane yields from this study compared to the literature

Author	Substrate	BMP Yield ($m^3_nCH_4$/tVS)	Retention time (days)	Temp Range
This study	ssFW	467-529	30 days	37 ± 1 °C
Zhang et al., (2012) [12]	ssFW	455-456	30 days	36 ± 1° C
Davidsson et al. (2007) [30]	ssOFMSW	300-400	15 days	55°C
Cecchi et al., (2003) [29]	ssOFMSW	158-397	-	-
	ssFW	401-489		

4.3.5 Assessing the biomethane potential of source separated food waste

In 2010, approximately 2 million tonnes of biodegradable municipal waste was produced in Ireland of which 820,000 t would be deemed OFMSW [6]. By 2016, it is estimated that 950,000 tonnes of OFMSW will be produced annually in Ireland of which a *minimum* of 530,000 t will require biological treatment [6]. Table 4.9 outlines an assessment of the bioresource of OFMSW biomethane. A conservative BMP yield of 470 L CH_4 kg VS^{-1} added is chosen. The analysis (Table 4.2) suggests each tonne of food waste equates to 280 kg of VS. The resource is equivalent to 70 Million m_n^3 of biomethane per annum (Table 4.9) equivalent to 70 million litres of diesel. Thamsiriroj et al. [31] suggest that biomethane is an ideal biofuel when coupled with a natural gas vehicle (NGV) industry. The biogas would need to be upgraded and injected into the natural gas grid. The natural gas grid is Ireland is in place in 153 cities and towns and at least 40% have houses are connected to this grid. This allows home fill systems. However NGV buses are seen as the best method for initiating such an industry. There are 400,000 NGV buses in operation worldwide [31]. The first NGV bus in Ireland started operation in July 2012. Biofuels produced from residues are liable to a double credit in line with the Renewable Energy Directive [16]. Thus the bioresource of food waste is equivalent to 2.8% Renewable Energy Supply in Transport (RES-T). This is significant. To put this in context, Ireland has a very ambitious plan to have 10% of the private transport fleet operating

on electricity by 2020. This involves about 300,000 electric vehicles (EVs) which would put Ireland in the forefront of the EV market in the world. However if this plan was realised and this level of infrastructure was in place, this would only generate 1.6% RES-T [32]. It is to Ireland's (and other EU states) advantage to put in place a biological treatment infrastructure for food waste and to couple this with the production of renewable gaseous transport biofuel. The idea of using the food waste of a city to fuel the bus fleet of the city is gaining momentum in the EU in cities such as Barcelona and Oslo. In the EU this bioresource may only be obtained if food waste is source segregated. At present approximately 25% of all households in Ireland are provided with a brown bin collection service [6]. However the most recent waste management policy document states that household food waste regulations will be introduced requiring the separation and diversion of food waste to more productive uses than landfill [33].

Table 4.9 Bioresource of OFMSW beyond 2016

Parameter	Value
Quantity of OFMSW	530,000 t/a
Quantity of VS (29.4% DS of which 95.3% VS)	148,500 t VS/a
BMP range 467 to 520 m^3_n CH_4/tVS	470 m_n^3 CH_4/tVS
Biomethane production	70 million m_n^3/a
Energy Value of Methane (STP)	37.78 MJ/m_n^3
Biomethane production	2.65 PJ/a
Expected transport energy in Ireland 2020	188PJ/a
Biomethane production (RES-T)	1.4%
Biomethane production (RES-T) including for credit	2.8%

4.4 Conclusions

To evaluate the biomethane resource an optimum biomethane potential methodology must be employed. This paper has shown that wet samples give slightly higher BMP results than dried samples, that inoculum should be from a healthy, stable AD process, and that inoculum which has previously been acclimatised to a given substrate gives the best BMP results. The range of results for the same food waste samples ranged from 314 to 529 L CH_4 kg VS^{-1} added depending on the apparatus used and the source of inoculum. This range would obviously have a very significant impact on the calculated renewable energy resource associated with OFMSW.

From this study food waste has the potential to provide 2.8% renewable energy supply in transport. The Animal By-Products Regulations does not permit digestate from food waste to be applied to agricultural land unless it is source segregated. Therefore in order to realise the full bioresource from food waste source segregation of municipal waste must be fully implemented at national level.

Acknowledgments

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5 Evaluation of the biomethane potential from multiple waste streams for a proposed community scale anaerobic digester

Evaluation of the biomethane potential from multiple waste streams for a proposed community scale anaerobic digester

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Abstract

This paper examines the biomethane potential from organic waste for a proposed community scale anaerobic digester in a rural town. The biomethane potential test is used to assess the suitability of waste streams for biomethane production and to examine the variation in biomethane potential between waste sub streams. A methodology for accurately estimating the biomethane potential from multiple heterogeneous organic waste substrates is sought. Five main waste streams were identified as possible substrates for biogas production, namely: Abattoir waste, (consisting of paunch and dewatered activated sludge); cheese factory effluent; commercial and domestic food waste; pig slurry; and waste water treatment sludge. The biomethane potential of these waste streams ranged from as low as 99 L CH_4 $kgVS^{-1}$ for pig slurry to as high as 787 L CH_4 $kgVS^{-1}$ for dissolved air floatation sludge from a cheese effluent treatment plant. The kinetic behaviour of the biomethane production in the batch test is also examined. The objective of the paper is to suggest an optimum substrate mix in terms of biomethane yield per unit substrate for the proposed anaerobic digester. This should maximise the yield of biomethane per capital investment. Food waste displayed the highest biomethane yield (128 $m_n^3 t^{-1}$) followed by cheese waste (38 $m_n^3 t^{-1}$) and abattoir waste (36 $m_n^3 t^{-1}$). It was suggested that waste water sludge (16 $m_n^3 t^{-1}$) and pig slurry (4 $m_n^3 t^{-1}$) should not be digested. However the biomethane potential test does not give information on the continuous operation of an anaerobic digester.

Keywords: anaerobic digestion; biogas; biomethane potential test; waste to energy;

5.1 Introduction

5.1.1 Benefits of anaerobic digestion in waste treatment and energy recovery

Anaerobic digestion uses a large variety of organic substrates to produce biogas. Germany has over 6,000 anaerobic digesters with energy crops as the dominant feedstock [1]. However with world food prices continuing to rise into the foreseeable future, there is much international concern over the use of energy crops for fuel production. This concern can be seen in the latest amendment to the EU renewable energy directive [2] as Europe seeks to introduce a limit to the contribution made from liquid biofuels produced from food crops, such as those based on cereals and other starch rich crops, sugars and oil crops. Attention has been redirected to utilising waste and residues for energy recovery. The Renewable Energy Directive [3] states that biofuels produced from wastes, residues, non-food cellulosic material and ligno-cellulosic material shall be considered at twice their energy value for assessment of compliance with the 2020 target of 10% renewable energy supply in transport. This suggests that compressed biomethane produced from food waste and residues are more sustainable transport biofuels than first generation food crop based biofuels such as ethanol produced from wheat. The typical greenhouse gas savings (as compared to the displaced fossil fuel) for compressed biomethane from municipal solid waste (MSW) is quoted as 80%. This may be compared with 32% for wheat ethanol and 45% for rapeseed biodiesel [4]. One of the advantages of anaerobic digestion is the flexibility in substrates that may be used to produce biogas and the flexibility in the use of the biogas. Biogas (which is between 50 and 70% methane) may be used as renewable heat, renewable electricity or if upgraded to biomethane (~98% methane) it may be used as a renewable gaseous transport biofuel in compressed natural gas vehicles.

5.1.2 Anaerobic co-digestion of organic wastes

There have been many previous studies on the co-digestion of agricultural slurries and energy crops or organic wastes, however there are limited publications on the assessment of multiple waste streams for a single anaerobic digestion process. As the spectrum of potential substrates for biogas production broadens to include more organic wastes and residues, a suitable method to determine the methane potential of

a potential substrate is the biochemical methane potential (BMP) test. Such tests can provide information such as the rate of material degradation and the expected methane yield per gram of material added, which is known as the specific methane yield.

5.1.3 Feedstock sampling and screening for biomethane potential

As the demand for selecting and pricing biomass substrate for anaerobic digestion continues to increase the biomethane potential test is an increasingly recognised tool for screening potential feedstocks for biomethane potential. Many anaerobic digesters treat a variety of organic wastes that may change throughout the year. Representative sampling can often be difficult to achieve in practise due to heterogeneity of certain waste streams, fluctuations can occur in daily waste production and in sampling location. Within certain processes there may be several sub streams of waste production which can have widely different characteristics and therefore will affect widely different biomethane yields. The importance of accurate feedstock sampling and analysis for biogas production cannot be under estimated [5]. The biomethane potential (BMP) test is arguably the most significant part of an initial substrate analysis for biogas production and has a major impact on the design of an anaerobic digester. The methodology used in the BMP test is extremely important. Various authors have indicated a potential for different results depending on the methodology chosen [6-9]. The BMP test aims to assess the biomethane yield per unit of mass of feedstock under favourable anaerobic conditions. The BMP result is usually seen as the maximum methane potential for a particular feedstock, however, the BMP does not exactly replicate conditions in a continuously feed AD system and therefore the BMP result should not be viewed as an absolute value. Thamsiriroj and Murphy [10] suggest that some reactor configurations and process parameters, such as a high solid retention time, may result in higher methane yields than the BMP test.

5.1.4 Aims and Objectives

This paper sets out a methodology to assess and screen potential substrates from five major waste streams for a proposed anaerobic co-digestion facility using the biochemical methane potential (BMP) test as a selection tool. The BMP test is also

used to assess the level of variability of biomethane potential within the waste streams. The objective is to select substrates with a high methane production per unit mass which will lead to an economic digester design. This paper is part I of two papers in this issue. The second paper [11] examines the biomethane production and bioreactor performance from continuously fed laboratory trials over a period of 8 months based on the selection strategy of this paper.

5.2 Materials and Methods

5.2.1 Methodology for assessing potential substrates for biomethane production

The methodology used by the authors to assess the suitability of substrates for biogas production is as follows;

1. Carry out an ultimate and proximate analysis on samples of all potential substrates
2. Using values from ultimate analysis (CHN) use the Buswell equation to get a theoretical biomethane yield
3. Carry out a BMP test on each sample in triplicate
4. Compare the BMP yield to the theoretical yield to get a biodegradability index
5. Use BMP test data to select substrates for a preliminary design on expected biomethane yield
6. Carry out continuous lab scale AD trials to determine parameters such as organic loading rate and any inhibitory effects from the substrates (paper 2)

The results of the ultimate analysis were used to calculate the theoretical methane yield using the Buswell equation [12] (Equation (5.1)) and the carbon to nitrogen ratio for each waste stream.

$$C_nH_aO_b + (n - a/4 - b/2)\cdot H_2O \rightarrow (n/2 - a/8 + b/4)\cdot CO_2 + (n/2 + a/8 - b/4)\cdot CH_4 \quad (5.1)$$

The biodegradability index is defined as the ratio of the biomethane yield from the BMP test expressed as a percentage of the maximum theoretical value based on the

Buswell equation. This parameter can be used to assess the associated methane conversion efficiency of the waste material.

5.2.2 Experimental Outline

Two rounds of BMP tests were conducted. The first round of tests was conducted to assess the BMP yield from composite waste samples collected by the waste producers. These samples were deemed to be representative samples for each of the five major waste streams (as shown in Figure 5.1) according to the waste producers. The second round of BMP tests was carried out to check for variation in BMP yield within waste streams and to check the difference between the BMP result of the composite samples and the weighted average BMP sub samples from the second round. Nine sub samples were tested for BMP in round 2. All samples were tested in triplicate to get a mean and standard deviation. By sampling each individual sub stream a more accurate estimation of the variation of biogas yield within each main waste stream can be achieved. In total there were 14 samples tested in triplicate for BMP between round 1 and 2.

The five major waste streams which were investigated in round 1 were as follows:

1. Abattoir waste mix (paunch grass, green sludge and dewatered activated sludge at equal ratios based on mass of fresh matter)
2. Cheese process waste
3. Food waste mix (domestic and commercial food waste at equal ratios based on mass of fresh matter)
4. Pig slurry mix (slurry from weaners and fatteners at equal ratios based on mass of fresh matter)
5. Waste water treatment sludge – final sedimentation sludge

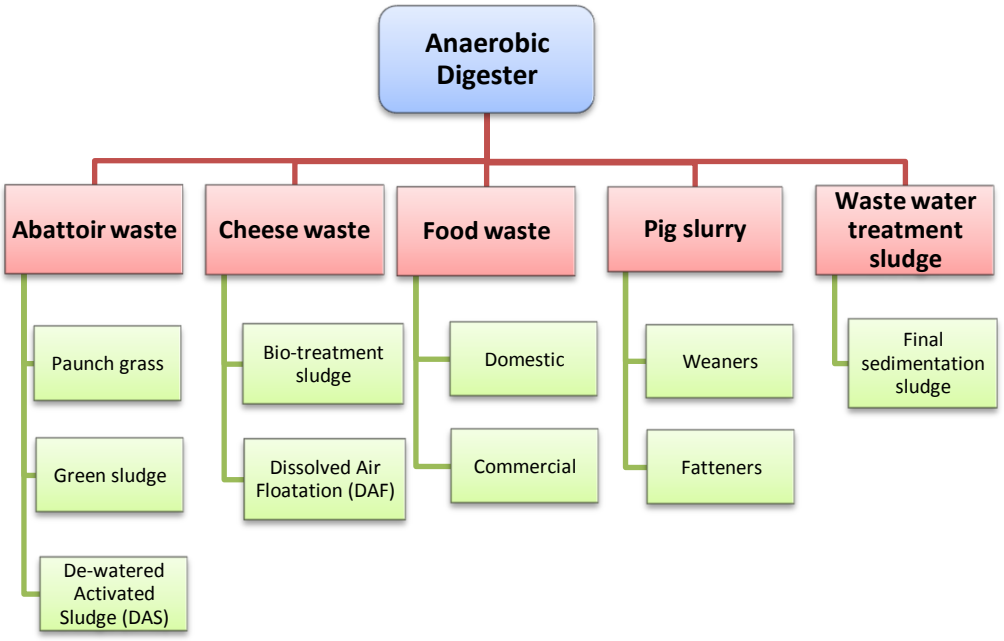


Figure 5.1 Major waste streams and sub streams considered for the anaerobic co-digestion facility

5.2.3 Waste Materials

The five major waste streams and associated sub streams to be investigated for BMP for the proposed AD plant are shown in Figure 5.1. These five waste streams were identified as possible substrate sources for the proposed anaerobic digester as they are the most available locally produced wastes within a 20 km radius of the proposed site.

1. **Abattoir Waste:** A local abattoir produces about 4700 tonnes per annum (ta^{-1}) of paunch content from the slaughter of cattle. Three categories of paunch and process sludge material were produced: paunch grass; green sludge; and dewatered activated sludge (DAS).
2. **Cheese processing waste:** A cheese factory produces approximately 6000 (ta^{-1}) of treated sludge which includes biologically treated effluent (5000 ta^{-1}) and dissolved air floatation (DAF) sludge (1000 ta^{-1}).
3. **Food waste:** A local waste collector operates a collection service for 1000 ta^{-1} of source segregated domestic and commercial food waste. The quantity of domestic household source separated food waste is expected to significantly increase over the next two years due to the implementation of national organic

waste separation policy. It is estimated that approximately 5000 tonnes per annum of source separated domestic food waste will be collected in the area once the waste separation policy is implemented.

4. **Pig slurry:** a local pig farm produces 20,500 ta^{-1} of pig slurry. The pigs are housed on concrete slats which allow slurry to flow to under-floor pits. Slurry samples were collected from weaners (young pigs from 3 months) and from fatteners (maturing pigs for market).
5. **Waste water treatment sludge:** the local waste water treatment plant is licensed to treat a maximum of 6,500 population equivalent. The characteristics of the waste samples are shown in Table 5.1.

Table 5.1 Characterisation of potential substrates for biogas production

Source	**TS (%)**	**VS (%)**	**VS/TS**	**C (% TS)**	**H (% TS)**	**N (% TS)**	**C:N ratio**
Abattoir waste							
Paunch grass	17.0(0.07)	15.6(0.08)	0.92	46.5(0.09)	6.3(0.03)	2.8(0.2)	16.6
Green sludge	19.6(0.6)	18.1(0.6)	0.93	57.3(0.3)	8.4(0.07)	3.0(0.2)	19.1
DAS	13.3(0.08)	10.7(0.06)	0.81	41.0(0.1)	5.8(0.02)	6.5(0.1)	6.3
Cheese processing effluent							
Bio-treatment sludge	9.4(0.3)	7.6(0.3)	0.81	43.9(0.1)	6.8(0.04)	5.6(0.3)	7.8
DAF	7.8(0.3)	6.8(0.3)	0.88	65.1(0.5)	10.3(0.03)	1.3(0.3)	50
Food waste							
Domestic	21.9(0.7)	19.9(0.7)	0.91	46.8(0.2)	6.3(0.07)	2.7(0.1)	17.3
Commercial	35.4(0.7)	30.1(0.3)	0.85	49.0(0.5)	7.0(0.06)	3.4(0.2)	14.4
Pig slurry							
weaners	4.7(0.01)	3.3(0.02)	0.70	38.3(0.4)	5.2(0.07)	3.1(0.3)	12.4
fatteners	6.5(0.03)	4.8(0.01)	0.74	40.3(0.5)	5.3(0.07)	2.5(0.2)	16.1
Waste water treatment sludge	8.6(0.08)	6.7(0.05)	0.77	43.3(0.2)	5.8(0.06)	2.2(0.4)	19.7

Values are presented as mean with (standard deviation)

5.2.4 Sampling Technique

The standards VDI [13] and ISO 5667 [14] were followed for sampling methodology. For solid material such as brown bin waste, a representative sample was obtained by taking a large sample from different locations in the bulk material. This large sample was spread on a clean surface and then mixed well. A cross was drawn through the middle of the spread sample, and two opposite quarters were removed. The remaining two quarters were spread and mixed again, and again a cross was drawn and two quarters removed. This process was repeated until the required amount of sample was obtained [5]. Liquid feedstocks were sampled at different frequencies, liquid levels and process streams to ensure good representation. Solid waste materials such as abattoir waste, food waste and waste water treatment sludge were processed through a food mincer (Buffalo 800W) to a particle size of less than 5mm. Liquid waste such as pig slurry and cheese processing effluent were homogenised in a blender. All samples were stored in a freezer at -20°C until required.

5.2.5 Source of Inocula

The inoculum for round 1 of the BMP tests was obtained from a farm scale anaerobic digester (farm A) operating at mesophilic temperatures, treating mostly cattle slurry and a small portion of grease trap waste from a local catering premises. The approximate feed ratio of cattle slurry to grease trap waste was 9:1 on a volumetric basis. Inoculum from farm A was incubated at 35 °C for 3 weeks prior to the BMP round 1. The inoculum had a pH of 7.9, total solids (TS) of 33.0 gTS kg^{-1} and volatile solids (VS) content of 17.1 gVS kg^{-1} after passing through a 2mm sieve. Inoculum used in round 2 BMP tests was sourced from another farm scale anaerobic digester (farm B) operating at mesophilic temperatures treating a mixture of cattle slurry, poultry litter and a small quantity of grease trap waste at an approximate ratio of 5:4:1 respectively, on a volumetric basis. The inoculum from farm B was incubated at 35 °C for 1 week prior to BMP round 2. The inoculum from round 2 had a pH of 7.95, TS of 59.4 gTS kg^{-1} and VS content of 42.9 gVS kg^{-1} after passing through a 2 mm sieve. The higher VS content in the inoculum from round 2 is due to the operation of higher total solids digestion process on the second farm which

included finely macerated straw associated with the poultry litter as part of the substrate.

Both samples of inoculum were taken from stable anaerobic digesters operating on substrate mixes dominated by cattle slurry and at similar temperatures. Inoculum from both rounds was tested using cellulose as a standard control substrate (C_{12} H_{20} O_{10}). The maximum theoretical methane yield from cellulose according to the Buswell equation is 415 L CH_4 $kgVS^{-1}$. Inoculum from source A gave a specific methane yield of 354 ± 6 L CH_4 $kgVS^{-1}$ while inoculum from source B gave 371 ± 4 L CH_4 $kgVS^{-1}$. As both sources of inoculum gave over 85% of the theoretical max, this proves that a healthy consortium of anaerobic microbes were present in both rounds. Indeed some recent research carried out by Holliger and colleagues (2012) indicate that there is little or no influence on the source of inoculum or its adaptation on the BMP result for the tested substrates, provided the inoculum contains sufficiently diverse microbial communities to cope with the degradation of complex substrates [15]. In the study by Holliger and colleagues (2012) no significant difference was found between BMP results using four different sources of inoculum. In another inter-laboratory study by Raposo and colleagues (2011), related to BMP testing four substrates (starch, cellulose, gelatine and mung bean) the influence of inocula source was insignificant with respect to the extent of anaerobic biodegradation [16]. However the source of inoculum can have an effect on the kinetic rate of degradation.

5.2.6 BMP Apparatus

The apparatus used to conduct the BMP tests was the Automatic Methane Potential Test System II (Bioprocess Control Sweden AB). This laboratory instrument is specially designed for determination of the BMP of a substrate. The AMPTS II system consists of three major parts as can be seen in Figure 5.2.

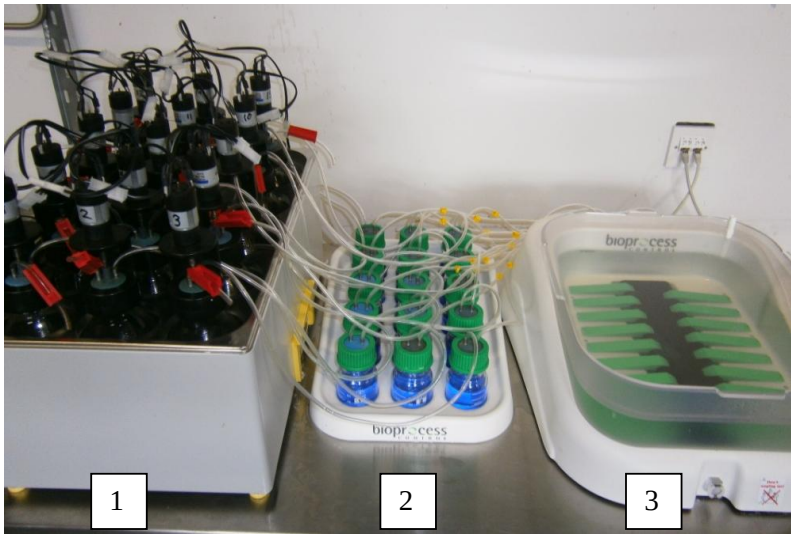


Figure 5.2 BMP apparatus used in the paper: Automatic Methane Potential Test System II (Bioprocess Control Sweden AB). 1. Water bath with 15 No. 500 ml bottle reactors: 2. Carbon dioxide fixing unit: 3. Gas flow measuring unit

1. A temperature controlled water bath with 15 bottle reactors of 500 ml volume, each equipped with a mixer that can be run in either continuous or intermittent mode
2. A carbon dioxide fixing unit with an alkaline solution (3N sodium hydroxide) that absorbs the carbon dioxide and hydrogen sulphide produced during the anaerobic digestion process
3. A gas measuring unit consisting of 15 parallel operating cells, where the gas is measured through water displacement. When approximately 10 ml of gas has been accumulated each cell opens and releases the gas. For each opening, the time, temperature and pressure are registered and stored locally in an embedded Central Processing Unit (CPU). Based on these measurements, normalised (0°C, 1 atm and dry gas) accumulated gas production and gas flow rate are calculated.

The BMP tests were performed with a working volume of 400 ml. The ratio of inoculum to substrate was chosen to be 2:1 on a volatile solids (VS) basis. The inoculum to substrate ratio is a critical parameter in conducting a BMP test according to the Anaerobic Digestion Specialist Group of the International Water Association [6]. A ratio of 2:1 or greater of inoculum to substrate on a VS basis is recommended for BMP trials to limit any inhibitory effects due to the chemical

composition of the substrate such as inhibition associated with accumulation of ammonia and volatile fatty acids (VFA) [6, 7, 16].

If several substrates are to be tested with the same inoculum, the amount of inoculum used in each bottle is calculated in accordance with the substrate with the lowest VS content. This amount of inoculum is then subsequently used for the other substrates and the amount of substrate is then adjusted so that the desired VS ratio is achieved. In this way only one set of blanks (corresponding to the amount of inoculum added in each reactor) is used. If some reactors contain a total volume less than 400 ml then these reactors are topped up to 400 ml with de-ionized water. The amount of inoculum to be used is calculated in accordance with equation 5.4 which is derived from equations 5.2 and 5.3. The mass of substrate on a VS basis is calculated based on equation 5.5. The adjusted mass for the other test substrates is calculated using equation 5.6.

$$\frac{M_{in} \cdot VS_{in}}{M_{out} \cdot VS_{out}} = 2 \tag{5.2}$$

$$M_{sub} + M_{in} = 400 \tag{5.3}$$

$$M_{in} = \frac{800 \cdot VS_{sub}}{VS_{in} + 2 \cdot VS_{sub}} \tag{5.4}$$

$$M_{sub} = 400 - M_{in} \tag{5.5}$$

$$M_{sub} = \frac{M_{in} \cdot VS_{in}}{2 \cdot VS_{sub}} \tag{5.6}$$

Where M_{in} is the mass of inoculum, M_{sub} is the mass of substrate, VS_{in} is the volatile solids content of the inoculum and VS_{sub} is the volatile solids content of the substrate.

The headspace volume (260ml) in each of the reactor bottles was flushed with nitrogen for 3-4 minutes at a rate of 500ml per minute to eliminate oxygen and create a fully anaerobic environment.

The BMP tests were run for a period of 30 days or until biogas production was less than 5ml day $^{-1}$. The reactor bottles were maintained at a constant temperature 37^{o}C (± 0.5 °C) by means of a water bath. The biogas is passed through a solution of sodium hydroxide (3 N NaOH) to remove carbon dioxide and other non methane gases. The methane is then passed through individual gas tippers which automatically count and record gas flow. This is a well established method for removing carbon dioxide from the biogas in order to get an accurate measurement of methane flow rate [5]. Removing carbon dioxide using an alkaline solution prior to measuring the gas flow is desirable for volumetric methods based on water displacement since a certain amount of carbon dioxide will always dissolve in water leading to inaccurate measurements [17, 18].

5.2.7 Analytical methods

The total solids (TS) and volatile solids (VS) were determined gravimetrically using the methods described in APHA 2005 [19]. Each waste stream was sampled and tested in triplicate for total carbon (C), hydrogen (H) and nitrogen (N) on a total solids basis and was attained by ultimate analysis using element analyser (CE 440 Model) at the Chemistry Department in University College Cork, Ireland.

5.3 Results and Discussion

5.3.1 Results from BMP trials

The cumulative biomethane potential yields for round 1 and 2 of BMP tests are shown in Table 5.2. Methane yields are reported as the average of triplicate samples with standard deviations.

Table 5.2 Biomethane potential and biodegradability of composite samples and sub streams

Waste Source	Sub stream	Round	BMP (L CH_4 $kgVS^{-1}$)	Theoretical BMP (Buswell eq)	Bio-degradability (BMP/BMP_T)
Abattoir	Composite sample	1	336 ± 15.0	481	71
	Paunch grass	2	238 ± 15.9	469	51
	Green sludge	2	403 ± 15.1	683	59
	DAS	2	165 ± 7.7	408	40
Cheese	Composite sample	1	454 ± 19.3	508	89
	Bio-effluent	2	461 ± 30.8	492	94
	DAF	2	787 ± 46.7	826	95
Food waste	Composite sample	1	508 ± 21.5	537	95
	Domestic	2	419 ± 45.3	471	86
	Commercial	2	535 ± 20.0	550	97
Pig slurry	Composite sample	1	99 ± 8.4	340	34
	Weaners	2	38 ± 2.0	352	11
	Fatteners	2	70 ± 12.8	328	21
WWTS	Final sedimentation	1	247 ± 10	406	61

5.3.2 Abattoir Waste

In the first round of BMP trials the mixed abattoir waste sample gave an average specific methane yield of 336 L CH_4 $kgVS^{-1}_{added}$ with a standard deviation (SD) of 4.5% (Table 5.2). The biodegradability of the abattoir waste from round one was 71% of the theoretical methane yield calculated by the Buswell equation. The composite abattoir waste sample tested in the first round of BMP tests consisted of equal parts paunch grass, green sludge and dewatered activated sludge on a fresh matter basis. Based on the volatile solids content of each abattoir sub stream, the ratio of the mixture on a volatile solids basis is 0.35 grass paunch, 0.41 green sludge and 0.24 DAS.

The BMP results from round 2 shows that there is large variation in specific methane yield between the three sub streams of abattoir waste. The grass paunch sub stream gave an average methane yield of 238 L CH_4 $kgVS^{-1}_{added}$ with a SD of 6.7%; the

green sludge gave an average specific methane yield of 403 L CH_4 $kgVS^{-1}_{added}$ with a SD of 3.7%, while the de-watered activated sludge yielded the lowest average methane potential at 165 L CH_4 $kgVS^{-1}_{added}$ with SD of 4.6%. As shown in Table 5.2 all three abattoir sub streams had lower biodegradability than the composite sample in round 1. It is expected that the de-watered activated sludge (DAS) which has undergone a biological treatment process would have a reduced biomethane potential due to biological aerobic degradation of the waste stream.

To compare the BMP results from round 1 and 2 the weighted average BMP of the 3 sub streams from round 2 is compared to that of round 1. The weighted BMP mix is calculated based on the specific methane yield of each abattoir sub stream (in round 2) multiplied by the respective ratio of sub stream used in round 1 on a volatile solids basis.

Weighted BMP mix = (0.35 * Paunch grass) + (0.41 * Green sludge) + (0.24 * DAS)

The mean weighted BMP result is 288 ± 11 L CH_4 kg VS^{-1}_{added}. Based on this calculation the average specific methane yield from round 2 is approximately 14% less than was achieved in round 1. Using the two-sample t-test for equal variances ($t = 4.51$, $p < 0.0107$), there is a statistically significant difference between the weighted BMP from round 2 and the actual BMP result of the composite mixed sample in round 1 with 95% confidence. This indicates a positive synergistic effect in co-digestion of the three sub streams as opposed to mono digestion of each sub stream. This can be attributed to improvement of the C:N ratio. For example the C:N ratio of the DAS is 6.3, while the C:N ratio of the composite is 15.2.

Although there have been many studies done on anaerobic digestion of mixed slaughter house waste, few studies assess only the paunch content from ruminants. Palatsi and colleagues (2011) achieved methane potentials of 270-300 L CH_4 kg COD^{-1} (208-230 L CH_4 kg VS^{-1}) from mixed pig and cattle slaughterhouse wastes [20]. Wang and Banks (2003) previously achieved 210 L CH_4 per kg TS added using a two-stage anaerobic digestion system for treating mixed abattoir wastes [21]. Abattoir waste such as paunch content from ruminants is desirable as a co-substrate for AD due to the presence of ruminant bacteria which produce enzymes that help hydrolyse complex carbohydrates such as cellulose [22].

The abattoir waste stream as produced at the cattle slaughtering facility in this study produces different quantities of waste sub streams. The abattoir waste is dominated by the paunch grass sub stream at the approximate ratio of 2.5 paunch grass to 1.5 de-watered activated sludge (DAS) to 0.7 green sludge on a fresh matter basis. The weighted average biomethane potential from the abattoir waste is calculated based on the BMP results from round 2 multiplied by the proportions at which each material occurs.

Weighted average methane yield from abattoir waste as it occurs in the processing plant is estimated as follows;
$[(2.5 * 238) + (1.5 * 165) + (0.7 * 403)] / 4.7 = 239$ L CH_4 $kgVS^{-1}_{added}$.
This can be viewed as a conservative estimate as the BMP results from the composite sample in round 1 indicate that there may be positive synergetic effects from the co-digestion of the three sub-streams which may increase the actual BMP yield of the mix.

5.3.3 Cheese Processing Waste

The cheese process effluent from round 1 gave a maximum BMP of 454 L CH_4 $kgVS^{-1}_{added}$ with a SD of 4.3%; this was 89% of the theoretical methane yield calculated by the Buswell equation (Table 5.2). In round 2 the dissolved air floatation (DAF) sludge yielded a BMP of 787 L CH_4 kg VS^{-1}_{added}. DAF is the highest methane yielding substrate of all sub streams tested; this can be attributed to the high carbon to nitrogen ratio of 50 which is also the highest of all substrates tested. DAF is known to contain dissolved fats from the cheese process effluent. The bio-treatment sludge gave an average methane yield of 461 L CH_4 kg VS^{-1}_{added} which is 1.5% higher than the previous BMP result for cheese waste in round 1 and is within the standard variation of 4.3% of the previous BMP result from round 1. It was noted that the composite cheese process sample from round 1 was very similar to the bio-effluent sample in round 2. After further enquiries from the waste producers it was discovered that on the day of sampling the composite sample of cheese process waste from round 1 contained only the biologically treated effluent as the Dissolved Air Floatation (DAF) tank was not connected. Therefore the BMP

results for cheese process waste in round 1 are representative of the bio-effluent sub stream.

The two sub streams of cheese waste effluent tested in round 2 showed a relatively large difference in BMP with the DAF yielding 71% extra specific methane yield than the bio-effluent sludge. Typically there are 5 parts biologically treated effluent to 1 part DAF at the cheese processing plant. This gives a weighted average of 515 L CH_4 kg VS^{-1}_{added} for the combined sub streams. This value is higher than other reported values for cheese processing waste. Erguder and colleagues (2001) achieved a maximum of 424mL CH_4 $gCOD^{-1}$ using cheese whey [23] while Labatut et al. (2011) reported a BMP yield of 423.6 mL CH_4 gVS^{-1}_{added} for cheese whey [24]. It can be concluded that the higher methane yields from cheese effluent in this study is attributed to the DAF portion of the waste stream which consists mostly of dissolved fats which contribute to higher methane yields.

Harvest 2020- A vision for Irish agri-food and fisheries [25] has projected an increase of 50% in milk production to supply increasing world demand for dairy products. This will result in more cheese processing effluent requiring further treatment and additional waste management options. To this effect the inclusion of cheese processing sludge as a substrate for biogas production is an attractive waste to energy concept.

5.3.4 Food Waste

The composite mixed sample of domestic and commercial source separated food waste gave the highest specific methane yield of round one with an average BMP of 508 L CH_4 $kgVS^{-1}_{added}$ with a standard deviation of 4.2%, giving approximately 95% of the theoretical methane as per the Buswell equation. Previously reported BMP yields from canteen food waste are similar to these results (480-530 L CH_4 $kgVS^{-1}$) [9].

A large variation in biomethane potential was also noted between the two main sub streams of source segregated food waste. Commercial food waste which is typically collected from canteens, restaurants, hotels and catering premises gives a relatively

high methane potential of 535 L CH_4 g VS^{-1}_{added} with a SD of 3.7%. The biodegradability of the commercial food waste is 97% of the theoretical which indicates very good degradation under anaerobic conditions. This BMP result for commercial food waste is similar to the maximum BMP yield from university canteen waste of 527 L CH_4 g VS^{-1}_{added} previous observed by Browne and Murphy (2013) for canteen food waste [9].

The domestic food waste samples gave an average methane potential of 419 L CH_4 kg VS^{-1}_{added} with a larger SD of 11% and biodegradability of 85%. Zhang and colleagues (2012) achieved between 445-456 L CH_4 kg VS^{-1}_{added} from domestic source segregated food waste [26]. The BMP result for domestic food waste is approximately 22% lower than the BMP for commercial food waste and is due to the physiochemical differences between the two food waste sub streams as shown in Table 5.1. The variability in BMP yield from the domestic food waste stream is larger than that of the commercial waste stream; however the variability in BMP yield between waste streams was not found to be statistically significant using the F-test two sample for variances in Excel ($p<=0.183$, $F=4.47$).

The weighted average BMP from food waste in round 2 is 477 L CH_4 kg VS^{-1}_{added}. This is 6.1% less than the BMP from round 1 (composite mixed sample). Using the two-sample t-test for equal variances $t = 1.87$, $p < 0.135$ (two tail), there is no significant difference between the weighted BMP from round 2 and the actual BMP result of the composite mixed sample in round 1 with 95% confidence. This indicates that the difference in BMP result between round 1 and 2 for food waste is attributed to the level of variability of BMP yields within the food waste streams. The BMP results for food waste samples in this study are higher than other reported methane yields for similar food waste substrates, Davidsson and colleagues (2007) reported methane yields of between 300-400 L CH_4 kg VS^{-1}_{added} for a large number of source sorted OFMSW samples which had all been through different pre-treatment processes [27]. In the current study, food waste samples were collected as produced therefore ensuring the samples had not undergone degradation and produced relatively higher methane yields.

5.3.5 Pig Slurry

The pig slurry gave much lower BMP results than expected, with an average methane yield of 99.3 L CH_4 $kgVS^{-1}_{added}$ in round 1. This is about half the expected BMP yield reported in the scientific literature for pig slurry [28], typically in the range of 200-250 L CH_4 $kgVS^{-1}$. Astals and co-workers (2011) achieved methane yields of 188 ml CH_4 gVS^{-1}_{added} from batch mono-digestion of pig slurry [29]. Kafle and Kim (2013) reported BMP yields for pig slurry in the range of 259-268 ml CH_4 g COD_{added} [30].

In round 2 pig slurry sub stream samples from weaners (young pigs about 28 days old) and fatteners (older pigs being prepared for market) were tested to confirm if the initial BMP results for mixed slurry were accurate. Similar to the pig slurry mix in round 1, slurry taken from the fattener's sub stream of pig slurry, with a volatile solids concentration of 4.76% of total mass, gave a reduced average methane yield of 70 L CH_4 kg VS^{-1}_{added}. The slurry collected from the weaner's slurry tank which had a lower volatile solids content of 3.28% of the total mass, yielded an extremely low specific methane yield of 38 L CH_4 kg VS^{-1}_{added}. The cumulative methane curve started to decrease after day 7 (at 38 L CH_4 kg VS^{-1}_{added}) and dropped to only 18 L CH_4 kg VS^{-1}added by day 30. The rate of methane production from the inoculum alone (blank) was greater than that of the weaner pig slurry (with the same amount of inoculum as the blank). This indicates that the weaner pig slurry sampled may have contained toxins or inhibitors to the anaerobic inoculum. The first sample of mixed pig slurry used in round 1 BMP trials had a volatile solids concentration of only 1.35% of the total mass. It was initially thought that the low methane yield from pig slurry in round 1 was possibly due to an error in sampling. However after additional sampling and testing of individual sub streams of pig slurry in round 2, even lower BMP yields were achieved.

The reason as to the low methane yields from pig slurry is unclear; great effort was taken in the second round of BMP trials to attain slurry samples from different depths in the slurry tank and samples were well mixed and homogenised prior to the BMP tests. One hypothesis is that the weaner slurry may have been contaminated with a bio-toxic substance such as an anti-biotic. However a bio-toxicology test is

beyond the scope of this paper. In this particular case study it is recommended that pig slurry would not be included as part of the substrate mix due to its low methane yield and low solids content.

5.3.6 Biomethane kinetics

The characteristics of biomethane production were examined by using the modified Gompertz equation to predict cumulative biomethane production in batch mode [30-32]. Biomethane production can be predicted as follows;

$$M = P.exp\left\{-exp\left[\frac{R_{max} \cdot e}{P}(\lambda - t) + 1\right]\right\} \quad (5.7)$$

Where,

M is the cumulative methane yield a given time (ml CH_4 g VS^{-1}),

P is the max methane potential (L CH_4 kg VS^{-1}) from BMP test,

R_{max} is the maximum methane production rate (L CH_4 kg VS^{-1} day^{-1}),

e is the mathematical constant = 2.7183,

λ is the lag phase for methane production to begin (days),

t is the time (days).

R_{max} and λ are can be determined by non linear regression using the SOLVER function in Microsoft Excel, which employs an iterative least squares fitting routine to produce the optimal goodness of fit between data and function. The statistical indicators, correlation coefficient (R^2) and root mean square error were calculated [33].

The cumulative methane production curves from round 1 BMP tests shown in figure 5.3 have a slightly S-shape or sigmoid shaped cumulative curves which indicate a delay in methane production. This time lag is most noticeable for samples tested using inoculum from farm A during round 1 BMP trials. This inoculum was incubated for a longer period of time (3 weeks) prior to the commencement of BMP tests than inoculum from farm B (1 week). The lag time in the first round of BMP tests is between 6.4 and 7.3 days for abattoir, cheese and food waste but is 0.5 day for wastewater treatment sludge and 0 for slurry. All substrates have a BMP half life (BMP $T_{0.5}$) of less than 13 days which indicates that these waste materials are readily biodegradable under favourable anaerobic conditions. The model curve fitting generated using the modified Gompertz equation, gave a coefficient of determination

of greater than 0.95 for the all waste streams in round 1, which indicates a very close fit.

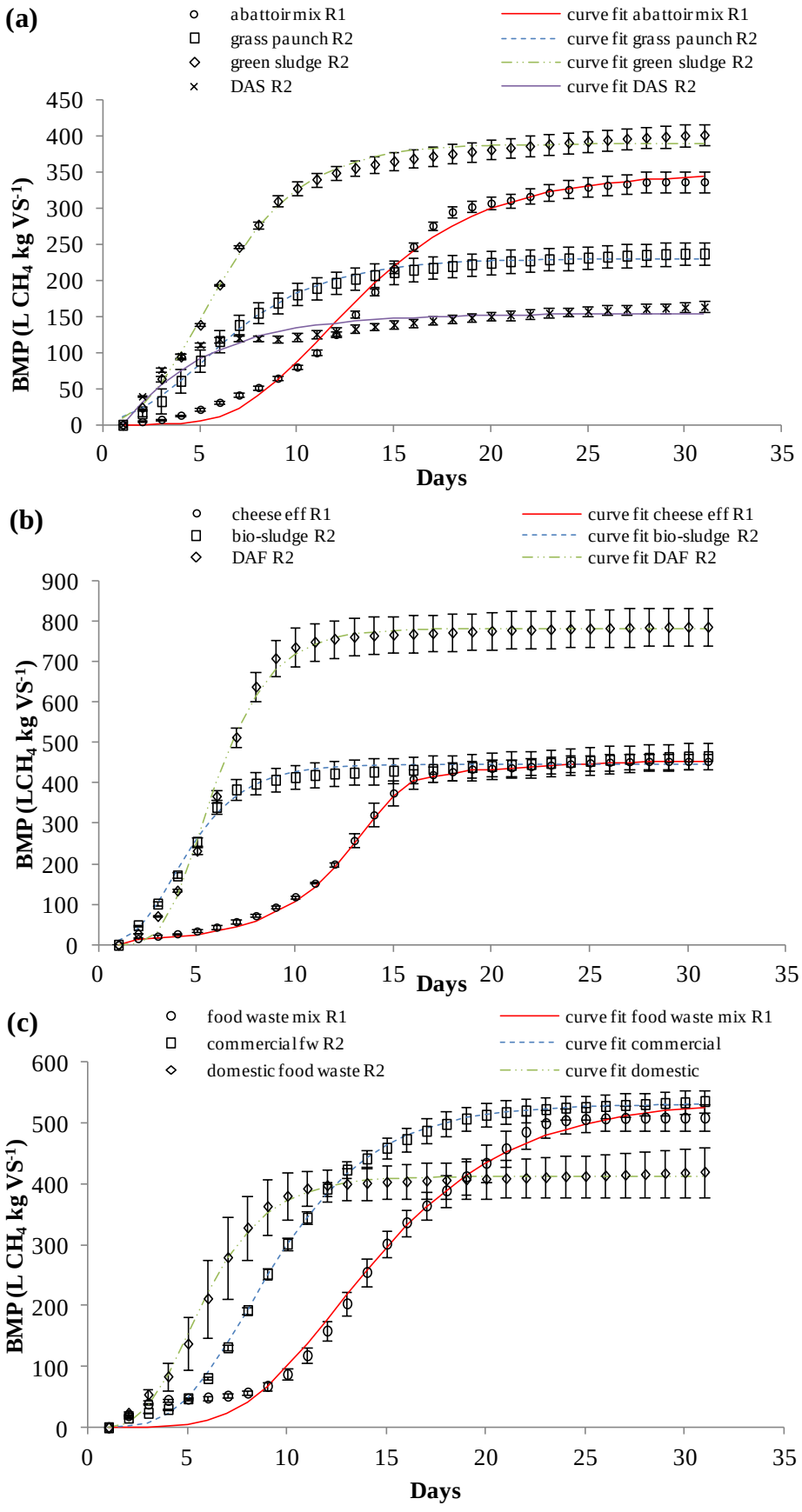


Figure 5.3 (a) BMP of abattoir waste round 1 & 2 (b) BMP of cheese processing waste round 1 & 2 (c) BMP of food waste round 1 & 2

The time lag for methane production in the second BMP trial was found to range from 0 to 3 days. All substrate samples tested in round two have a BMP half life (BMP $T_{0.5}$) of less than 9 days which indicates that these waste materials are readily biodegradable under favourable anaerobic conditions. Except for the weaner's pig slurry sample, the curve fits for all the waste streams in round 2 have a coefficient of determination of greater than 0.95 which indicates a very close fit. The kinetic parameters of the modified Gompertz equation are shown in Table 5.3.

Table 5.3 Biomethane kinetics using the modified Gompertz equation

Waste Source	Sub stream	Round	BMP (LCH_4 $kgVS^{-1}$)	R_{max} (LCH_4 $kgVS^{-1}$ day^{-1})	BMP $T_{0.5}$ (days)	Time lag λ (days)
Abattoir	composite sample	1	336 ± 15.0	28.5	5.5	6
	Paunch grass	2	238 ± 15.9	24.3	5.6	0.5
	Green sludge	2	403 ± 15.1	47.9	5.3	0.9
	DAS	2	165 ± 7.7	28.4	4.2	0
Cheese	composite sample	1	454 ± 19.3	55	11.2	7
	Bio-effluent	2	468 ± 30.8	82.8	3.7	0.8
	DAF	2	787 ± 46.7	149.6	5.0	2.3
Food waste	composite sample	1	508 ± 21.5	40.9	12.8	6.7
	Domestic	2	419 ± 45.3	69.4	4.9	1.8
	Commercial	2	535 ± 20.0	55.5	8.4	3.5
Pig slurry	composite sample	1	99 ± 8.4	13	5	0
	Weaners	2	38 ± 2.0	-	-	-
	Fatteners	2	70 ± 12.8	-	-	-
WWTS	Final sedimentation	1	247 ± 10	60.8	2.6	0.5

5.3.7 Methane potential per mass of substrate

Typically for an operator of an anaerobic digester the input substrate is best described in terms of wet weight (ww) or actual weight arriving at the facility. Methane production is best understood in terms of m_n^3 of methane per tonne of substrate delivered to the facility. The methane potential per tonne of substrate is outlined in Table 5.4. The food waste is the highest yielding substrate per tonne of wet weight (128 m_n^3 CH_4 t^{-1}ww) followed by the cheese waste and the abattoir waste (38 and 36 m_n^3 CH_4 t^{-1} ww respectively). The wastewater sludge and the pig slurry are the weakest substrates (17 and 4.2 m_n^3 CH_4 t^{-1} ww respectively). The significance of volatile solids content may be noted immediately. The weighted average BMP result of cheese waste yielded 515 L CH_4 $kgVS^{-1}$ with an average VS content of 7.5% VS, this equates to 38 m_n^3 CH_4 t^{-1} ww. This may be compared to the food wastes samples which yielded a similar weighted average BMP of 512 L CH_4 $kgVS^{-1}$ at a VS content of 25% of total weight equating to 128 m_n^3 CH_4t^{-1} ww.

Table 5.4 Weighted average methane potential per tonne of feedstock from round 2

Source	Quantity available (tonne annum^{-1})	BMP (L CH_4kg VS^{-1})	Volatile Solids (% total weight)	Methane Yield	
				m^3 CH_4tww^{-1}	$m_n^3a^{-1}$
Abattoir					
DAS	1500	165	10.7	17.7	
Green sludge	700	403	18.1	72.9	
Paunch grass	2,500	238	15.6	37.1	
Sub total	4,700				
Weighted average		239	14.4	36.2	170,140
Cheese					
Bio-treatment	5,000	461	7.6	35.0	
DAF	1,000	787	6.8	53.8	
Sub-total	6,000				
Weighted average		515	7.46	38.1	228,600
Food waste					
Commercial	800	535	30.1	164.3	
Domestic	200	419	19.9	84.4	
Sub-total	1,000				
Weighted average		512	25.0	128.0	128,000
Pig slurry					
Fatteners		38	5.0	1.9	
Weaners		70	3.3	2.3	
Mix [a]		99	4.2	4.2	85,920
Sub-total	20,457				
WWTS	1,000	247	6.7	16.5	16,500
Total Feedstock	33,157	250	6.9	19.0	629,160

[a] The pig slurry mix taken from round 1

5.3.8 Suitability of waste substrates for commercial biogas production

The total quantity of substrate available is approximately 33,000 tonnes per annum with an average methane yield of $19 m_n^3 t^{-1}$ ww which would be expected to generate approximately 629,000 m^3 of methane annually. This is a low average methane yield per tonne of feedstock and would not be deemed conducive to a financially viable biogas system. The Danish model typically is built upon a minimum average methane yield of 30 $m_n^3 CH_4 t^{-1}$[34]. With reference to Table 5.4 it may be noted that pig slurry accounts for approximately 67% of the total available feedstock. However it would only contribute approximately 14% of the total estimated methane yield. The value for the maximum BMP of pig slurry is particularly low (maximum of 99 L CH_4 $kgVS^{-1}$ added). The authors recommend that pig slurry should not be part of the feedstock for this digester system.

The waste water treatment sludge (WWTS) only provides 2% of the total estimated methane yield from 3% of the total available waste. Final sludge from a typical extended aeration basin, as is used in this location, is considered a low methane yielding feedstock for anaerobic digestion. It is not recommended that the WWTS is part of this digester system based on the relatively low BMP yield of 19 $m_n^3 t^{-1}$ of feedstock.

Conversely in the case of food waste, 21% of the total estimated methane yield energy comes from only 3% of the total available feedstock. The objective of this proposed waste to biogas anaerobic digester is to have a cost effective design with an optimum specific volumetric methane yield. Therefore it is recommended that pig slurry and waste water treatment sludge be removed from the proposed AD substrates. The authors recommend that the design of the biogas plant should be based on three substrates: abattoir waste, cheese waste and food waste.

5.3.9 Recommended waste substrates for proposed digester

The scenarios include for substrates with a high specific methane capacity. Information from waste collectors in the region would suggest that the availability of source segregated food waste will increase (from a low base) over the next few years as landfill levies rise. An assumption is made that 4300 ta^{-1} of source separated food waste may be sourced. From Table 5.5 it may be noted that 947,600 m_n^3 of CH_4 may be produced for 15,000 t of substrate. This equates to 63 m_n^3 CH_4 per tonne of substrate. This is more than a three-fold increase in the specific methane capacity than from digestion of all substrates (see Table 5.4: 19 m_n^3 CH_4t^{-1}). By eliminating the lower methane yielding feedstocks such as pig slurry and WWTS a smaller digester volume with a higher volumetric methane yield will be achieved. This will improve the biomethane yield per unit of capital cost.

Table 5.5 Suggested input feedstock for proposed digester

Source	Quantity ($t\ a^{-1}$)	% of total substrate	Methane Yield (m^3CH_4/t ww)	% CH4	Methane yield ($m^3\ CH_4$)	C:N
Abattoir	4700	31%	36	169, 200	18%	14
Cheese	6000	40%	38	228, 000	24%	15
Food waste	4300	29%	128	550, 400	58%	15
Total	15,000	100%	63	947,600	100%	14.7

5.3.10 Limitation of designing anaerobic facilities based on BMP results

The results of BMP tests yield data on the potential biomethane yield from substrates digested in an anaerobic digester. The test is however limited in its ability to model a continuous AD process. A continuously fed AD trial is required to assess important parameters such as determining the optimum organic loading rate and hydrolytic retention time. The monitoring of inhibitory compounds such as the accumulation of volatile fatty acids and ammonia is required to assess the long term suitability of substrates at a specific organic loading rate.

5.4 Conclusions

The BMP test can be used to find the variability of biomethane potential between waste sub streams, identify any potential toxic substrates and can also be used to examine the kinetics of biomethane production. The BMP results as presented in this paper suggest that abattoir waste, source separated food waste and cheese process effluent sludge are all potentially high methane yielding feedstocks. However waste water treatment sludge and pig slurry in particular were deemed to be unsuitable for commercial scale digestion due to their low solids content and low specific methane yield. Of the potential waste substrates the best estimated methane yields range from 128 m_n^3 t^{-1} ww for source separated food waste to 36 m_n^3 t^{-1} ww for abattoir waste. However there are limitations to the test as it is essentially a batch reactor with optimum conditions for biomethane production. A small scale continuously feed AD trial is necessary to more accurately assess the long term digestion stability of the nitrogen rich substrates outlined in this paper. This is dealt with in a following paper in this journal [11].

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6 Improving hydrolysis of food waste in a two phase reactor

Improving hydrolysis of food waste in a leach bed reactor

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Abstract:

This paper examines the rate of degradation of food waste in a leach bed reactor under four different operating conditions. The effects of leachate recirculation at a low and high flow rate are examined with and without connection to an upflow anaerobic sludge blanket (UASB). Two dilution rates of the effective volume of the leach bed reactors were investigated: 1 and 6 dilutions per LBR per day. The increase in dilution rate improved the destruction of volatile solids without connection to the UASB. However connection to the UASB greatly improved the destruction of volatile solids by almost 60% at the low recirculation rate of 1 dilution per day. The increase in volatile solids destruction with connection to the UASB was attributed to an increase in leachate pH and buffering capacity provided by recirculated effluent from the UASB to the leach beds. The destruction of volatile solids for both the low and high dilution rates was similar with connection to the UASB, giving 82% and 88% volatile solids destruction respectively. This suggests that the most efficient leaching condition is 1 dilution per day with connection to the UASB.

Keywords: hydrolysis; food waste; biogas; UASB.

6.1 Introduction

6.1.1 Introduction to municipal biowaste treatment

Municipal biowaste often referred to as the organic fraction of municipal solid waste (OFMSW) consists of food and garden waste from domestic, commercial and street cleanings. It is the main cause of smell and nuisance in municipal solid waste (MSW) and is responsible for most of the environmental hazards associated with municipal waste management, such as the formation of polluting leachate and methane gas under anaerobic conditions. As EU countries are obliged to divert biodegradable waste from landfill under the terms set out in the Landfill Directive 1999 [1], new treatment methods are sought in many countries to treat OFMSW in the most environmentally and economically sound way. The use of anaerobic digestion (AD) in treating OFMSW is becoming increasingly popular across Europe [2]. However OFMSW is a complex and heterogeneous material and many questions still remain about the most effective AD process for OFMSW digestion and even if it is suitable for long term continuous mono-digestion [3]. A significant portion of OFMSW consists of food waste with a total solids (TS) content of 20-30% [4]. As of June 2010, commercial premises in Ireland which produce greater than 50kg of food waste per week are legally required to provide designated bins for source separated food waste (SSFW) [5]. It is estimated that over a million tonnes per annum of OFMSW will have to be diverted from landfill in Ireland by 2016 to meet the EU Landfill Directive [1]. Currently alternative waste treatment infrastructure is insufficient to meet this demand [6]. Due to the recent EC proposal [7] to limit biofuels from food crops to 2011 levels (ca. 5%) the potential to upgrade biogas from food waste to biomethane [8] and use as a transport fuel [9] can help EU states to meet the 10% renewable energy in transport target.

6.1.2 Anaerobic Digestion Technology

The most commonly known and used digester type is the continuously stirred tank reactor (CSTR) which is operated at a low total solids content, typically 5-10% TS [3, 10, 11]. Food waste has a total solids content of between 20-30% therefore wet AD systems may require dilution with water or agricultural slurry to facilitate homogenization and mixing. As water has a relatively large specific heat capacity

(4.2 kJ/kg/°C) the required heat energy would be larger due to the increased volumes to be treated as would the energy required for pumping and mixing [12]. It is commonly cited in the waste management industry that food waste even when it is collected in a designated bin, can be heavily contaminated with other household waste materials such as plastics and textiles. Thus the CSTR design may not be best suited to treat food waste unless it is source segregated. As an alternative to wet AD processes, the concept of dry fermentation has been developed for treating high solids biowaste such as food waste. In continental Europe many dry fermentation processes have been employed for the treatment of municipal food waste such as Bekon©, Bioferm© and DRANCO©. Such systems generally achieve greater than 60% volatile solids (VS) reduction during dry fermentation and usually require a significant post composting process to meet waste stabilisation standards. This can lead to significant investment costs due to the need for extra storage capacity and digestate handling for the composting and post maturation stages. Often the end product compost is not suitable for horticulture as it can be contaminated with plastics but can be used as landfill cover.

6.1.3 Two Phase Anaerobic Digestion of Food Waste

As the array of potential biomass feedstocks for biogas production continues to expand, it has been suggested that two phase AD could offer greater flexibility and increase process efficiency [13]. Employing a primary reactor where hydrolysis and acidification are promoted, followed by a secondary high rate bioreactor, such as the upward anaerobic sludge blanket (UASB), where acetogenesis and methanogenesis stages are optimised, has previously been studied for high solids feedstocks such as food waste and grass silage [13, 14]. High removal efficiencies can be expected from well developed UASB systems (i.e. up to 95% chemical oxygen demand (COD) removal). Using a number of leach beds in sequence an approximately constant level of COD can be supplied to the UASB ensuring a smoother production of biogas [15]. The system employed by Nizami and Murphy (2011) was a two phase system with 6 sequential fed leach bed reactors (SLBR) coupled with an UASB. Two phase AD is ideally suited to feedstocks with relatively high dry solids content and can lead to higher organic loading rates (i.e. more biowaste through put) expressed in terms of mass volatile solids per unit working volume of the leach bed reactor (LBR).

6.1.4 Optimisation of first phase reactor

The concept of the first phase reactor is to convert solid material into organic acids by providing suitable conditions for hydrolysis and acidification. Hydrolysis involves enzymatic degradation of high solid substrates to soluble products which are further degraded to volatile fatty acids (VFA). To promote this conversion of solid material to soluble COD, a leach bed reactor (LBR) is used as the primary bioreactor. Liquid leachate (initially water or water with inoculum) is circulated over a solid bed of biomass, removing soluble COD and distributing microbes throughout the biomass. The leachate percolates through the biomass and filter layers by gravity to a leachate holding tank where it may be either recirculated or pumped to the UASB (second stage reactor). The LBR is designed to retain solid particulate matter but allow soluble material to flow through to the leachate holding tank. Although the use of LBRs as the primary bioreactor in two phase systems has been previously studied, many questions pertain as to the optimum operating parameters for this process. It has been previously shown that parameters such as temperature, pH, flow rate, organic loading rate and solid retention time have an impact on the effectiveness of the system. In addition the kinetic disintegration parameters of the feedstock itself, based on the composition of the feedstock (i.e. percentage of proteins, carbohydrates and lipids) also impact the rate of hydrolysis and acidification. The efficiency of the first phase digester is monitored by calculating the mass of volatile solids (VS) dissolved in the leachate for a given flow rate and solid retention time. This was achieved by subtracting the remaining solid mass from the initial mass thus giving the mass of total solids which were dissolved in the leaching process.

6.1.5 Aim of paper

The aim of this paper is to determine the optimum operating conditions for digesting food waste (or OFMSW) in a two stage SLBR-UASB system. A major feature of this process is the conversion of food waste to soluble COD which can then be converted to methane in the UASB. Evaluation of the optimum initial parameters for the leaching process will allow greater UASB performance and thus greater biogas/biomethane yields can be expected.

6.2 Materials and Methods

6.2.1 Leach Bed Reactors Design

The leach bed reactors used in these laboratory trials were stainless steel tanks with a total volume of approximately 50L. The total volume is divided into three equal sections of approximately 17L. The top section incorporates a leachate sprinkling head and headspace, the middle section is the effective reactor volume (incorporating biomass retaining vessel, sieves and meshes) and the bottom section facilitates leachate percolation and collection. The effective reactor volume (middle section) is made up of a biomass retaining cage with a 3mm mesh, this sits on top of a 50mm layer of 10mm gravel supported by a 1mm sieve. The leach bed reactors were loaded in the same manner for each trial. Each leach bed cage was loaded with 4 kg food waste in a nylon mesh with a pore size of about 1mm. The height of the food waste layer was kept the same for each LBR (approximately 60mm). Each LBR had the same sprinkling head configuration to ensure even distribution of leachate over the food waste layer. The nylon mesh had the effect of retaining the leachate for a short period of time so that the entire food waste layer was in contact with the leachate before it drained into the leachate holding tank. This ensured that operational conditions were the same in all LBRs. The filtering system is designed to retain solid particles in the biomass retaining vessel and prevent wash through of solid particulate matter. This leach bed reactor was originally designed for leaching of grass silage by Nizami and Murphy (2010) [15] and was modified to accommodate food waste. A schematic diagram of the leach bed reactor is shown in Figure 6.1.

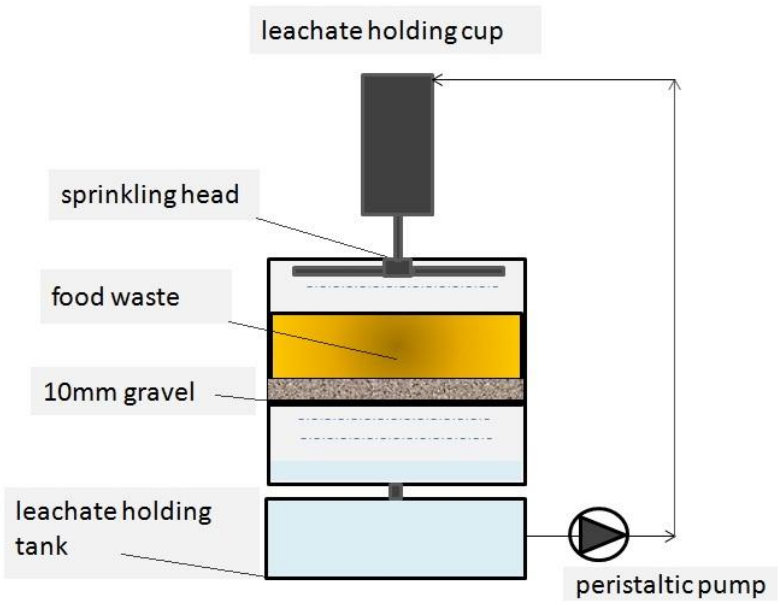


Figure 6.1 Leach bed reactor (LBR) schematic diagram

A custom made sprinkle head system was installed on the bottom of the cover lid to distribute leachate over the SSFW. A leachate holding cup of approximately 1.5L in volume holds the leachate until a timer activates a solenoid valve allowing leachate to flow to the sprinkle head and pass over the biomass in the LBR. The leachate then percolates down through the substrate and is collected in a 40L leachate holding tank. A peristaltic pump (Watson Marlow 323S) conveys leachate from the leachate holding tank to the leachate holding cups. A heating coil located below the leachate holding tank is used to control the temperature of both the leach bed and leachate holding tank.

6.2.2 Upflow anaerobic sludge blanket

The dimensions of the upflow anaerobic sludge blanket (UASB) are working height 1.01m, internal diameter 0.204m. Total working volume = 0.033 m^3 – volume of heating bar (0.00046 m^3) = 0.0325 m^3. The upflow anaerobic sludge blanket has a working volume of 32.5 L. A drawing showing the front elevation of the full system is shown in Figure 6.2.

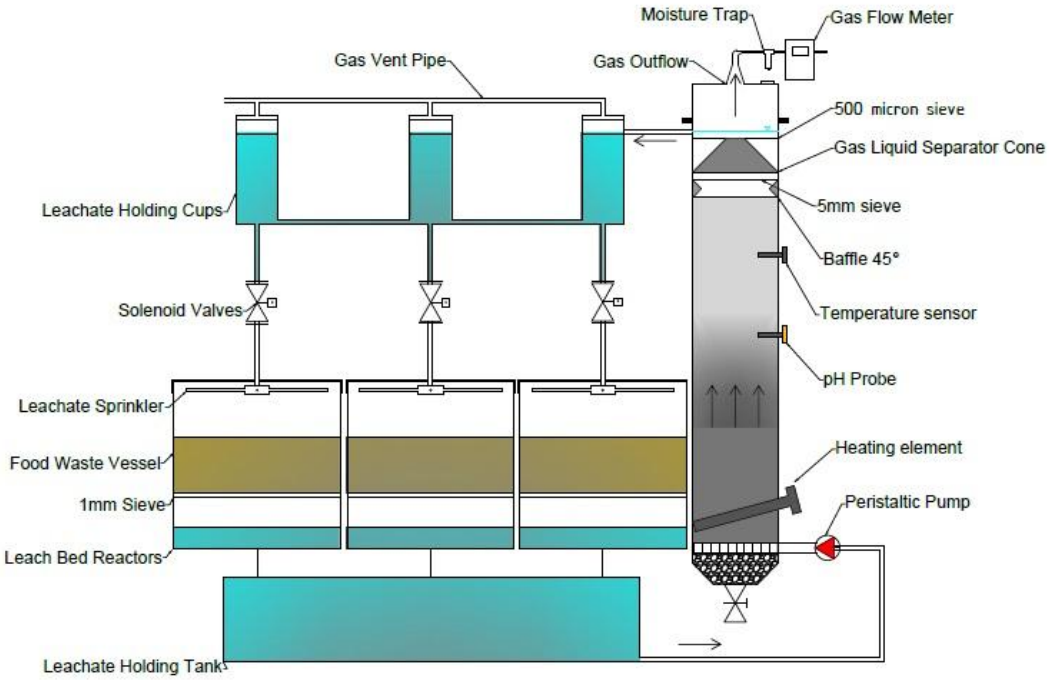


Figure 6.2 Sequentially fed leach bed reactors connected to upflow anaerobic sludge blanket (SLBR-UASB)

6.2.3 Food waste

As food waste is a heterogeneous substrate that can change depending on the season and region it is difficult to model for lab scale experimental work. It has been shown by several authors that source separated food waste gives higher methane yields than co-mingled MSW [3, 16]. Source separate food waste (SSFW) from the university canteen (University College Cork, Ireland) was chosen as the substrate to be used in the two phase AD process. It was decided to take a large bulk quantity of SSFW in an effort to get a representative sample. Approximately 200 kg of mixed SSFW was collected from the main campus restaurant. The SSFW was manually screened for non biodegradable contaminants such as plastic bags and cutlery. The SSFW was first manually chopped and screened so that particle size was less than 12mm and mixed thoroughly which is required by the Department of Agriculture, Food and Fisheries (DAFF) in Ireland, under the Animal By-Products Regulations (DAFF, 2009). The well mixed bulk material was then passed through a Buffalo 850W mincer (Figure 6.3) and then mixed again in a large plastic container. The food waste samples were then stored in 8L containers at -20°C until required for the leaching

experiments. The samples were then defrosted at room temperature for 24 hours prior to experimental use. The food waste was characterised as per Table 6.1.



Figure 6.3 Collection and mixing of canteen food waste

Table 6.1 Characteristics of food waste and granular sludge inoculum

Parameters	Food waste	Granular sludge
pH	4.1	7.3
Total Solids (%)	29.4	11.3
Total Volatile Solids (% TS)	95.1	81.0
Proteins (% TS)	18.1	-
Carbohydrates (% TS)	59.0	-
Lipids (fats) (% TS)	18.0	-
% C (% TS)	49.6	42.1
% H (% TS)	7.3	5.8
% N (% TS)	3.5	7.3
% Ash (% TS)	4.9	19.0
Biomethane Potential [1] ($L\ CH_4\ kg\ VS^{-1}$)	528	-

[1] Biomethane potential taken from (Browne and Murphy, 2013) using the same food waste sample

6.2.4 Granular Sludge

For the leaching trials with connection to the upflow anaerobic sludge blanket (UASB) granular sludge taken from a commercial UASB treatment system which treated high strength COD from cheese, whey and alcohol processing effluent. The granular sludge was sieved through a series of standard sieves down to 150 microns to separate the granules from the liquid digestate. Granular sludge was then sampled for total solids TS and VS content (11.3% TS and 81% VS: Table 6.1). The UASB was filled with 15L of granular sludge i.e. approximately half the working volume, with the remainder filled with the separated liquid digestate.

6.2.5 Chemical oxygen demand of food waste

The theoretical chemical oxygen demand of an organic compound can be calculated by the following equation;

$C_n H_a O_b N_c + (n + a/4 – b/2 -3/4c) O_2 \rightarrow nCO_2 + (a/2 -3/2c) H_2O + cNH_3$ (6.1)

Where;

n = the number of moles of carbon; a = the number of moles of hydrogen

b = the number of moles of oxygen; c = the number of moles of nitrogen.

Table 6.2 describes the percentage carbon, hydrogen and nitrogen from an elemental analysis. From this a mole of food waste on a dry basis can be written as $C_{16.4} H_{29} O_{9.8} N$ which has a molar mass of 397.3 g $mole^{-1}$. Using equation 6.1 above gives:

$C_{16.4} H_{29} O_{9.8} N + 17.93 O_2 \rightarrow 16.4 CO_2 + 12.89 H_2O + 1 NH_3$ (6.2)

Table 6.2 Chemical formula for food sample on dry matter basis

Element	Number of moles	Molar mass (g $mole^{-1}$)	Mass contribution (g kg^{-1})
C	16.4 (41.3)	12.01	495.8
H	28.8 (72.4)	1.01	73.2
O*	9.8 (24.7)	16.00	395.8
N	1 (2.5)	14.01	35.3

* The mass contribution from oxygen is calculated by O = 1000 – (C+H+N)

Therefore 17.93 moles of oxygen are required to oxidize 1 mole of food waste on a dry matter basis to carbon dioxide, ammonia and water. This means that for 397.3 g TS food waste, 573.7g O_2 is required for oxidation giving the relationship of 1.44 g COD g TS^{-1} food waste. As UCC canteen food waste has a volatile solids content of 0.951 g VS per g TS, the relationship may be expressed as 1.52 g COD g VS^{-1}.

6.2.6 Overview of leaching experiments

Leaching experiments were carried out using four different leaching conditions (Table 6.3). The recirculation of leachate over the LBRs was examined at two flow rates (low and high) with and without connection to the upflow anaerobic sludge

blanket. As the effective reactor volume of the LBR is 17 L, the low recirculation flow rate was chosen as 17 L day^{-1} which corresponds to a hydraulic retention time (HRT) of 1 day and a dilution rate of 1 per day. The high recirculation flow rate was chosen as 102 L day^{-1} which corresponds to a HRT of 0.167 day (4 hours) and a dilution rate of 6 per day. The high flow rate was previously used by Nizami and colleagues (2010) in accessing optimal hydrolysis of grass silage [17]. Equations (6.3) and (6.4) describe a simple model of the leaching system.

Table 6.3 Leaching experimental overview

Leaching Case No.	Flow rate (L day^{-1})	Dilution rate (day^{-1})	UASB connection	Solid retention time (days)
1	17	1	No	24
2	102	6	No	24
3	17	1	Yes	24
4	102	6	Yes	24

$$HRT = V_e / Q \quad (6.3)$$

The dilution rate (Φ) is defined as;

$$\Phi = 1/HRT = Q / V_e \quad (6.4)$$

Where Q is the recirculation flow rate (L day^{-1}) and V_e is the effective reactor volume (L)

6.2.7 Leaching without UASB

Leaching trials 1 and 2 were carried out in duplicate with each LBR fitted with an individual leachate holding tank, as shown in Figure 6.1. A leachate holding tank of approximately 40L in volume was filled with water and was heated to 37°C. It is reported that hot water improves leaching of COD from the feedstock in the LBR [11]. Liquid leachate was sampled daily from the leachate tank and concentrations of chemical oxygen demand (COD), total volatile fatty acids (VFA) and pH were recorded. Each leach bed was loaded with 4 kg of food waste which equated to approximately 1.12 kg volatile solids (VS) (4 kg TS * 30% TS * 95% VS).

6.2.8 Leaching with UASB

Leaching trials with connection to the UASB were effected using 6 LBRs in sequentially fed mode. LBRs 1-6 were loaded sequentially every 4 days with 4 kg food waste (w/w) with a solid retention time of 24 days for each LBR (i.e. LBR1 fed day 0, LBR2 day 4, LBR 3 day 8, LBR4 day 12, LBR 5 day 16, LBR 5 day 20, LBR1 emptied and refilled day 24 and so on). It was postulated that the recirculation of effluent from the UASB would improve VS removal in the LBRs. By passing the COD rich leachate through the UASB the build up of VFAs would be prevented and the flow through of inoculum from the UASB to the LBR would also help hydrolysis of the slower degrading material within the food waste.

In leaching case 3 the low recirculation flow rate of 17 L day^{-1} LBR^{-1} was achieved using a leachate flow rate of 102 L day^{-1} over 6 LBRs. The flow rate of 102 L day^{-1} corresponds to an upflow velocity of 0.13 m per hour in the UASB, which is at the higher end of the recommended flow for granular sludge development [14]. In leaching case 4 the high flow rate of 102 L day^{-1} over each leach bed was achieved using two peristaltic pumps, the first feeding the UASB at 80 L day^{-1} (corresponding to the recommended upflow velocity of 0.1 m $hour^{-1}$) and the second pump recirculating leachate at a rate of 532 L day^{-1} giving a total of 612 L day^{-1} over 6 LBRs i.e. 102 L day^{-1} LBR^{-1}.

6.2.9 Analytical Methods

TS and VS were measured using methods described by the American Public Health Association 2005 [18]. The COD concentration was measured by a COD analyzer set (Hach DRB200 and DR 2800). The C, H, N contents of the FW were analyzed by the Department of Chemistry, University College Cork, using the ultimate analysis method. VFAs were measure by titration following the procedures outlined by Ripley and co-workers (1986) [19]. The pH was measured using a Hanna bench top pH meter.

6.3 Results

6.3.1 Case 1: Leaching at low re-circulation flow rate

In the first leaching trial without connection to the UASB, a flow rate of 17 L day^{-1} achieved a maximum average volatile solids removal of 51.5% at a solid retention time of 24 days. The yield of theoretical COD is calculated via Equation (6.5):

$$[VS_{IN}\ (g) - VS_{OUT}\ (g)] * 1.52\ gCOD\ gVS^{-1} / \text{total volume of Leachate (L)} \quad (6.5)$$

The theoretic yield of COD after 24 days is calculated as;

$$[(1116g\ VS_{IN} - 541g\ VS_{OUT}) * 1.52\ gCOD\ gVS^{-1} / 40L] = 21.85\ g\ COD\ L^{-1}$$

The observed COD at day 24 was 11.44g L^{-1} which indicates that 10.41 g COD L^{-1} is lost to respiration and oxidation in the leach bed i.e. almost 47.5% of the theoretical COD is degraded in the leach bed. A cumulative curve of the theoretical COD was plotted using a first order degradation equation (equation 6.6 below). The theoretical COD produced at intervals of 6, 12 and 24 days were calculated by multiplying the mass of volatile solids destroyed at each time interval by the conversion factor 1.52 g COD g VS^{-1}. The destruction of volatile solids at time intervals of 6 and 12 days were derived from additional leaching trials. A plot of cumulative theoretical COD and actual measured COD in the liquid phase is shown in Figure 6.4.

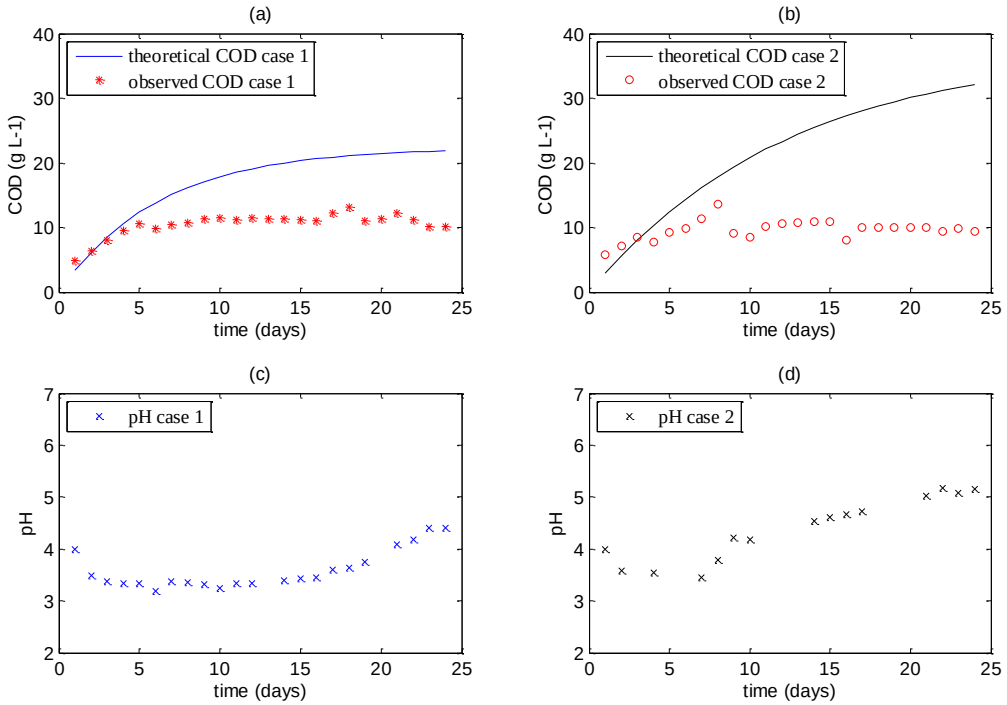


Figure 6.4 COD and pH in leaching case 1 and 2

$$S = \alpha S_{max} * (1 - \exp(-kt)) \quad (6.6)$$

Where;

S is the theoretical COD concentration at a given time t; α is the conversion coefficient of volatile solids to theoretical COD; S_{max} is the theoretical maximum concentration of COD and k is the hydrolysis kinetic constant. The theoretical COD production curve for case 1 is shown in Figure 6.4 (a). The parameters α, S_{max} and k are found using non linear regression using Microsoft Excel solver function and are shown in Table 6.4.

Table 6.4 Comparison of low and high leachate flow rate on volatile solids destruction

Case	**Flow rate (L day^{-1})**	**Dilution (day^{-1})**	**Hydrolysis kinetic constant (k)**	**VS destroyed (%)**	**Coefficient of conversion (α)**	**COD destroyed (%)**
1	17	1	0.16	51.5	0.553	47.5
2	102	6	0.08	72.7	0.85	47

During this period the pH of the leachate remained very acidic and ranged from 3 to 4.5. This low pH is well below the optimum reported pH range for stabile hydrolysis and acidification of pH 5.5 - 6.5. Figure 6.4 (c) shows that the pH of the leachate starts off very low at 4, drops almost as far as 3 and then increases very gradually with time approaching 4.5 by day 24. The level of total volatile fatty acids was also monitored and followed a similar accumulation pattern to the COD increasing from 462 mg L^{-1} on day 2 up to 2628 mg L^{-1}on day 24. Below pH 4 reduced microbial activity results in less degradation of the substrate and therefore less conversion of complex carbohydrates, proteins and lipids.

6.3.2 Case 2: Leaching at high recirculation flow rate

At the higher flow rate of 102 L day^{-1}, a much improved VS removal rate of 72.7% was achieved at a retention time of 24 days. Using equation 6.5 the theoretical COD yield is calculated as 32.15 gCOD L^{-1}, however by day 24 the COD concentration in the leachate was only 9.44 gCOD L^{-1} as shown in Figure 6.4 (b). This indicates that up to 70.6% of the theoretical COD was lost in the leach beds. However after 24 days solid retention time the leachate holding tank had accumulated a sedimentation layer of fine food waste particles (<1mm) on the bottom of the tank due to the high flow rate of leachate. This sedimentation layer contributed approximately 5 gVS L^{-1} which is theoretically 7.6 gCOD L^{-1}. This indicates that actual losses from the leach bed represent approximately 47% of initial theoretical COD which is very similar to case 1. As the leach beds are not fully anaerobic (i.e. the head space was not initially flushed with nitrogen) it is hypothesised that the COD may have been oxidised by a combination of microbial activity in the leach beds and the increased sprinkling rate of leachate (6 times greater than case 1). The higher flow rate did not fully prevent the drop in pH which also occurred at the lower flow rate of 17 L day^{-1} but the pH recovered faster and reached over 5 by day 24. It is postulated that the gradual increase in pH is as a result of the oxidation of volatile organic acids in the LBRs via the sprinkling of leachate in the LBR headspace over time.

6.3.3 Case 3: leaching at low rate with UASB

Operation of the LBRs in sequentially fed mode with connection to the UASB resulted in an average of 81.8% VS reduction with a solid retention time of 24 days

at steady state conditions. This is a significant increase in removal of VS compared with case 1 (51.5% VS removal) at the same flow rate without connection to the UASB. The increase in VS removal was attributed to the positive effects of recirculating leachate from the UASB back to the LBRs. The recirculation of effluent from the UASB improved the rate of hydrolysis and solubilisation of particulate matter in the LBR by keeping the pH of the LBRs in the range of 7-8 and also supplied fresh inoculum to the LBRs. At steady state the UASB yielded an average of 332.4 L CH_4 $kgVS^{-1}$ added, which is approximately 63% of the max biomethane potential from UCC canteen food waste (Table 6.1). Gas from the leach beds was also measured during this trial and yielded approximately 7.2 L CH_4 $kgVS^{-1}$ added which is 2.2 % of the methane produced by the UASB. Table 6.5 indicates that the SLBR-UASB system had an efficiency of 82.6 % in converting COD to methane. The remaining losses are associated with microbial growth and oxidation of COD via sprinkling in the LBRs.

Table 6.5 Assessment of VS reduction in Case 3: Leaching at low rate with UASB

Volatile solids destruction of 81.8% theoretically should yield: 1.52 g COD gVS^{-1} * 1140g VS_{IN} * 0.818 = 1417 gCOD removed from each LBR 1417 * 6 = 8506 gCOD removed from total SLBR system COD concentration in the leachate 12 ± 1.3 g L^{-1} = 480g COD 8506 gCOD removed – 480 gCOD in leachate = 8025 g COD destroyed. Total methane yield from SLBR-UASB system was 2320 L CH_4. 2320 L CH_4 / 8025 gCOD = 289 mL CH_4 $gCOD^{-1}$ destroyed Maximum theoretical methane yield 350 mL CH_4 $gCOD^{-1}$ destroyed (Sperling and Chernicharo, 2005). 100* (289/350) = 82.6% efficiency of SLBR-UASB system converting COD to methane. Thus 17.4% of COD destroyed in the LBR

6.3.4 Case 4: leaching at high rate with UASB

Leaching at the high flow rate with connection to the UASB resulted in very high destruction of volatile solids in the leach beds with an average VS removal of 87.5%. During case 4 problems with the gas flow from the UASB were encountered. As shown in Figure 6.5, the concentration of COD in the leachate continued to rise from 9.2 g L^{-1} to 20.7 g L^{-1}, the conversion efficiency of the UASB dropped as low as 5% COD removal. On further examination it was found that excessive foaming had occurred in the gas-liquid separation (GLS) phase of the UASB. This foaming caused the gas pipe to become blocked and therefore gas was forced out through the effluent outflow pipe undetected.

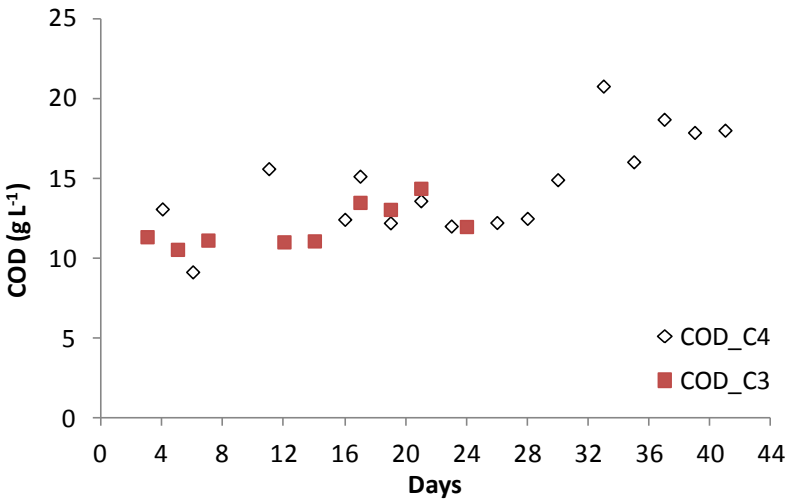


Figure 6.5 Observed COD in cases 3 and 4

The excessive foaming in the UASB during leaching case 4 may have been caused by a number of factors such as organic over-loading, surface active agents (such as proteins and lipids), sudden temperature change and the presence of filamentous microorganisms in the liquor [20]. However as food waste contains relatively large quantities of proteins and lipids (18.1 and 18% of TS respectively) it is postulated that foaming in this instance is a result of overloading the UASB and accumulation of large quantities of suspended solids and partially degraded particulate matter which is due to wash out of substrate from the LBR caused by high recirculation flow rate on the top layer of the UASB.

To overcome the overloading problem sequential loading of the LBRs in the second run was stopped. The retention time in the LBRs was extended sequentially by 4-24 days from LBR No. 6 – 1. This resulted in LBR 6 having a second round SRT of 28 days (as opposed to 24 days in the first round) and LBR 1 having a second round SRT of 48 days. Although the UASB effectively failed due to organic overloading, the performance of VS removal in the LBRs was extremely good with approximately 95% VS removal in LBRs in 28 days. Beyond 28 days no significant difference in VS removal was noted.

6.4 Discussion of Results

6.4.1 Recommended operation of the SLBR-UASB system

It is clear that connection to the UASB gives improved destruction of volatile solids in the LBRs (as shown in Figure 6.6). This is most obvious when comparing the results of case 1 and case 3 where the destruction of volatile solids increased from 51.5 – 81.8% VS destroyed. The increase in volatile solids destruction corresponds to an increase in leachate pH from 4 up to 7.8 in cases 1 and 3 respectively. Recirculation of effluent from the UASB increases the pH and buffering capacity of the leachate and leads to improved degradation of food waste in the LBRs.

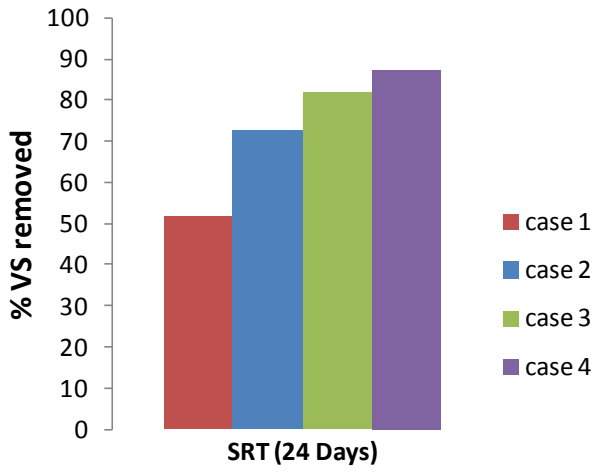


Figure 6.6 Volatile solids removal as percentage of initial volatile mass

The relatively low destruction of volatile solids in case 1 shows that hydrolysis is negatively affected by a low pH. It was observed that the post leaching food waste

was heavily covered with white fungi and was foul smelling during cases 1 and 2. Improving the rate of hydrolysis and acidification in the LBR by means of pH control, addition of inoculum and water dilution has been previously tested with various levels of success. Thamsiriroj and colleagues (2012) [21] showed that the flow rate of leachate through the LBR significantly improved the removal of VS while varying the solid retention time also affected the efficiency of the system. Xie and co-workers (2012) [22] showed that the addition of inoculum improved hydrolysis yields relative to leaching without inoculum. This is also in line with leaching experiments carried out by Jagadabhi and colleagues (2011) [12] which highlighted the importance of recycling UASB effluent back to the LBRs for continuous replenishments of anaerobic inoculum. However Xie and colleagues (2012) [22] also showed that pH control in the optimum range of 6-6.5 and dilution of leachate with fresh water had positive effects on hydrolysis and VS removal and proved more beneficial than just inoculum addition alone.

Although the increase in dilution rate per LBR in case 2 and 4 resulted in improved VS destruction in the LBRs, it also resulted in wash out of material from the LBRs to the leachate holding tank. This is not desirable for stable operation of the UASB which is sensitive to high levels of suspended solids and partially degraded material. The high dilution rate also required additional opening and closing of the leachate holding cups which lead to numerous, significant pressure fluxes in the system. It resulted in suction of produced gas through the effluent pipe (route of liquor) and not through the gas flow meter (desired route of gas). At commercial scale it may not be economically advantageous to operate at such a high dilution rate due to pumping costs.

It is recommended that the SLBR-UASB should be operated as in case 3 with 1 dilution per LBR per day. Under these conditions an average VS destruction rate of 81.8% can be achieved producing approximately 340 L CH_4 $kgVS^{-1}$ with a solid retention time of 24 days. This is about 64% of the maximum biomethane potential from canteen food waste. Higher specific methane yields have been reported using continuously stirred tank reactors e.g. Zhang et al (2012) reported a specific methane yield of 420 L CH4 $kgVS^{-1}$ with VS destruction of 84% using source segregated food waste [16]. However the advantage of the SLBR-UASB system is the

separation of the solid and liquid phases where the residual solid material can be easily separated from the liquid phase and can be further processed into compost, fibres or combusted as refuse derived fuel in the case of mixed municipal waste. In addition the utilisation of leach beds requires less energy input than conventional systems for mixing and pre-treatment which can be significant when treating municipal food waste.

6.4.2 Overloading of upflow anaerobic sludge blanket

The failure of the UASB during case 4 was attributed to overloading of the UASB. The flow rate to the UASB in case 4 was set at 80 L day^{-1} which equates to the recommended upflow velocity for the UASB at 0.1 m $hour^{-1}$ [14]. As the concentration of COD increased from 9.2 g L^{-1} to 20.7 g L^{-1} the daily flow rate of COD to the UASB increased from 736 gCOD day^{-1} to 1656 gCOD day^{-1}. The maximum COD capacity of the UASB was calculated as 730 g COD day^{-1} in Table 6.6. This suggests that the system was overloaded by a factor of 2.27.

Table 6.6 Maximum loading of the UASB

UASB granular sludge is designed to treat up to 0.6g COD g VS^{-1} inoculum day^{-1} (Supplied by Paques, Netherlands)
Granular sludge = 9.01% VS (of total mass) = 90.1gVS/L
COD conversion efficiency of the inoculum = 90% (Nizami et al., 2011)
COD capacity for 15L of granular sludge
=15 L * 90.1 g VS L^{-1} * 0.6gCOD.gVS^{-1}.day^{-1} * 0.9 removal = 729.8 g COD day^{-1}

Degradation of food waste occurs quite rapidly in comparison to other substrates such as grass silage. Nizami and Murphy (2011) reported a 72% destruction of volatiles in grass silage over 30 days at a high recirculation rate. This paper reports 87.5% destruction of volatiles in 24 days. Work by the authors would suggest that the kinetic decay constant (k) for food waste is approximately twice that of grass silage which suggests that food waste will break down twice as fast as grass silage. Thus higher loading rates will occur on the system using food waste as compared to grass silage. Observational measurements of COD suggest that there is a large increase in COD over the first 4-5 days of leaching in the LBR. During sequential

loading of LBRs care must be taken to ensure that the daily flow rate of COD to the UASB does not exceed its capacity. Potentially the system was overloaded by a factor of 2.27. Remedies to this include reducing the feedstock by 56% (from 1.12 kg VS per batch to 0.493 kg VS per batch) or decreasing the daily flow rate to the UASB by timing the pump on 26 minutes and off for 34 minutes in every hour, thus reducing the daily COD flow rate by a factor of 2.3.

6.4.3 Flow rate mechanism

There is a degree of ambiguity in the scientific literature as to whether the biomass in the LBR should be submerged or sprinkled with re-circulating leachate. Nizami and co-workers (2010) previously found that operating the LBR under flooding conditions using grass silage inhibited the rate of COD conversion in comparison to sprinkling. The reason postulated was that under flooding conditions a build up of volatile fatty acids caused a drop in pH below the recommended levels for hydrolysis and thus led to an ensiling affect on the process [17]. However in this experiment the leachate was constantly re-circulated over the feedstock without connection to the UASB which may have contributed to the build up of acids. Previous leaching experiments on food waste by Shin and co-workers (2001) used the LBRs in a saturated state: however pH was controlled at 6.5 and the flow rate was adjusted to prevent build up of acids in the LBR [13]. The LBRs were also inoculated with digestate from an existing AD plant which was not done in the leaching trials of Nizami and co-workers (2010). It is fair to suggest that the design and operation of LBRs is a relatively recent and immature technology and more detailed studies on the operating parameters is needed before moving onto to full scale development.

6.4.4 COD losses in the leach bed reactors

In cases 1 and 2 approximately 47% of the theoretical COD is not accounted for in either in the leachate or in the produced biogas (Table 6.4 and 6.5). As the LBRs were not fully anaerobic i.e. initially air is present in the head space of the leach bed reactors prior to loading, it is plausible that COD was converted to carbon dioxide by the abundance of white fungi present on the remaining biomass, particularly in leaching cases 1 and 2. This is not ideal for two phase digestion as COD is

effectively lost i.e. not available for methane production. This is in agreement with findings of Nizami and co-workers (2010) who suggested aerobic respiration in a recirculating leachate system occurs over time [17]. The higher flow rate had the effect of washing partially degraded material through the LBR and into the leachate tank. This is also undesirable as a build up of suspended solids and partially degraded material can contribute to foaming in the UASB.

6.5 Conclusions

From the leaching trials conducted a number of conclusions can be drawn:

- Increasing the flow rate from 17 L day^{-1} to 102 L day^{-1} without connection to the UASB resulted in a 41% increase in VS removal (51.5% -72.7%). However the high dilution rate results in partially degraded material wash out from the LBRs into the leachate holding tank.
- Connection to the UASB greatly improved VS destruction in the LBRs. In particular VS destruction increased by almost 60% from case 1 to case 3 with the low recirculation rate of 1 dilution per LBR per day
- Recirculation of effluent from the UASB increased the pH and buffering capacity of the leachate and resulted in better destruction of volatile solids, less fungal growth and improved odour in the LBRs in both cases 3 and 4
- The high recirculation rate caused operational problems to the SLBR-UASB system. The frequent opening and closing of head cups resulted in biogas losses from the UASB through the effluent pipe. The high dilution rate of the LBRs resulted in material wash out from the LBRs into the leachate holding tank. The increase in suspended solids and partially degraded material in the leachate resulted in foaming and organic over-loading of the UASB.
- It is recommended that the SLBR-UASB system should be operated under case 3 conditions with 1 dilution per LBR per day. The organic loading rate to the UASB should be monitored and controlled carefully to avoid overloading, foaming and process inhibition.

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7 The impact of increasing organic loading in two phase digestion of food waste

The impact of increasing organic loading in two phase digestion of food waste

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Abstract:
This paper examines the impact of increasing organic loading in a two phase digestion system treating commercial food waste. The first phase is a series of sequentially fed leach bed reactors (LBRs). The second phase is an Upflow Anaerobic Sludge Bed (UASB). Leachate from the leach beds, form the influent to the UASB. Effluent from the UASB is re-circulated over the leach beds. Flow rates corresponded to 1 volume of leachate per effective LBR volume per day. The theoretical organic loading rate (OLR) of the UASB is based on the conversion of VS in the LBR to chemical oxygen demand (COD). The experiment was set up such that the theoretical OLR would rise from 7.1 to 8.8 to 11.8 kg COD $m^{-3}d^{-1}$.
The system operated effectively at the lowest organic loading rate producing 384 L CH_4 kg VS^{-1} which corresponded to 72% of the value obtained in a BMP test. COD conversion efficiency was recorded at 75%. The accumulation of COD over the life of the experiment led to a situation whereby the volumetric OLR (product of COD concentration in the leachate by the flow rate) was over twice the theoretical OLR at the end of the experiment (24.3 kg VS $m^{-3}d^{-1}$ versus 11.8 kg VS $m^{-3}d^{-1}$). At the highest loading rate TAN reached levels of 4500 mg L^{-1} with pH levels of 8.15. This resulted in significant reduction of methane production.

Keywords: two phase digestion; food waste; UASB.

7.1 Introduction

7.1.1 Anaerobic digestion of food waste

The organic fraction of municipal solid waste (OFMSW) collected from households and commercial premises is dominated by food waste which accounts for approximately 33.5% of municipal solid waste (MSW) in Ireland [1]. EU states are obliged to divert biodegradable waste from landfill under the Landfill Directive 1999 [2]. Generation of biomethane from digestion of OFMSW is seen as a very sustainable transport biofuel with a green house gas saving of 80% when compared to diesel [3]. As a result anaerobic digestion of OFMSW is becoming increasingly popular across Europe [4]. Digestion of OFMSW with a total solids (TS) content of 20-40% and potential for up to 15% non-organic material such as plastic requires different reactor engineering to biogas systems for digestion of slurries and sludges.

7.1.2 Benefits of leach bed systems for digestion of OFMSW

Innovative biogas solutions to digestion of OFMSW includes for dry digestion systems such as the leach bed reactor (LBR). These involve digestion of organic materials (with moisture content in the range 50 to 75%) in static piles with recirculation of liquid leachate over the fermenting material. The main advantage of the leach bed reactor is in the simplicity of the design with little or no moving parts, and reduced heat demand. The ubiquitous continuously stirred tank reactors (CSTR) operate at a solids content of less than 10%. This would necessitate pre-treatment and/or dilution of organic material with high solids content. OFMSW may contain material that can be problematic for stirring mechanisms. These include garden waste and physical contaminants. CSTR systems require an energy intensive pre-treatment stage where the material is shredded, separated and slurried to the desired consistency. The parasitic energy demand for heating and stirring a CSTR can amount to about 30% of the total energy produced by the system [5]. Leach bed reactors are designed for organic material with higher solids content (25-50% total solids) and do not employ mechanical stirring. As such the parasitic demand should be considerable less.

7.1.3 Two phase digestion of OFMSW

Dry batch digestion can be performed either as a one phase or two phase process. Single phase systems can be performed in hermetically sealed chamber often referred to as vertical garage door system. In a two phase process a high rate methane reactor is connected downstream of the primary leach bed reactor. Liquid is sprayed over the top of the pile and percolates down through it, assimilating soluble fermentation products such as volatile organic acids. As the organic content of the liquid increases, usually measured in terms of chemical oxygen demand (COD), it can be transferred to a high rate methane reactor such as an upflow anaerobic sludge blanket (UASB) for more efficient methane production.

7.1.4 Previous studies on leach bed reactors connected to high rate methane reactors

The concept of two phase digestion to digest high solids biomass has been tested on a number of substrates such as grass silage [6, 7], maize silage [8], canteen food waste [9] and OFMSW [10]. Lehtomaki and colleagues (2008) found that 66% of the biomethane potential of grass could be achieved when combining a leach bed reactor to a second stage UASB, whereas in the one-stage leach bed process only 20% of the methane potential was extracted [6]. Nizami and Murphy (2011) achieved 341 L CH_4 kg VS^{-1} which was approximately 70% of the maximum methane potential of perennial rye grass [7]. Murto and colleagues (2013) tested the performance of a leach bed reactor system coupled with an upflow anaerobic filter with and without the addition of structural material (wood chip). Their substrate was the mechanically separated dry fraction of organic municipal waste. The system which employed wood chip achieved 89% of the biomethane potential whilst the system without wood chip only achieved 37% of the BMP result [10].

7.1.5 Aims of Paper

The aim of this paper is to assess the biomethane yields and process performance of a two phase anaerobic digestion system incorporating sequentially fed leach bed reactors connected to an upflow anaerobic sludge blanket, treating source segregated food waste under increasing organic loading rates.

7.2 Materials and Methods

7.2.1 Characterisation of food waste

Approximately 100 kg of source segregated food waste was sampled from a large quantity of organic waste which had been collected from over 20 catering premises in the city. The food waste was manually screened for non biodegradable contaminants such as plastic bags and cutlery and was then passed through a Buffalo 850W food mincer to a particle size of less than 6mm (Figure 7.1). The processed food waste was then mixed manually, weighed and stored in 8kg bags at -20°C until required. The bags were defrosted at room temperature for 24 hours prior to experimental use.



Figure 7.1: Collection and preparation of food waste

Table 7.1 gives detailed information on the physiochemical characteristics of food waste. The empirical formulae ($C_n H_a O_b N_c S_d$) can be calculated from an ultimate analysis. Using the Buswell equation the stoichiometric conversion of the organic matter to methane and carbon dioxide can be found.

Table 7.1: Characterisation of commercial food waste used in trial

Characteristics	Value
pH	4.85 ± 0.05
TS (%)	31.5 ± 0.25
VS (% TS)	91.2 ± 0.94
Ash (% TS)	8.8 ± 0.94
C (% TS)	49.0 ± 0.58
H (% TS)	7.0 ± 0.06
N (% TS)	3.4 ± 0.2
O* (% TS)	31.8 ± 0.6
C:N	14.4
Proteins (% TS)	29.6 ± 1.6
Fats (% TS)	26.7 ± 0.4
Carbohydrates (% TS)	34.7 ± 2.8
COD_{Th} (g OD g VS^{-1})	1.6
BMP_{Th} (L CH_4 kg VS^{-1}) (Boyle's eq)	569

*%O = 100% - (% C + H + N + ash)

The theoretical specific methane yield (mL CH_4 gVS^{-1}) can be calculated as follows:

$$BMP_{Th} = \frac{\left[\left(\frac{n}{2}\right)+\left(\frac{a}{8}\right)-\left(\frac{b}{4}\right)\right]\cdot 22400}{(12n+a+16b)} \quad (7.1)$$

Where;

n is the number of atoms of carbon;

a is the number of atoms of hydrogen;

b is the number of atoms of oxygen;

At standard pressure and temperature (1 atm, 273K) the volume of 1 mol of methane is 22400 mL. However, when proteins are present, ammonia and hydrogen sulphide are released and must be taken into consideration using Boyle's equation:

$$BMP_{Th} = \frac{\left[\left(\frac{n}{2}\right)+\left(\frac{a}{8}\right)-\left(\frac{b}{4}\right)-\left(\frac{3c}{8}\right)-\left(\frac{d}{4}\right)\right]\cdot 22400}{(12n+a+16b)} \quad (7.2)$$

Where;

c is the number of atoms of nitrogen;

d is the number of atoms of sulphur;

An alternative method for estimating the methane potential of a substrate can be calculated if the organic fraction composition is known (i.e. proteins, lipids and carbohydrates)

$$BMP_{Th} = 415 \cdot \%Carbohydrates + 496 \cdot \%\,\text{Proteins} + 1014 \cdot \%\,\text{Lipids} \qquad (7.3)$$

The theoretical oxygen demand can also be calculated based on the atomic composition from elemental analysis using the following equation 7.4:

$$COD_{Th} = \frac{\left[\left(2n\right) + (\text{a}/2) - b - (3c/2)\right] \cdot 16}{\left(12n + a + 16b + 14c\right)} \qquad (7.4)$$

7.2.2 Leach Bed Reactors

The leach bed reactors used in these laboratory trials were stainless steel tanks with a total volume of approximately 50L. The total volume is divided into three equal sections of approximately 17L. The top section incorporates a leachate sprinkling head and headspace, the middle section is the effective reactor volume (incorporating biomass retaining vessel, sieves and meshes) and the bottom section facilitates leachate percolation and collection. The effective reactor volume (middle section) is made up of a biomass retaining vessel with a 3mm mesh. The filtering system is designed to retain solid particles in the biomass retaining vessel and prevent wash through of solid particulate matter. This leach bed reactor was originally designed for leaching of grass silage by Nizami and Murphy (2010) [11] and was modified to accommodate food waste. A schematic diagram of the leach bed reactors connected to the UASB is shown in Figure 7.2. The leachate holding tank which is common to all LBRs was initially filled with 40L of water and heated to 37 °C prior to commencement of leaching.

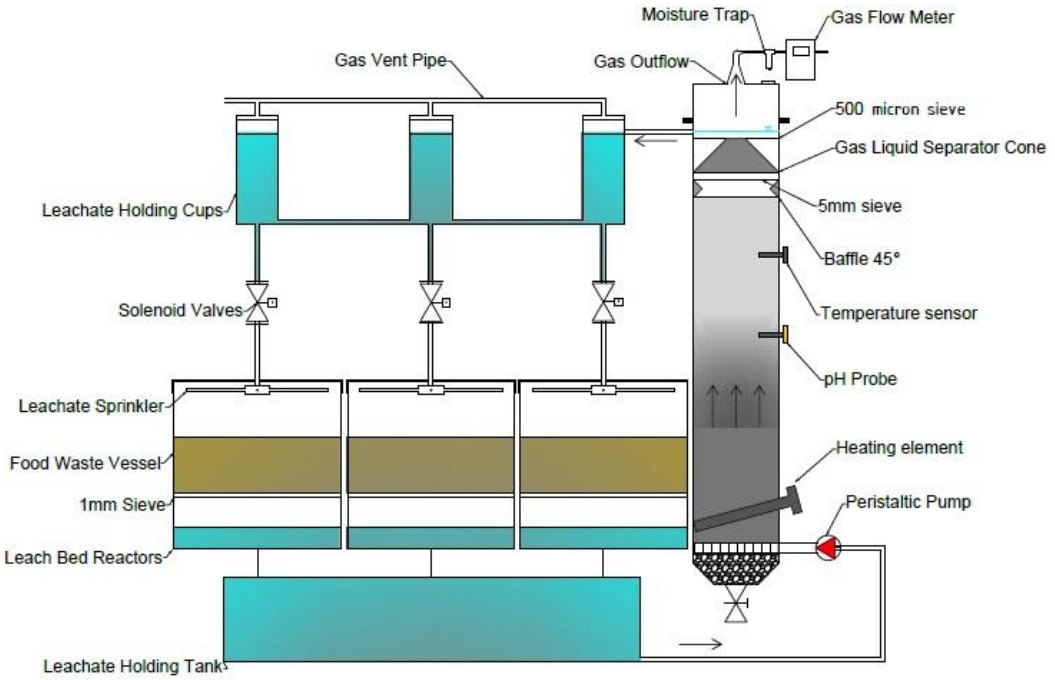


Figure 7.2 Sequentially fed leach bed reactors connected to upflow anaerobic sludge blanket (taken from [12])

7.2.3 Upflow anaerobic sludge blanket

The upflow anaerobic sludge blanket (UASB) has a working height 1.01m, and an internal diameter of 0.204m. The total working volume excluding the heating bar is 32.5L. The temperature in the UASB is controlled via a temperature sensor and a heating element to 37 ± 0.5 °C. A wet gas flow meter is connected to the gas outline pipe in the gas liquid separator to measure the flow of biogas. A pH probe is also installed in the UASB. All sensors are linked to a SCADA system where all measurements are recorded on an average hourly basis. A peristaltic pump (Watson Marlow 323S) is used to supply a flow of leachate from the leachate holding tank to the UASB.

7.2.4 Granular sludge inoculum

The granular sludge used in the lab scale UASB was taken from an industrial UASB treatment system which treated high strength wastewater (average effluent COD 15,000 mg L^{-1}) from cheese, whey and alcohol processing effluent. The granular sludge was sieved through a series of standard sieves down to 150 microns to

separate the granules from the liquid digestate. Granular sludge was then sampled for total solids TS and VS content (11.3% TS and 81% VS). The UASB was filled with 15L of granular sludge i.e. approximately half the working volume, with the remainder filled with the separated liquid digestate.

7.2.5 Experimental outline

In a previous study by the authors [12] the destruction of volatile solids in the LBRs was examined under 4 different conditions: 2 cases with a dilution rate of 1 reactor volume per day (low flow rate) and 2 cases with a dilution rate of 6 reactor volumes per day (high flow). The outcome of this trial showed that when the leach beds were connected to an upflow anaerobic sludge blanket with recirculation of effluent over the leach beds an improved rate of volatile solids destruction was observed in the LBRs as shown in Table 7.2.

Table 7.2: Results from previous leaching trials on volatile solids destruction in LBRs

Leaching Case No.	Flow rate (L day^{-1})	Dilution rate (day^{-1})	UASB connection	VS destruction (%)
1	17	1	No	51.5
2	102	6	No	72.7
3	102	6	Yes	81.8
4	17	1	Yes	87.5

Interestingly the destruction of volatile solids was similar for both the high and low flow rates with connection to the UASB. This flow rate allows for a design upflow of 0.1 m hr^{-1} in the UASB and a dilution rate of 1 volume of leachate per volume of leach bed per day. The system is a closed loop which at full scale should result in a low energy input system. The SLBR-UASB trial ran continuously for approximately 200 days. This run time can be broken into 4 distinct time periods with each period consisting of 2 solid retention times (SRT) at a fixed loading rate to the LBRs. The theoretical organic loading of the system is outlined as follows:

Period 1 (day 0-59): This period incorporated the start up of the sequentially fed leach bed reactor system, the acclimatisation period for the UASB and

troubleshooting with gas flow measurements from the UASB and SLBR. Each LBR was loaded with 2 kg of fresh matter food waste (0.574 kg VS per LBR). The SRT for each leach bed was initially set at 30 days (6 LBRs fed sequentially every five days). To estimate the theoretical organic loading rate on the UASB the daily theoretical COD production from LBRs is first calculated as:

$$DailyCOD_{Th} = VS_{In} \cdot COD_{Th} \cdot VS_{re} / SRT \quad (7.5)$$

Where;

VS_{In} is the total input of 6 LBRS (kg VS)

COD_{Th} is the theoretical ratio of COD to VS (1.6 gO_2 gVS^{-1})

VS_{re} is the max percentage removal from LBRs (%)

SRT is the solid retention time in days.

The daily theoretical organic loading rate in the UASB is equal to the daily COD produced divided by the volume of the UASB. For period 1: 184 g COD is produced per day (574 g VS per LBR * 1.6 g COD.g^{-1} VS / 5 days). The theoretical organic loading rate on the UASB is calculated as 5.67 kg COD m^{-3} day^{-1} (0.184 g COD d^{-1} / 32.5L) assuming that 100% of COD is destroyed per day. The theoretical daily COD and organic loading rate to the UASB for each period are shown in Table 7.3.

Table 7.3 Theoretical COD production and organic loading rate for each experimental period

Experimental Time (days)	**Period**	**Food waste per LBR (kg VS)**	**Solid Retention Time per LBR (days)**	**Daily theoretical COD (g COD day^{-1})**	**Theoretical OLR UASB (kg COD m^{-3} day^{-1})**
(0-59)	1	0.574	30	184	5.67
(59-107)	2	0.574	24	230	7.1
(107-155)	3	0.718	24	287	8.8
(155-191)	4	0.718	18	383	11.8

Period 2 (day 59-107): The solid retention time (SRT) for each leach bed reactor was reduced to 24 days (LBRs fed every 4 days) to increase the daily concentration of COD in the leachate. Each LBR was loaded with 2 kg of fresh matter food waste (0.574 kg VS per LBR). The maximum theoretical daily production of COD from

the LBRs is calculated as 230 g COD day^{-1} which corresponds to a theoretical organic loading rate in the UASB of 7.1 kg COD m^{-3} day^{-1}.

Period 3 (day 107-155): The organic loading on the system was increased to 2.5 kg fresh matter food waste per LBR (0.718 kg VS per LBR). The SRT remained at 24 days per LBR. This gave a theoretical COD production of 287 g COD day^{-1} and a theoretical organic loading rate in the UASB of 8.8 kg COD m^{-3} day^{-1}.

Period 4 (day 155-191): The organic loading per LBR remained at 2.5 kg fresh matter per LBR (0.718 kg VS per LBR). However the SRT was reduced to 18 days (LBRs fed every 3 days). This would have the effect of further increasing the daily production of COD and therefore increasing the organic loading rate of the UASB. The theoretical daily production of COD in period 4 was calculated as 383 g COD day^{-1} which corresponds to a theoretical organic loading rate in the UASB of 11.8 kg COD m^{-3} day^{-1}.

7.2.6 Biochemical methane potential tests

The food waste was assessed for biomethane potential. The BMP analysis was performed using the automatic methane potential test system (AMPTS II, Bioprocess Control, Lund, Sweden). This apparatus and the BMP methodology are described in detail in [13]. The BMP tests were performed at 37°C. Digestate from a continuous lab scale reactor treating a mixture of cattle slurry and food waste was used as the source of inoculum. The inoculum had a volatile solids content of 21.4 g kg^{-1} and initial pH of 7.8.

7.2.7 Analytical methods

The total solids (TS) and volatile solids (VS) were measured according to Standard Methods 2540 G. The pH was determined using a pH metre (Jenway 3510) calibrated with buffers at pH 4.0, 7.0 and 10.0. Elemental composition (C, H, N, O) of the food waste was attained by ultimate analysis using element analyser (CE 440 Model). Carbohydrates, proteins and fats were analysed by a private laboratory Exova (Ireland) Ltd. Biogas composition was analysed using a portable gas detector (Type PGD3-IR Biogas) supplied by Status Scientific Controls Ltd. All biomethane

yields are reported at standard temperature and pressure (1atm, 273K). The total ammonia nitrogen in the leachate was measured weekly using Hach Lange cuvette tubes 69, high range ammonia 0-50 mg L^{-1} N. The total and soluble COD were measured every second day using Hach COD vials heating block and spectrophotometer DR 3900. The soluble COD samples were first filtered through glass micro fibre filters (GF/A Whatman). The total volatile fatty acids (TVFA), total alkalinity and TVFA/alkalinity ratio were determined by the Nordmann titration method. The sample was centrifuged (3000 RPM for 30 min) and titrated with 0.1N sulphuric acid using a Titronic Universal titrator. TVFA and alkalinity were calculated by using empirical equations (Nordmann method).

7.3 Results

7.3.1 Results of BMP test

The BMP test on the input food waste material gave a specific methane yield of 534.5 ± 5 L CH_4 kg VS^{-1}. This is 94% of the theoretical methane potential (Table 7.1) according to Boyle's equation (7.2). The relatively high BMP yield can be attributed to the high portion of lipids (26.7% TS) in the commercial food waste. Lipids have a high theoretical methane yield (as seen from equation 7.3).

7.3.2 Period 1 - Start up of SLBR-UASB

The SLBR-UASB system start-up and commissioning phase ran for a period of 60 days. During this period the hydraulic loading rate to the UASB was gradually increased step-wise by increasing the leachate flow rate up to 78.4 L day^{-1}. During this start up period problems with gas flow measurement occurred whereby a large portion of daily biogas produced in the UASB escaped out through the effluent pipe. These problems were associated with blockages in the gas liquid separator (Figure 7.3), which forced the biogas out through the effluent pipe and therefore gas production was not all accounted for during this start-up period. The gas liquid separator (GLS) was modified to reduce the risk of clogging by the introduction of coarse and fine meshes to help retain the granular sludge in the UASB. The pipe which connected the GLS directly to the flow meter was altered so that the gas would be directed into the headspace of the UASB prior to gas measurement (Figure

7.3). This prevented any liquid or solid particles entering the gas out flow pipe and reduced the risk of blockages. The results from the start-up phase are not presented.

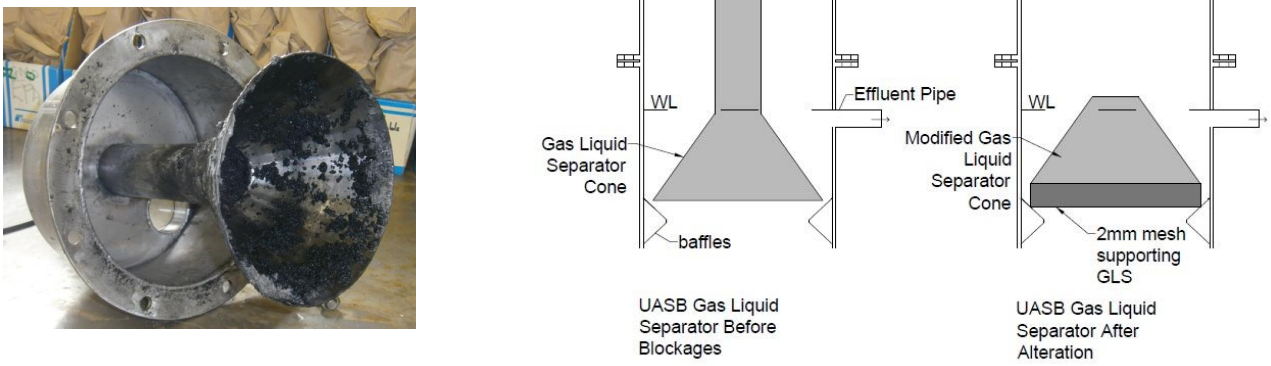


Figure 7.3 Blockage of the original gas liquid separator and subsequent modification

7.4 Period 2

7.4.1 Methane production from SLBR UASB

The UASB produced a specific methane yield of 337 L CH_4 kg VS^{-1} during the first SRT of period 2 and 382 L CH_4 kg VS^{-1} during the second SRT in period 2. The average methane yield from the UASB during period 2 is calculated as 360 L CH_4 kg VS^{-1}. An additional methane yield of 23.7 L CH_4 kg VS^{-1} was produced in the LBRs in period 2 bringing the total average methane yield of the full SLBR-UASB system for period 2 to 384 L CH_4 kg VS^{-1} (Table 7.4). This is 72% of the biomethane potential based on the BMP test of input food waste (535 L CH_4 kg VS^{-1}). The average percentage of methane in the biogas from the UASB in period 2 was 62.7 ± 2.6%. The average destruction of volatile solids in the LBRs was 89.5 ± 0.6 %.

7.4.2 Conversion of COD to methane

Theoretically 0.350 L of methane at STP (1 atm, 273K) can be obtained from the removal of 1 g COD (Raposo et al., 2011). The relative efficiency of conversion of COD to methane may be evaluated using Equation (7.6)

$$BMP_{ThCOD} = VS_{added} \cdot (gCOD / gVS) \cdot 350 \cdot VS_{destroyed} \quad (7.6)$$

Where:

BMP_{thCOD} is the theoretical conversion efficiency of COD to biomethane

Six leach beds each filled with 2 kg of food waste at 28.7% VS is equivalent to 3.44 kg VS. This converts to 4.93 kg COD (1.6 kg COD kg^{-1} VS destroyed) at 89.5% destruction. Allowing for 350 L CH_4 / kg COD the theoretical production is 1726 L CH_4. The actual recorded production of methane in period 2 is 1320 L. Thus COD conversion efficiency is 76% (Table 7.4).

7.4.3 Comparison of volumetric and theoretic OLR

In continuous operation of the SLBR-UASB the volumetric organic loading rate (VOLR) of the UASB was calculated as follows:

$$VOLR = COD_i \cdot Q_i / V \quad (7.7)$$

Where:

COD_i is the average concentration of COD in the influent leachate (mg L^{-1});

Q_i is the influent flow rate to the UASB (L day^{-1});

V is the reactor volume of the UASB (L)

Based on the average soluble COD concentration the volumetric organic loading rate was 12.4 kg COD m^{-3} day^{-1} (Table 7.4). This may be compared with the theoretical OLR of 7.1 kg COD m^{-3} day^{-1}. This is of considerable issue. The UASB is loaded at a higher rate than would be considered from a design theoretical perspective. This is due to the incomplete conversion of COD to methane in the UASB (76% in period 2) and its accumulation over time.

7.4.4 Process stability in period 2

During period 2 the average total COD in the leachate was 8829 ± 1617 mg L^{-1} while the soluble COD was 5151 ± 1166 mg L^{-1}(Table 7.4). The average concentration of total volatile fatty acids (TVFA) was 2439 ± 216 mg HAc_{eq} L^{-1} while the total alkalinity (TA) was 9878 ± 427 mg $CaCO_3$ L^{-1}. The ratio of TVFA to TA was on

average 0.25 for period 2 indicating that the AD process was stable. The pH during period 2 was 8.06 ± 0.1 which is relatively high for a methanogenic reactor; however substrates containing high levels of nitrogen such as food waste are known to exhibit higher pH values due to the higher buffering capacity associated with the higher concentrations of total ammonia nitrogen (TAN) in the liquid phase [14].

7.5 Period 3

7.5.1 Specific methane yields

The specific methane yield from the first SRT in period 3 was 355.8 L CH_4 kg VS^{-1} while a reduced specific methane yield of 321.3 L CH_4 kg VS^{-1} was generated for the second SRT of period 3. The average specific methane yield for the UASB in period 3 is calculated as 338.6 L CH_4 kg VS^{-1}which is 6 % lower than the average methane yield from the UASB in period 2. An additional methane yield of 16.7 L CH_4 kg VS^{-1} was generated in the LBRs generating an average methane production from the full SLBR-UASB system during period 3 of 355.2 L CH_4 kg VS^{-1}. This is 7.5% less than for period 2. The average percentage of methane in the biogas from the UASB in period 3 was 63.7 ± 2.7% CH_4 which was slightly higher than period 2 (Table 7.4).

Table 7.4 Summary of process monitoring in SLBR-UASB trial

AD process parameters	Period 2 (Day 59-107)	Period 3 (Day 107-155)	Period 4 (Day 155-191)
BMP_{ex} (L CH_4 kg VS^{-1})	534.5 ± 5		
Total specific methane yield SLBR-UASB (L CH_4 kgVS^{-1})	384	355	209
Average percentage CH_4 in UASB biogas (%)	62.7 ± 2.6	63.7 ± 2.7	55.9 ± 8.3
Percentage of BMP (%)	71.8	66.4	39.1
VS destruction in LBRs (%)	89.5 ± 0.6	84.3 ± 5.8	83.9 ± 5.2
Conversion efficiency COD to CH_4 (%)	76	75	39.1
Soluble COD (mg L^{-1})	5151 ± 1166	7088 ± 627	10093 ± 569
Total COD (mg L^{-1})	8829 ± 1617	12779 ± 1670	18507 ± 1174
Theoretical OLR UASB (kg COD m^{-3} day^{-1})	7.1	8.8	11.8
VOLR UASB (kg COD m^{-3} day^{-1})	12.4 ± 2.8	17.1 ± 1.5	24.3 ± 1.4
TVFA (mg HAc_{eq} L^{-1})	2439 ± 216	4289 ± 743	6302 ± 410
TA (mg $CaCO_3$ L^{-1})	9878 ± 426	13378 ± 919	15332 ± 252
TVFA/TA	0.25	0.32	0.41
pH	8.06 ± 0.1	8.13 ± 0.07	8.15 ± 0.03
TAN (mg N L^{-1})	3042 ± 522	4348 ± 153	4524 ± 133
NH_3 (mg N L^{-1})	397 ± 145	610 ± 42	697 ± 64

The average destruction of volatile solids in the LBRs was 84.3 ± 5.8 %. The maximum theoretical methane yield based on VS destruction per SRT in period 3 was calculated (using equation 7.6) as 2032 L CH_4. The average experimental methane produced per SRT in period 3 was 1528.3 L CH_4. This equates to a conversion efficiency of 75% of COD to methane for the full SLBR-UASB system.

7.5.2 Modification of the leach beds

The significant drop in methane yield associated with the second SRT in period 3 was caused by a reduction in leachate flow to the UASB towards the end of period 3. A large decrease in methane production in the UASB was noticed from about day 154 – 159 (Figure 7.4 (a)). It was discovered that the flow of leachate to the UASB had been severely reduced as the LBRs had become clogged and were retaining

leachate. This problem was overcome by cutting V-notch weirs (Figure 7.5) in the holding cages to allow excess leachate overflow from the LBRs and into the leachate holding tank.

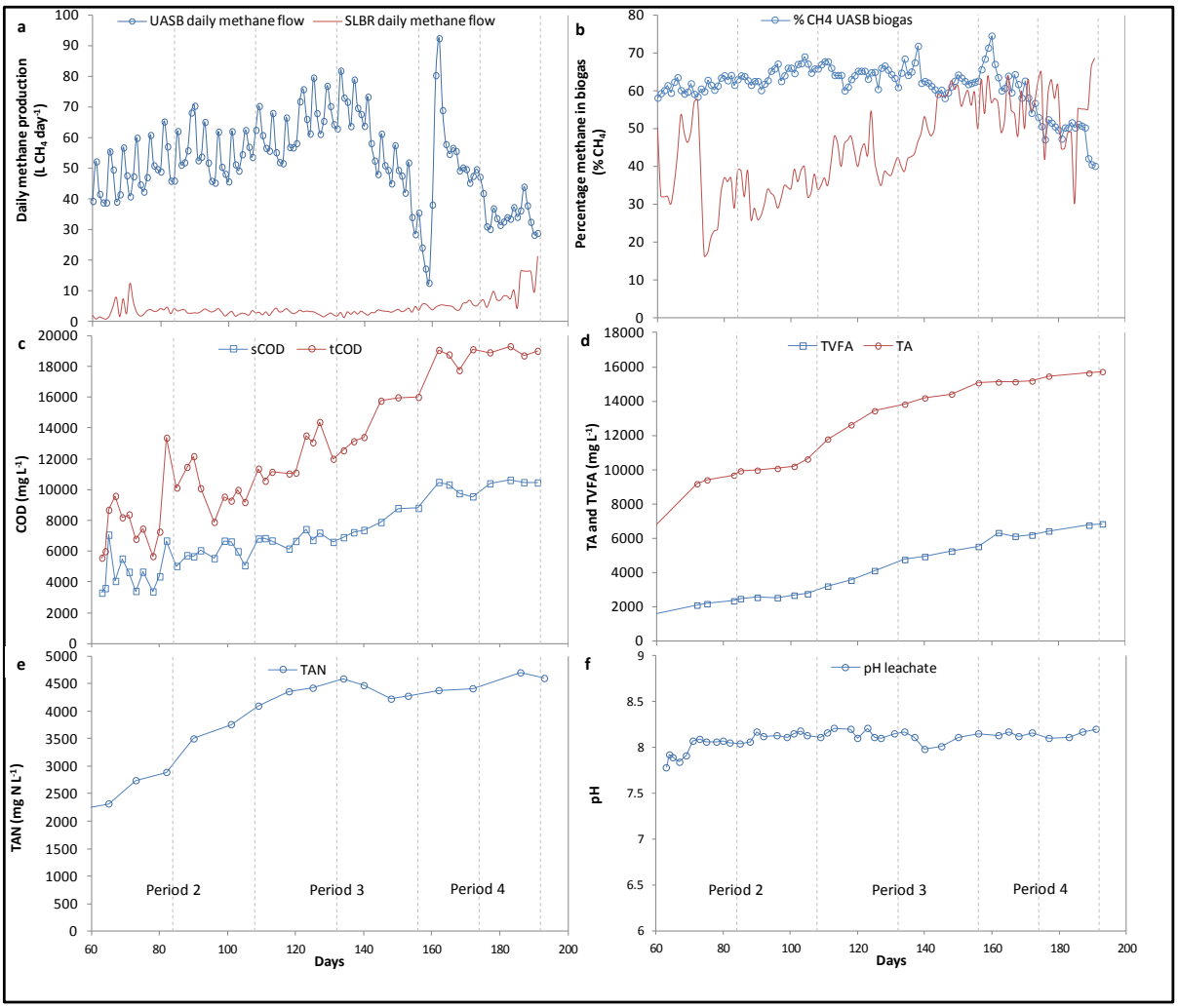


Figure 7.4 Gas and liquid monitoring of the SLBR UASB process



Figure 7.5: V notch weir cut into biomass holding cage

7.5.3 Process stability in period 3

In period 3 the organic load in the LBRs was increased by inputting 2.5 kg (w/w) food waste per LBR (an increase of 25% VS input from period 2). The increases in organic load per LBR led to an increase in the daily methane production in the UASB (Figure 7.4 (a)). The average total and soluble COD in the leachate was 12779 ± 1670 and 7088 ± 627 mg L^{-1} respectively in period 3 (Table 7.4). The volumetric organic loading rate on the UASB (based on the soluble COD) was an average of 17.1 ± 1.5 kg COD m^{-3} day^{-1} which was an increase of about 38% from period 2. The actual observed soluble COD in period 3 was approximately 13% greater than the theoretical amount predicted in Table 7.2. This additional COD can be attributed to a slight accumulation of COD from period 2. The efficiency of COD conversion from period 2 was 76% and if 10% of the COD is utilised for biomass growth (i.e. new bacteria) approximately 14% of the COD remains in the leachate. The concentration of total volatile fatty acids (TVFA) in period 3 was 4289 ± 743 mg HAc_{eq} L^{-1} while the total alkalinity (TA) was 13378 ± 919 mg $CaCO_3$ L^{-1}. The ratio of TVFA to TA was on average 0.32 for period 3 indicating that the AD process was stable (i.e. TVFA/Ta < 0.4). This ratio had increased from period 2 (TVFA/TA =0.25). The pH during period 3 increased slightly from period 2 to an average of 8.13 which is relatively high for a methanogenic reactor. The concentration of total ammonia also increased in period 3 with an average of 4348 ± 153 mg N L^{-1}. The increase in total ammonia coupled with the increase in pH led to a corresponding increase in the concentration of un-ionised ammonia (NH_3) to 610 ± 42 which is the more toxic form for methanogens.

7.6 Period 4

7.6.1 Large decrease in methane production

After the reduction in leachate flow to the UASB had been overcome from the end of period 3, an initial increase in the daily methane production from the UASB was observed from around day 160 with a spike in methane production at day 162. However methane production in the UASB soon began to drop again after the initial spike in production as can be seen in Figure 7.4(a) and from about day 174 a noticeable decrease in the percentage methane in the biogas from the UASB was

observed, as shown in Figure 7.4(b). The specific methane yield produced in the UASB for the first SRT in period 4 was 205.8 L CH_4 kg VS^{-1} and 146.7 L CH_4 kg VS^{-1} for the second SRT, giving an average of 176.3 L CH_4 kg VS^{-1} from the UASB in period 4. This was a reduction of approximately 48% from period 3 and showed that the UASB had reached a state of inhibited methane production. Meanwhile methane production from the LBRs increased to 23 L CH_4 kg VS^{-1}in the first SRT of period 4 and 42.6 L CH_4 kg VS^{-1}in the second SRT of period 4. The average total specific methane yield for the full SLBR-UASB system in period 4 was 209.1 L CH_4 kg VS^{-1}. This is only 37% of the BMP of the input material and shows that the system had reached severe inhibition. The level of volatile solids destruction in the LBRs remained similar to period 3 at around 84%. The theoretical maximum methane potential per SRT in period 4 based on destruction of volatile solids in the LBRs was calculated as 2023 L CH_4, however an average of 791 L CH_4 was generated by the SLBR-UASB system corresponding to a greatly reduced efficiency of 39.1% in conversion of COD to methane. The percentage methane in the biogas from the UASB decreased dramatically from the middle of the first SRT in period 4 from 62.6% CH_4 on day 170 to as low as 40.1% CH_4 by day 191. It was decided to stop the loading of the SLBR as the UASB had clearly reached a state of inhibition. Interestingly the percentage methane in the biogas from the LBRs increased substantially during period 4 as did the daily methane production rate particularly in the second SRT of period 4.

7.6.2 Process monitoring in period 4

In period 4 the solid retention time in the LBRs was reduced from 24 to 18 days (LBRs sequentially fed every 3 days). Theoretically this should increase the daily COD production by 25% from period 3 (as shown in Table 7.2). The average total and soluble COD in the leachate was 18507 ± 1174 and 10093 ± 569 mg L^{-1} respectively in period 4. The volumetric organic loading rate in the UASB (based on the soluble COD) was 24.3 ± 1.4 kg COD m^{-3} day^{-1} which was an increase of 42.1% from period 3. This value is above the limit of 20 kg COD m^{-3} day^{-1} which would be deemed the upper limit on loading of a UASB. The concentration of total volatile fatty acids (TVFA) in period 4 was 6302 ± 410 mg HAc_{eq} L^{-1}. The total alkalinity (TA) was 15332 ± 252 mg $CaCO_3$ L^{-1}. The ratio of TVFA to TA was on average

0.41 for period 4 which is slightly above the recommended ratio for stable AD processes. The pH during period 4 increased slightly from period 3 to an average of 8.15 which is significantly above the optimum range of 7-7.5 pH for a methane reactor. The concentration of total ammonia also increased in period 4 with an average of 4524 ± 133 mg N L^{-1}. The increase in total ammonia coupled with the increase in pH lead to a corresponding increase in the concentration of un-ionised ammonia (NH_3) to 697 ± 64 mg N L^{-1} which is reportedly more toxic for methanogens than the ionised form (NH_4^+).

7.6.3 Increased gas production from leachate holding tank

During period 4 when opening the LBRs for unloading and loading, evidence of solid material washed out from the LBR holding cages into the leachate holding tank was observed. This was confirmed by the relatively large concentration of solid material which remained at the bottom of the leachate tank at the end of the trial period. On removing the leachate at the end of the experimental run the leachate was found to contain an average of 2.8 ± 0.3% VS. This effectively means that 1.12 kg VS remained in the leachate tank and was not converted to methane. Theoretically this remaining solid material could yield a maximum methane potential of 392 L CH_4 which is approximately 19.4% of the theoretical methane yield based on the destruction of VS in period 4. Effectively the leachate holding tank became an additional methane bioreactor over time. This can be seen in Figure 7.4 (a) and (b) where an increase in daily methane production and in the percentage methane in the biogas from the LBRs can be seen, particularly in the final period 4. The recirculation of effluent from the UASB ensured the pH remained high in the leachate holding tank. In addition the inevitable wash out of some granular sludge from the UASB to the leachate tank provided a source of methanogenic inoculum. The relatively large fluctuations in the methane content of the SLBR biogas is explained by the fact that the LBRs were emptied and fed sequentially every 4 days in period 2 and 3, and every 3 days in period 4.

7.7 Discussion of Results

7.7.1 Inhibition of methane production in UASB

In period 4 a large drop in both daily biogas production and percentage methane in the biogas from the UASB was observed. It can be seen that the increase in organic loading rate to the UASB had a negative effect on methane production in the UASB. This is in agreement with Shin and colleagues (2001) who showed that organic loading rates above 20 kg COD m^{-3} day^{-1} resulted in greatly reduced conversion of COD to methane [9]. The accumulation of COD and VFAs in the leachate in period 4 can be clearly seen in Figures 7.4 c and 7.3 d with concentrations of total VFAs being well above recommended levels for stable AD (6302 ± 410 mg HAc_{eq} L^{-1}). This further increased the organic loading rate on the UASB and ultimately led to severe process inhibition by the end of the period 4. The accumulation of VFAs indicates strong inhibition of acetoclastic methanogenesis which has previously been linked to inhibition of methane production by the accumulation of total ammonia nitrogen (TAN) in the leachate over time [15].

7.7.2 Ammonia inhibition of acetoclastic methanogenesis

Ammonia is released through the degradation of amino acids and proteins and comes in the form of either ionized ammonia (NH_4^+) or free ammonia (NH_3). The balance between ionized and free ammonia is pH and temperature dependent [16]. Elevated levels of TAN are known to cause inhibitory effects at concentrations above 3000 mg N L^{-1} [17] and the effects are more pronounced at higher pH due to the associated swing towards free ammonia (NH_3) which is thought to be the cause of inhibition for acetoclastic methanogens. Research into ammonia inhibition indicates that acetoclastic methanogens are more sensitive to high levels of ammonia than the hydrogenotrophic methanogens [18, 19]. In another study, the increase in total ammonia concentrations to 4051-5734 mg N L^{-1} caused a 56.5% reduction in methanogenic activity [20].

7.7.3 Ammonia inhibition in digestion of substrates with low carbon to nitrogen ratios

It has been previously observed that long term digestion of food waste follows a pattern of production and accumulation of VFAs over time in line with increasing concentrations of TAN [15]. Accumulation of TAN is most often associated with organic substrates with a low carbon to nitrogen (C:N) ratio [21]. It is usually recommend to a have a C:N ratio of between 20-30. In this trial the commercial food waste had a C:N ratio of 14.4 (Table 7.1). According to Banks and Heaven (2013) once free ammonia has reached a critical concentration a portion of the metabolic capacity will be inhibited which in extreme cases lead to the total failure of the digester [16]. Despite a number of studies which have looked at ammonia inhibition exact values for the concentration at which it becomes toxic are hard to predict. Allen and colleagues (2013) achieved good specific methane yields from the co-digestion of food waste, paunch content and cheese effluent which all have low carbon to nitrogen ratios. In that study concentrations of 478 mg N L^{-1} free ammonia were reported without disruption to methane production. However the trial was operated at a temperature of 35 ° C and the pH was below 8 for most of the trial [22]. In this trial the concentration of TAN for periods 3 and 4 was between 4096-4702 mg N L^{-1} as shown in Figure 7.4 (e) while the concentration of free ammonia ranged from 610 ± 42 to 697 ± 64 mg N L^{-1}. This responded to an increase in VFAs and a large decrease in specific methane yield.

7.7.4 Control of ammonia and pH levels

One of the possible methods for controlling the concentration of free ammonia is lowering the pH in a reactor (e.g. from 8 to 7). Theoretically this could convert much of the free ammonia to the less harmful disassociated ammonium form. Strik and co-workers (2006) reported the reduction of free ammonia levels (NH_3) to less than inhibitory levels by pH-based control (using 17% HCL) however the methane yield was also severely reduced [23].

7.8 Conclusions

Two phase digestion of food destroyed 89% of volatile solids at a theoretical organic loading rate of the UASB of 7.1 kg VS $m^{-3}d^{-1}$ whilst producing 384 L CH_4 kg VS^{-1},

72% of the value obtained in a BMP test. The COD conversion efficiency was 76%. This incomplete conversion of COD to methane led to an accumulation of COD over the lifetime of the experiment (191 days). This caused a significant difference between what the theoretical OLR was expected to be at design stage (11.8 kg VS $m^{-3}d^{-1}$ for period 3) and what the Volumetric OLR actually was in operation (24.3 kg VS $m^{-3}d^{-1}$ for period 3). As loading rates were increased the ratio of acids to total alkalinity rose from 0.25 to 0.41 indicating the level of stress on the system. The low C:N ratio of the substrate proved problematic. Levels of free ammonia rose from 397 to 697 mg NH_3-N/L. This resulted in significant reduction of methane production and what would be deemed a failure of the system.

Acknowledgements

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8 Assessing biomethane production from the organic fraction of municipal solid waste in batch and continuous operation

Assessing biomethane production from the organic fraction of municipal solid waste in batch and continuous operation

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Abstract:

This paper examines the variability in biomethane potential from the organic fraction of municipal solid waste (OFMSW) depending on source of origin. Eight organic waste streams were examined for biochemical methane potential (BMP). Specific methane yields of between 274-368 mL CH_4 gVS^{-1} for household waste and 491-535 mL CH_4 gVS^{-1} for commercial waste were achieved. Inclusion of garden waste reduced methane yields. A semi continuous trial on commercial food waste produced an average of 560 ± 29 mL CH_4 gVS^{-1} at a moderate organic loading rate (OLR) of 2 kg VS m^{-3} day^{-1} with a hydraulic retention time (HRT) of 30 days. Raising the OLR to 4 kg VS m^{-3} day^{-1} led to a reduction in specific methane yield. The low carbon to nitrogen (C:N) ratio of commercial food waste (14.4) led to process instability due to levels in excess of 7000 mg L^{-1} towards the end of the trial.

Keywords: anaerobic digestion; food waste; BMP; CSTR

8.1 Introduction

Food waste accounts for approximately 25% of domestic household waste in Ireland [1]. Many commercial organic waste streams are also dominated by food waste, particularly catering premises such as restaurants, hotels and office canteens. National and European legislation place restrictions on the amount of organic waste which may be sent to landfill [2]. The current EU Waste Framework Directive [3] seeks to encourage waste separation at source and biological treatment of organic waste. Anaerobic digestion is a vector which can maximise the value of organic waste. The methane component of biogas, produced from the anaerobic process, is a valuable renewable gaseous fuel. The digestate from the biogas process may be used as a mineral rich fertilizer and reduce synthetic fertilizer consumption [4].
This paper seeks to outline the variability in methane yields from OFMSW depending on the waste source and type of collection. A selection of organic waste samples from domestic, commercial and food processing waste streams were investigated. The biochemical methane potential (BMP) test was used to assess the methane yield for each substrate. Based on the results of the BMP test the waste stream with the highest BMP was chosen as the feedstock for a semi continuous anaerobic digestion trial. This trial was used to assess the long term process stability at increasing organic loading rates.

8.2 Materials and methods

8.2.1 Collection, preparation and characterisation of waste samples

Samples were collected in a large centralised facility (Acorn Recycling Ltd.) licensed to treat 45,000 tonnes per annum of organic municipal waste (referred to as brown bin waste in Ireland). This facility treats a wide range of municipal organic waste streams from across the province of Munster in Ireland (population circa 1.25 million people). As shown in Figure 8.1, a total of 8 different waste streams were sampled; 4 household, 2 commercial and 2 food processing streams. Each sample consisted of approximately 10 kg of material sampled across a large bulk quantity of each waste stream. The German VDI guidelines were followed on sampling solid material [5]. The samples were screened for non organic material and were then

passed through a Buffalo food mincer to a particle size of less than 5mm. All samples were stored in a freezer at -20°C until required as previously described by [6]. A proximate and elemental analysis was carried out in triplicate on samples from each waste stream as shown in Table 8.1.

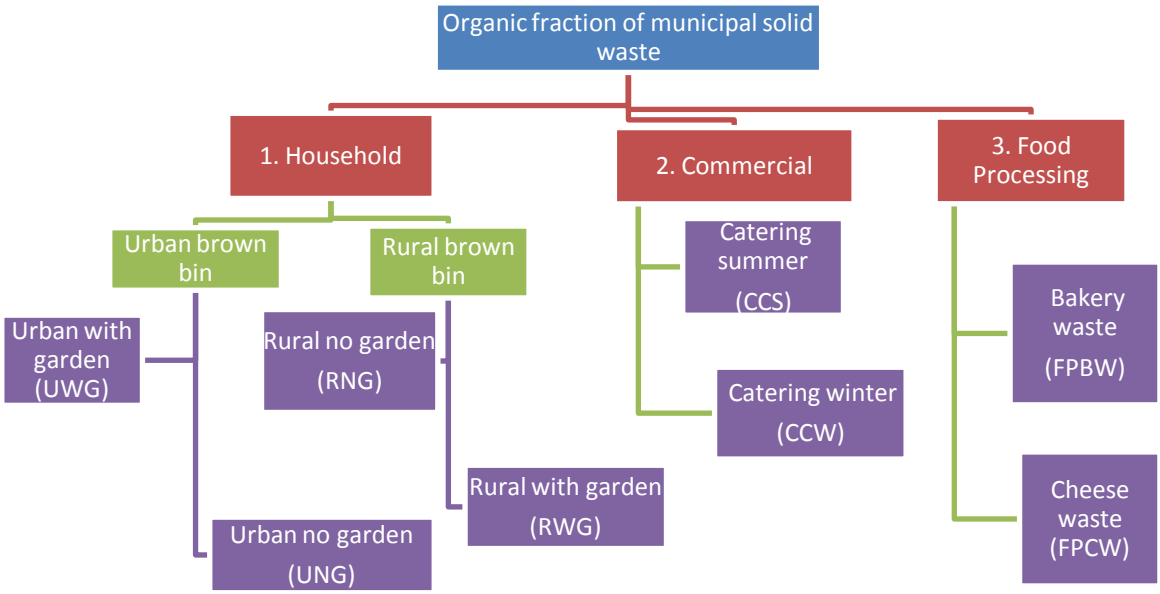


Figure 8.1 Illustration of samples taken from the organic fraction of municipal solid waste (with and without garden waste)

Table 8.1 Characterisation of OFMSW samples

Samples	Total solids (%)	Volatile solids (% TS)	Total carbon (%TS)	Total hydrogen (%TS)	Total nitrogen (%TS)	C:N
Household brown bin						
Rural with garden (RWG)	33.4 (0.4)	82.3 (0.2)	43.3 (0.2)	5.9 (0.1)	2.7 (0.1)	16
Rural no garden (RNG)	30.6 (3.3)	88.4 (0.4)	44.9 (0.2)	6.6 (0.1)	3.1 (0.2)	14.5
Urban with garden (UWG)	25.66 (0.1)	73.6 (0.4)	41.3 (0.2)	5.2 (0.1)	2.6 (0.4)	16
Urban no garden (UNG)	31.0 (2.4)	93.8 (0.3)	46.5 (0.2)	7.3 (0.1)	3.7 (0.1)	12.6
Commercial waste						
Commercial canteen summer (CCS)	32.8 (0.1)	92.6 (0.3)	49.0 (0.6)	7.0 (0.1)	3.4 (0.2)	14.4
Commercial canteen winter (CCW)	23.8 (0.5)	90.0 (0.3)	48.2 (0.2)	7.0 (0.04)	3.6 (0.2)	13.4
Food processing						
Food processing bakery waste (FPBW)	45.7 (0.4)	91.9 (0.6)	52.7 (0.2)	8.2 (0.05)	2.8 (0.2)	18.8
Food processing cheese waste (FPCW)	15.9 (0.1)	55.6 (0.3)	24.9 (0.1)	4.1 (0.03)	4.6 (0.03)	5.4

All values are presented as mean and (standard deviation)

8.2.2 BMP tests

The apparatus used to conduct the BMP tests was the Automatic Methane Potential Test System II (Bioprocess Control Sweden AB). This laboratory instrument is specially designed for determination of the BMP of a substrate. The AMPTS II system consists of three major parts as follows:

1. A temperature controlled water bath with 15 bottle reactors of 500 ml volume, each equipped with a mixer that can be run in either continuous or intermittent mode.
2. A carbon dioxide fixing unit with an alkaline solution (3N sodium hydroxide) that absorbs the carbon dioxide and hydrogen sulphide produced during the anaerobic digestion process.
3. A gas measuring unit consisting of 15 parallel operating cells, where the gas is measured through water displacement. When approximately 10 ml of gas has been accumulated each cell opens and releases the gas. For each opening, the time, temperature and pressure are registered and stored locally in an embedded Central Processing Unit (CPU). Based on these measurements, normalised (0°C, 1 atm and dry gas) accumulated gas production and gas flow rate are calculated.

The BMP tests were performed with a working volume of 400 ml. The ratio of inoculum to substrate was chosen to be 2:1 on a volatile solids (VS) basis. The inoculum to substrate ratio is a critical parameter in conducting a BMP test according to the Anaerobic Digestion Specialist Group of the International Water Association [7]. A ratio of 2:1 or greater of inoculum to substrate on a VS basis is recommended for BMP trials to limit any inhibitory effects due to the chemical composition of the substrate such as inhibition associated with accumulation of ammonia and volatile fatty acids (VFA) [8]. All samples were tested for BMP in triplicate. A BMP test of the inoculum alone (referred to as a blank) was conducted in triplicate. The average methane yield from the blanks was subtracted from the samples of OFMSW with inoculum to accurately assess the BMP yields from the samples only. A triplicate BMP test was also carried out on cellulose for quality control as the maximum BMP from cellulose is known and can be compared with

the BMP yield. The percentage volatile solids destroyed during the batch process was calculated as follows:

$$\% \text{ VS destruction} = 100 \cdot (1 - (VS_f - VS_{fb})/(VS_i - VS_{ib}) \quad (8.1)$$

Where;

VS_i is the amount of total input VS (g), VS_f is the amount of total VS at the end of the BMP test (g), VS_{ib} is the amount of VS (g) in the inoculum (blank) at the beginning of the BMP test and VS_{fb} is the amount of VS (g) in the inoculum (blank) at the end of the test.

The Buswell equation was used to calculate the theoretical maximum methane potential [9].

$$BMP_{Th} = \frac{\left[\left(\frac{n}{2}\right)+\left(\frac{a}{8}\right)-\left(\frac{b}{4}\right)\right]\cdot 22400}{(12n+a+16b)} \quad (8.2)$$

Where;

n is the number of atoms of carbon;

a is the number of atoms of hydrogen;

b is the number of atoms of oxygen;

The biodegradability index is the ratio of the measured BMP divided by the theoretical methane yield according to the Buswell equation and is used to assess the level of biodegradability of a substrate.

8.2.3 Source and characteristics of inoculum for BMP tests

The inoculum for the BMP tests was obtained from a lab scale 300L digester treating mostly cattle slurry and a small portion of food waste operating at mesophilic temperatures (35 °C). After an incubation period of one week the inoculum had a pH of 7.9, total solids (TS) of 34.2 gVS kg^{-1} and volatile solids (VS) content of 21.4 gVS kg^{-1} after passing through a 2mm sieve. Inoculum from both rounds was tested using cellulose as a standard control substrate (C_{12} H_{20} O_{10}). The maximum theoretical methane yield from cellulose according to the Buswell equation is 415 L CH_4 $kgVS^{-}$

[1]. The specific methane yield produced from the cellulose was 371±4 LCH_4 $kgVS^{-1}$. This is almost 90% of the theoretical maximum indicating that a healthy inoculum.

8.2.4 Kinetic modelling of BMP tests

Two first order kinetic models were used to fit the cumulative methane production data from the BMP tests. Assuming first-order kinetics for the hydrolysis of particulate organic matter, the cumulative methane production can be described by means of the following equation:

$$Y(t) = Y_m \cdot (1 - \exp(^{-kt})) \quad (8.3)$$

Where,
Y(t) is the cumulative methane yield at digestion time t days (mL CH_4 g VS^{-1} added), Y_m is methane potential of the substrate (mL CH_4 g VS^{-1} added), k is methane production rate constant (first order disintegration rate constant) (day^{-1}), t is the time (days).

The duration of the lag phase is also an important factor in determining the efficiency of anaerobic digestion. The lag phase (k) can be calculated with the modified Gompertz model as described by [10] as follows:

$$M = P.exp\left\{-exp\left[\frac{R_{max} \cdot e}{P}(\lambda - t) + 1\right]\right\} \quad (8.4)$$

Where,
M is the cumulative methane yield at a given time (ml CH_4 g VS^{-1}), P is the max methane potential (L CH_4 kg VS^{-1}) from the BMP test, R_{max} is the maximum methane production rate (L CH_4 kg VS^{-1} day^{-1}), e is the mathematical constant = 2.7183, λ is the lag phase for methane production to begin (days), t is the time (days).
A nonlinear least-square regression analysis was performed using Excel to determine λ, R_{max}, k, and the predicted methane yield. The predicted methane yield obtained from the regression analysis was plotted with the measured methane yield. The statistical indicators, Correlation coefficient (R^2) and root mean square error (RMSE) were calculated to assess the goodness of fit [11].

8.2.5 Statistical analysis

The significance of differences in the average methane yields was determined by using single factor Analysis of Variance (ANOVA) in Excel software 2007. If the calculated F value was higher than the tabulated F value, the minimum significant difference (MSD) was calculated to judge whether two or more averages were significantly different or not (Tuckey test). MSD was calculated at P = 0.05 ($MSD_{0.05}$) [12].

8.2.6 Semi-continuous trial

The semi continuous trial was carried out in a continuously stirred tank reactor (CSTR) with a total volume of 5L (working volume of 4L) and ran for a period of 25 weeks. The reactor was maintained at a temperature of 37 $\pm$ 1 ^{o}C and was continuously stirred at a rate of 100 rpm. The reactor was constructed out of thick walled plastic with a vertically mounted stirring mechanism as shown in Figure 8.2. The reactor was placed inside a coiled copper pipe frame which was heated by a thermo-circulator. Biogas flow was measured using a tipping bucket mechanism whereby the number of tips was recorded and multiplied by the calibrated gas volume of the tipping bucket (78 ml per tip). Biogas was sampled downstream of the gas flow tipping meter in 1L Tedlar gas bags and analysed for methane, carbon dioxide and hydrogen sulphide.

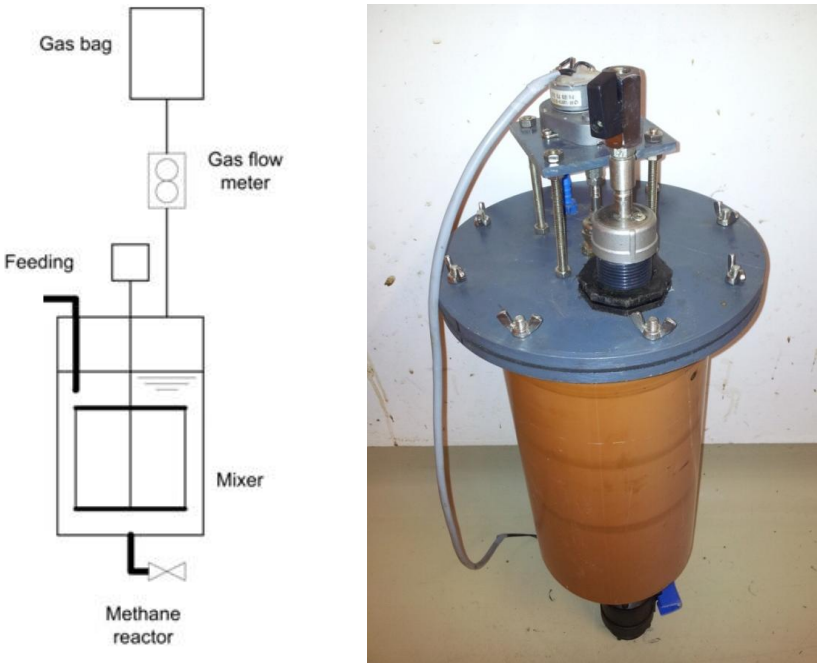


Figure 8.2 Continuously stirrer tank reactor (5L) used for semi continuous trial

8.2.7 Analytical methods

Total solids and volatile solids were determined gravimetrically following the standard methods (APHA, 2005). The biogas composition in the semi continuous trial was measured by infra red gas analyser (Status Scientific Control I-R biogas analyzer). The instrument was calibrated before the commencement of the trial and showed an accuracy of ± 1% when tested weekly on a standard mixture of 65% methane 35% carbon dioxide provided by BOC specialty gases. All methane yields were adjusted to standard temperature of 273 K and 1 atmosphere (1013 hPa). Volatile organic acids and total alkalinity were measured using the Nordmann titration method (1978) using 0.1N sulphuric acid and a Titronic Universal Titrator. The pH of the digestate was measure daily using a Jenway 3510 pH meter. Total ammonia was measured using the Hach NH_3-N vials and spectrophotometer DR 3900.

8.3 Results and Discussion

8.3.1 Results from the BMP tests

The results from the BMP test are shown in Table 8.2. Household waste streams ranged in methane potential from 274 – 368 mL CH4 gVS^{-1}, commercial waste samples ranged from 491 – 535 mL CH4 gVS^{-1} while food processing samples exhibit the largest difference between samples (529 mL CH4 gVS^{-1} for bakery waste and only 188 mL CH4 gVS^{-1} for cheese waste activated sludge). The commercial waste samples exhibited a much higher degree of biodegradability and volatile solids reduction than the household waste samples. In particular the household waste streams which consisted of mostly garden waste had a much lower biodegradability index than waste streams without garden waste. The BMP result for the cheese waste was much lower than expected. In a previous study by the authors [6] a sample of cheese processing treatment sludge from a different location yielded 461 L CH_4 kg VS^{-1}. This demonstrates that the type of existing biological waste treatment processes at dairy plants can produce waste sludge with hugely different biomethane potential. A one way Anova analysis suggests a statistical difference between the mean biomethane potential results depending on the source of OFMSW ($F_{7,16}$ = 332.6, $P < 0.01$.Where there are 7 degrees of freedom between samples and 16 degrees of freedom within samples. Multiple comparisons using the Tuckey test ($MSD_{0.05}$ = 34.4 mL gVS^{-1}, $P < 0.05$) revealed that there is a significant difference in biomethane potential between almost 90% of the waste samples depending on source, however there were some notable exceptions. In the household waste stream there was no significant difference between urban and rural samples that came from a similar collection system ($P > 0.05$). However there was a significant difference in methane potential depending whether garden waste was included or not. For example samples without garden waste gave higher methane yields than samples which consisted mostly of garden waste. Canteen waste samples gave significantly higher BMP yields than from household waste streams. However there was a significant difference between canteen waste samples depending on the season. Samples taken from the same waste collection run in summer (June 2012) gave 9% higher BMP yields than winter (December 2012). In the food processing stream bakery waste samples gave vastly greater methane yields (529 mL CH4 gVS^{-1}) than from cheese

waste activated sludge (188.5 mL CH4 gVS^{-1}). Interestingly the bakery waste sample did not differ significantly from the canteen waste (CCS). The results from the commercial waste samples are similar to previously reported BMP yields from canteen food waste (480-530 L CH_4 $kgVS^{-1}$) [13].

Table 8.2 Spectrum of food waste – samples collected

Source	BMP (30 days) (ml CH_4 g VS^{-1})	Theoretical BMP Buswell equation	Biodegradability Index	Volatile solids destruction as measured (% VS)
Rural with garden (RWG)	274.1 (4.6)	577	0.48	47
Rural no garden (RNG)	367.8 (6.2)	566	0.65	69
Urban with garden (UWG)	296.7 (6.1)	625	0.47	51
Urban no garden (UNG)	343.7 (2.7)	564	0.61	60
Commercial canteen summer (CCS)	534.5 (5.0)	620	0.86	81
Commercial canteen winter (CCW)	490.9 (4.8)	620	0.79	80
Food processing bakery waste (FPBW)	529.2 (25.4)	696	0.76	81
Food processing cheese waste (FPCW)	188.5 (1.2)	530	0.36	42

8.3.2 Kinetic study results

The results of the kinetics analysis using the first order kinetic model and the modified Gompertz model are summarised in Table 8.3 (a) and (b) respectively. The first order kinetic model gave k values ranging from 0.12 – 0.17 day^{-1} for household samples, 0.07 - 0.09 day^{-1} for commercial samples and 0.08 - 0.13 day^{-1} for food

processing samples. The commercial food waste samples had higher percentages of proteins and lipids which take longer to digest than carbohydrates therefore resulting in lower k values [14]. The modified Gompertz model showed a lag time of 1.2 and 3 days for all samples tested. The time taken to reach 90% of the maximum BMP value was shown to range from 9 – 15 days indicating that all OFMSW substrates were readily degradable. Both models exhibited a good fit when plotted against the measured data with the coefficient of determination (R^2) ranging from 0.93 -0.95 for the first order model and 0.99 for the Gompertz model. The RMSE ranged from 10.7 – 48.8 mL CH_4 gVS^{-1} for the first order model while the Gompertz model gave lower values of over 0.7 – 9.9 mL CH_4 gVS^{-1}. Both models can be used to predict the maximum methane potential. The modified Gompertz model gave slightly lower predicted maximum BMP yields than the measured data ranging from -0.8 to -9.3% while the first order model generally gave higher predicted methane yields than measured ranging from -1.8 to +19.2%. In 87.5% of cases the model Gompertz gave a more accurate predicted max biomethane yield than the first order equation. Based on the statistical indicators (RMSE and R^2) the modified Gompertz model was found to demonstrate the best fit for the samples tested. The cumulative methane yields of the BMP tests are shown in Figure 8.3. The first order kinetic model fits are shown in dashed curves while the modified Gompertz model fits are shown in unbroken curves.

Table 8.3 (a) Results of BMP kinetic analysis using the first order kinetic equation

Sample	BMP measured (mL CH_4 gVS^{-1})	BMP predicted (mL CH_4 gVS^{-1})	Difference (%)	RMSE (mL CH_4 gVS^{-1})	R^2	k (day^{-1})
Household waste						
RWG	274.1 (4.6)	292	+ 6.5	21.6	0.93	0.12
RNG	367.8 (6.2)	388	+ 5.5	28.7	0.93	0.14
UWG	296.7 (6.1)	302	+ 1.8	18.0	0.95	0.17
UNG	343.7 (2.7)	369	+ 7.4	27.2	0.93	0.12
Commercial waste						
CCS	534.5 (5.0)	603	+12.8	40.2	0.94	0.09
CCW	490.9 (4.8)	585	+ 19.2	36.7	0.95	0.07
Food processing waste						
FPBW	529.2 (25.4)	623	+ 17.7	48.8	0.92	0.08
FPCW	188.5 (1.2)	185	- 1.8	10.7	0.95	0.13

Table 8.3(b) Results of BMP kinetic analysis using the modified Gompertz equation

Sample	BMP measured (mL CH_4 gVS^{-1})	BMP predicted (mL CH_4 gVS^{-1})	Difference (%)	R^2	RMSE (mL CH_4 gVS^{-1})	Lag phase (days)	T_{90} (days)
Household waste							
RWG	274.1 (4.6)	268	- 2.2	0.99	2.9	2.2	11
RNG	367.8 (6.2)	363	- 1.3	0.99	4.1	2.0	10.2
UWG	296.7 (6.1)	288	- 2.9	0.99	0.8	1.3	8.7
UNG	343.7 (2.7)	338	- 1.7	0.99	3.3	2.2	11.3
Commercial waste							
CCS	534.5 (5.0)	530	- 0.8	0.99	3.4	2.3	13.4
CCW	490.9 (4.8)	484	- 1.4	0.99	0.7	2.5	15.3
Food processing waste							
FPBW	529.2 (25.4)	528	- 0.2	0.99	9.9	3.0	14.3
FPCW	188.5 (1.2)	171	- 9.3	0.97	0.7	1.2	10.8

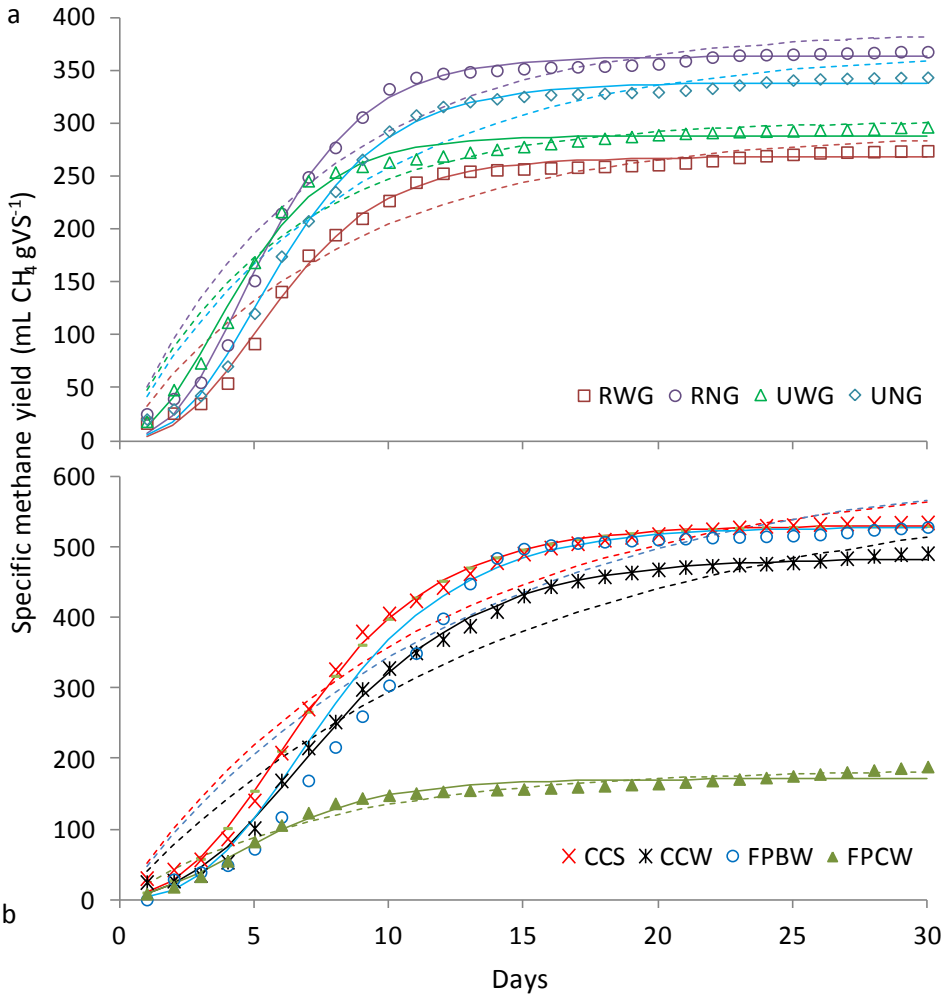


Figure 8.3 BMP cumulative methane yields for **(a)** household samples and **(b)** commercial & processing samples

8.4 Results from semi continuous trial

8.4.1 Specific methane yields in period 1

The semi continuous trial was operated for 176 days using commercial canteen food waste from the same collection as sample CCS in the BMP trials. This waste stream was chosen as a substrate for the semi-continuous trial because the same material had been used in separate AD trials conducted by the authors [15]. The semi-continuous system was started at a moderate organic loading rate (OLR) of 2 kg VS m^{-3} day^{-1}. The hydraulic retention time (HRT) was initially set at 30 days. This was achieved by adding a portion of digestate back in with the input feed keeping the total solids content of the input feed to 10% which facilitated easy stirring of digester

contents. The reactor was maintained at this OLR for 3 HRTs (period 1). The first HRT incorporated the start up and acclimatisation period. By the end of the first HRT the system had reached a steady state of methane production. Methane yields from the second and third HRT were used to calculate average specific methane yield for period 1 (OLR of 2 kg VS m^{-3} day^{-1}) which was 560.1 ± 29.3 mL CH_4 g VS^{-1} added. The standard deviation in the second and third HRT was only 5% of the total yield and clearly showed that the reactor was in steady state. The weekly average specific methane yield is shown in Figure 8.4 (a). The daily percentage methane in the biogas is shown in Figure 8.4(b). In the start-up period the percentage methane increased from 40.4% to 60% over the first 30 days with the weighted average methane percentage in the biogas remaining at 60 ± 1.3 % for period 1.

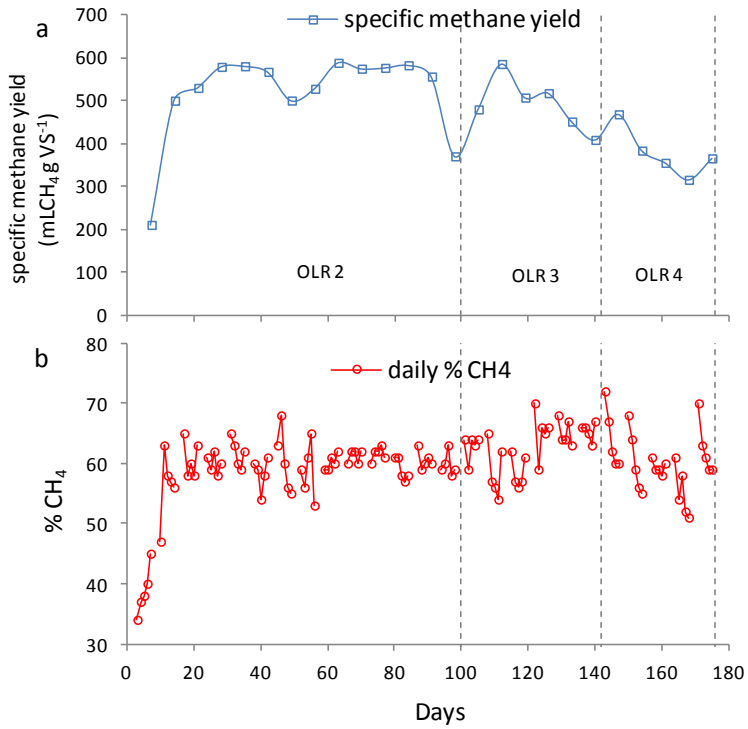


Figure 8.4 (a) Weekly average specific methane yield and **(b)** daily methane percentage

8.4.2 Specific methane yields in period 2

After completing 3 HRTs at the initial feeding rate, the OLR was increased to 3 kg VS m^{-3} day^{-1} at day 99. By increasing the OLR to 3 the HRT was reduced to 21 days as the solids content of the input material was kept at 10% TS by recirculation of an

increased amount of digestate. The OLR was maintained at 3 kg VS m^{-3} day^{-1} for 2 HRTs (42 days). The average SMY for period 2 was 484 ± 72.0 mL CH_4 g VS^{-1}. This is a reduction of about 13% from the previous SMY in period 1. The standard deviation in period 2 is approximately 15% of the average SMY and shows that there was greater fluctuation in daily gas production at the higher OLR of 3 kg VS m^{-3} day^{-1}. The weighted average methane content in the biogas increased to 61.5 ± 2.8 % in period 2.

8.4.3 Specific methane yields in period 3

On day 142 the OLR was further increased to 4 kg VS m^{-3} day^{-1} which resulted in a reduced HRT of 17 days. The trial was completed on day 176. The average SMY in the final period was 381.5 ± 52.0 mL CH_4 g VS^{-1} which was a 21% decrease in SMY from period 2 and a 32% decrease from period 1. The average methane content was 60.7±3.6%.

8.4.4 Conversion of volatile solids to gas

To assess the conversion of VS to gas the following equation 8.5 taken from [16] is used:

$$M_R = L_N \cdot ((16 \cdot CH_4\%) + (44 \cdot CO_2\%))/22.413 \quad (8.5)$$

Where;

MR is the daily average mass of volatile solids removed (g VS); L_N is the average daily normalised biogas volume (L) at standard temperature and pressure (STP); CH_4 % is the methane content in the biogas; CO_2 is the carbon dioxide content in the biogas; There are 22.413 L per mole of gas at STP. According to this equation the average removal of VS in period 1 was 84% with a HRT of 30 days. This decreased to 72% in period 2 with a HRT of 21 days and further reduced to 54% in period 3 with a HRT of 17 days. The average concentration of total solids in the digestate increased from 5.1 ± 0.5 % TS in period 1 to 5.5 ± 0.3 % TS in period 2 and 6.7 ± 0.9 % TS in the final period. This indicates that reducing the HRT also reduces the degradation of volatile solids. However the large drop in specific methane yield

towards the end of the trial may not be entirely as a result of the reduced HRT as signs of process instability emerged towards the end of the trial at an OLR of 4 kg VS m^{-3} day^{-1}.

8.4.5 Monitoring process stability in semi-continuous trial

During the semi-continuous trial the total volatile fatty acids (VFA), total alkalinity (TA), pH and total ammonia nitrogen (TAN) were monitored to assess the stability of the digestion process. The average results from the three time periods are shown in Table 8.4. In Period 1 (OLR 2 kgVS m^{-3} day^{-1}) the concentration of total VFAs was 1128 ± 281 mg Ac_{eq} L^{-1}. A small increase was observed during Period 2 (OLR of 3 kgVS m^{-3} day^{-1}) with an average of 1511 ± 77 mg Ac_{eq} L^{-1}. The concentration of VFAs rose sharply towards the end of the trial during Period 3 (OLR of 4 kgVS m^{-3} day^{-1}) as shown in Figure 8.5 (a), with an average of 2595 ± 750 mg Ac_{eq} L^{-1}. The sharp increase in VFA concentration indicated that the biological system was stressed.

Table 8.4 Summary of results from semi-continuous AD trial of canteen food waste

Period	**1**	**2**	**3**
OLR (kg VS m^{-3} day^{-1})	2	3	4
HRT (days)	30 x 3	21 x 2	17 x 2
SYM (mL CH4 g VS^{-1})	560.1 (29.3)	483.9 (72.0)	381.5 (52.0)
% CH4 (Weighted Average)	60.1 (1.3)	61.5 (2.8)	60 (3.6)
% VS conversion to gas	84	72	54
% TS (digestate)	5.1 (0.5)	5.5 (0.3)	6.7 (0.9)
% VS (digestate)	3.5 (0.3)	3.9 (0.2)	4.7 (0.7)
pH	7.7 (0.13)	7.9 (0.14)	8.1 (0.11)
TAN (mg L^{-1})	3543 (525)	5342 (485)	7205 (280)
NH_3 (mg L^{-1})	237 (50)	433 (185)	952 (75)
VFAs (mg HAc_{eq} L^{-1})	1128 (281)	1511 (77)	2595 (750)
Alkalinity (mg $CaCO_3$ L^{-1})	8093 (970)	9830 (159)	10230 (185)
VFA/TA	0.14	0.15	0.25

Results are indicated as a mean with standard deviation is in brackets

The average total alkalinity for the period 1 was 8093 ± 970 mg $CaCO_3$ L^{-1}. This increased to 9839 ± 159 mg $CaCO_3$ L^{-1} in period 2 and 10230 ± 185 mg $CaCO_3$ L^{-1} in period 3. The ratio of TVFA/TA is often used to assess the stability of the AD process. A ratio of 0.4 or less indicates that the process is stable while ratios over 0.8 indicate organic overloading and process instability. During the trial the VFA/TA ratio remained below 0.4, however it is clear that even though the ratio was within stable limits, high concentrations of total ammonia nitrogen (TAN) coupled with a large decrease in SMY towards the end of the trial indicate that a state of semi-inhibited methanogenesis had been reached.

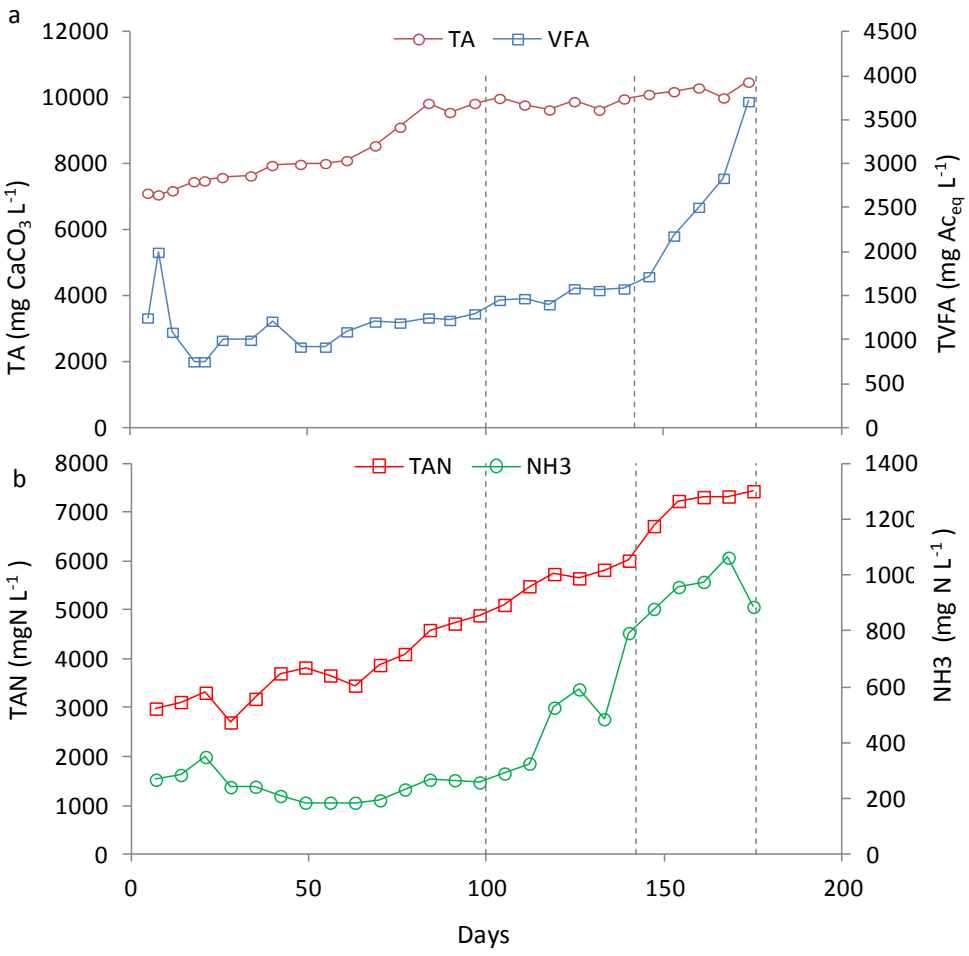


Figure 8.5 (a) Monitoring of total alkalinity (TA) and total volatile fatty acids (TVFA) **(b)** total ammonia nitrogen (TAN) and free ammonia (NH_3) in the semi-continuous trial

8.4.6 The inhibitory effects of high ammonia concentrations

There is a linear relationship between decreased specific methane yield and increasing concentrations of free ammonia in the liquid phase. Total ammonia

nitrogen (TAN) contributes to the buffering capacity of the system but can be toxic to methanogens at higher pH values. A rise in pH from 7 to 8 can result in a 10 fold increase in the concentration of free ammonia. During the trial the pH increased from an average of 7.7 ± 0.1 in period 1 to 8.1 ± 0.1 in the final period. The high pH is of concern when combined with high levels of TAN as the relationship between ionised ammonium (NH_4^+) and unionised (free) ammonia (NH_3) is pH and temperature dependent. The concentration of TAN increased linearly for the duration of the trial with final concentrations in excess of 7000 mg N L^{-1}, as shown in Figure 8.5(b). This is a very high concentration of TAN and would be considered to be well in the toxicity range for methane production [17]. It is well documented that high concentrations of free ammonia (NH_3) can cause inhibition to methane production, [18]. [19] reported that free ammonia concentrations above 1000 mg N L^{-1} are inhibitory for methanogenesis. Banks and colleagues (2012) reported high concentrations of total ammonia at high organic loading rates using source separated food waste. They showed that at elevated levels of total ammonia the acetoclatic methanogens were virtually nonexistent with the methane production coming from the hydrogenotrophic route. To overcome the inhibitory effects of high levels of ammonia the addition of trace elements such as iron, cobalt, selenium and molybdenum were successfully shown to improve methane yields at high organic loading rates (e.g. 5 kg VS m^{-3} day^{-1}) [20].

8.4.7 Comparison of methane yield from food waste

The specific methane yield (SMY) produced during period 1 of the semi continuous trial was relatively high in comparison to other reported methane yields from food waste. The highest average SMY of 560 ± 29.3 mL CH_4 gVS^{-1} was achieved at an OLR of 2 kg VS m^{-3} day^{-1} and HRT of 30 days. This is 90.3% of the Buswell Equation value. It is however 7% higher than the average BMP result from the same sample. This indicates that at moderate organic loading rates a continuous AD process may equal or even exceed methane yields from the BMP test. This may be due to acclimatisation of the inoculum with time. Other workers have recorded higher SMYs in continuous digestion than in BMP mode [21]. Zhang and colleagues (2012) achieved 425 L CH_4 kg VS^{-1} from continuous digestion of source segregated food waste at an OLR of 2 kg VS m^{-3} day^{-1}. The same material gave BMP results of

between 445-456 L CH_4 kg VS^{-1} [22]. Davidsson and colleagues (2007) reported methane yields of between 300-400 L CH_4 kg VS^{-1}_{added} for a large number of source sorted OFMSW samples which had all been through different pre-treatment processes [23]. Separate trials by the authors [15] on a two phase AD system involving sequentially fed leach beds connected to an upflow anaerobic sludge blanket, treating the same commercial food waste, produced 384 L CH_4 kg VS^{-1} which corresponded to 72% of the value obtained in the BMP test. This is approximately 70% of the highest average methane yield achieved in the semi continuous trial and suggests that a conventional CSTR may be the best reactor configuration for maximising methane yield from food waste.

8.5 Conclusions

The characteristics of OFMSW can vary largely depending on the source and type of collection with BMP values of between 274 - 535 mL CH_4 gVS^{-1}. A semi continuous trial on commercial food waste produced an average of 560 ± 29 mL CH_4 gVS^{-1} at a moderate OLR of 2 kg VS m^{-3} day^{-1} with a HRT of 30 days. At higher OLRs (4 kg VS m^{-3} day^{-1}) increasing concentrations of VFAs (2595 mg L^{-1}) coupled with high concentrations of free ammonia (952 mg L^{-1}) led to a greatly reduced average specific methane yield (344 mL CH_4 gVS^{-1}).

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9 Conclusions and recommendations

9.1 Conclusions of Thesis

The conclusions of the thesis are as follows:

- Compressed biomethane from OFMSW is potentially one of the cheapest renewable transport fuels available today with a production cost (including VAT) of €0.36 m^{-3} CH_4 assuming a modest gate fee of €70 per tonne of waste.
- The upper bound results of biochemical methane potential (BMP) tests on canteen food waste yielded relatively high methane potential of 467-529 L CH_4 kg VS^{-1}. It was found that higher BMP yields were achieved using inoculum sourced from a stable AD process which had been previously acclimatised to the substrate.
- If the quantity of OFMSW (ca. 530,000 tonnes) which is required to be diverted from landfill by 2016 under the terms of the EU Landfill Directive is used for biomethane production, the potential bioresource from OFMSW could meet 2.8% renewable energy in transport.
- The BMP test was found to be a very useful methodology for screening and assessing potential organic waste streams especially when investigating heterogeneous or case specific waste streams. Important kinetic parameters such as the predicted maximum methane yield, decay rate constant lag time and time taken to reach 90% of maximum BMP can be found using first order kinetic models on observed BMP data.
- In a real world case study abattoir, cheese processing and food waste were found to be the highest methane yielding organic waste streams available for a community scale AD facility.
- Increasing the portion of food waste in semi continuous co-digestion trials using these three substrates led to higher specific methane yields.
- A novel two phase AD system consisting of sequentially fed leach bed reactors connected with an upflow anaerobic sludge blanket showed excellent conversion of organic solids to chemical oxygen demand with up to 90% conversion of volatile solids. At low to medium organic loading rates the UASB performed well producing 72% of the BMP value (an average of 384 L

CH_4 kg VS^{-1}). However at higher volumetric organic loading rates the specific methane yields decreased.

- Further research is required to improve the efficiency in converting COD into methane at high organic loading rates in the SLBR-UASB system
- A single stage semi continuous trial using a conventional CSTR bioreactor on the same commercial food waste produced an average of 560 ± 29 L CH_4 kg VS^{-1} at a moderate organic loading rate of 2 kg VS m^{-3} day^{-1} and hydraulic retention time of 30 days. This was 5% higher than the average BMP value and over 30% higher than the best average specific methane yield from the SLBR UASB system. Lower specific methane yields were observed at higher organic loading rates and reduced hydraulic retention times.
- In both the continuous CSTR and SLBR-UASB trials the accumulation of ammonia in the system over time was linked to the inhibition of methanogenesis phase.
- The organic fraction of municipal solid waste has significant potential for biomethane production ranging from 75 -160 m^3 CH_4 per tonne of waste depending on source.
- In particular food waste from catering premises exhibited a very high specific methane yield ranging from 470-535 L CH_4 per kg volatile solids added.
- Domestic organic waste streams can contain significant portions of garden waste which can lead to lower specific methane yields 274-419 L CH_4 $kgVS^{-1}$.
- Agri-food processing waste streams such as abattoir waste and cheese processing waste also present significant biomethane potential but the methane yields are highly variable depending on the existing waste treatment processes such as forced aeration of liquid waste streams (BMP results from cheese processing waste varied between 190 to 460 L CH_4 $kgVS^{-1}$ depending on source).

9.2 Recommendations for further research

It has been demonstrated that food waste can yield very high specific methane yields can be generated at moderate organic loading rates and long hydraulic retention times. However further research is required to maintain high methane yields at high organic loading rates and shorter retention times.
As food waste has a lower than optimal carbon to nitrogen ratio high concentrations of ammonia may build up in the reactor over time inhibiting methane production. A method for controlling or removing the ammonia from the process would be advantageous. Ammonia nitrogen has a market value as a fertiliser and may add value to the process.

The SLBR-UASB has great potential to be up scaled as novel high solids two phase AD system. The low energy input requirements of the system and the separation of solid and liquid phases are two key advantages over conventional AD systems. However more research is needed to improve the efficiency of converting COD in the liquid phase to methane and reduce losses in the system. The constant recirculation of effluent from the UASB back to the LBRs leads to an increase in the pH above optimal levels for hydrolysis and acidification (> pH 8). In long term operation this may result in the full system becoming like a second stage methane reactor. The high pH also increases the portion of free ammonia which is temperature and pH dependant and more toxic to methanogenic archaea.

The following trials should be carried out to improve specific methane yields:

- Control the pH in the leachate beds (pH 5.5 -6.5) and the UASB (7-7.5). This may lead to increased degradation and acidification of solid material and prevent methane losses in the leach beds. It may also benefit the methanogenis phase by reducing the concentration of free ammonia in the UASB between 7 and 7.5
- Other studies have shown that food waste is deficient in micro nutrients such as selenium, molybdenum and cobalt. Addition of these trace elements may improve the specific methane yields at high organic loading rates and should be tried on the SLBR-UASB system.

- The periodical replacement of a portion of leachate with fresh water has been previously shown to improve solubilisation of COD. This may also be an effective way to limit the pH from increasing above the optimum range in the leach beds and may also help regulate the concentration of inhibitory substances such as ammonia.
- Improving the structure of the leach bed by adding a well defined structural co-substrate such as wood chip, cardboard or a mature stage lignified grass may improve leachate distribution throughout the material and also increase the carbon to nitrogen ration of the feedstock therefore reducing the concentration of ammonia nitrogen in the liquid phase
- There is scope for collaboration with micro biologists on tracking the dynamics of the microbial community structures in the bioreactor over time and under increasing organic loading. By indentifying the key microbial communities, bio-catalytic pathways and optimum community structures may be enhanced leading to higher process efficiency particularly at higher organic loading rates.

Appendix A: Evaluation of the biomethane yield from anaerobic co-digestion of nitrogenous substrates

Evaluation of the biomethane yield from anaerobic co-digestion of nitrogenous substrates

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Abstract

This paper examines three substrates for anaerobic co-digestion (AcoD): abattoir waste; cheese waste and food waste. These substrates were assessed in detail for suitability for biomethane production. Biomethane potential (BMP) assays were carried out in mono and co-digestion for the three substrates and two mixes: T1 (40% abattoir waste; 50% cheese waste; 10% food waste on a wet weight (w/w) basis) and T2 (30% abattoir waste; 40% cheese waste; 30% food waste). The C:N ratio of both mixes was below optimum. Low levels suggest that the production of free ammonia (NH_3) in semi-continuous digestion was of primary concern. Both mixes were digested in a semi-continuous process for 25 weeks. The recommended operating condition for T1 was a loading rate of 3 kg $VSm_n^{-3}day^{-1}$ at a retention time of 23 days. The biomethane yield was 305 $LCH_4\,kg^{-1}$ VS which was 87% of the BMP value and 61% biodegradability. For T2 (with the higher C:N ratio) a higher loading rate of 4 kg VS $m_n^{-3}day^{-1}$ at a lower retention time of 15 days was recommended. The biomethane yield was 439 $LCH_4\ kg^{-1}$ VS (99% of the BMP value and 84% biodegradability). At these conditions levels of Total Ammonia Nitrogen (TAN) were 4109 and 4831 mg L^{-1} for T1 and T2 respectively. These values are on the large side according to the literature. The temperature was reduced to 35^{o}C to minimise toxicity associated with TAN. Ratios of volatile acids to total alkalinity were typically in the range 0.2 to 0.3 suggesting stable operation.

Keywords: biomethane; biogas; abattoir waste; food waste.

Introduction

Importance of biofuel production from residues

The EU Renewable Energy Directive [1] allows a double credit to biofuels produced from residues. In October 2012 the European Commission [2] published a proposal to limit food-based biofuels to 5% of renewable energy in transport. Biofuel production at present is very close to this level and as such the Commission is placing barriers to the development of further first generation liquid biofuel systems. Their objective is to stimulate second generation biofuels from non-food substrates such as wastes which do not interfere with food production. Greenhouse gas emissions from biofuels must effect a 60% reduction in greenhouse gas emissions on a whole life cycle basis as compared to the fossil fuel displaced [1, 2]. Typical values are given in The EU Renewable Energy Directive for biofuel systems, including for: 83% for compressed biomethane generated from residues; 32% for wheat ethanol and 45% for rapeseed biodiesel [1, 3]. This paper interrogates the optimum production of biomethane from residues available in a rural community and builds upon a paper by Browne and co-workers [4].

Outline of scenarios to be investigated

Browne and co-workers [4] examined the potential for biomethane production from a community from five substrates: abattoir waste; cheese waste; food waste; pig slurry and wastewater treatment sludge. They highlighted the requirement for detailed sampling of the various components of the substrates. For example abattoir waste had three components (paunch grass, green sludge and waste activated sludge). These three components yielded different specific biomethane production (L $CH_4 kg^{-1}$ VS) rates and were available in different quantities. Based on the analysis of fifteen BMP assays Browne and co-workers [4] suggested that pig slurry and wastewater treatment sludge should be omitted from this community digester if optimisation of gas production per unit substrate was required. Food waste was shown to have the highest yield per volume of substrate ($131 m_n^3$ CH_4 t^{-1}). This substrate is also beneficial as it generates a gate fee [5]. At present source segregation of food waste only allows for 1000 t a^{-1} of available substrate in this community. It is very possible with new legislation that 5000 t a^{-1} will be available in the short term. Thus two trials will be investigated as outline in Table A1.

Table A1 Individual substrates, proposed mixes and BMP results

	C:N ratio	**TS (%)**	**VS (%)**	**C (%)**	**H (%)**	**N (%)**	**BMP mono-digestion L CH_4 kg^{-1} VS**	**Trial T1 proportion of mix**		**Trial T2 proportion of mix**	
								ww basis (%)	VS basis (%)	ww basis (%)	VS basis (%)
Abattoir	13.6	12	10.6	47.2	5.8	3.4	239	40	42	30	24
Cheese factory	14.8	8.3	6.9	48.5	8.0	3.3	515	50	34	40	21
Food waste	15	28	24.5	48.8	7.3	3.3	535	10	24	30	55
C:N ratio								14.3		14.6	
TS (%)								11.7		15.3	
VS (%)								10.1		13.2	
BMP weighted mono-digestion								403		459	
BMP actual co-digestion								350 $\pm$ 12		443 $\pm$ 14	

Operational parameters of concern for semi-continuous digestion

A limitation with preliminary design of anaerobic digesters using the results of BMP assays is that little information is given on organic loading rate (OLR), hydraulic retention time (HRT) or parameters which indicate the stability of the process, such as: levels of total ammonia nitrogen (TAN); and the ratio of volatile fatty acids (VFAs) to alkalinity. A low carbon to nitrogen (C:N) ratio is an indication of a nitrogen rich substrate and the potential for significant ammonia production within the digester when digested. The un-dissociated form of ammonia nitrogen, NH_3 is the toxic component. The concentration of NH_3 is temperature and pH dependent. Inhibition starts somewhere between 1500 to 3000 mg TAN, but higher concentrations (up to 8500 mg L^{-1}) can be tolerated [6] but often with a reduction in biomethane production. It is important to monitor the ratio of VFAs to alkalinity. Typically a ratio greater than 0.3 indicates that the process is beginning to become unstable and levels at 0.8 suggest that the process is in failure [7]. In this paper the ratio of volatile fatty acids (VFAs) measured in mgHAceq L^{-1} (which is equivalent to the measurement of acetic acid), to alkalinity measured in mg $CaCO_3$ L^{-1} was also assessed.

Literature on digestion of food waste

Food waste is not a homogenous substrate and its composition varies from place to place. It also depends on whether the food waste has been source segregated or is from a co-mingled source, separated at a materials recovery facility. The organic fraction of municipal solid waste (OFMSW) is another source of food waste which includes for more refractory material (paper, cardboard and textiles) and potentially is a poorer source of biomethane [5]. Data on biomethane production from source segregated food waste found in the literature include: 401 – 489 LCH_4 kg^{-1} VS [8], 455 L CH_4 kg^{-1} VS [9] and 467 – 529 L CH_4 kg^{-1} VS [5].

Lower values are encountered for mechanically separated organic fraction of municipal solid waste. Cecchi et al. (2003) quote values of 158 to 397 L CH_4 kg^{-1} VS [8] while Davidsson et al. (2007) quote values of 300 – 400 L CH_4 kg^{-1} VS [10].

Literature on digestion of abattoir waste

Banks et al. (2011) highlighted the high level of nitrogen (and the corresponding low C:N ratio) in kitchen waste leading to high levels of ammonia in the digester which may be responsible for accumulation of volatile fatty acids [11]. For similar reasons anaerobic digestion of slaughterhouse waste may be problematic. A digester in Austria [12] digested floatation fat, pig blood, hind gut of pig and bovine rumen content. TAN levels of between 4500 and 7500 mg L^{-1} are documented; at the higher levels, gas production decreased. NH_3 which is temperature dependent is the toxic form of ammonia nitrogen; at lower temperatures, less NH_3 is produced [7]. The slaughterhouse waste digester in Austria maintained the temperature of the digester at or below 35^oC to minimise production of NH_3 and maximise production of bio methane [7]. Edstrom et al., (2003) document the problems in mono-digestion of slaughter wastes (stomach and intestinal content, animal low risk excluding blood and blood) [13]. Again the primary issue is the significant production of TAN, accumulation of VFAs and limiting methane production. To successfully operate a pilot scale facility they co-digested the slaughter waste with food waste and eventually operated at 3 kg VS m_n^{-3} d^{-1}. Ammonia nitrogen levels were of the order of 4500 mg L^{-1}. The biomethane yield was 560 mn^3 CH_4 kg^{-1} VS with a methane concentration of 70% [13].

Literature on digestion of cheese waste

Waste from cheese production is also a high nitrogen content substrate, typically with a C:N ratio below 15 [4, 14]. In a trial experiment to establish an optimum loading rate for cheese waste Jihen et al., (2010) added biological waste from a dairy farm in order to increase the C:N ratio. This resulted in both higher levels of biodegradability and increased methane content [14]. To overcome high ammonia levels, Comino et al., (2012) reduced the operating temperature to 35^oC in co-digesting cheese waste and cattle slurry (1:1 mix). Biomethane yields of 343 L CH_4 kg^{-1} VS were obtained [15].

Inhibition associated with TAN

Ammonia (NH_3) is a compound that can be present in both gaseous and soluble form.

$NH_3(aq) + H_2O(l) \Rightarrow NH_4^+(aq) + OH^-(aq)$

Gerardi (2003) reported on the relationship of ammonia in an anaerobic digester as follows [16]: Ammonia is released through the degradation of amino acids and proteins and comes in the form of either ammonium ions (ionized ammonia NH_4^+) or dissolved ammonia gas (free ammonia NH_3). The release of ammonia increases the digester alkalinity which is an important buffering step in the digestion process. However, at certain concentrations ammonia can become toxic to methanogens and may result in digester failure. The dissolved ammonia gas (free ammonia NH_3) is the more toxic component specifically to acetoclastic methanogens. Ammonium ions (NH_4^+) are less toxic and are used by the bacteria as a nutrient source for nitrogen. Both free ammonia (NH_3) and ammonium ions (NH_4^+) are reduced forms of nitrogen. The two forms are in equilibrium as the conversion of free ammonia to ammonium ions is pH dependent. A higher pH results in the production of free ammonia (NH_3), while lower pH results in the production of ammonium ions (NH_4^+). Dropping the pH in a reactor can convert much of the free ammonia to the less harmful ammonium ions. Deublein and Steinhauser (2008) similarly stated that the equilibrium relationship is also temperature dependent and that a rise in temperature will shift the equilibrium in favour of free ammonia (NH_3), thereby increasing the chances of inhibition [17]. Dropping the temperature by a few degrees celsius can improve reactor stability. Banks and Heaven (2012) described an equation relating production of free ammonia to the pH and temperature [18]:

$$\frac{\text{Free NH}_3}{\text{Total NH}_3} = \left(1 + \frac{10^{-\text{pH}}}{10^{-\left(0.09018 + \frac{2729.92}{T(\text{K})}\right)}}\right)^{-1}$$

The term TAN will be used in this paper.

Aims and Objectives of paper

An ambition of this paper is to evaluate the relevance, and highlight the limitation of the BMP assay as a method for undertaking design of a community digester facility.

To facilitate this ambition, semi-continuous digestion was undertaken of two mixes of substrates (with different C:N ratios as outlined in Table A1) over 175 days. The objectives of the paper are to:

- Compare the BMP assays of these substrates in mono-digestion and AcoD;
- Assess the ideal operational parameters (OLR and HRT) for the two mixes (Table A1) in semi-continuous digestion;
- Assess the performance of the reactors at these operational conditions, in particular specific methane yields (L CH_4 kg^{-1} VS), ratio of VFA/ total alkalinity and levels of TAN mg/l;
- Compare the biomethane yield to that obtained using BMP assays.

Materials and Methods

Materials

The three substrates were sourced in significant quantities to allow representative samples to be taken and to allow for 25 weeks of laboratory assessment. The samples were macerated to a particle size of less than 2mm and placed in a freezer set at -20^{o}C. The samples were previously described in Browne et al., (2013) and summarised below [4]:

Abattoir Waste: Slaughter wastes containing 53% grass-like paunch; 32% dewatered activated sludge (DAS) and 15% green sludge.

Cheese Waste: Liquid sludge which includes 83% biologically treated effluent and 17% dissolved air floatation (DAF) sludge.

Food waste: Source segregated domestic and commercial waste. Present levels of 1,000 t a^{-1} are expected to rise to 5,000 t a^{-1} over the next four years.

Of issue with the substrates is the low C:N ratio (Table A1). Ideally the C:N ratio of the substrates in an anaerobic process should be in the range of 20:1 to 30:1 [7]. The levels here (14.3:1 for Trial 1 and 14.6:1 for Trial 2) suggest excess nitrogen and as such elevated levels of TAN in mg/l [6, 11].

Biomethane Potential Assays

BMP assays are in essence a batch digestion process. Inoculum at a ratio of 2:1 or greater to feedstock on a volatile solids (VS) basis is recommended in laboratory

BMP trials [19]. This reduces the chances of process inhibition from excess VFAs or ammonia. The same process was used here as in Browne et al., (2013) using the automatic methane potential test system (AMPTS) developed by Bioprocess™ [4]. All assays were carried out in triplicate. The assays were run until biogas production was minimal (less than 5ml day^{-1}). Glass bottles with a working volume of 400ml mixed by electric stirrers are maintained at a constant temperature. Carbon dioxide is removed from the biogas by passing through a solution of 3N sodium hydroxide. Individual gas tippers automatically count and record biomethane flow.
BMP assays were preformed on both the individual substrates (mono-digestion) and the mix of the substrates (co-digestion). BMP assays were also carried out on the digestate removed from the semi-continuous reactors at the end of the process to quantify the biomethane potential remaining in the digestate.

Semi-continuous Digestion Trials

Semi-continuous trials were carried out in two parallel continuously stirred tank reactors (CSTR). The reactors were referred to as T1 (Tank 1 used for Trial 1 mix) and T2 (Tank 2 used for Trial 2 mix). The trials ran for a period of 25 and 24 weeks respectively. The reactors were initially maintained at 37 $\pm$ 1 ^{o}C and continuously stirred at a rate of 100rpm. The temperature was reduced to 35 $\pm$ 1 ^{o}C at the start of week 13, when the OLR increased to 3 kg VS m_n^{-3} d^{-1}. The reactors were constructed out of thick walled plastic with a vertically mounted stirring mechanism. The tank volumes were 5L with a working volume of 4L. Each reactor was placed inside a coiled copper pipe frame which was heated by a thermo-circulator; an insulated cover was placed over the system to reduce heat loss (Figure A1).

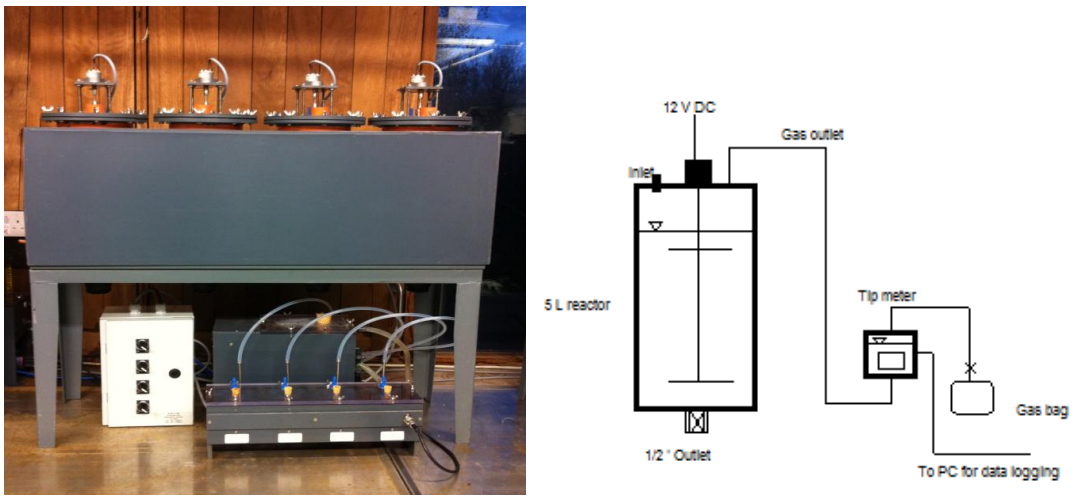


Figure A1 Semi-continuous AD digestion system consisting of 5 L reactors and tipping bucket measuring device

Inoculum, start-up, feeding and operation

Inoculum for both the BMP assays and the semi-continuous trials were sourced from a working reactor which co-digested dairy and poultry manure and food waste. For the semi-continuous trials the inoculum was placed in the reactors two weeks before the start of the trial; this was done to de-gas, and digest any residual volatile solids in the inoculum. An organic loading rate (OLR) of 2 kg VS $m_n^{-3}d^{-1}$ was chosen as a start up feeding rate. The substrate was macerated and weighed and placed in 100ml containers for each of the two systems. An ultimate analysis (percentage Carbon, Hydrogen, Oxygen) and a proximate analysis (total solids, volatile solids and ash content) were carried out for both mixes in the containers to insure minimal variations. Each reactor was fed 5 days a week (not on Saturdays or Sundays).
In order to reduce hydraulic retention time (HRT) and to minimise stress on the stirring mechanism, the substrates were reduced to a maximum of 10% total solid (TS) content. This was achieved by recirculation of liquor digestate from the reactor output to the inlet. The organic loading rate was determined by analysing the volatile solids in all substrates. The two mixes (Table A1) were based on a wet weight basis. To determine accurate destruction rates and maintain a constant liquor level in both tank reactors a mass balance was conducted including for biomethane yields; this allowed calculation of the amounts of digestate to be removed daily from both T1 and T2 (Table A2).

Table A2 Mass balance of T1 at organic loading rate of 2 kg VS $m^{-3}.day^{-1}$

Mix T1 (40% Abattoir Waste, 50% Cheese Waste and 10% Food Waste on a ww basis)
11.7% TS and 10.1% VS
Feeding and recirculation
Organic Loading Rate 2 kg VS $m_n^{-3}d^{-1}$ * 4L effective volume = 8g VS d^{-1}
8g VS d^{-1} at 10.1% VS = 79 g ww d^{-1}
Expect 90% destruction of volatiles; 7.2 g VS converted to methane d^{-1}
79 g ww d^{-1} added with destruction of 7.2 g d^{-1} implies addition of 71.8 g d^{-1}
To keep liquor level constant remove 71.8g of digestate d^{-1}
DS of liquor is 6%:
79g ww T1 mix at 11.7% TS plus 34g liquor at 6% TS = 113 g ww at 10% DS
Hydraulic Retention Time
4000 L of effective volume equates to ca. 4000g of mass
HRT including recirculation is 4000 g/113g d^{-1} = 35 days
HRT excluding recirculation is 4000 g/79g d^{-1}= 51 days

Gas measurement in semi-continuous trials

The cumulative gas yield for the full week was recorded and divided by the grams of volatile solids (VS) fed over the week (5 days of feeding). Biogas was collected in Tedlar gas bags and analysed for composition (percentage CH_4, CO_2 and H_2S in ppm). The measuring system used incorporated gas tipping buckets. A set volume of gas (ca. 78ml) causes the tipping mechanism to tip. The number of tips was recorded and translated into volume of biogas. Measurement of the percentage of methane in the biogas allowed calculation of biomethane production.

Analysis and parameter calculations

The following parameters were recorded:

- The composition of the biogas was measured on 2 hand held gas measuring devices which were checked with a standard solution of calibration gas each week for accuracy to $\pm$ 1% CH_4 (1171580) using a 35% CO_2 in CH_4 balance. Two infrared analysers were used: a Drager X-AM 7,000 and a Status Scientific Control ComBI-R Biogas analyser. All biogas and biomethane

yields were reported in L CH_4 kg^{-1} VS and adjusted for standard temperature at 273 K and pressure at 1013 mbar.

- The VFAs were measured in mg HAceq L^{-1}. Alkalinity was measured in mg$CaCo_3$ L^{-1}. The Nordmann titration method [20] was used to measure both the VFA and alkalinity, using a sample of 0.1 n Sulphuric acid using a Titronic Universal titrator.
- The ratio of volatile organic acids to alkalinity was measured using the FOS/TAC method as described by Weiland (2008) [21]. The titration is first carried out until a pH of 5.0 (bicarbonate alkalinity) and then until 4.4 (alkalinity caused by organic acids).
- Total solids and volatile solids were determined by APHA standards [22]. Samples were taken twice weekly.
- pH was measured daily on samples of digestate using a Jenway 3510 pH meter
- Total Ammonia Nitrogen was measured weekly using a Hach DR 3900 spectrophotometer (Hach test kit number CLK 303)

Results

BMP results

The three substrates underwent mono-digestion in BMP assays and AcoD in mixes with results as outlined in table A1. BMP based on actual AcoD varied from the calculated specific methane yield based on weighted mono-digestion. For mix T2 there was a slight reduction in yield (3.5%). In mix T1 there was a variance of 52 L CH_4 kg^{-1} VS or a 13% reduction in the BMP from AcoD as compared to the expected yield based on weighted mono-digestion.

Initial loading and retention time for semi-continuous trials

The two systems operated in parallel. They were initially run on a low OLR (2 kg VS $m^{-3}day^{-1}$) to allow a period of acclimatisation and ensure a healthy start up for the reactors. The TS content of the two mixes for T1 and T2 were 11.74 % and 15.31 %. Calculated quantities of liquor return were added to dilute the solids content of the feed to a level of ca. 10%. This had the added effect of reducing HRT from 51 days

to 35 days for reactor T1 and from 66 day to 31 days for T2. Table A2 outlines the loading regime for T1.

Results of semi-continuous trials at an OLR of 2 kg VS m^{-3} day^{-1}

For a period of 13 weeks both reactors were operated at a temperature of 37$\pm$ 1 ^{o}C and an OLR of 2 kg VS m_n^{-3} d^{-1} to allow for an adequate start up phase (equated to three HRTs). A summary of results is shown in Table A3 and Table A4. The maximum yield recorded for T1 (378 L CH_4 kg^{-1} VS) over the entire 25 week experimental period was recorded in the first retention time of the OLR of 2 VS m^{-3} day^{-1}. There was a decline in yields from the first HRT to the second HRT (Figure A2). The third HRT was a more stable period for biomethane production. The methane production ranged $\pm$ 22 L CH_4 kg^{-1} VS for HRT 3 as compared to $\pm$ 129, and $\pm$ 52 L CH_4 kg^{-1} VS for HRT 1 and HRT 2 respectively.

T2 did not produce any significant levels of biogas for the first two weeks of operation; biogas production in T2 started in week 3 (Figure A2 (a)). There was a similar trend for T2 as for T1 (Figure A2 (a)). A sharp rise in biomethane levels were recorded in the first retention period, followed by a decline to lower levels in the second HRT and a steady state in the third HRT as indicated by a smaller deviation in biomethane yields. The ratio of VFA/alkalinity in T1 and T2 was predominately below 0.2 only rising above this limit for 2 weeks out of a total of 13 weeks in the first reactor (Table A5). T2 had a higher VFA/ alkalinity ratio but was within the upper bound of stable limits, reaching 0.37 at its maximum. This suggests that steady state had been reached. Biomethane production values in Table A3 exclude the initial period of start up (the first three weeks). The methane content in the biogas (shown in Figure A2 (b); Table A4) indicates the time to stable operation is of the order of 5 weeks.

Table A3 Summary of results of biomethane yields for T1 and T2

Method	**T1 Specific methane yield (L CH_4 kg^{-1} VS)**	**T2 Specific methane yield (L CH_4 kg^{-1}VS)**
Theoretical maximum based on Buswell Equation		
	501	525
BMP		
Weighed based on mono-digestion	407	438
Co-digestion	350 $\pm$ 12	443 $\pm$ 14
Results from 25 weeks of continuous trials		
Average (25 weeks)	267	378
Average, after start up	312	413
OLR 2 kg VS m^{-3} day^{-1}		
HRT 1 after start up	266	189
HRT 2	267	366
HRT 3	281	398
Average after start up	280	380
OLR 3 VS m^{-3} day^{-1}		
HRT 1	267	386
HRT 2	334	440
Average	305	410
OLR 4kg VS m^{-3} day^{-1}		
HRT 1	291	469
HRT 2	290	420
Average	291	439

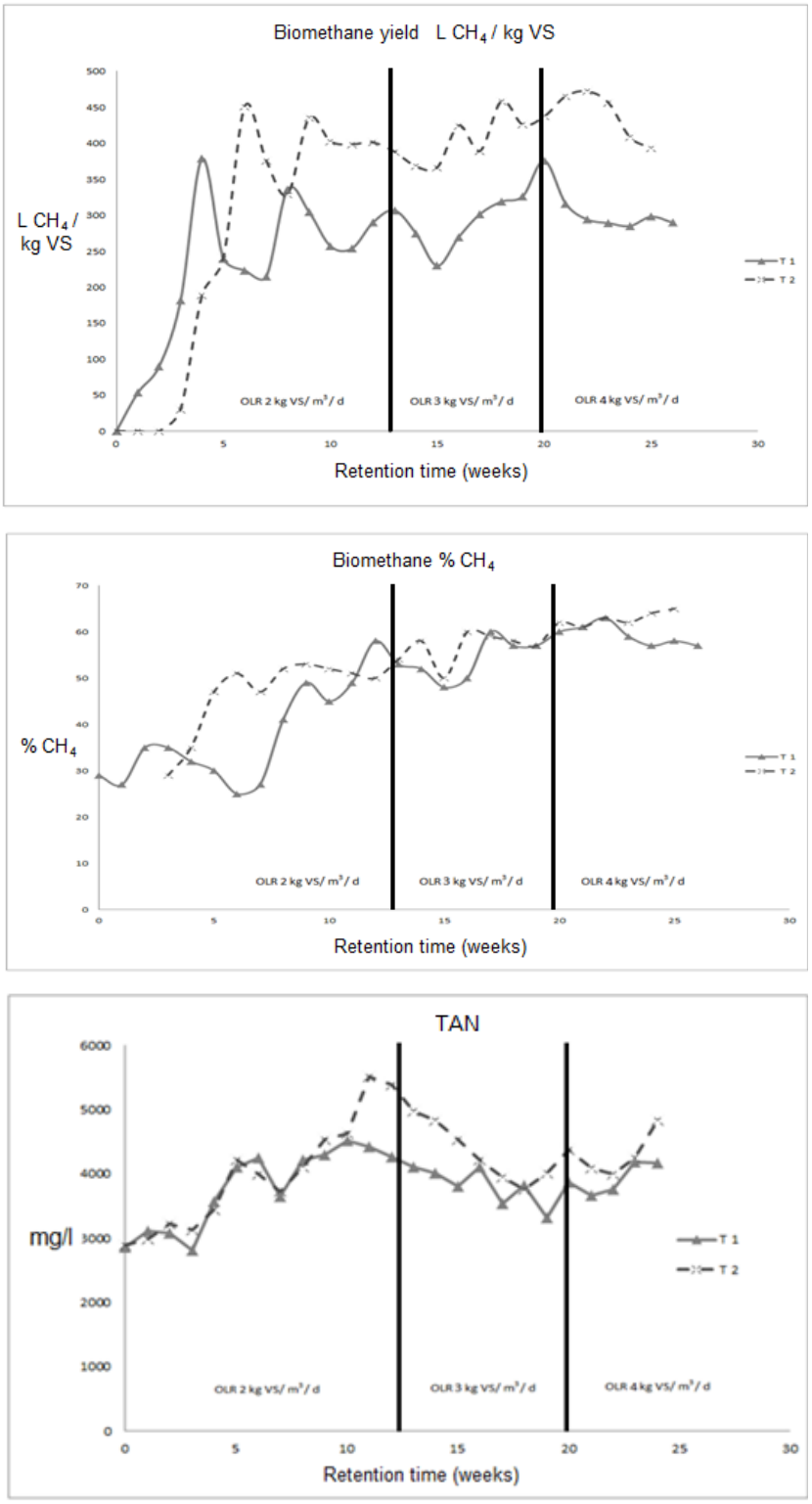


Figure A2 (a) Biomethane yield **(b)** Methane content and **(c)** TAN for T1 and T2.

Table A4 Summary of biomethane production efficiency in semi continuous trials

Reactor	**T1**			**T2**		
OLR (kg VS m_n^{-3} d^{-1})	2	3	4	2	3	4
Yield/ BMP	0.80	0.87	0.85	0.86	0.95	0.99
Biodegradability index	0.56	0.61	0.60	0.72	0.79	0.83
CH_4 %	63.11	63.45	66.93	63.48	64.07	66.85
Specific CH_4 yield (L CH_4 kg^{-1} VS)	279.7	305.3	291.0	380.0	409.8	439.0
Specific yield $m_n^3CH_4$ t^{-1}	28.3	30.9	29.44	50.46	54.42	58.30

Table A5 Summary of AD semi continuous process operation of T1 and T2

Reactor	**T1**			**T2**		
OLR (kg VS m_n^{-3} d^{-1})	2	3	4	2	3	4
HRT (ignore recirculation) d	51	34	25	66	44	33
HRT (with recirculation) d	35	23	17	31	20	15
Operating parameters						
TAN (mg L^{-1})	4518	4109	4187	5501	4834	4831
Free Ammonia (mg N L^{-1})	413	376	400	341	442	478
pH	7.63 ± .11	7.89 ± .09	8.00 ± .07	7.69 ± .16	7.91 ± .12	8.03 ± .09
VFA (mg HAceq L^{-1})	1205	653	1322	1687	1109	956
Alkalinity (mg CaCO3 L^{-1})	5239	3110	5508	4559	3824	4780
VFA/alkalinity	0.23	0.21	0.24	0.37	0.29	0.20

Results of semi-continuous trials at an OLR of 3 kg VS m^{-3} day^{-1}

The OLR was increased from 2 to 3 kg VS m^{-3} day^{-1} in both reactors and the temperature was dropped to 35± 1 ^oC to reduce the toxic effect of free ammonia. With return of liquors the HRT was calculated as 23 days and 20 days for T1 and T2 respectively (Table A5). An initial decrease in biomethane yields was recorded for both reactors, but this levelled out (Figure A2 a) and a more stable production of biomethane was observed. T1 yields for this organic loading rate averaged 305 L CH_4 kg^{-1} VS; this may be compared with an average of 280 L CH_4 kg^{-1} VS for the lower OLR. The average yield raised from 267 to 334 L CH_4 kg^{-1} VS from retention period 1 to 2 (Table A3). The ratio of VOA/ alkalinity averaged 0.21 for this period (Table A5) indicating a lack of stress on the system. The pH rose somewhat from 7.63 to 7.89 (Table A5). TAN levels (Figure A2 c) dropped off somewhat from 4518 (at an OLR of 2 kg VS m^{-3} day^{-1}) to 4109 mg/L (at 3 kg VS m^{-3} day^{-1}). This may be

explained by the drop in temperature from 37 to 35°C.Trends for T2 were similar to T1. Biomethane production averaged 410 L CH_4 kg^{-1} VS as compared to an average of 380 L CH_4 kg^{-1} VS for the lower OLR. The average yield raised from 386 to 440 L CH_4 kg^{-1} VS from retention period 1 to 2 (Table A3). VFA/ alkalinity averaged 0.29 for this period (Table A5) down from 0.37 from the previous loading rate. The pH rose from 7.69 to 7.91 (Table A5). TAN levels (Figure A2 c) dropped from 5501 (at an OLR of 2 kg VS m^{-3} day^{-1}) to 4834 mg/L (at 3 VS m^{-3} day^{-1}) again this can be attributed to the drop in temperature.

Results of semi-continuous trials at an OLR of 4 kg VS m^{-3} day^{-1}

Again the systems were operated for two retention times. Reactor T1 averaged 291 LCH_4 kg^{-1} VS which was a decline of 4.6% from the previous average production at the lower OLR (Table A3). The biomethane yield was quiet stable; variation in average yield between the first and second retention period was only $\pm$1 %. TAN was very similar to the lower OLR (4187 compared to 4109 mg L^{-1}). VFA/ alkalinity was low at 0.24 (up from 0.21). The pH increased to 8 which is considered high; ammonia is more toxic at higher pH [7]. The authors believe that the system had reached a steady state with slightly less biomethane production than at the lower OLR (3 kg VS m_n^{-3} d^{-1}). This would suggest that for T1 the optimum OLR lies somewhere between 3 and 4 kg VS m^{-3} day^{-1}.

Reactor T2 produced increased biomethane yields; from an average of 410 L CH_4 kg^{-1} VS at 3 kg VS m^{-3} day^{-1} to 439 L CH_4 kg^{-1} VS at 4 kg VS m^{-3} day^{-1} (an increase of 7.3%; Table A3). VFA/ alkalinity ration was 0.2. The TAN reached concentrations of 4831mg L^{-1} (Table A5). The pH was recorded in excess of 8 which is high and of issue when associated with high ammonia levels [7]. The biomethane level achieved is very similar to the BMP result. Using the weighted BMPs for the individual substrates a value of 459 L CH_4 kg^{-1} VS is calculated. The BMP of the substrate mix T2 was recorded at 443 L CH_4 kg^{-1} VS. The semi-continuous system has a specific methane yield very close to these values (Table A6). The result of the semi-continuous trial for an OLR of 4 kg VS m^{-3} day^{-1} is within 1% of the BMP of the mixture. The authors would suggest that 4 kg VS m_n^{-3} d^{-1} is very close to optimum performance at this feeding ratio. The retention time is low at 15 days including for recirculation.

Table A6 Summary of evaluation of methane yield from multiple waste streams

Parameters measured	**T1**	**T2**
Theoretical maximum based on Buswell Equation (L CH_4 kg^{-1} VS)	501	525
BMP weighted based on mono-digestion (L CH_4 kg^{-1} VS)	403	459
BMP co-digestion (L CH_4 kg^{-1} VS)	350 $\pm$ 12	443 $\pm$ 14
Recommended OLR (kg VS m^{-3} day^{-1})	3	4
Hydraulic Retention time without recirculation (days)	34	33
Hydraulic Retention time without recirculation (days)	23	15
Corresponding biomethane production (L CH_4 kg^{-1} VS)	305	439
Biomethane production as a ratio of BMP	0.87	0.99
Biodegradability index (based on Buswell Equation)	0.61	0.84
TAN (mg L^{-1})	4109	4831
VFA/Total Alkalinity	0.21	0.2
pH	7.89	8.03

Discussion of Results

Biodegradability of substrates and efficiency of AD process

Efficiency was estimated using two different metrics (shown in Table A4):

- Dividing the average biomethane yield produced in semi-continuous trials by the maximum theoretical yield derived from the Buswell equation [23]. This is known as the biodegradability index and is expressed as a ratio.
- Dividing the average biomethane yield produced in semi-continuous trials by the BMP yield recorded in BMP assays. Many authors report that the BMP is an upper limit of the specific biomethane yield and as such this value should not be greater than 1.

Reactor T1 had its highest rates of biomethane production (Table A4) at an OLR of 3 kg VS m^{-3} day^{-1}; (0.87 (ratio of BMP) and 0.61 (biodegradability index)).
Reactor T2 had the highest biomethane production (Table A4) at an OLR of 4 kg VS m^{-3} day^{-1}; (0.99 (ratio of BMP) and 0.83 (biodegradability index)).
The BMP is often considered the upper level of biomethane production but a number of researchers [24 – 26] have recorded methane yields from semi-continuous processes in excess of values obtained in BMP assays.
Table A4 outlines the specific yields of the 2 mixes for the different organic loading rates and also lists these values in yields per unit mass on a wet weight basis. For

example at an organic loading rate of 4 kg VS m_n^{-3} d^{-1} T1 yields 29 m_n^3 CH_4 t^{-1} as compared to 58 m_n^3 CH_4 t for T2. This is almost double the yield. This highlights the higher methane potential and dry solids content of food waste (535 L CH_4 kg^{-1} VS at 24.5% VS = 131m_n^3 t^{-1}) as compared to abattoir waste (239L CH_4 kg^{-1} VS at 10.6% VS = 25m_n^3 t^{-1}).

Total Ammonia Levels

TAN levels in both T1 and T2 were measured weekly (shown in Figure A2 c) and reached their highest level after 10 weeks in T1 and 11 weeks in T2 (4518 mg L^{-1} and 5501 mg L^{-1} respectively). These levels are considered high with respect to the scientific literature [6, 7]. Drosg et al., (2013) suggests inhibition can start at 3000 mg L^{-1}[6]. A slaughter waste digester in Austria [12] operated with TAN levels of between 4500 and 7500 mg L^{-1} and experienced reduced biomethane production at the higher levels. Initially (up to week 13) the temperature was set at 37^{o}C, but as ammonia levels began to rise the temperature was dropped to 35^{o}C and maintained at this level for the remainder of the experiment. The objective of this was to reduce the concentration of free ammonia (NH_3) (which is reported to be the more toxic form for methanogens) and maintain stability as recommended by Hansel et al.,(1999) [27].

The inoculum used in this experiment was taken from a commercial scale digester operating on poultry manure and food waste. This inoculum would be expected to have high levels of TAN even before feeding commenced. Levels of TAN in the inoculum before a period of de-gassing took place were 3368 mg L^{-1}. At the start of the experiment the level was 2860 mg L^{-1}. However after a suitable period of acclimatisation had been allowed to take place the ammonia decreased in concentration. At week 13 when the OLR was increased and the temperature dropped the concentration of TAN reduced to just over 4106 mg L^{-1} in T1 and 4966 mg L^{-1} in T2. It continued to decrease to a level of 3316mg L^{-1} in T1. At the OLR of 4 kg VS m^{-3} day^{-1} it averaged 4187 mg L^{-1}. T2 had a similar curve profile but at a slightly elevated level; it reached a lower level of 3750 mg L^{-1} at week 18 and averaged 4831 mg L^{-1} at an OLR of 4 kg VS m^{-3} day^{-1}. Free ammonia concentrations are reported in Table A5.For stable anaerobic digestion at high ammonia concentrations, the following parameters are a prerequisite [6]:

- good adaptation of the microbes,
- good trace element availability and
- low to medium hydrogen sulphide concentrations.

Stability of Process

The ratio of VFA/ alkalinity recorded during the trial was not high. Levels remained in the range of 0.15 and 0.3 in both reactors. An average level of 0.37 was experienced in T2 at the lowest organic loading rate but this dropped as the system evolved. This suggests that both consortia of microbial bacteria were healthy and not under undue stress. The pH in both reactors was at satisfactory levels (7.5 for T1 and 7.6 for T2) for the period with an OLR of 2 kg VS m_n^{-3} d^{-1}. The pH rose to above 8.0 at an OLR of 4 kg VS m^{-3} day^{-1} for both T1 and T2. This is problematic when coupled with high total ammonia levels [6, 7].

Biogas composition

Biogas composition showed increases in volume of CH_4 from an average of 63% CH_4 (after start up) in T1 and T2 at an OLR of 2 kg VS m^{-3} day^{-1} to 64% CH_4 in T1 and T2 for an OLR of 3 kg VS m^{-3} day^{-1} (Table A4). This further increased to 67% CH_4 for the final OLR. Methane composition in the biogas was predominantly higher on the day after the two day feeding lull (Saturday and Sunday). Percentages reached on average 2-3% CH_4 higher on Mondays as compared to the weekly average. Biogas composition was similar in both reactors throughout the trial. H_2S levels did not register in the biogas composition until week 9 in both reactors (Figure A3). It remained under 500 ppm until week 20 when the OLR was increased to 4 kg VS m_n^{-3} d^{-1}. The initial device (Status Scientific Control ComBI-R Biogas analyser) could not measure levels in excess of 500ppm. A new device (Drager X-AM 7,000) was purchased (in place in week 23) with a larger measuring range for H_2S. Levels of up to 860ppm were recorded in T1 and 980 ppm in T2 (Figure A3). The Drager recorded levels of Hydrogen over 2000ppm from week 23 when it was purchased to week 25 (termination of experiment).

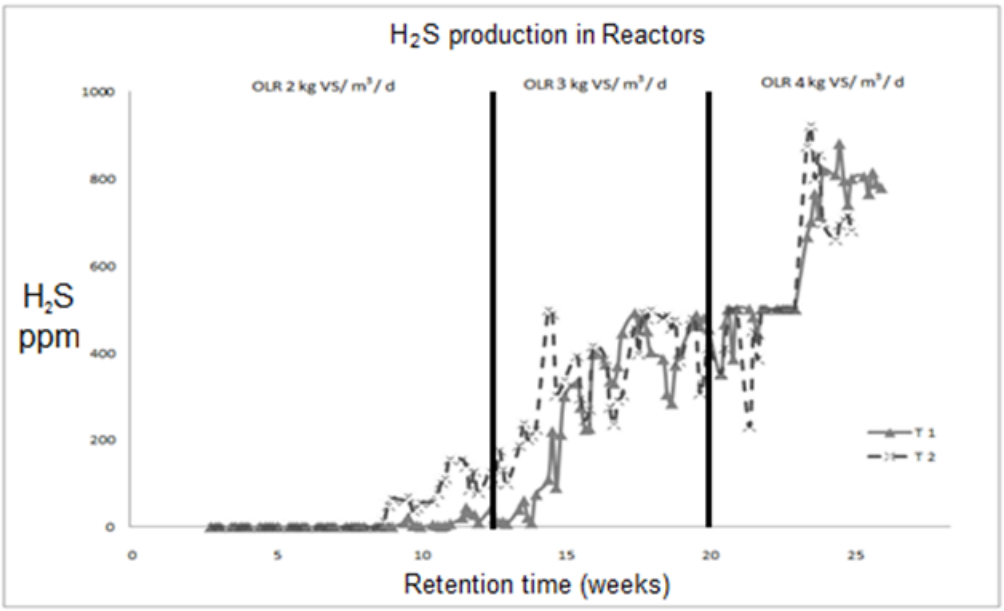


Figure A3 Concentration of H_2S (ppm) in biogas from T1 and T2.

Conclusions

The results of this paper and previous work [4] allow a comparison of biomethane yields using four methodologies including for three different laboratory procedures. The methods include:

- Theoretical maximum calculated using the Buswell equation based on the ultimate analyses of the substrates.
- The first laboratory procedure is based on mono-digestion BMP trials.
- The second laboratory procedure is based on BMP trials of actual mixes.
- The third laboratory procedure included for 25 weeks of semi-continuous digestion at three different organic loading rates.

The results of the semi-continuous trials are summarised in Table A6. The result of the BMP assay from AcoD is not the same as would be calculated using a weighting of mono-digestion results. There is actually a small decrease for T2 (3%) and a more significant decrease for T1 (13%).The recommended OLR is lower (3 kg VS m_n^{-3} d^{-1}) for T1 than for T2 (4 kg VS m_n^{-3} d^{-1}). The HRT (with recirculation) is recommended at 23 days for T1 and 15 days for T2. The ratio of VFA/ alkalinity is typically below 0.3 for both trials. This suggests stability though the pH was slightly higher than expected at 7.89 and 8.03 respectively for T1 and T2.The ratio of the biomethane yield from the semi-continuous trials to that obtained using BMP assays

is 0.87 for Trial 1 and 0.99 for Trial 2. It is suggested that using only a BMP test for a preliminary design of an anaerobic reactor does not yield sufficient data for choosing operating conditions.

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