METHANE OXIDATION POTENTIAL OF UNCOMPOSTED YARD WASTE AS A LANDFILL BIOCOVER

Submitted by

Gomathy Radhakrishna Iyer

DISSERTATION

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy in Civil Engineering at
The University of Texas at Arlington
December 2018
Arlington, Texas

Supervising Committee:

Dr. Melanie Sattler, Supervising Professor

Dr. Tarek Abichou

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ABSTRACT

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GOMATHY RADHAKRISHNA IYER, Ph.D.

The University of Texas at Arlington, 2018

Supervising Professor: Dr. Melanie Sattler

Biocovers are widely used in landfills to oxidize emissions of the greenhouse gas methane. Biocovers used till date are fully or partially made of composts. Compost takes time and effort to create, and costs about $10 per cubic yard on an average. Even more importantly, however, production of compost, although theoretically an aerobic process, actually generates methane, from 3.2 to 362 kg CO_2-equivalents per ton of wet waste composted, depending on the type of waste, whether open or enclosed composting technology is used, and other factors.

To reduce the net greenhouse gas emissions from biocovers, this research explores the potential of uncomposted yard waste as a landfill biocover to oxidize methane. The components of yard waste were separated as grass clippings, leaves, and mixed yard waste and physical and chemical characteristics were analyzed. The characteristics of biosolids and different fly ashes were also analyzed with the intention of biosolids helping the yard waste in enhancing the microbial community and nutrients, and fly ash helping in keeping the yard waste compact. These materials by themselves and in combination were tested in batches for methane removal.

The grass clippings and a mixture of grass, biosolids, and fly ash showed the highest performance in batch tests were further tested in columns which replicated landfill conditions. The biocover performance index for the uncomposted grass, biosolids & fly ash biocover mixture was 43.3 µg/g/hr vs. 29.0 for a traditional compost biofilter. Also, upon biological analysis of column reactor samples, presence of methanotrophs were confirmed in both grass and biocover mixture. However, upon analyzing the leaching characteristics of fly ash, it was found there is leaching of silver, arsenic, cadmium, chromium and thallium greater than the permissible limit in drinking water. This study therefore suggests using of grass and biosolids as biocover mixture to remove methane emissions from landfills.

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Thanks are due to my lab mates in helping me throughout my research with their valuable time and support. I thank Dr. Arpita Bhatt for guiding me and being there whenever I was stuck and needed help. I express my sincere thanks to Aiswarya Acharath Mohanakrishnan who has been a great helping hand for my research and fine friend ever since I met her.

Family is always the backbone of any researcher and I express my sincere thanks to my husband Dr.Ramesh Padmanabhan, for guiding me the right path always, being my toughest critic and a big support. Thanks to my two big pillars, my mother Gomathy and brother Ramakrishna Iyer, who have been with me in each step. Without them I wouldn’t have made it until here. I am always thankful to my mother-in-law Raji Padmanabhan for her continuous prayers and encouragement. I am blessed to have my wonderful

cousin Sivaram Krishnamoorthy, who has been a constant motivator right from the beginning.

Thanks to Almighty for always being with me, showering your love and blessings.

DEDICATION

I dedicate this dissertation to my father, the late Radhakrishna Iyer,

who taught me the very basics of engineering and how to approach things practically. He was the one who taught me to dream and motivated me to reach heights. He made me think and work independently and always told me, that I should not step back anytime anywhere because I am a girl. Dedicating this dissertation to my father is the slightest appreciation I can ever give to him. You will always be missed, Appa!

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Chapter 1

Introduction

1.1 Background:

Landfilling of solid waste is a common and popular practice worldwide nowadays. Microorganisms break down the organic constituents of the solid wastes into methane, carbon dioxide and other trace gases. Landfills are therefore one of the major sources of anthropogenic methane emissions. In the US, they are the 3rd largest source, or 18% of the US total (US EPA, 2013). This is particularly a problem because methane has a global warming effect 28 times greater than carbon dioxide on a 100-year time horizon (IPCC, 2013). Although there are several methods to reduce the methane emissions such as landfill gas collection systems, the amount of methane escaping these systems is still around 25% (US EPA, 2005).

Landfill covers serve as a major factor in curbing landfill gas emissions. Recent researches focus on oxidizing the methane emissions escaping the landfills using landfill covers. Several materials, including composts, sewage sludge, peat, and saw dust, have been investigated. Biologically active landfill covers with such biodegradable materials are called biocovers. Biocovers are found to be more efficient than other landfill covers with respect to oxidizing methane to carbon dioxide. Waste materials which end up being landfilled and taking up space, such as yard waste, fly ash, paper waste, and brewery waste, are also attracting attention as potential landfill biocovers. Biocovers are expected to:

- Serve the purpose of conventional landfill covers,
- Maintain bacterial activity useful for biological oxidation,
- Oxidize methane to carbon dioxide.

1.2 Problem statement:

Most current large engineered landfills have gas extraction systems in place, which are useful during the active phase of landfilling (Barlaz et al., 2009), although previously closed landfills may not. Although the majority of the landfill gas generated is taken care by gas extraction systems, additional control measures are still required to prevent methane emissions completely (Scheutz et al., 2011; Wong et al., 2016). Several studies have revealed that the efficiency of gas extraction system varies from 50-95 %, depending upon the type of cover system: daily, interim or final (Spokas et al., 2006). Daily covers are implemented at the end of each day's landfilling, interim covers are to cover that part of the landfill cell where waste may not be placed for at least another year and final cover covers are implemented as a final cap once the landfill capacity is achieved (Barlaz et al., 2009; Spokas et al., 2011).

Since landfill gas extraction systems are less than 100% efficient, additional measures are needed to curb methane emissions. Apart from the primary role served by the landfill covers which is to prevent waste exposure to the outside environment and prevent storm water and surface water infiltration, they are currently being researched to reduce maximum methane emissions, either to replace or along with the gas extraction system (Marion et al., 2009; Muenmee et al., 2015; Scheutz et al., 2011). Methane is oxidized to carbon dioxide as it is transported through the cover soils. Biological oxidation of methane occurs due to methanotrophs, a form of bacteria which uses methane as their primary source of energy for cell synthesis, using an enzyme called methane monoxygenase (Scheutz et al., 2009; Scheutz et al., 2004). Soil has been used for conventional landfill covers. The mean methane oxidation in landfill soil covers vary from 22- 55% in clayey to sandy soil (Chanton et al., 2009).

As an effort to enhance methane oxidation, several biocovers have been implemented globally as well (Hilger et al. 2003; Marion et al., 2008; Stern et al., 2007). Biocovers are biologically active landfill covers that can support and maintain methanotrophic populations (Yazdani, 2010). There are two specific layers considered in an engineered biocover system: the upper oxidation layer, which is made of organic materials such as composts or sewage sludge, and the basal distribution layer, which can distribute LFG evenly to the oxidation layer (Scheutz et al., 2009). There have been various laboratory scale studies with controlled experimental settings which focus on factors responsible for biocover performance (Nikiema et al., 2007).

Although there have been researches on biocovers for the last 15 years, none of the researches report a fully efficient biocover system that curbs methane emission completely. Typical methane oxidation by biocovers at landfill field sites are reported up to 96% (He et al., 2012), although lab studies show up to 100% oxidation. For one of the field studies done in Denmark at Skellingsted landfill, the percentage methane oxidation was as low as 40% (Scheutz et al., 2009). There are other shortcomings, however, associated with traditional biocovers. Compost takes time and effort to create, and costs about $10 per cubic yard on an average. Even more importantly, however, production of compost, although theoretically an aerobic process, actually generates methane. According to Boldrin et al. (2009), the composting process can generate from 3.2 to 362 kg CO_2-equivalents per ton of wet waste composted, depending on the type of waste composted, whether open or enclosed composting technology is used, and other factors. These emissions include direct emissions from waste degradation during composting, activities at the composting site, and upstream activities such as production of materials. Direct emissions from waste degradation are primarily CO_2, but also include methane and nitrous oxide (more potent greenhouse gases), depending on the management process. Methane is formed in anaerobic pockets of the compost material. According to Edelmann et al. (2000), 5.1-13.5% of degraded carbon is emitted as methane, depending on the management of the composting process.

Un-composted yard waste is a potential alternative to compost and other traditional biocovers. Using un-composted yard waste would be expected to reduce the cost, time, and effort involved in creating compost, as well as the methane emissions from the composting process. Yard waste constitutes 13.3% of the solid waste stream (USEPA, 2014). Yard waste also contains ample organic content to sustain methanotrophic activity (Humer and Lechner, 1999). Un-composted yard waste may possess permeability issues and compaction issues (too permeable, and not able to be sufficiently compacted) due to its particle structure, which could be resolved if it is used in combination with other materials as an oxidation layer. It could also potentially be used by itself as a gas distribution layer.

Two materials that could be combined with yard waste to address the permeability and compaction issues include biosolids and fly ash. Biosolids contain macronutrients nitrogen and phosphorous, which could be helpful in supporting the growth of methanotrophs that oxidize methane (Lu et al., 2012). Biosolids have been used in the past as part of final covers for supporting vegetation due to their nutrition value (Lamb et al., 2012). The engineering properties of biosolids - high compaction and low permeability - make them a good component that can be added with yard waste to obtain a good biocover (Arulrajah et al., 2011).

Class C fly ash is cementitious and could bond with the yard waste upon compaction to decrease the yard waste permeability (Cokca and Yilmaz, 2004). Re-use of fly ash in landfill covers is potentially important, due to new US Environmental Protection Agency (EPA) rules governing utility on-site storage of fly ash, which will likely increase the amount of fly ash directed to MSW landfills in the next few years. This fly ash will consume valuable landfill volume unless ways are found to re-use it. An optimal amount of fly ash, however, would need to be determined for use in a landfill cover to avoid cover cracking during waste settlement.

1.3 Research Objectives

The goal of this research is to develop a daily, intermediate, and final cover effective in oxidizing methane by varying the proportions of yard waste, biosolids, and fly ash in the upper oxidation layer of the biocover.

Specific aims of this research are:

1. To assess physical and chemical properties of the proposed cover materials.
2. To perform batch tests to study the oxidation capacity of material mixtures with different C/N ratios.
3. To perform column tests to optimize the mix proportions of materials to achieve desired permeability and compaction and finalize the biocover mix.
4. To perform a life cycle analysis of methane emissions from biocovers composed of uncomposted yard waste vs. composted yard waste.

The 2 proposed advantages of uncomposted yard waste biocovers over composted yard waste biocovers are:

1. Lower life cycle emissions of methane, due to reduction of methane generated during the composting process;
2. Convenience, since time and effort are not required to create compost.

Chapter 2

Literature Review

2.1 Introduction

Waste generation has been increasing day by day due to population growth, urbanization and standards of living (Noor, Yusuf, Abba, Abu Hassan, and Mohd Din, 2013). The waste production in United States has increased from 1.2 kg/capita during 1960s to 2.01 kg/capita during 2014 (USEPA, 2017) . Solid waste management has evolved from open dumping to integrated waste management which focuses on source reduction. In spite of various strategies followed for waste management, 47.4% of municipal solid waste still goes to landfills. According to USEPA 2014 reports, 135.92 million tons of municipal solid waste is disposed of at 1956 landfills (USEPA, 2017)

A typical municipal solid waste (MSW) landfill will have incoming wastes comprising of plastics, wood, paper, metals, Styrofoam, food, and other organics as well as inorganic wastes. When the wastes are compacted in the landfills, the water content in the waste materials along with storm water if any forms the leachate and percolates down the landfill, which is taken care by leachate collection system in an engineered landfill. The organic waste in the landfill gets decomposed anaerobically by methanogens to methane, carbon dioxide and other trace gases, which migrates upwards towards the landfill cover. The trace gases include hydrogen, nitrogen, oxygen, non-methane organic compounds, ammonia, and sulfides.

The generation of landfill gases is a major problem faced due to landfilling (Lou and Nair, 2009). The major constituents of landfill gas produced by decomposition of organic matter are methane (40-60%) and carbon dioxide, which are major greenhouse gases as well (Chiemchaisri et al., 2007). Methane is third most important greenhouse gas in the atmosphere after water vapor and carbon dioxide (Hansen, 1998). Lifetime of methane is 12 years, which is lesser than that of carbon dioxide 172.9 years. However the radiation efficiency of methane is over 28 times greater than that of carbon dioxide. Anthropogenic sources are found to contribute 70% of annual methane emissions and landfill emissions are 6% of them. (IPCC, 2014; NASA, 2016). Table 2.1 shows range of composition of various gas in landfill gas.

Table 2.1: Composition of landfill gas (Tchobanoglous et al., 1993)

Components	Percentage by Volume
Methane	45-60
Carbon dioxide	40-60
Nitrogen	2-5
Oxygen	0.1-1
Ammonia	0.1-1
Non methane organic compounds (NMOCs)	0.01-0.6
Sulfides	0-1
Hydrogen	0-0.2
Carbon monoxide	0-0.2

2.2 Landfill gas production

Landfill gas is produced in three stages: Bacterial decomposition, volatilization, and chemical reaction.

<u>Bacterial Decomposition</u>: Most of the landfill gas is produced by bacterial decomposition, which occurs when organic waste is broken down by the methanogenic bacteria present in the wastes and cover soil. Organic wastes include food, garden waste, street sweepings, textiles, and wood and paper products. Bacteria decompose organic waste in four phases (aerobic decomposition, Acidogenesis, acetogenisis and methangogenisis), and the composition of the gas changes during each phase. (M. A. Barlaz, 1997). The last stage involves conversion of complex polymers to methane, which requires methane-producing microorganisms, methanogens, which use the growth substrates acetate, carbon dioxide and hydrogen, formate, methanol and methylated amines and dimethyl sulfides (Barlaz, 1997; Keltjens and Vogels, 1993). Figure 2.1 shows stages in landfill gas production.

The bacterial decomposition happens in four stages:

Aerobic decomposition: In this phase of decomposition, aerobic bacteria breaks down long molecular chains of complex carbohydrates, proteins, and lipids that comprise organic waste, with the help of oxygen. The primary byproduct of this process is carbon dioxide.

Acidogenesis: Once the oxygen is fully utilized, the anerobic bacteria convert the products of aerobic bacteria in to acetic, lactic, and formic acids and alcohols such as methanol and ethanol. The landfill becomes highly acidic. These acids mix with moisture in the landfill and dissolve nitrogen and phosphorous. If at some point, oxygen gets introduced, aerobic decomposition will be reinitiated.

Accelerated methane production phase: Certain bacteria consume organic acids produced in phase II and form acetate. This gives a supporting environment for methane-producing bacteria. Acid-producing bacteria create compounds for the methanogenic bacteria to consume and in turn, methanogenic bacteria consume the carbon dioxide and acetate, too much of which would be toxic to the acid-producing bacteria.

Decelerated methane production phase: This phase occurs when both the composition and production rates of landfill gas remain relatively constant. Gas is produced at a stable rate in Phase IV, typically for about 20 years; however, gas will continue to be emitted for 50 or more years after the waste is placed in the landfill (Crawford and Smith, 1985).

Volatilization: Landfill gases can be created when certain wastes, particularly organic compounds, change from a liquid or a solid into a vapor. This process is known as volatilization. NMOCs in landfill gas may be the result of volatilization of certain chemicals disposed of in the landfill.

Chemical Reactions: Landfill gas, including NMOCs, can be created by the reactions of certain chemicals present in waste. For example, if chlorine bleach and ammonia come in contact with each other within the landfill, a harmful gas is produced.

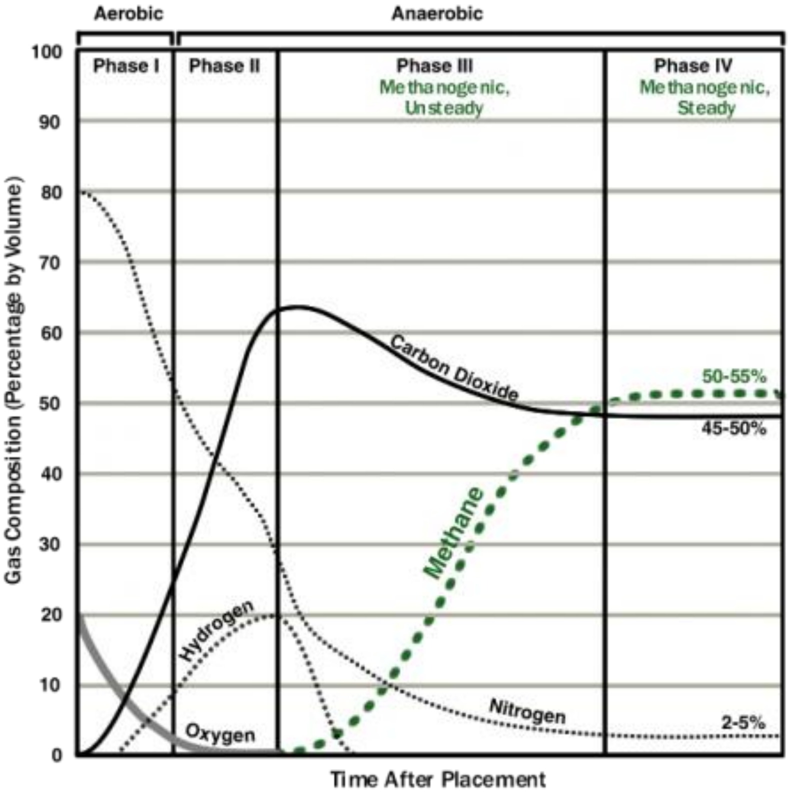

Figure 2.1: Stages of landfill gas production (Source: EPA, 1997)

Methanotrophs which exist in aerobic conditions in a landfill in turn oxidize methane to carbon dioxide and water. Methanotrophs and methanogens are linked for their abilities to convert perchloroethylene and trichloroethylene to carbon dioxide (Little et al., 1988; Wilson and Wilson, 1985).

About 160-250 cubic meters of landfill gas is generated from a ton of municipal solid waste (Humer and Lechner, 1999). Considerable amounts of methane are released over a time span of 2-3 decades, depending upon the landfill operation technologies, organic content in the waste landfilled and the degradation conditions in the landfill, which is termed as the active phase of a landfill. Even post closure of the landfill, trace amounts of methane are expected to be released for about 100 years (Marion et al., 2009).

Methane emission mechanisms through landfill covers include advection via Darcy flow, diffusion, and wind induced advection. The pressure gradient is formed by either wind or due to change in pressure due to pressure build up by gas generation (Poulsen and Møldrup, 2006). When there is vegetation present in cover soils, the plant-mediated transport can also affect observed flux (Chanton, 2005). Lateral methane migration is possible during wet periods in unlined landfills constructed on coarse sediments or fractured rocks. During saturation, internal gas pressure is developed rather than diffusing to atmosphere (Christophersen and Kjeldsen, 2001; Franzidis et al., 2008). The landfill gas may also get adsorbed into the solid particles in the landfill, or get dissolved in the water particle surrounding it, which also impacts the movement of methane generated (Franzidis et al., 2008).

2.3 Landfill Gas Mitigation

As a means to convert the landfill gas to energy and as a method to mitigate landfill gas emissions, currently, all the landfills are equipped with gas extraction and collection systems. As of 2014, there are 637 landfill gas to energy projects in the United states (USEIA, 2017). Since most of the landfill gas is generated during the active phase of the landfill, the gas extraction system is also most effective during that period (Cheimchaisri et al., 2007). The gas collection system needs to be installed within the first few years after closure, or within 5 years since last refuse is placed in the landfill (IPCC, 2007). One report states that 66 % of landfill gas can be captured with an efficient landfill gas capturing system and converted to energy, although the capture percent can vary considerably depending on the operation of the system and phase of waste degradation (USEPA, 2015) . The amount of landfill gas that escapes the landfill after installation of a gas extraction system depends on its efficiency, and time since cover was installed and efficiency of the landfill cover (Borjesson et al., 2007; Spokas et al., 2006). The landfill gases are also found to escape through vents around the collection systems which are known as hotspots (Pedersen et al., 20011).

For efficient operation and management of a LFG collection system, it is essential to know the components and temporal variations in gas production. With respect to this, there have been several LFG generation models developed (Shariatmadari, 2011). First- order decay models are more realistic approach to determine LFG production rates. The various landfill gas production models available are LandGEM (Landfill Gas Emissions Model), GasSim, Afvalzorg, IPCC (International Panel for Climate Control), EPERFrance (European Pollutant Emission Register), SWANA (Solid Waste Association of North America), TNO (a Dutch research institute) model and Mexico Gas model (an initiative of Landfill Methane Outreach Program by USEPA) (Shariatmadari, 2011). A landfill gas emission model was also developed by University of Texas, Arlington students named CLEEN (Capturing Landfill Emissions for Energy Needs) which could predict the landfill gas emissions from landfills anywhere across the world.

Landfill gas flaring is also a common practice in landfills where the methane extraction is low and uneconomical (Marion et al., 2008; Scheutz et al., 2009). Flaring is beneficial when there is excess gas extraction than the capacity of the generators to produce electricity, as well as during maintenance times. Hence, generally landfill gas extraction systems are equipped with flaring, which releases carbon dioxide, a less powerful greenhouse gas. However LFG flaring still poses a risk of releasing harmful byproducts such as unburnt hydrocarbons and sulfur that may cause health concerns (Hettiarachchi et al., 2009). Biofiltration is seen as a good treatment method in place of flaring (Strosher, 1996). Landfill aeration is also a widely implemented concept to mitigate methane emissions (Rizkowski and Stegnamm, 2012).

Even when a landfill gas collection and energy recovery or flaring system is in place, the amount of methane escaping landfills is still around 25 % (US EPA, 2005). The efficiency of landfill covers by itself thus plays a significant role in mitigating landfill gas emissions (Barlaz et al., 2004). Landfill covers are now being used either in place of or along with gas extraction systems to efficiently mitigate methane emissions (Chiemchaisri et al., 2012; Scheutz et al., 2009). Aerobic soils exhibit the highest methane oxidation rates with elevated levels of methane (Le Mer and Roger, 2001). This oxidation is usually mediated by methanotrophs (Bogner et al., 1997; Kightley et al., 1995). Studies also indicate that if amendments rich in organic content are implemented in landfill cover soil, the methane oxidation rate can be increased (Sadasivam and Reddy, 2014). Chemical oxidation of methane with catalysts such as palladium and rhodium has also been reported (Gong et al., 2014; Li et al., 2003; Naito et al., 2008). Semi-oxidized methane can be used for synthetic gas production (Naito et al., 2008).

2.4 Traditional soil landfill covers and methane oxidation

Landfills covers are implemented based on time frame for which the cover is required - Daily, Intermediate or Final. Daily covers are implemented after each day, after the waste is placed and the work is completed; Intermediate covers are provided when the cell is not used for landfilling for 6 months or more; final covers are provided once the landfill capacity is reached, to cap the landfill (Spokas et al., 2011).

The percentage oxidation potential in landfill cover soils can vary from negligible to more than a hundred (meaning the cover is oxidizing methane from the atmosphere) according to a study by Bogner and team (Bogner et al., 1997). Oxidation rates in landfill cover soils are affected by moisture, temperature, methane soil gas concentrations, soil pH, and nutrient availability (Albanna et al., 2007). Oxidation rates also depend on landfill cover material, landfill gas flux, climatic conditions, and type of vegetation (Cao and Staszewska, 2013).

2.4.1 Role of methanotrophs in methane oxidation

One of the most important factors controlling methane oxidation by landfill covers is methanotrophic communities (Hu and Long, 2016). The microorganisms use the enzyme methane monoxygenase, or MMO, to catalyze the oxidation of methane to methanol, and subsequently formaldehyde and formate. Figure 2.2 shows pathway for microbial oxidation of methane to carbon dioxide.

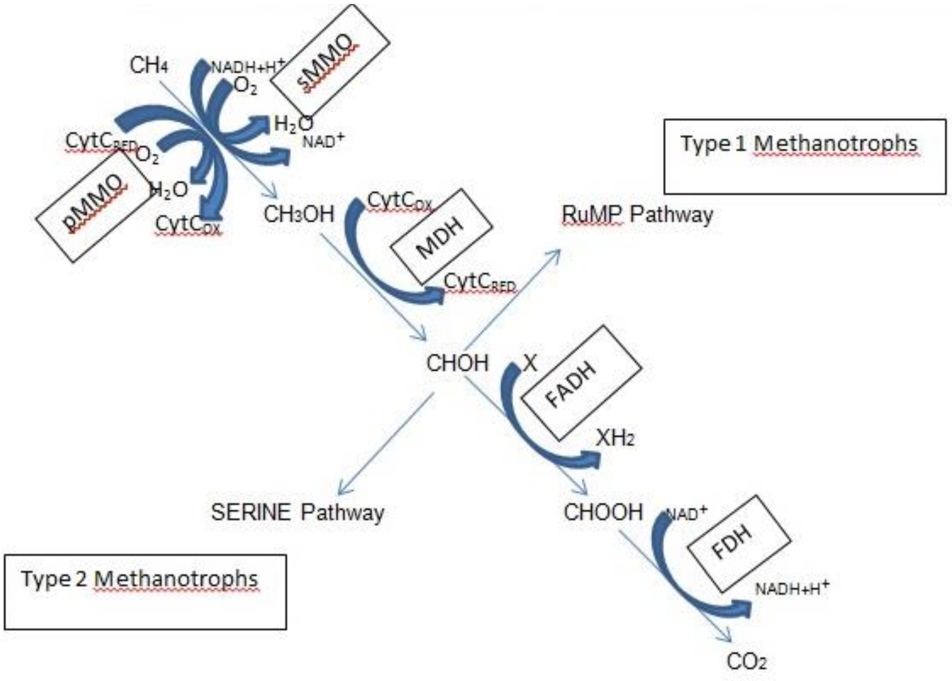

Figure 2.2: Microbial methane oxidation pathway (Scheutz et al., 2009)

Based on the differences in morphological and physiological characteristics, methanotrophs together comprise a total of 11 genera (Hanson et al., 1996) and are divided in to two groups: type 1 and type 2. Recently several other genera of methanotrophs have been identified, leaving the community more diverse (Hanson et al., 1996). Table 2.2 below shows methanotrophs identified till date.

Table 2.2: Methanotrophs, their type and nitrogen fixation property

Genus	Type of MMO	Nitrogen fixation
Methylobacter	pMMO	No
Methylocaldum	pMMO	No
Methylocapsa	pMMO	Yes
Methylocella	sMMO	Yes
Methylococcus	pMMO	Yes
Methylocystis	sMMO/ pMMO	Yes
Methylomicrobium	pMMO	No
Methylomonas	pMMO	No
Methylosinus	sMMO/ pMMO	Yes
Methylophaera	pMMO	No
Methylothermus	pMMO	n.d

The type 1 included methylococcus, methylomicrobium, methylobacter and methylococcaceae. Type 2 included methylosinus and methylocystis. Most type 1 methanotrophs are incapable of fixing nitrogen, whereas type 2 are capable of doing that (Bowman et al., 1993).

Methanotrophs can exist even in severe conditions (Horz et al., 2002; Heyer, 2002). They were found to exist in temperatures as low as -25 °C to as high as 72 °C and at acidic pH of 2.2 to basic pH of 10.5 (Bodrossy et al., 1999; Dunfield et al., 2007; Kaluzhnaya et al., 2001; Knoblauch et al., 2008). Studies say that there are two types of methanotrophs with respect to their methane affinity 1) those with high methane affinity, resulting in low methane oxidation, and 2) those with low methane affinity favoring high methane oxidation (Bogner et al., 1997; Sadasivam and Reddy, 2014). The first group has high affinity to methane and hence favors low methane, high oxygen concentration. The second group has low affinity to methane and hence favors high methane low oxygen concentration. Hence the type one are mostly found in the upper surface and group two are found in the bottom surface of cover soils. Natural soils which are exposed to CH_4 concentration are found to have high affinity and low activity (Bender and Conrad, 1994; Whalen, 1990). Many studies further has revealed that type 2 methanotrophs survive high methane low oxygen concentrations and also high nitrogen conditions. Both Type 1 and 2 are found in a landfill cover soil, whereas type 1 methanotrophs are mostly found in sewage sludge landfill covers, mostly due to high nutrient content (Borjesson and Svensson, 1997).

When the methane and oxygen are present at the same time in the biosphere, aerobic microbial oxidation takes place. In the upper portions of landfill covers, there will be methane due to the anaerobic degradation of waste and oxygen due to influx of air from the atmosphere. This will provide conditions for methanotrophic bacteria to flourish; hence, the aerobic oxidation of methane occurs according to the following reaction:

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$+ heat (Scheutz et al., 2009).

Methanotrophic bacteria are mostly aerobic. Their activity depends on the methane and O_2 concentrations and hence are confined to narrow horizontal bands within the landfill covers (Hanson, 1996). According to several studies done in simulated landfills, the greatest oxidation potential is found below a depth of 20 cm in most of the soil covers (Yazdani, 2010; Scheutz et al., 2004). Figure 2.3 below shows gas concentration profile measured at Skellingsted Landfill (Zealand, Denmark) and methane oxidation rates vs. sampling depth in batch tests by Scheutz et al. (2009).

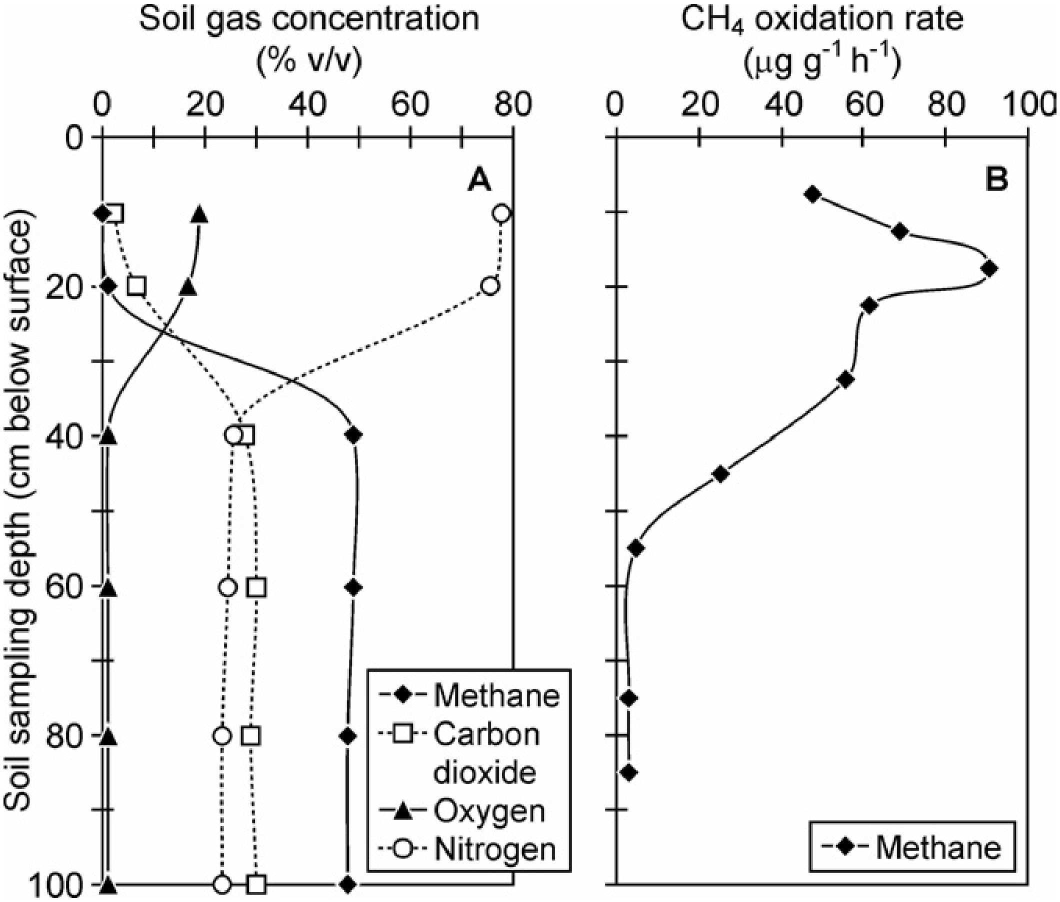

Figure 2.3: Gas concentration profile: methane oxidation rates vs. sampling depth (Scheutz et al., 2009)

The oxidation is significant until a depth of 60 cm from the cover surface and is less from there on because of limited oxygen availability. However, at sites having low methane emissions, there may be the presence of an oxidative zone (Scheutz et al., 2009).

The methane oxidation kinetics in landfill covers is often described by Michaelis-Menton kinetics:

$$r = \frac{\mathrm{V}_{\mathrm{max}}\{\mathrm{CH}_4]}{\mathrm{K}_{\mathrm{m}} + [\mathrm{CH}_4]}$$

where r is the methane oxidation rate, V_{max} is the maximum methane oxidation rate, K_m is the Michaelis Menton reaction constant and [CH_4] is the methane concentration.

2.4.2 Factors influencing methane oxidation

The methane oxidation in cover soils is also influenced by various environmental factors such as temperature, moisture content of the cover soil, porosity, permeability, availability of oxygen, and presence of nitrogen. Temperature can play a vital role in existence of methanotrophs. Most of them found in pure culture are mesophiles (Hanson, 1996). An optimum temperature for methanotrophs to carry on methane oxidation is 25-35 °C, although they can survive and support oxidation in negative temperatures (Bodrossy et al., 1999). The majority or all of the methanotrophs found until now which can adopt to lower temperatures are from Type 1 (Borjesson et al., 2007). Methane oxidation may stop in cold areas when the temperature is 5-10 °C for type 2.

Soil moisture is yet another important factor which plays an important role in methane oxidation by soil covers. Moisture serves as medium for nutrient supply and also help sin in removing residual metabolic compounds. However, gas transport may be affected by excess soil moisture because molecular diffusion is slower in water than in air. When the soil cover is saturated with water, the gases will diffuse i to water and this will reduce the availability of methane and oxygen and hence lower the methane oxidation (Scheutz et al., 2009). Water saturation can also lead to lateral transport of landfill gas, which may cause emissions at places adjacent to the landfill (Franzidis et al., 2008). At optimum moisture content, there is both maximum molecular diffusion and methane oxidation happening (Scheutz et al., 2004). The pore size distribution and air capacity also have an important role related to soil moisture. Air capacity is the share of pores maintained by the soil cover once water is drained and water available in the soil cover is held just by capillary forces. The desired air capacity is >50 %. The optimum range of soil moisture in cover soils ranges between 10%w/w to 20%w/w (Hettiarachchi et al., 2009; Scheutz et al., 2004; Whalen, 1990).

Oxygen supply also plays important role in methane oxidation. Although methane oxidation is possible at even very low oxygen concentrations, methane oxidation drops significantly below an oxygen mixing ratio of 3% (Wilshusen et al., 2004). There are also studies which support the fact that methane oxidation starts only in concentrations of 1.7-2.6% (Gebert and Groengroeft, 2006). Although clay is preferentially used as a soil cover in many landfills, clay tends to saturate during heavy precipitation, thereby decreasing gas transport, and desiccate during dry seasons, thereby increasing emissions.

The presence of nitrogen in the form of ammonium ions will inhibit methane oxidation due to pH decrease during nitrification. The methane oxidation may remain unaltered up to an ammonium ion concentration of 14 mg-N/kg (Scheutz et al., 2004). It has also been found that ammonium-based fertilization for longer time inhibits growth and activity of methane oxidizers, even when the concentration is less than 1 mg-N/kg. After a certain lag, the methanotrophs seem to grow back, although much evidence on this theory is unavailable (Bodelier and Laanbroek, 2004). The presence of nitrogen and nitrate is beneficial to the methanotrophs, unless there is a large volume of ammonia-oxidizing bacteria present, which may impose competitive inhibition (Bodelier and Laanbroek, 2004).

2.4.3 Previous researches on methane oxidation by traditional soil landfill covers

Research on landfill covers on oxidation of methane has been going on since last 15 years (Yazdani, 2010). Methane oxidation capacity of soils is either studied in batch tests or in packed column reactors (column test). Batch tests are less expensive, less laborious, and also technically simple. Although the batch reactors are more flexible with respect to number of soils to be tested and with incubation conditions like temperature, moisture, column tests are more suitable when the dynamic gas transport and long-term gas exposure are to be tested. Column tests also allow for simulation of compaction appropriate for field-scale conditions. The oxidation rate obtained in columns may not be compared with that of batch experiments due changes in the system and procedure of testing (Scheutz et al., 2009). Table 2.3 and Table 2.4 show batch and column studies, respectively, for methane oxidation rates of different landfill covers.

Table 2.3: Methane oxidation rates in conventional soil landfill covers from batch studies

Soil cover type	**Max. CH_4 oxidation rate ($\mu g\ CH_4\ g^{-1}\ h^{-1}$)**	**Initial methane concentration (%v/v)**	**Organic content %w/dw**	**Optimum soil moisture content (%w/dw)**	**Reference**
Sandy loam	26	3	3.4		Visscher, 1999
Sandy loam	47.2	2	3.4		De Visscher, Schippers, and Van Cleemput, 2001
Sandy loam	48	5		35	Börjesson and Svensson, 1997

Soil cover type	Max CH4 oxidation rate (µg CH4 g^{-1} h^{-1})	Initial methane concentration (%v/v)	Organic content %w/dw	Optimum soil moisture content (%w/dw)	Reference
Loamy sand	118	15	3.2	25	Scheutz et al., 2004
Loam	28	15	1.86	20	Schuetz, 2003
Humic soil	86.4	10	7.2	21	Scheutz et al., 2009
Biowaste compost	128	10	31.6		
Sand-clay loam	41.5	1.7-2	1.8	15	
Till	40	10	4.4	12	
Silty-loam	173	5	22-30	61	

Table 2.4: Column studies showing methane oxidation with conventional soil cover materials

Type of soil cover	Methane inlet concentration %	Methane load (g CH_4 m^{-2} day^{-1})	Steady state oxidation rate (g CH_4 m^{-2} day^{-1})	Oxidation %	Maximum oxidation rate %	Duration days	Reference
Landfill coarse sand	99	266	166	61	83	180	Kightley et al., 1995
Landfill sandy loam	50	368	230	65	79	65	Hilger et al., 2000
Topsoil	100	150	55	37	47	51	Humer and Lechner, 1999
Landfill sandy soil	50	26-32	22	70-85		95	Scheutz et al., 2009
Agri-cultural loam	50	216	98	45	81	127	De Visscher, 1999

The highest for oxidation rates have been reported for sandy soils with 2 to 5% of w/w organic content; however, they do not meet the permeability requirement by USEPA of 10-^{5} cm/s and would thus need to obtain a permit as an alternative cover. Other environmental factors which can affect the methane oxidation rate were studied as well, including moisture content and temperature. Some of the columns were operated with 100% methane concentration, where some were operated with inlet concentration of 50% methane so as to replicate the landfill gas. The methane load typically varied between 200 to 300 g CH_4/m^2/day (Bogner et al., 1997). For a 20-meter layer of waste, this load will be equal to 11-17 m^3 LFG/ m^3 waste/ year, which is expected within 10 to 15 years after disposal (Scheutz et al., 2009). The Table also depicts maximum oxidation rate and steady-state methane oxidation rate. Also, the maximum duration for which the columns were operated was 250 days. The oxidation rates were found to vary between 100 to 150 g CH_4/m^2/day, with maximum rates up to 250 g CH_4/m^2/day. Since long-term column experiments often exhibit a peak, followed by a steady-state value, there are both steady-state oxidation rates as well as maximum oxidation rates mentioned in the Table (Hilger et al., 2000; Kightley et al., 1995).

One of the best methods to quantify the methane oxidized by landfill cover material is the isotope method. The measurement of emitted ^{13}C compared to unoxidized ^{13}C in the anaerobic zone will give a robust quantification of methane oxidized (Chanton and Liptay, 2000). Prior to the isotope method, researchers used batch incubation tests with known methane to calculate percentage methane oxidized (Bogner et al., 1997). There have been reports that in the 1980s, mass ratios and mass balances were used to quantify methane oxidation.

2.5 Biocovers

There have been various materials tested as landfill covers including soil, rubber chips, compost of garden waste, municipal solid waste compost, wood chips, sawdust compost, biosolids, biochar, and so on. Since a large quantity of material is required for landfill covers, the selection of cover material usually depends on availability and cost (Bohn et al., 2011). Highly porous materials such as composts and wood chips will facilitate water penetration, thereby preventing drying of clay and also allowing vertical flow of gas (Abichou et al., 2011; Stern et al., 2007). However, they do not meet EPA's permeability requirements. Materials with high organic contents are found to support methanotrophic activity and growth compared to other materials (Jugnia3, 2010). High porosity and high water holding capacity materials are also found to provide a medium for methanotrophs (Kettunen et al., 2006). Mature composts have been widely studied and haven been found to meet the criteria of landfill covers for practical application in reducing methane emissions (Marion et al., 2008). Both biochemical based behavior and geotechnical based behavior have been studied in the laboratory as well as in the field by several researchers (Bogner et al., 2005; Humer and Lechner, 1999; Khoshand and Fall, 2014). The covers rich in organics and tested under successful lab systems were subsequently tested in fields and were called biocovers (Barlaz et al., 2004; Bogner et al., 2005; Marion et al., 2008).

2.5.1 Methane Oxidation in Biocovers

A biocover acts as a system which can provide ambient conditions for oxidation of methane in a biotic environment. A biocover will generally consist of a basal gas distribution layer, which is highly permeable and will homogenize the LFG fluxes, followed by an oxidation layer which will support the methanotrophs for methane oxidation. For heterogeneous biocover materials like composts, batch tests may not be feasible since batch tests may not give long term changes in the reactor with continuous flow of methane. However, batch tests can help in finding suitable materials for biocovers. In order to quantify the actual methane oxidation rates, column tests are preferred to provide biocovers with a continuous supply of methane (Marion, 2004; Scheutz et al., 2009). There have been studies conducted on microbial methane oxidation of composts from MSW and sewage sludge (Humer and Lechner, 1999; Wilshusen et al., 2004), compost-perlite mix (Werf, 2005), mix of wood chips and compost (Wilshusen et al., 2004) as stated in Table 2.5. Better methane oxidation has been reported by composts which are well mature and have lower C/N ratio and ammonia concentration. A balanced grain size distribution will ensure gas permeability at high moisture contents, which is also a detrimental factor in methane oxidation capacity of biocovers (Scheutz et al., 2009).

Table 2.5 Column tests on biocover performance (1)

Biocover material	Moisture content (% w/dw)	Methane load (g CH_4 m^{-2} day^{-1})	Steady state methane oxidation rate (g CH_4 m^{-2} day^{-1})	% steady state oxidation	Max. % oxidation	Duration In days	Reference
Mature sewage sludge+ deinking waste+sand (4:2:4)	57	30.7 35.7 41.4	31.4 27.9 9.3	97 77 22		10-21 22-41 42-65	Kettunen et al., 2006
Mature sewage sludge+ deinking waste+bark chips (4:2:4)	164	32.9 37.1 42.1	25.7 6.4 0.7	74 16 >1		10-21 22-41 42-65	
SS-compost+sand mix (70/30)	45	180	135	75	100	53	Humer and Lechner, 1999

Biocover material	**Moisture content (% w/dw)**	**Methane load ($g\ CH_4\ m^{-2}\ day^{-1}$)**	**Steady state methane oxidation rate ($g\ CH_4\ m^{-2}\ day^{-1}$)**	**% steady state oxidation**	**Max. % oxidation**	**Duration In days**	**Reference**
Composted pine bark+perlite mix		54	38	70		120	Plessis et al., 2003
Compost + polystyrene pellets		250-500	242	69	72	86	Powelson et al., 2006
Sedge peat moss	316	160 319	88 93	55 29	90 50	351 351	Stein, 2001
30cm compost-sand mix on top of 90 cm sand	14.2/ 10.7	55	52-54 (day 45) 48-54 (day 60) 31-50 (day 49) 44 (day 56)	94-98 88-98 57-90 80	98 98 90 80	45 60 49 56 Total:229 days	Berger et al., 2005

Biocover material	**Moisture content (% w/dw)**	**Methane load (g CH_4 m^{-2} day^{-1})**	**Steady state methane oxidation rate (g CH_4 m^{-2} day^{-1})**	**% steady state oxidation**	**Max. % oxidation**	**Duration In days**	**Reference**
MSW Compost-	85	400					Humer, 2001; Scheutz et al., 2009
60 weeks old	82	400	400	100	100	187	
20 weeks old	47	216	212	53	100	187	
36 weeks old			212	98	100	84	
SS Compost+ wood chips-							
Matured	96	180	180	100	70	53	
Fresh	85	94	33	35	100	35	
Yard waste compost	32.2	589	583	96	100	369	Haubrichs and Widmann, 2006
Yard waste compost+ wood chips	92.5	485	476	93	100	369	

Biocover material	**Moisture content (% w/dw)**	**Methane load (g CH_4 m^{-2} day^{-1})**	**Steady state methane oxidation rate (g CH_4 m^{-2} day^{-1})**	**% steady state oxidation**	**Max. % oxidation**	**Duration In days**	**Reference**
Compost+ wood chips	68	229-254	161	58	100	255	Scheutz et al., 2009
Compost+ sand	30	229-254	-31	-10	48	255	
Supermuld	14	229-254	29	12	60	255	
Leaves compost	124	520	100	19	77	600	Wilshusen, Hettiaratchi, and Stein, 2004
Garden compost	122	520	0	0	10	220	
Wood compost	123	520	100	19	19	220	

Biocover material	Moisture content (% w/dw)	Methane load (g CH_4 m^{-2} day^{-1})	Steady state methane oxidation rate (g CH_4 m^{-2} day^{-1})	% steady state oxidation	Max. % oxidation	Duration In days	Reference
Mechanical biological treatment residual- 22 week	79	30	30	100		5-39	Einola, Karhu, and Rintala, 2008
		60-78	53-82	88-100		39-52	
		78	64-74	82-95		52-77	
		78	56	71		77-87	
		78	39	50		87-124	
Mechanical biological treatment residual- 57 week	104	30	30	100		5-39	
		60-78	53-82	88-100		39-52	
		78	72-79	92		52-77	
		78	61	78		77-87	
		78	22	28		87-124	

The high water retention capacity of biocovers also produces high leachate volumes (Marion, 2004). Almost 90% of water infiltration into the biocover can be prevented by vegetation (Marion, 2004). There is also evidence that vegetation can increase biological methane uptake (Hilger et al., 2000). The negative side of vegetation is that it competes with the methanotrophs for the limited oxygen available (Keppler, 2006). Several field measurement experiences with biocovers have been reported by various authors (Scheutz et al., 2009). It has been found that the biocovers are capable of oxidizing methane emissions from the landfill when the collection systems are turned off and also are capable of drawing methane from atmosphere and oxidizing it (M. A. Barlaz et al., 2004). Many recycled waste materials have been found suitable for the gas distribution layer (Bogner et al., 2005).

2.5.2 Alternative Materials for Biocovers

Although Table 2.5 shows a number of biocovers achieving 100% methane oxidation, there are a couple of shortcomings associated with traditional biocovers. All of the biocovers that achieved 100% removal of methane, with the exception of the mechanical biological treatment residual, were made from compost. (Mechanical biological treatment is a treatment facility where mechanical treatment of wastes such as sorting and biological treatment such as composting takes place.) Compost takes time and effort to create, and costs about $10 per cubic yard on an average. Even more importantly, however, production of compost, although theoretically an aerobic process, actually generates methane. According to Boldrin et al. (2009), the composting process can generate from 3.2 to 362 kg CO_2-equivalents per ton of wet waste composted, depending on the type of waste composted, whether open or enclosed composting technology is used, and other factors. These emissions include direct emissions from waste degradation during composting, activities at the composting site, and upstream activities such as production of materials. Direct emissions from waste degradation are primarily CO_2, but also include methane and nitrous oxide (more potent greenhouse gases), depending on the management process.

Methane is formed in anaerobic pockets of the compost material. According to Edelmann et al. (2000), 5.1-13.5 % of degraded carbon is emitted as methane, depending on the management of the composting process.

Uncomposted yard waste is a potential alternative to compost and other traditional biocovers. Using uncomposted yard waste would be expected to reduce the cost, time, and effort involved in creating compost, as well as the methane emissions from the composting process.

2.5.2.1 Uncomposted yard waste

Yard waste constitutes 13.3 % of the solid waste stream (USEPA, 2015). 61.1% undergoes composting, 7.6 % undergoes combustion and 31.3 % undergoes landfilling. Yard waste has been recognized as tough material for landfilling by landfill managers due to its low compacted density of about 1500 pounds per cubic yard (Miller, 2001). Several states in United States have banned burning of yard waste due to potential air pollution and health problems.

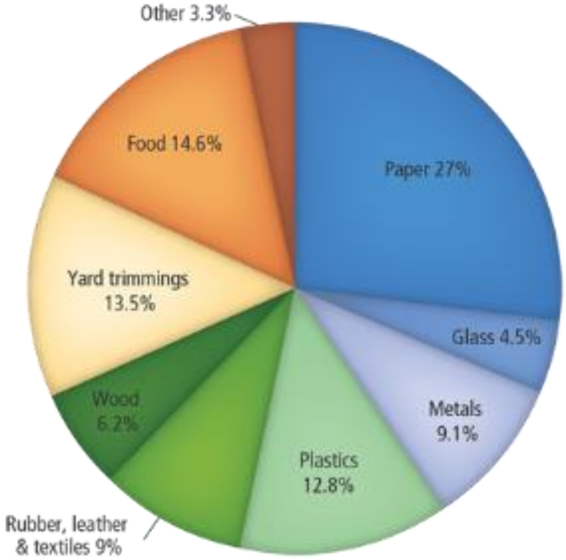

Figure 2.4: Total MSW generation (USEPA, 2015)

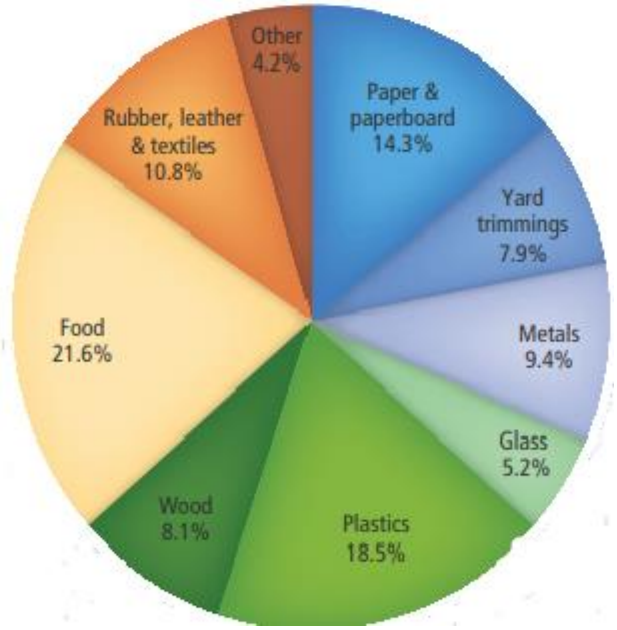

Figure 2.5 :Total MSW landfilled (USEPA, 2015)

Even though composting yard waste is a suitable solution for managing yard waste, the operational cost per cubic yard of compost is $10. Composting can also produce methane emissions, since anaerobic pockets typically exist in the compost pile, as Use of yard waste as a landfill cover material provides an alternative disposal route. Yard waste also contains ample organic content to sustain methanotrophic activity (Marion and Lechner, 1999). Uncomposted yard waste may possess permeability issues and compaction issues (too permeable, and not able to be sufficiently compacted) due to its particle structure, which could be resolved if it is used in combination with other materials – biosolids and fly ash.

2.5.2.2 Biosolids

Biosolids are solid residues obtained from treatment of sewage, which are rich in nutrients and organic material. Although sewage sludge and biosolids are two terms used interchangeably, both are different. Biosolids are treated sewage sludge in accordance with regulatory requirements by USEPA. Almost 7,100,000 tons of biosolids are generated in the US around a year and about 55% of them are used for land applications (Water

Environment Federation, 2010). According to EPA, composting of biosolids is found to be a more viable option than land application, since most of the pathogens will be removed during composting and the resultant is an organic material which can be used as a fertilizer. Still the 45 % of biosolids disposal is unaccounted for and 17% ends up in landfills as monofills (USEPA, 1998). Instead of landfilling, the biosolids can be used as landfill biocovers due to their high inoculum of microbes.

Biosolids have a reported dry density of 0.56 tons/m^3 when compacted with 85% moisture. This property of biosolids may be helpful in controlling the permeability of the yard waste. Also, biosolids are rich in microorganisms which can serve as an inoculum of microbes for biological oxidation of methane. There have been several reported biocovers using biosolids and their compost (Marion et al., 2008; Scheutz et al., 2009).

2.5.2.3 Fly Ash

Fly ash is a fine, powdery substance that "flies up" from the coal combustion chamber (boiler) and is captured by emissions controls, such as an electrostatic precipitator or fabric filter baghouse, and scrubbers. According to 2012 USEPA statistics, 110 million tons of coal combustion residue is produced in 47 states and Puerto Rico. This includes fly ash, bottom ash, and boiler slag and flue gas desulfurization gypsum (Figure 2.5).

Fly ash is well known for its cementitious properties and is expected to be helpful in controlling the permeability requirements of the biocover. There are class C and class F fly ash. The class may not be an issue, since the fly ash is used in the biocover to control porosity only. The color of fly ash varies from gray to black, depending on the amount of un-burnt carbon in the ash. Fly ash, has been utilized to neutralize soil acidity and increase availability of mineral for plant growth (Gangloff, 2003).

Figure 2.6: Fly ash use and statistics (2007)

Class C fly ash is produced from the burning of sub-bituminous coal and has self-cementing properties whereas class F fly ash lack self-cementing properties. In the presence of water, Class C fly ash hardens and gets stronger over time. Two types of Class F fly ash from two coal-fired plants designated as F1 F2 and F3. The two types of class C fly ash obtained from other to coal fired plants were designated as C1 and C2.

2.6 Modelling of methane oxidation in landfill covers

Methane oxidation in landfill covers involves many biochemical reactions which are different in each cover material. Simulation models help in estimating methane oxidation (Czepiel et al., 1996). They also help in learning the processes happening in landfill cover (Hilger et al., 1999). The existing methane oxidation models for can be categorized into empirical models, process-based models and collision models (Scheutz et al., 2009). The empirical models are formed based on empirical equations from experimental data. They pertain to conditions existing during the experiment and cannot be extrapolated (Czepiel et al., 1996). Process-based models involve mass transport equations and methane oxidation kinetics. Although they are highly realistic, they are of limited use because they require measuring many parameters (Hilger et al., 1999; Stein, 2001). The collision model tries to picturize process in landfill covers as collisions between gas molecules and soil particles (Bogner et al., 1997).

The model developed by Bogner et al. (1997) is attractive from a computational point of view, but its underlying assumptions are unconventional. The model describes pressure-driven gas flow as “non-equimolar counter-diffusion as a result of a gradient of the total concentration.” This may not be true since the pressure gradient itself can act as a source of mass transport (Hilger et al., 1999) was based on the Stefan Maxwell equation. The biofilm model was used with thick biofilm and oxygen as the limiting substrate. Although this is true, the model is static and hence the methanotrophic activity profile needs to be known if this model is to be used. The model developed by Stein (2001) incorporated flow and Fickian diffusion with concentration-dependent diffusion. Although the model was dynamic with respect to gas concentrations, it was static with respect to methanotrophic activity.

Among the methane oxidation models available for cover soils, California Landfill Methane Inventory Model (CALMIM) is the best model available. It is a freely available JAVA tool which models a typical annual cycle for CH_4 emissions from site-specific daily, intermediate, and final landfill cover designs. CALMIM has been field validated with data from 40 landfills at 29 international sites and is compliant with Tier III criteria of IPCC, which relies on validated higher quality methods and site-specific data. CALMIM models typical annual emissions based on 1-D diffusional flux and seasonal oxidation in site-specific cover soils, focusing specifically on inputs and outputs which can be validated at field scale (Bogner, 2014).

2.7 Research Goal and Objectives

The goal of this research is to develop more sustainable daily, intermediate, and final cover effective in oxidizing methane by varying the proportions of yard waste, biosolids, and fly ash in the upper oxidation layer of the biocover. This is based on the hypothesis that a cover with un composted yard waste can be developed, which has a lesser carbon footprint compared to covers made from composted yard waste. This could be made with uncomposted yard waste, biosolids, and fly ash so as to meet final cover permeability requirements.

Specific aims of this research are:

1. To assess suitability of yard waste, biosolids, and fly ash as biocover materials by measuring physical/chemical properties.
2. To evaluate the oxidation capacity of the proposed biocover materials, individually and in combination, using batch tests.
3. To measure methane oxidation under simulated actual-landfill conditions via column tests, for the most promising cover materials identified in batch tests.
4. To determine whether un-composted yard waste biocovers reduce net methane emissions. compared to biocovers made from composted yard waste, by conducting a life-cycle-analysis for methane.

The 2 proposed advantages of uncomposted yard waste biocovers over composted yard waste biocovers are:

1. Lower life cycle emissions of methane, due to reduction of methane generated during the composting process;
2. Convenience, since time and effort are not required to create compost.

Chapter 3

Materials and Methodology

The goal of this research is to develop a daily biocover and an intermediate biocover effective in oxidizing methane by varying the proportions of yard waste, biosolids, and fly ash in the upper oxidation layer of the biocover. This chapter discusses the materials used for the biocover and methods to analyze their properties; construction and analysis of batch reactors; permeability test on the biocovers; experimental design, construction, and data collection from the column reactors.

3.1 Biocover materials

The materials used for developing biocover in this project include yard waste, biosolids and fly ash.

The physical parameters and chemicals parameters play a big role in the behavior of biocover oxidation of methane (Marion et al., 2009). The physical parameters tested on the biocover materials include pH, moisture content, bulk density, air filled pore volume and water holding capacity. The chemical parameters tested on biocover materials include nitrate, nitrite, ammonia, sulfate, phosphate, C/N ratio.

3.1.1 Physical Parameter Analysis

Preparation of samples

The yard waste was collected from the UTA recycle and composting facility, and grass clippings and green leaves were separated as two individual samples and the mixed yard waste a third sample. The biosolids were collected from the City of Fort Worth Village Creek wastewater treatment facility 10 g of each yard waste sample were ground with 30 ml of water and extract was obtained by filtration. Duplicates were prepared for each sample. 10 g of raw biosolids, lime treated biosolids, fly ashes F1, F2, F3, C1 and C2 were taken in a conical flask along with 30 ml of water and placed in a shaker unit for 30 minutes. Duplicates were made for the slurry also. The slurry was made to rest for 10 minutes and extract was obtained after filtration.

Physical parameters analysis

a) pH:

pH was tested on the extracted liquid samples of each biocover material using Hach HQ40D meter (Figure 3.1). The pH probe (InteliCAL of Hach) was calibrated with pH 4, pH 7 and pH 10 calibration solution and the measurements of pH of each extract were recorded.

Figure 3.1 pH analysis

b) Moisture content

Moisture content of each of the biocover materials was tested using ASTM D2216 method. 10 crucibles were washed and oven dried at 110 °C and the empty weight of each crucible was noted. 50 grams of grass clippings, leaves, mixed yard waste, treated biosolids, raw biosolids and class C and F fly ash were each taken in a crucible and initial weight was noted. All the crucibles with biocover materials were transferred to an oven at a preset temperature of 110 °C for 24 hours. After 24 hours, the crucibles were taken out and transferred to a desiccator to allow them to cool down to room temperature. A final reading of weight of each crucible was taken and moisture content of each sample was calculated as below:

Moisture content = $\frac{Final\ weight\ of\ crucible\ with\ sample - initial\ weight\ of\ crucible\ with\ sample}{Initial\ weight\ of\ crucible\ with\ sample - empty\ weight\ of\ the\ crucible}$ * 100

c) Bulk density

Bulk density of the biocover waste materials was tested using ASTM E1109-86 method for testing bulk density of solid waste fractions (ASTM, 2004) (Figure 3.2). A 500 ml measuring jar was taken and initial weight was noted. Grass clippings were poured in to the measuring jar until it overflowed, without compaction and final weight was taken. This procedure was carried out for rest of the materials also. The readings were recorded and bulk density was calculated as per the following equation:

Bulk density kg/m^3 = $\frac{Final\ weight\ of\ measuring\ jar - Initial\ weight\ of\ measuring\ jar}{volume\ of\ measuring\ jar\ in\ ml}$

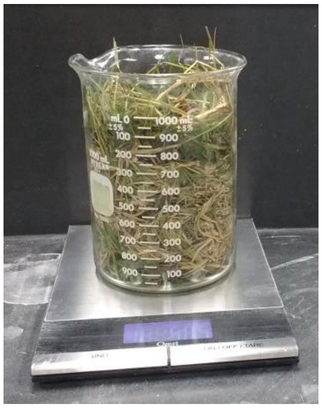

Figure 3.2: Bulk density analysis

d) Air-filled pore volume

Air-filled pore volume was determined as per the practical method available for determining air-filled pore volume of compost (Jason S. Annan, 2010). The biocover material was poured into a 1- L beaker to reach the 1-L graduation. Weight measurement of the beaker with the biocover material was taken. Empty weight of the beaker and the beaker containing water up to 1- L graduation was measured. Air-filled pore volume was calculated by the equation:

% Air-filled pore volume =

$$\frac{\left[\frac{\text{Weight of beaker with biocover and water in kg} - \text{weight of beaker with biocover in kg}}{1000}\right]}{\left[\frac{\text{Weight of beaker with water in kg} - \text{weight of empty beaker in kg}}{1000}\right]} * 100$$

This equation assumes that water occupies the volume filled by air during the experiment and on density of water, 1000 kg/l

3.1.2 Chemical analysis

The nitrate, nitrite, sulfate, ammonia and phosphorous were tested on the sample extracts using Hach D2800 Spectrophotometer (Figure 3.3 and 3.4). The Hach testing kits corresponding to each component were used for analysis. Table 3-1 lists the testing kits used for analysis of various chemical components.

The C/N ratio was tested using CHNS analyzer at Chemistry Department of University of Texas, Arlington by Dr. Roy N. Mc Dougald, Jr. The sample preparation was carried out for the CHNS analysis separately. 20 grams of each biocover material was taken, oven dried at 110 °C and fine powdered using a powdering blender and handed over for CHNS analysis.

Table 3.1: Hach spectrophotometer testing kits used for chemical properties analysis

Component	Testing kit used
Nitrate	TNT 836
Nitrite	TNT 839
Ammonia	TNT 832
Phosphorous	TNT 844
Sulfate	TNT 865

Figure 3.3 and Figure 3.4: Spectrophotometer analysis

3.2 Batch tests

3.2.1 Batch test methodology

Batch tests were conducted in Wheaton Serum bottles of 125 ml volume, which are made of borosilicate glass. 20 grams of biocover material was placed in the bottle and was sealed using aluminum crimp seal with PTFE/Butyl septa of 20 mm closure size using a crimper (Figure 3.5).

Figure 3.5: Serum bottle with butyl septa

12 % of volume of bottle air (15 ml) was taken out of the batch reactor using a syringe and needle. 5 ml of 100% methane (4 % by volume of bottle) was introduced into the reactor by syringe injection. 10 ml of pure oxygen (8 % by volume of bottle) was introduced into the reactor to add additional oxygen to ensure that the bottle would stay aerobic longer.

3.2.2 Methane oxidation measurement

Methane oxidation was calculated by measuring methane, carbon dioxide and oxygen concentration in headspace of each reactor. A SRI Gas Chromatograph-8610 C was used to measure the gas concentration (Figure 3.6). A Haysep packed column was used for analysis with flame ionization detector (FID) equipped with methanizer for detecting methane concentration and electron capture detector (ECD) for detecting oxygen concentration. The column temperature was 100° C, held steady. Ultra-purity grade Nitrogen was used as the carrier gas. For the first 24 hours, hourly samples of 50 µl were taken from the headspace of each batch reactor and analyzed. Then samples were analyzed every 12 hours for 48 hours and then daily samples were analyzed for a week. Weekly samples were analyzed until the oxidation was observed to be nearly complete.

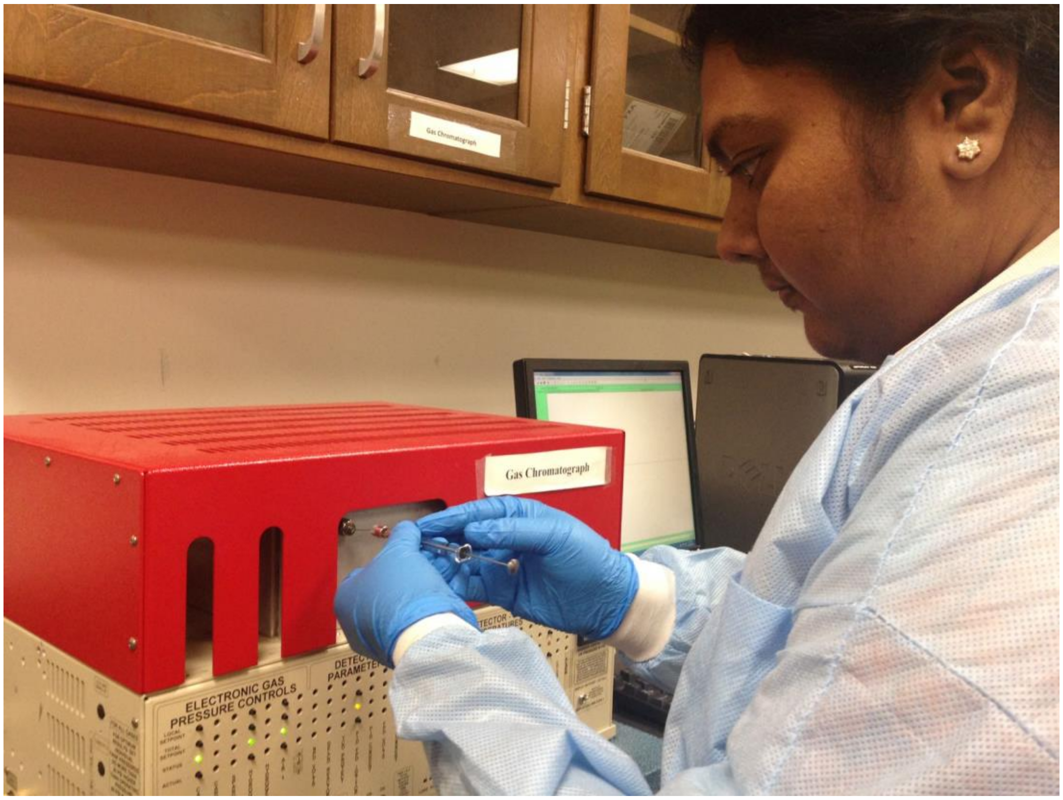

Figure 3.6: Gas chromatography analysis of headspace gas in the reactors

3.2.3 Batch test experimental design

The batch tests were initially designed on the basis of C/N ratio of the biocover materials. Batch tests were conducted in 3 phases. According to the literature review, a C/N ratio of 12-18 was considered good for efficient performance of biocover. Hence, during the first phase, combined C/N ratio of 12 and 13 were considered for mixtures of materials, since varying the C/N ratio of grass and biosolids beyond 12 and 13 was impractical due to their self C/N ratios being 11.9 for grass and 12.5 for biosolids. The basic aim of the first batch test was to see how well the grass and biosolids performed as a biocover. The following equation was used to find the weight of each material required to make a particular C/N ratio:

$$Q2 = \frac{Q1\ x\ N1\ x\ \left(R - \frac{C1}{N1}\right) x\ (100 - M1)}{N2\ x\ \left(\frac{C2}{N2} - R\right)\ X\ (100 - M2)}$$

Where Q1: Quantity of material 1 in the mixture to attain desired C/N ratio

Q2: Quantity of material 2 in the mixture to attain desired C/N ratio

C1, C2: % C in the material 1 and material 2, respectively

N1, N2: % N in the material 1 and material 2, respectively

M1, M2: moisture content in material 1 and 2, respectively

R: Desired C/N ratio

During the second set of batch tests, C/N ratio was varied from 8 to 11 for biosolids and F3 fly ash mix, and 14 to 18 for biosolids and F2 fly ash mix., considering workable C/N ratio with the materials proposed and to check if it helps to increase oxidation capacity if C/N ratio is lowered. For the third set of batch tests, the best material combination of the first two batch tests was selected and varied in proportions.

3.2.4 Batch test 1

Batch test 1 was conducted aiming at a preliminary analysis of combinations of grass, biosolids and fly ash with the C/N ratio in the range of 12.and 13 (Figure 3.7). The material mix is as per Table 3.2 Duplicates were run for each mix. As per earlier researches, biocovers behaved the best when C/N ratio is between 12 and 18. The high presence of nitrate (supporter of methane oxidation) and other favorable chemical concentrations (refer to results) made grass the first choice in selection of biocover materials among the yard wastes.

The chemical reaction occurring during methane oxidation is:

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

The biosolids were expected to provide an inoculation of microbes and nutrients. Lime-treated biosolids were avoided due to high pH levels, which act as an inhibitor. The influence of fly ash had to be known since it is to be used for adjusting the permeability. The grass and biosolids by themselves were also tested for their oxidation capacity of methane.

Figure 3.7: Batch Test 1 reactors

Table 3.2: Materials mix for Batch test 1

Biocover material	**Grass (g)**	**Biosolids (g)**	**Fly ash (g)**
Grass clippings	20	0	0
Biosolids	0	20	0
Grass + biosolids (C/N 12)	15.57	4.43	0
Biosolids + fly ash3 (C/N 12)	0	19.9	0.1
Biosolids + fly ash2 (C/N 13)	0	18.2	1.8

3.2.5 Batch test 2:

In Batch test 2, the leaves, which were second in nitrate level, were tested in combination with the biosolids for C/N ratios ranging from 14 to 18 (Table 3.3). Leaves could be varied from a C/N ratio of 14 and higher only due to individual C/N ratio of biosolids being low. Fly ash, on the other hand, has low C/N ratio and could be mixed from 8 to 17. Lower ranges were tested to check if they have good oxidation in that range. Fly ash by itself was also tested for oxidation capacity as a control. Biosolids and combination of grass and biosolids with C/N 12 were tested again for replicability. Figure 3.8 shows the reactor setup.

Figure 3.8: Batch Test 2 reactors

Table 3.3 Materials mix used in Batch Test 2

Biocover material	**Grass (g)**	**Biosolids (g)**	**Fly ash (g)**	**Leaves (g)**
Leaves	0	0	0	20
Leaves + Biosolids (C/N 14)	0	1.3	0	18.7
Leaves+ Biosolids (C/N 15)	0	2.2	0	17.8
Leaves+ Biosolids (C/N 16)	0	2.9	0	17.1
Biosolids + Fly ash 3 (C/N 11)	0	19.7	0.3	0
Biosolids + Fly ash 3 (C/N 10)	0	19.3	0.6	0
Biosolids + Fly ash 3 (C/N 9)	0	18.9	1.1	0
Biosolids + Fly ash 3 (C/N 8)	0	18.4	1.6	0
Biosolids + Fly ash 2 (C/N 14)	0	15.2	4.8	0
Biosolids + Fly ash 2 (C/N 15)	0	12.98	7.02	0
Biosolids + Fly ash 2 (C/N 16)	0	11.1	8.9	0
Biosolids + Fly ash 2 (C/N 17)	0	9.9	10.1	0
Biosolids + Fly ash 2 (C/N 18)	0	8.8	11.2	0
Grass+ Fly ash 1 (C/N 12)	0	18.2	1.8	0
Grass+ Biosolids (C/N 12)	15.57	4.43	0	0
Biosolids	0	20	0	0
Fly ash F1	0	0	20	0
Fly ash F2	0	0	20	0
Fly ash F3	0	0	20	0
Fly ash C1	0	0	20	0
Fly ash C2	0	0	20	0

A duplicate of each reactor was made, and gas concentrations were measured from the two reactors on alternate days. Steady-state values were then averaged.

3.2.6 Batch Test 3

From the batch test 1 and 2 observations, the grass with biosolids was found to be a promising combination for oxidizing methane. In order to find out a workable design in terms of percentage of grass, biosolids and fly ash, a third set of batch tests was conducted (Figure 3.9). Since grass clippings were helping the oxidation the most, its percentage was varied from 90 to 50, while, the percentage of biosolids and fly ash mix was varied correspondingly from 10 to 50. There were 5 biosolids-fly ash mixes which were tried with each of the grass percentages, making a total of 25 combinations. A duplicate for each combination was also made and gas measurements were taken alternatively from reactors having same combinations. The combination of grass, biosolids and fly ash were varied with respect to relative percentages, as shown in Table 3.4 below. A duplicate for each reactor was run. The grass and biosolids used in this set of batch tests were freshly collected in early Spring season.

Figure 3.9: Batch Test 3 reactors

Table 3.4: Materials mixes used in Batch test 3

Sample id	% Grass	% of Biosolids: fly ash mix	Resultant C/N ratio of the mix
1	90	10% 9:1 mix	7.79
2	90	10% 8:2 mix	8.05
3	90	10% 7:3 mix	8.35
4	90	10% 6:4 mix	8.70
5	90	10% 5:5 mix	9.11
6	80	20% 9:1 mix	6.37
7	80	20% 8:2 mix	6.59
8	80	20% 7:3 mix	6.85
9	80	20% 6:4 mix	7.17
10	80	20% 5:5 mix	7.57
11	70	30% 9:1 mix	5.68
12	70	30% 8:2 mix	5.86
13	70	30% 7:3 mix	6.07
14	70	30% 6:4 mix	6.34
15	70	30% 5:5 mix	6.69
16	60	40% 9:1 mix	5.28
17	60	40% 8:2 mix	5.42
18	60	40% 7:3 mix	5.60
19	60	40% 6:4 mix	5.82
20	60	40% 5:5 mix	6.12
21	50	50% 9:1 mix	5.02
22	50	50% 8:2 mix	5.13
23	50	50% 7:3 mix	5.28
24	50	50% 6:4 mix	5.47
25	50	50% 5:5 mix	5.72

3.2.7 Additional batch tests

Additional batch tests were conducted with leaves and grass in combination for information purposes. Two reactors were made with one having 70 % grass and 30 % leaves, and another one with 50 % grass and 50 % leaves (Figure 3.10). This was done to see if the presence of leaves affects the percent removal of methane significantly, since grass and leaves are not separated during collection ideally.

Figure 3.10: Additional batch reactors

3.2.8 Test for other methane loss

Tests for other methane loss were conducted for grass clippings, biosolids and fly ash. First, the materials were left in UV light under sterile conditions overnight to kill microbes, if any. 20 gram each of grass, biosolids and fly ash were filled in their respective reactors (Fig. 3.11).

Figure 3.11: Other methane loss test reactors

The reactors were sealed, and methane was introduced in to the reactors like a normal batch test. Duplicates were made in a similar way. UV treatment of materials ensured that removal of methane that happens in the reactor are due to adsorption only. The reactors were observed for next 8 weeks.

3.2.9 Methane generation test

Methane generation tests were conducted for grass, biosolids, leaves and fly ash respectively. 20 grams of each material were filled in reactors and were sealed. The headspace in these reactors contained room air and no methane (Fig. 3.12). Duplicates were also made for each reactor. The reactors were observed for methane generation if any for next 8 weeks.

Figure 3.12: Methane generation

3.3 Measurement of change in density with compaction

Due to the low density of grass, compaction tests were conducted to see if the compacted bulk density with natural moisture content of grass can satisfy the recommended bulk

Figure 3.13: Compaction test on the biocover materials

density for a biocover (0.8 -1.1 kg/l) using Proctor compaction test (ASTM D698). The same was tested for the prospective column test mix design of 70 % grass, 21 % biosolids and 9 % fly ash and with leaves since it showed a good percentage change of methane in the batch tests.

3.4 Column reactors

Column reactors were set up to analyze the oxidation of biocovers when there is a continuous flow of methane- carbon dioxide, replicating actual landfill conditions. The best biocover mix design containing grass, biosolids and fly ash was tested, along with grass as control, and yard waste compost as an additional control. Column reactors replicated a section of actual landfill cover conditions with a continuous upward flow of 50% methane and 50% carbon- dioxide from the bottom of the reactor and air (79 % N_2, 21% O_2) at the top. The column reactors were set up according to the schematic below in Figure 3.14.

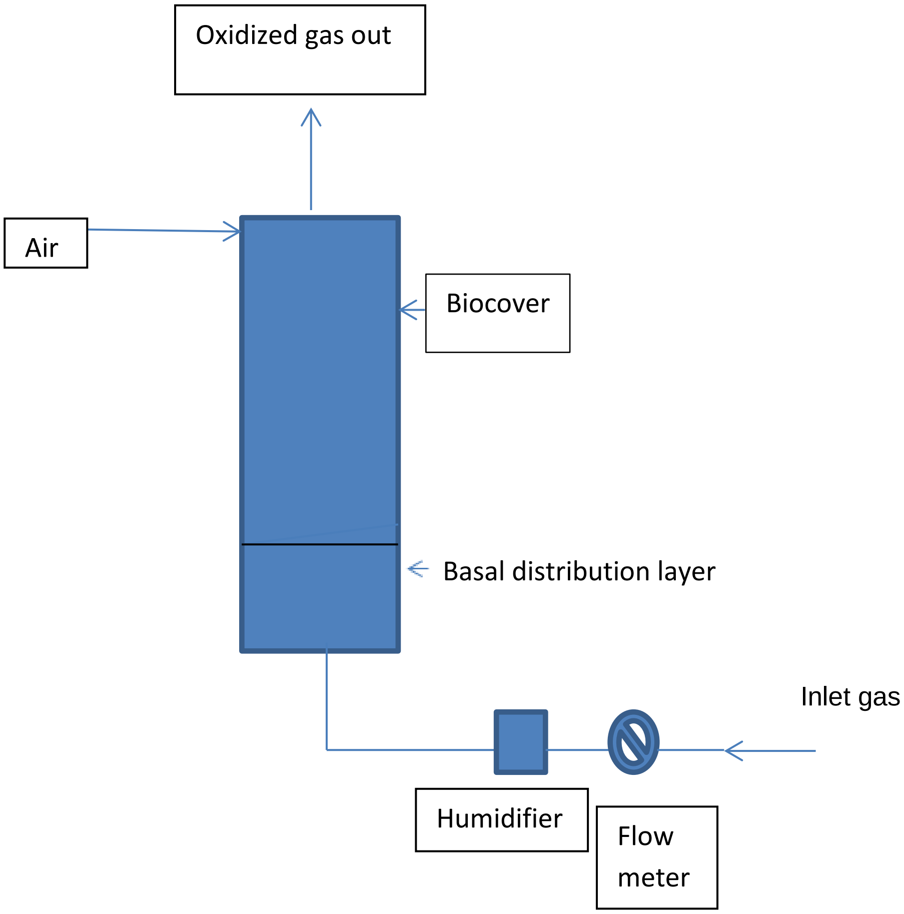

Figure 3.14: Schematic of column reactor set up

All column reactors were made of plexiglass, 8.25 in inner diameter with 0.5 inches thickness and of 35 inches of height. The columns were sealed at the bottom with a square plexiglass plate of dimension 12in x 12 in. Two circular groves of diameter 32in. and 37 in. were carved with a depth of 1/16 in. and 1/8 in. respectively. O-rings were placed in these groves to ensure air tightness of the column with the sealing. At the center of the sealing plate, a hole of half inch diameter was made for the tubing for inlet gas. The entire column reactor resting on the sealing plate was structurally supported by 4 threaded steel rods of 3/8 inch diameter with 16 threads per inch. The steel rods were equidistant from center of the column along the four corners of the sealing plate as shown in Figure 3.15.

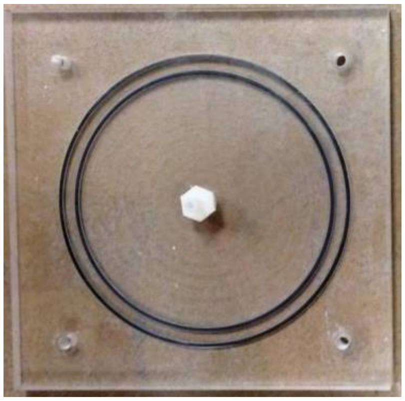

Figure 3.15: Sealing plate

A flowmeter manifold ensured distribution of inlet gas with uniform pressure and required flow rate. There were 16 Matheson flowmeters in the manifold, out of which 5 flowmeters on the bottom of the manifold were operated for the reactors for this research (Fig. 3.16).

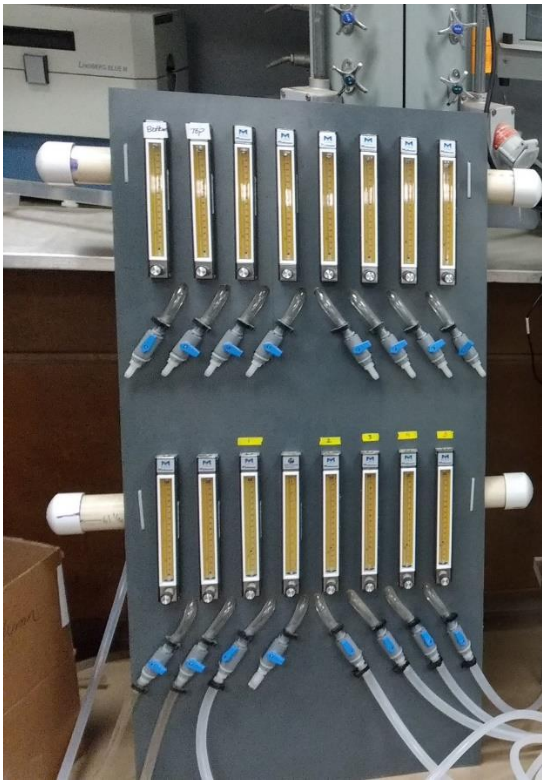

Figure 3.16: Manifold for distributing inlet gas

The flowmeters were attached to the front side of the manifold and the tubing connections were on the rear side. The manifold consisted of long thick PVC pipe, on the rear side, capped at the two ends with tubing coming out from equidistant threaded holes of the PVC pipe that went to the column reactors. The Matheson flowmeters used were FM-1050 series high accuracy flowmeters (150 mm reference), stainless steel float with E100(6-150 sccm air) flow tube and 1/8" NPT female standard connections. In order to turn the inlet gas on and off to the column reactor, miniature PVC high flow ball valves on inclined ¼ in. NPT female connection with 3/8 in. to 5/8 in. barb below the flowmeter were used.

The sampling ports were installed 6 inches apart from the base, along the height of the column reactor. They were made of half inch NPT compression fitting with 17 mm septa placed in between the connections which ensured an air tight seal. The connections for the sampling port and inlet port are shown in Figure 3.17. The tubing used for suppling the inlet gas was 3/8 inch inner diameter chemical resistant PVC tubing.

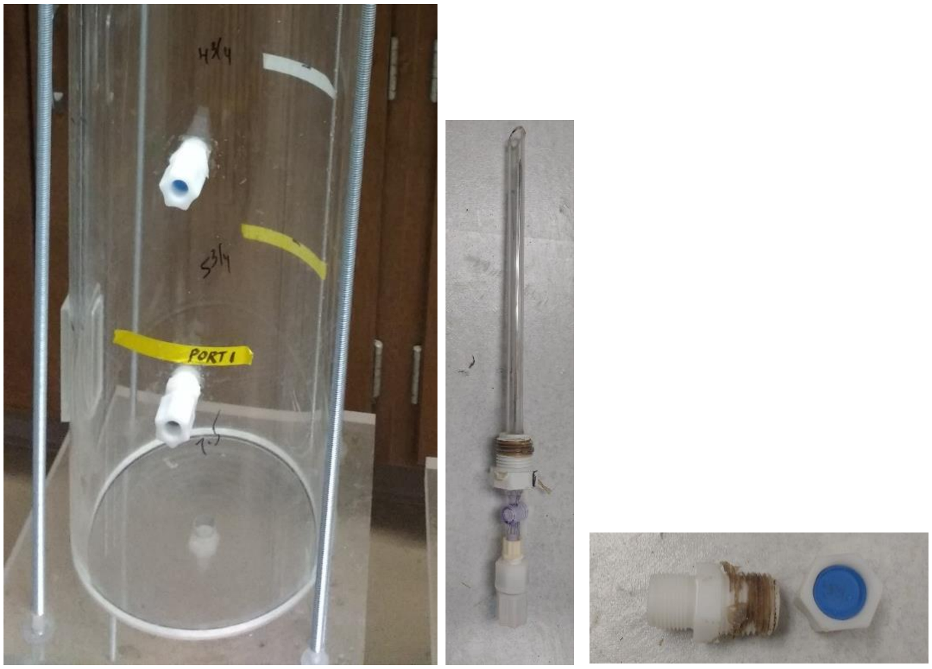

Figure 3.17: Sampling port connections and inlet port

These fittings were secured to the column reactor at the final stage, through the threaded half inch holes, before starting the column run. The connection to the inlet of the column was made with a half inch barbed fitting.

3.4.1 Biocover materials procurement

The grass clippings obtained for the column reactors were primarily two places. The grass used for reactors 1, 2 and 4 were collected from a residential area directly and were freshly mowed. Grass used for column reactor 3 was from Arlington City Landfill. All grass was not collected from the landfill because there were no fresh grass available and the available grass were exposed to rain on previous days and showed signs of decay.

Figure 3.18: Grass clippings that were collected for filling reactors

The biosolids were collected from Village Creek waste water treatment plant from the sludge dewatering facility, as shown in Figure 3.19.

Figure 3.19: Biosolids from the sludge dewatering facility

3.4.2 Setting up of column reactors with grass clippings

First, the cylindrical plexiglass portion of the column was mounted on the mold, as shown in Figure 3.20. This was done to provide a firm base for the column during compaction. A fine mesh cut in a circular pattern to the diameter of the column was placed on the mold to prevent loss of particles. Grass was used for making the first column reactor. Considering 2 feet of landfill cover, it was decided to fill the column with biocover material in 4 layers of 6 inches each. Knowing the bulk density of the grass, the weight of grass required to approximately fill the first layer as calculated as 4.1 kg. This was weighed and placed on top of the mesh. The material was compacted using a standard proctor hammer. The next layer of 6 in. was also filled and compacted with 4.1 kg grass in the same way. After 1 foot, a moisture-temperature sensor was placed and the cable for that was drawn through the top-most port. Then, the third layer of grass (4.1 kg) was filled and compacted

Figure 3.20: setting up reactor to fill biocover material

. After filling the third layer, one more moisture-temperature sensor was placed. Finally, the fourth layer of grass was filled and compacted. A representative sample from this column material was taken for testing moisture content.

The cylindrical column was then inverted with the mesh facing upward. Gravel was filled into the space where the mold existed before, which was two inches deep. The bottom sealing plexiglass plate was placed in such a way that sampling ports would be projecting perpendicular to one of the sides of the plate. The 3/8 in. threaded steel rods were run through the corner holes of the sealing plates, as shown in Figure 3.21

Figure 3.21: Making of support for the reactor

3/8 in. washers and nuts were threaded onto the four steel rods such that they were equidistant from the sealing plate. This was crucial, since any difference in the length meant the column swaying to that side, leading to structural failure. The column reactor was tilted to a horizontal position without leaving the grip on the base sealing plate. The steel rods were checked for final adjustments to ensure equal length below the base sealing plate. Then the column reactor was tilted upright and moved close to the manifold, as shown in Figure 3.22.

Figure 3.22: Column reactor 1 after setting up

The sampling ports were installed. The cables from the two moisture sensor probes were secured safely. A small fan was fitted on top of the column to replicate landfill wind conditions, as shown in Figure. 3.23.

Figure 3.23: Simulating landfill wind conditions

Another column reactor was also constructed with grass as the biocover material, to serve as a duplicate to the first column, as shown in Figure 3.24.

Figure 3.24: Column reactor 2 with grass clipping as biocover material

3.4.3 Setting up of column reactors with grass, biosolids and fly ash

Bulk density of 70 % grass, 21 % biosolids and 9% fly ash was measured as 0.88 kg/l. From that, the total weight required for the reactor with the mix design was calculated as 3.25 kg of grass, 1.86 kg of biosolids and 1.7 kg of fly ash. The grass used in this reactor was from the composting facility at Arlington City landfill. This grass clippings were a few days old and had moisture upon collection due to previous day's rain.

For this reactor, the first layer was filled with 3.25 kg of grass which was compacted first, followed by a mix of biosolids and fly ash of 1.86 kg. On top of this next layer of 3.25 kg grass was placed and compacted. At this stage moisture- temperature probe was installed, and the cable was drawn to the top. Again, the next layer of 1.86 kg biosolids- fly ash mix was placed, followed by 3.25 kg of grass and were compacted. After installing the next moisture – temperature sensor, another layer 1.86 kg of biosolids- fly ash mix was placed, followed by 3.25 kg of grass and compaction. After filling gravel at the bottom and sealing it with plexiglass lid, the reactor was moved near to the manifold. The sampling ports were installed. The cables from the two moisture sensor probes were secured safely. A small fan was fitted on top of the column to replicate landfill wind conditions, as shown in Figure. 3.25.

Figure 3.25: Column reactor 3 with grass, biosolids and fly ash

Another column reactor was also constructed with grass, biosolids and fly ash as the biocover material, to serve as a duplicate to the third column, as shown in Figure 3.26. The grass used for this reactor was freshly mowed from a residential yard. The biosolids used for both the reactors were from Village Creek waste water treatment plant at Arlington, Texas.

Figure 3.26: Column reactor 4 with grass, biosolids and fly ash

3.4.4 Setting up of additional control reactor

Based on the literature review, compost performs well as a biocover. Hence an additional control reactor was set up with compost material in it. Fresh yard waste compost was collected from the recycling facility at University of Texas at Arlington. This reactor was built in the same way as the control column reactors (grass). The bulk density of the yard waste compost collected was measured as 1.5 kg/l. Correspondingly, the weight of the compost required to fill the column was calculated and the material was equally divided into four parts and filled in the column reactor in four layers, each layer being compacted with a standard proctor hammer. After filling the material, gravel was filled at the bottom and reactor was sealed with plexiglass lid and was moved near to the manifold. The sampling ports were installed. The cables from the two moisture sensor probes were secured safely. A small fan was fitted on top of the column to replicate landfill wind conditions, as shown in Figure. 3.27.

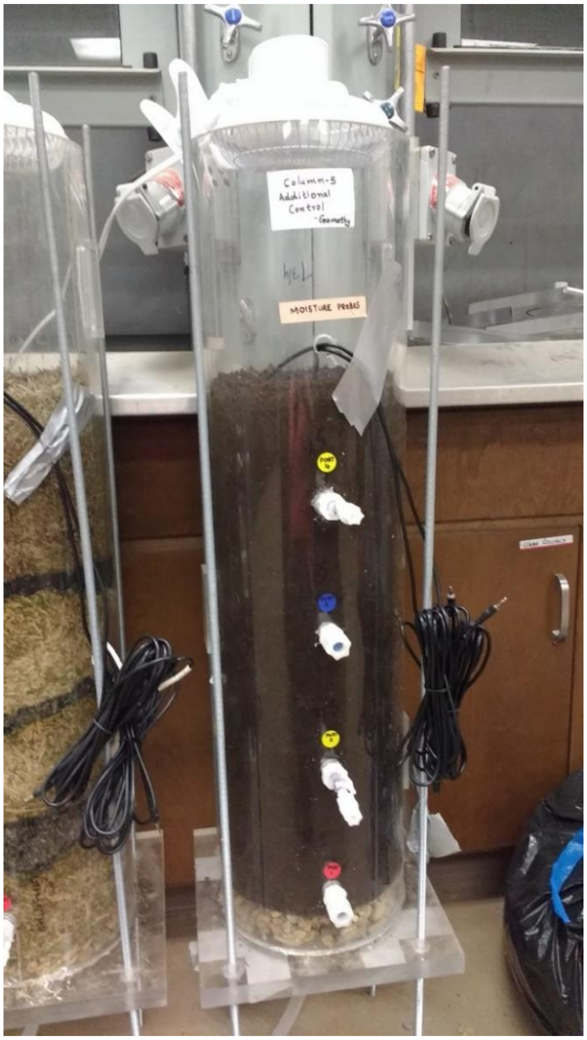

Figure 3.27: Column reactor 5 with compost

3.4.5 Setting up of inlet gas connections

50% methane – 50 % Carbon dioxide gas was passed through the inlet port of the column reactors at the base of the columns. The gas was passed through the manifold to each reactor as described earlier. The inlet gas was provided from Matheson 50% methane – 50 % Carbon dioxide cylinders set at 20 psi during the first week and at 7 psi from the 2nd week since the inlet gas did not require a greater pressure than that. The gas pressure was regulated using a 81 AF 350 regulator (Figure 3.28). Two gas cylinders were connected to the manifold and at a time only one cylinder was opened to provide gas supply. As the first cylinder gets empty, the second cylinder was opened to provide continuous supply of inlet gas. The emptied gas cylinder was then swapped with a new cylinder.

Figure 3.28: Gas cylinder regulator set up

The pressure at the flowmeters were maintained at 40 initially which read to 20 ml/min from the calibration chart for the flowmeters by Matheson (Figure 3.29). Then the flowmeters were maintained at 15ml/min of inlet gas flow rate.

Figure 3.29: Flow meters for controlling flow of inlet gas to the column reactors

3.4.6 Moisture content measurement, gas sampling and analysis

A Hamilton 22-gauge needle was used to sample gas from the column reactors. 50 µl of gas was sampled from all the 4 sampling ports in all the column reactors on alternate days and were analyzed immediately using a SRI Gas Chromatograph – 8610 C, as shown in Figure 3.30. A calibration graph was plotted each day using standard 50% methane, 50% carbon dioxide gas mixture for QA/QC.

Figure 3.30: Sampling of gas from reactor

Moisture content of all the five columns were measured every week using the Pro check 5M probes that were installed in the column reactors during filling the biocover material (shown in Figure 3.31). The lab temperature was maintained at 24 °C.

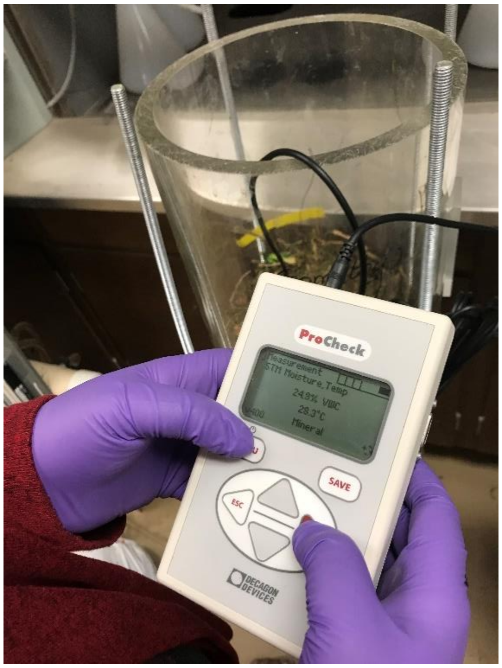

Figure 3.31: Moisture content testing equipment

3.4.7 Calculation of percentage change and biocover performance index from gas chromatogram

No. of moles of methane and Carbon dioxide from chromatography area was calculated by:

No. of moles of methane in sampling port = (Area $_{(methane)}$ * calibration factor for CH_4)/16

No. of moles of CO_2 in sampling port= (Area $_{(CO2)}$ * calibration factor for CO_2)/44

% methane in sampling port = $\frac{No{:}of\ moles\ of\ methane}{Total\ no{:}of\ moles\ of\ methane\ and\ CO2} * 100$

% removal of methane $= \frac{50-\%\, Methane\ in\ sampling\ port}{50} * 100$

50 is the percent methane entering the bottom of the column.

Biocover Performance Index for the column reactors were calculated as follows:

Weight of the column material was calculated from bulk density and volume of material.

Empty Bed residence time (EBRT) = volume of column material / flow rate of gas

Actual Residence time = EBRT * Void ratio

BPI $=\frac{(No{:}of\ moles\ of\ CH4\ in\ port\ 1-No{:}of\ moles\ of\ CH4\ in\ port\ 4)*16*volume\ of\ column\ material}{Weight\ of\ biocover\ material*actual\ residence\ time * volume\ of\ gas\ injected\ in\ to\ GC}$

3.4.8 Closed reactor gas sampling using Tedlar bag

At the end of the 90 days monitoring period, the top part of all the column reactors were closed and a Tedlar bag was installed as shown in Figure 3.32.

Figure 3.32: Tedlar bag installed on column reactors

The gas was collected in the Tedlar bag port every 3 days to understand the actual overall performance of the column reactor in methane removal. Gas collected in tedlar bag would be free of dilution of methane if any, that might happen in an open reactor. 50 µl sample from Tedlar bag was taken and analyzed using gas chromatograph.

3.4.9 Moisture content of column reactors

A representative sample of approximately 100 g was collected from materials used to fill each of the column reactors. Moisture content of each of the biocover materials was tested using ASTM D2216 method. Empty weight of five crucibles were taken. Samples from the column reactors was placed in each crucible and labelled accordingly. The weight of the crucibles with the samples was measured and recorded. The crucibles were transferred to an oven which was set at 110 °C for 24 hours, as shown in Figure 3.33.

Figure 3.33: Moisture content test of materials in column reactors

After 24 hours, they were transferred to a desiccator for cooling and were weighed. The weight of the crucibles with the samples were recorded. The moisture content of the column reactors was calculated as follows:

$$\text{Moisture content} = \frac{Final\ weight\ of\ crucible\ with\ sample - initial\ weight\ of\ crucible\ with\ sample}{Initial\ weight\ of\ crucible\ with\ sample - empty\ weight\ of\ the\ crucible} * 100$$

3.5 LEAF test on fly ash

Leaf Test was done to analyze the leaching characteristics of fly ash in the biocover. USEPA 1314: "Liquid-solid partitioning as a function of liquid-to-solid ratio for constituents in Solid Materials" Using a percolation column procedure was performed on fly ash. A plexi-glass column of ID 5 cm (approximate) and 30 cm in length was used to make the percolation column set up. 800 g of fly ash was mixed with water to attain the optimum moisture content of 14 % by weight of fly ash, obtained from the test. The top base lid of the percolation column was attached to the 30 cm long cylindrical Portion of the column and the set up was inverted so that base Portion faces the top. Quartz sand was placed up to 1 cm of height in the column. Moist fly ash was placed on top of it in 5 layers with slight tamping and leveling using a glass rod. The remaining Portion of the column was filled with quartz sand and the base lid was placed and glued. The column was inverted back so that the top Portion faces the top. The perimeter of the column connecting the base plates were sealed with silicone gel to prevent any leaks and was left for drying for next 24 hours. The percolation column was set up as shown in Figure 3.34.

An overhead tank was placed at a height and connected to a variable speed pump to supply deionized water (eluent) to the percolation tank. A 2 mm tubing was connected from the variable speed pump to the bottom of the percolation tank and another 2 mm tubing was connected from the top of the tank to the eluate collection apparatus. The tubing was primed with the eluent and the pump was switched on. The tap from overhead tank was opened to provide a minimal flow. The tap acted as a secondary flow controller to maintain the pump rate of 600-800 ml/day of eluent in to the percolation tank. The eluent rose inside the percolation tank and when it reached the top lid of the column, the pump was turned off. The column was allowed to saturate in the eluent for next 24 hours.

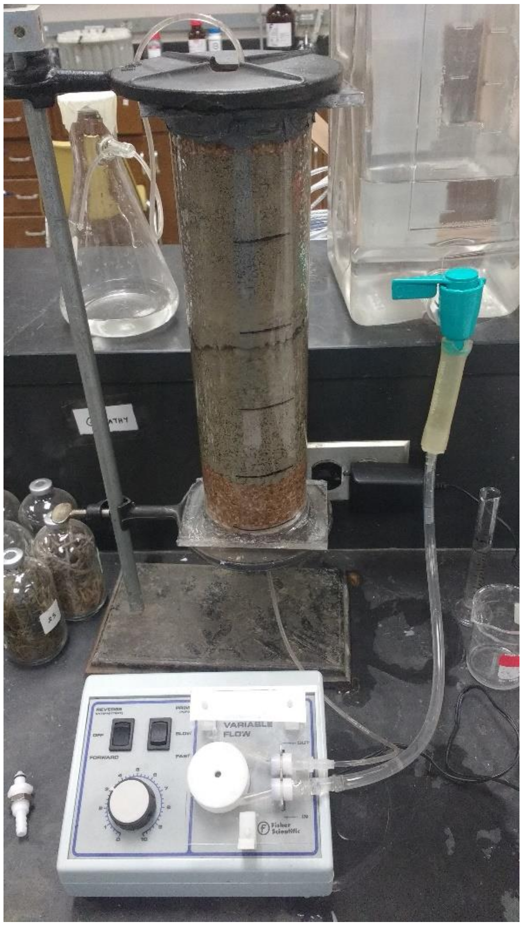

Figure 3.34: Percolation column set up for LEAF test

After 24 hours, the pump was switched on back again and adjusted to a pump rate of 800 ml/day. The eluate were collected at definite intervals of volume as per USEPA 1314. The time of eluate collection depended upon the actual flow rate inside the percolation column and it varied in each case from a few minutes to an hour from actual time interval for each eluate collection. Target time interval for each eluate collection was calculated as follows as given in USEPA 1314:

$$T_i = \frac{Mdry\ X\ \Sigma L/S}{Ri}$$

Where, T_i is the Target time interval for each eluate collection

M_{dry} is the dry weight of the fly ash used in the column

ΣL/S is the target cumulative L(Liquid)/S(Solid) for the interval time

R_i is the pump rate

Fraction volume is calculated as given in USEPA 1314 as:

Fraction volume = fraction L/S * packing mass in the column

Packing mass of fly ash in this percolation column is 800 g.

The target time interval used, volume of eluate collected with fraction of Liquid-solid ratio is given in Table 3.5. Fraction L/S is the Liquid-solid ratio for each collection interval. ΣL/S is the cumulative of fraction L/S as per USEPA 1314.

Table 3.5: Target time interval and eluate volume Table

Interval label	**End point ΣL/S (ml/g-dry)**	**Fraction L/S (ml/g-dry)**	**Target time interval (hours)**	**Fraction volume (ml)**
T01	0.2	0.2	4.8	160
T02	0.5	0.3	7.2	240
T03	1	0.5	12	400
T04	1.5	0.5	12	400
T05	2	0.5	12	400
T06	4.5	2.5	60	2000
T07	5	0.5	12	400
T08	9.5	4.5	108	3600
T09	10	0.5	12	400

3.6 Total Organic Carbon Analysis

Samples of materials that were used to build column reactors were collected. Each of them was dried in oven at 110 °C for 24 hrs and were powdered using mortar and pestle. These samples were preserved for TOC analysis. After the 90 days monitoring period, samples from each column reactor were collected, dried at 110 °C for 24 hours and powdered. These samples were outsourced for Total Organic Carbon (TOC) analysis to Huffman Hazen Laboratories.

3.7 Microbial Analysis

The samples taken from the column reactors, stored in deep freezers at -20°C, were taken to the Department of Life Science at University of Texas at Arlington. A Polymerase Chain Reaction (PCR) analysis was done on the samples to confirm the presence of methanotrophs and identify them. PCR is a widely used technology used in molecular biology, which can amplify even nano levels of nuciec acid (DNA or RNA) in a sample and make millions of copies of that DNA or RNA segment. A vast majority of PCR employs thermal cycling. Thermal cycling exposes reactants to repeated cycles of heating and cooling to permit different temperature-dependent reactions. In this set up we supply a forward and reverse primer complementary to the sequence of target DNA with PCR buffer containing magnesium.

Here, for analyzing samples from the column reactors, we used A189 and A682 primers, which were specific to the DNA of the methane-oxidizing monooxygenase enzyme. The ITS primers 1 (forward) and 2 (reverse) were used for identifying fungi. 200 µl sample was used to extract DNA. To extract DNA from the column reactor samples and the mock (water) a Qiagen power fecal kit was used. To extract DNA from E. Coli and Yeast (controls), Qiagen DNA minikit was used. A Qiagen kit works via binding nucleic acid on a silica membrane and eluting it. The DNA was extracted by following protocols of the Qiagen kits. A master mix of primers were made from which a diluted version was obtained for adding to DNA samples. The samples were prepped and were made to undergo PCR. The thermal cycle followed for PCR is shown in Figure 3.35. An agarose gel was cast, and the samples were collected after the PCR and transferred in to the wells of the gel along with primers and ethylene bromide dye. Electrical current was passed through the gel for the bands to differentiate according to the primers used. After an hour, the gel was taken out and read under UV light.

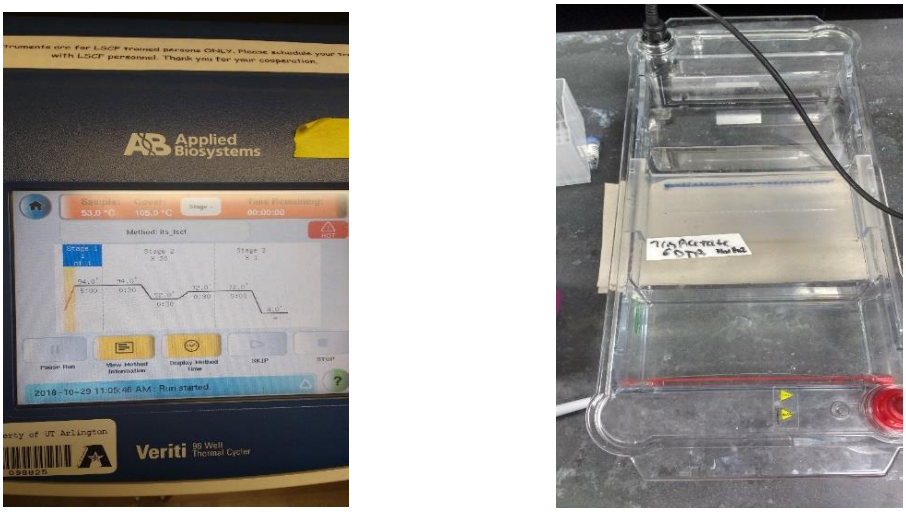

Figure 3.35: Thermal cycling in PCR and gel after adding sample and dye

Chapter 4

Results and Discussion

4.1 Physical characteristics

Table 4.1 gives the initial physical chemical analysis of materials considered for biocover application. The biosolids possessed the highest water content (80%) among all the materials and leaves (18.5%), the least. The moisture content for grass clippings (63.6 %) was just above the preferred value range of 30-60% suggested by Huber-Humer et al. (M. Huber-Humer et al., 2009). The preferred bulk density is 0.8-1.1 kg/l for biocovers, although this density would likely not meet landfill cover permeability requirements. Although the bulk density of the materials tested was less than this value, they can be compacted to achieve the preferred bulk density of biocovers.

Table 4.1: Physical characteristics of tested biocover materials

Material Tested	**Moisture content (%)**	**Bulk density (kg/l)**	**Air-filled pore volume (% v/v)**	**pH value**
Grass clippings	63.604	0.24	65.15	6.1
Leaves	18.492	0.16	72.32	6.8
Mixed yard waste	58.119	0.20	68.48	6.5
Biosolids	80.083	0.32	53.67	7.8
Lime-treated	81.508	0.345	55.28	10.1
Fly ash F1	0	1.64*	Not Applicable	7.3
Fly ash F2	0.01	1.58*	Not Applicable	8.1
Fly ash F3	0.02	1.68*	Not Applicable	6.1
Fly ash C1	0	1.78*	Not Applicable	8.5
Fly ash C2	0	1.34*	Not Applicable	7.8
Recommended values:	30-60	0.8-1.1	>25	6.5-8.5

*At optimum moisture content

The air-filled pore volume is much greater than the recommended volume of 25 % for all the materials. This should help in faster oxidation of methane since the transport of air will be easy. Such porosity, however, will not meet permeability requirements. As per literature, the pH value is an important factor in the oxidation of methane by landfill covers. Higher pH acts as an inhibitor of methane oxidation since methanotrophs do not flourish in basic pH. With respect to the physical parameter analysis, all materials, except lime-treated biosolids could be considered as biocover materials, either by themselves or in combination. Lime-treated biosolids possessed a pH of 10.1, which was a strong negative factor for methane oxidation capacity.

4.2 Chemical characteristics

The preliminary chemical analysis performed on the candidate biocover materials is given below in Table 4.2. The chemical characteristics played a vital role in deciding the combinations of materials that could be used as biocovers. The nitrate content is a strong supporter of methane oxidation. The higher the nitrate content, the greater is the oxidation as per literature (M. Huber-Humer et al., 2009). The grass clippings possessed the highest nitrate content among all the materials considered. The least was for biosolids; however, the biosolids could still act as a medium for microbes and also a material to control permeability and hence could be included in the biocover mixture.

Table 4.2: Chemical characteristics of tested biocover materials

	Nitrate	**Nitrite**	**Ammonia**	**Sulfate**	**Phosphate**	**C/N ratio**
Materials	ppm DM	ppm DM	ppm DM	ppm DM	% DM	
Grass clippings	420	1.196	213	3764	0.530	11.9
Leaves	254.8	6.280	25.6	4388	0.330	43.3
Mixed yard waste	328.4	4.920	94.4	4248	0.454	19.4
Biosolids (untreated)	3.5	1.608	340	3284	0.102	12.5
Lime-treated biosolids	32.5	3.004	282	378	0.094	8.5
Recommended values	no limit	<0.1	<400	>500	>0.3	10-20

The leaves possessed over half of the nitrate content possessed by grass clippings and could behave as a good oxidizing biocover material. Hence leaves were chosen as a secondary option if the grass clippings fail for some reason. The mixed yard waste possessed a C/N ratio more than 300 but was not considered for next level testing because of compacting difficulties that may occur.

The presence of nitrite is considered a strong inhibitor for methane oxidation by biocovers. Hence the lesser the nitrite content, the more efficient the biocover performance. The grass clippings possessed the least nitrite content. Although it exceeded the recommended value, it was not very high compared to nitrite content of other materials. Biosolids also possessed nitrite content close to the recommended value, which was considered a positive factor.

Higher ammonium values affect methane oxidation negatively. A value greater than 400 ppm DM has been found to affect the methane oxidation in biocovers. Hence ammonium concentration less than 400 ppm DM is desirable. All the materials tested in this project possessed ammonium concentration less than 400 ppm DM. Higher sulfate content (>500 ppm DM) could favor methane oxidation under anaerobic conditions and hence higher sulfate contents are preferred for biocover materials. All the materials tested except the lime treated biosolids possessed sulfate concentration greater than 500 ppm DM.

Phosphate is one of the nutrients that is required for growth of methanotrophs. A phosphate concentration of 0.3% DM is desired for the biocovers to help them for methane oxidation. The leaves marginally possess the recommended phosphate concentration. The grass clippings pass the recommendation criteria significantly. However, the biosolids and lime treated biosolids do not meet this requirement by themselves.

With respect to the physical and chemical parameters analyzed, the grass clippings pass all the recommended values, except for nitrite concentration and bulk density (which can be increased via compaction). Hence the grass clippings were selected as the major component for the biocover mixtures. Although the biosolids failed to possess many of the recommended criteria, the biosolids were selected to add to the grass clippings to support them to achieve required permeability and also to provide an inoculation of microorganisms and nutrients. The required parameters in terms of nitrate and phosphate could be achieved by mixing the biosolids with grass or leaves.

A C/N ratio of 10-20 was found as the working range for biocovers as per literature (Marion et al., 2009) Grass clippings possessed a C/N ratio of 11.9 and biosolids 12.5. The fly ash F1, F2, F3 possessed 13, 74.1 and 4.38, respectively. The leaves had a C/N ratio of 43.3 and mixed yard waste 19.3. This information was used to design the first set of batch reactors by combining the materials in different proportions to attain a particular C/N ratio. Fly ash surface characteristics were studied using Electron Spectroscopy for Chemical analysis. It showed presence of different chemicals and their percentages in the fly ashes tested. This was helpful in knowing what might leach in to the landfill when there is a potential rainfall. The results obtained are shown in Table 4.3.

Table 4.3: ESCA on fly ash

Fly ash ID	Al %w/w	C %w/w	Ca %w/w	Co %w/w	F %w/w	Fe %w/w	K %w/w	Mg %w/w	N %w/w	Na %w/w	O %w/w	S %w/w	Si %w/w
F1	0.19	3.42	1.8	0	0	3.91	3.32	0	0.49	6.32	50.73	11.34	13.42
F2	0.27	2.2	8.68	0	0.73	1.62	1.51	7.5	0	1.22	45.91	6.17	17.29
F3	0.23	13.04	1.52	0	0	3.96	0	0	1.22	1.25	48.7	9.39	14.61
C1	0.31	3.96	9.39	0	0	2.52	0	4.37	0	1.49	50.37	1.76	17.77
C2	0.3	2.89	9.84	1.16	0.64	1.62	0	3.75	0	2.22	46.54	6.64	16.61

4.3 Batch Test results

4.3.1 Batch Test 1

The Batch Test 1 consisted of reactors having grass clippings and biosolids by themselves, and combinations of grass, biosolids and fly ash. Table 4.3 shows the results in terms of maximum methane oxidation rate V_{max}.

Table 4.3: Biocover performance in Batch test 1

Biocover material	**V_{max} (nmol/kg/s)**	**K_m (%)**
Grass clippings	2121.7	2.12
Biosolids	1116.7	1.18
Grass+biosolids (C/N 12)	4410.8	2.45
Bio+fly ash 3 (C/N 12)	837.5	1.75
Bio+fly ash 2 (C/N 13)	558.3	1.73

The highest V_{max} value was shown by the reactor with grass and biosolids mixture of C/N ratio 12, followed by grass clippings by themselves. The trends in the hourly, daily and weekly concentrations of methane and carbon dioxide showed that there is a production of methane happening due to biodegradation of organic content in the grass clippings and biosolids; however, it was getting oxidized by the biocover mixture itself. There was a clear increase in the methane above the concentration of methane introduced into the reactor as well as a subsequent decrease showing the methane was getting oxidized to carbon dioxide (Figure 4.1).

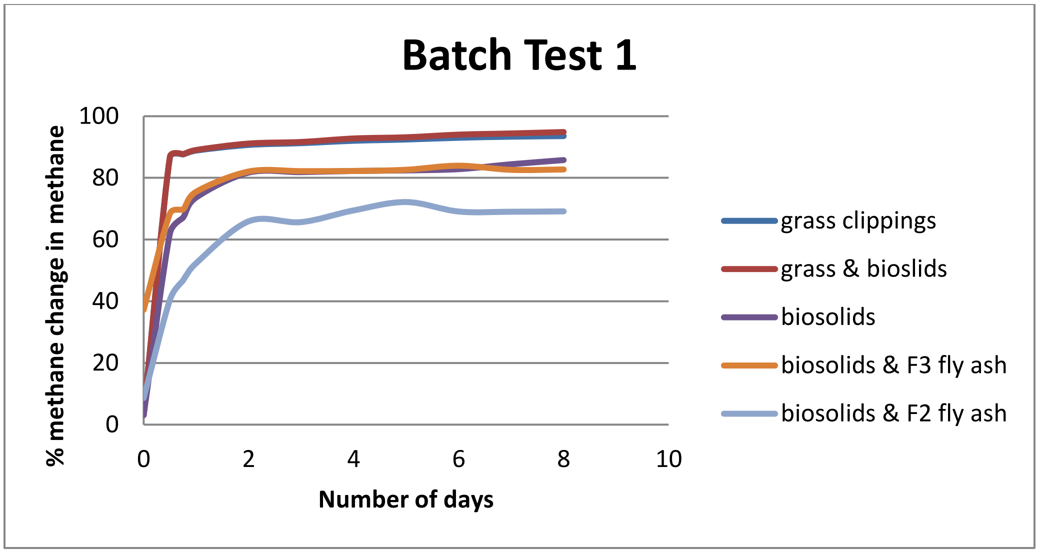

Figure: 4.1: Graph showing % methane oxidation in 9 days

These results helped in setting up the second set of batch reactors for further studies on combinations of biosolids, fly ash and leaves. Since the grass clippings possessed a C/N ratio of 11.9, and biosolids a C/N ratio of 12.5, they could not be tried with more combinations except for grass and biosolids mixture of C/N ratio. Hence leaves were tried as a choice to vary C/N ratio in the required range of 12-18.

4.3.2 Batch Test 2

In the second batch test, leaves and 2 types of class F fly ash were combined with biosolids in different C/N ratios and the following results were obtained. Leaves could be varied from a C/N ratio of 14 and higher only due to individual C/N ratio of biosolids being low. Fly ash, on the other hand, has low C/N ratio and could be mixed from 8 to 17. Lower ranges of C/N ratio were tested to check if they have good oxidation in that range. Fly ash by itself was also tested for oxidation capacity as a control. Biosolids and combination of grass and biosolids with C/N 12 were tested again for replicability.

The grass-biosolids mixture with C/N ratio 12, which was tested for reproducibility, yielded the same V_{max} value (4410.8 nmol/kg/s, Table 4.4). The biosolids and grass by itself yielded the same oxidation also. Leaves by themselves had a V_{max} value of 1391 nmol/kg/s. When leaves were combined with the biosolids for C/N ratios 14, 15 and 16, the V_{max} values were lower. This could have happened because of the microbes in biosolids supporting degradation of leaves, rather than oxidation. For the reactors with mixtures of fly ash F3 and biosolids, V_{max} values were also relatively low.

Table 4.4: Biocover performance in Batch test 2

Material	**C/N ratio**	**V_{max} (nmol/kg/s)**	**K_m (%)**
Grass	11.9	2121.7	2.12
Leaves	43.3	1390.8	1.94
Biosolids	12.5	1116.7	1.80
Grass & biosolids	12	4410.8	2.45
Leaves & Biosolids	14	558.3	1.40
Leaves & Biosolids	15	558.3	1.58
Leaves & Biosolids	16	319.5	1.62
Leaves & Biosolids	17	279.2	1.64
Biosolids & F3 fly ash	8	279.2	1.72
Biosolids & F3 fly ash	9	558.33	1.74
Biosolids & F3 fly ash	10	837.50	1.75
Biosolids & F3 fly ash	11	1085.30	1.77
Biosolids & F2 fly ash	12	837.50	1.75
Biosolids & F2 fly ash	13	558.30	1.73
Biosolids & F2 fly ash	14	325.20	1.72
Biosolids & F2 fly ash	15	265.50	1.55
Biosolids & F2 Fly ash	16	139.30	1.37

The individual reactors with the fly ash C1, C2, F1, F2, F3 show that they do not participate in methane oxidation. Leaves in combination with biosolids and leaves in combination with grass were not tested because of their vast difference in their C/N ratio which could not be mixed in the range between 12 and 18.

To summarize, the best combination of materials for biocover to enable methane oxidation would be a combination of grass and biosolids with fly ash F1 or F2 (that is, fly ash lower in carbon content). Fly ash is added in the mixture, despite producing methane for proving sufficient compaction required for biocovers (0.8- 1.1 kg/l). The combinations of grass, biosolids and fly ash and their efficiency on oxidizing methane is tested in the third batch test. Grass clippings and leaves by themselves could also be potential biocovers that can oxidize methane.

4.3.3 Batch Test 3

Table 4.5 shows results of the third batch test, which was conducted with the aim of coming up with the best combination of grass clippings, biosolids and fly ash to serve as a biocover to oxidize methane. The best oxidation out of the 25 designs was depicted by the design number 13, which corresponds to 70% grass, 21 % biosolids and 9 % fly ash. It is interesting to note that the grass-biosolids mixture with C/N ratio 12, which turned out to be the best biocover design among batch 1 and 2 tests, possessed 76.3% by grass and 23.7 % biosolids, which is almost the close to design 13.

Although 6.3% of grass and 2.7% of biosolids were replaced by fly ash in design 13, compared with the mixture tested in batch 1 and batch 2 tests, it did not affect the methane oxidation significantly. This opens the possibility of using fly ash as well to control the permeability requirements. The next highest cumulative % oxidation was given by design number 12, followed by design number 6. They had mixtures of 70% and 80% grass, 27% and 18% biosolids and 3% and 2% fly ash in their respective reactors. It is also interesting to note that, it is not the individual percentages of the grass or biosolids that determine the biocover performance in terms of methane oxidation, but their relative percentage along with the total C/N ratio that helps in the oxidation.

Table 4.5: Biocover performance in Batch test 3

Sample id	% Grass	% Biosolids: fly ash mix	V_{max} (nmol/kg/s)	K_m (%)
1	90	10% 9:1 mix	1327.50	2.67
2	90	10% 8:2 mix	1556.20	2.62
3	90	10% 7:3 mix	2175.5	2.67
4	90	10% 6:4 mix	1492.10	2.66
5	90	10% 5:5 mix	1365.20	2.63
6	80	20% 9:1 mix	1819.60	2.69
7	80	20% 8:2 mix	1917.50	2.62
8	80	20% 7:3 mix	2508.20	2.62
9	80	20% 6:4 mix	1862.38	2.64
10	80	20% 5:5 mix	1749.30	2.60
11	70	30% 9:1 mix	2475.20	2.65
12	70	30% 8:2 mix	3908.33	1.90
13	70	30% 7:3 mix	5862.50	2.17
14	70	30% 6:4 mix	3784.60	2.25
15	70	30% 5:5 mix	1395.83	2.34
16	60	40% 9:1 mix	1395.83	2.12
17	60	40% 8:2 mix	2233.33	2.13
18	60	40% 7:3 mix	2233.33	2.18
19	60	40% 6:4 mix	1675.00	1.98
20	60	40% 5:5 mix	1395.83	2.00
21	50	50% 9:1 mix	837.50	2.10
22	50	50% 8:2 mix	1395.83	2.14
23	50	50% 7:3 mix	1395.83	2.04
24	50	50% 6:4 mix	1395.83	2.10
25	50	50% 5:5 mix	558.33	2.14

A comparison of the cumulative methane oxidation percentages with their respective C/N ratios revealed that the cumulative methane oxidation generally increases as the C/N ratio is close to 6. However, it decreases with decreasing % of grass even if the C/N ratio is close to 6. Similarly, even if the percentage of grass is about 70 and C/N ratio close to 6, the methane oxidation decreases with increase in biosolids. Since the goal of the third batch experiment was to optimize the amount of grass and biosolids when fly ash is introduced for maximum cumulative methane oxidation, it is less important to learn about the impact of varying the material composition and C/N ratio in detail. Hence, from the three batch tests, the following biocover mixtures in Table 4.6 were tested for permeability and compaction requirements prior to the column experiment.

Table 4.6: Biocover mixtures selected for permeability and compaction testing

Design number	**%Grass**	**%biosolids**	**%fly ash**
13	**70**	**21**	**9**
12	**70**	**27**	**3**
6	**80**	**18**	**2**

4.3.4 Test on other methane loss

The other methane loss test conducted on grass clippings revealed that 4.38 % removal of methane in the reactor are due to adsorption. In biosolids, it was 3.78% and in fly ash it was 2.4 %. other methane loss test on leaves was the highest with 6.8 %. From this we can say that around 4 % of removal of methane in the batch reactors could be due to adsorption and rest due to oxidation.

4.3.5 Methane generation

Methane generation test was conducted with the biocover materials in the reactor and room air. There was no methane added externally. The reactor with grass clippings did not produce methane until 4 weeks of time. The 6th week measurement showed a methane production of 0.26 % by volume of the reactor. On the 8th week the methane production was 0.4 % and after three months, the methane production went up to 1.08 % by volume of reactor. Methane generation in biosolids went up to 1.9 % by volume of the reactor. However, fly ash did not produce any methane. Methane generation by leaves at the end of three months was 1.3 % by volume of the reactor.

4.3.6 Additional batch tests

Since the combination of grass and leaves was not tested previously, additional batch tests were performed with 70 % grass and 30% leaves, as well as 50 % grass and 50 % leaves. These combinations showed a percentage methane removal of 76.3 % and 69.8 %, respectively, at the end of three months. Their Vmax values were 1095.65 nmol/kg/s and 1125.72 nmol/kg/s, respectively.

4.4 Measurement of change in density with compaction

Grass was observed as the major component in the biocover mix that gave high % methane removal. A high percentage of grass in the mixture, however, meant low density of the biocover. Hence the best performing biocover mix with the least amount of grass was selected for the compaction test. The bulk density of compacted grass was measured as 0.81 kg/l and the bulk density of the compacted biocover mix was measured as 0.88 kg/l. Although the leaves by itself showed a good methane removal percentage, the density after compaction was 0.65 kg/l.

4.5 Column reactor test

The five column reactors were studied for a period of 90 days. The moisture content of the biocover materials used in the column reactors 1, 2, 3, 4 and 5 were 48.2 %, 48.6 %, 64.8 %, 56.1 % and 58.6 % by weight, respectively. The percentage change of methane was calculated for the four ports of each reactors. Biocover performance index in µg/g/hr was also calculated. The remaining sections discuss the percentage changes observed in each reactor and about their biocover performance indices.

4.5.1 Column reactor 1 - Grass

The column reactor 1 was filled with grass as the biocover material. The percentage change obtained from bottom (Port 1) to top (Port 4) of the reactor varied over the time as shown in Figure 4.2. The initial percentage change of methane from Port 1 itself was around 41%. The reason for this could have been because the Port1 was at a height of 3 in. from the base of the column reactor. So, the process of biological oxidation could have already started.

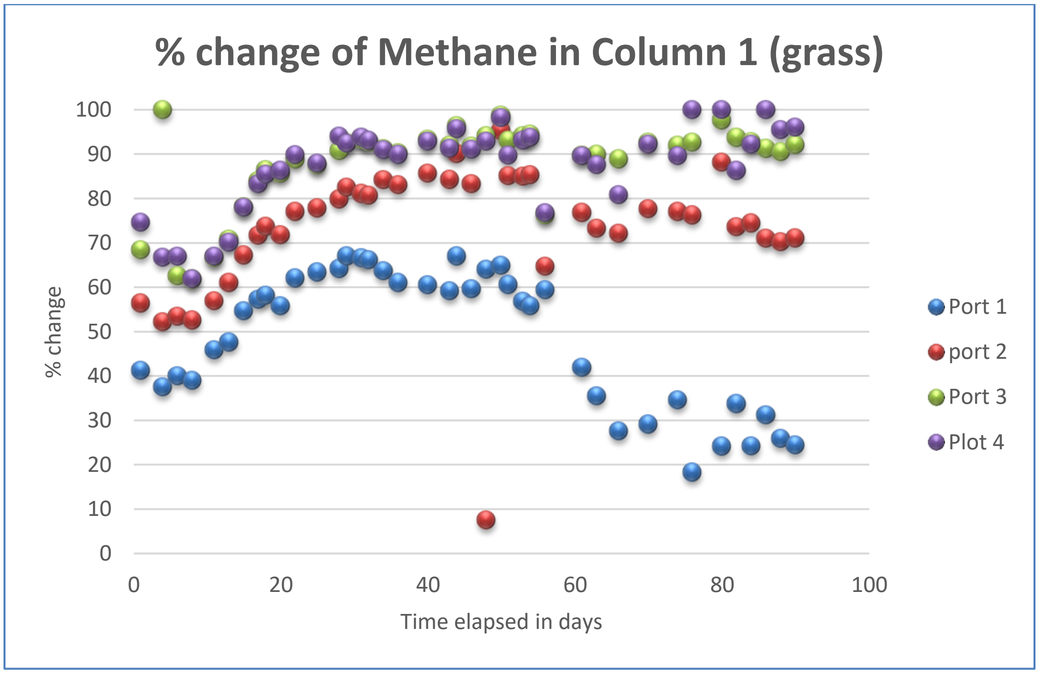

Figure 4.2: Percentage change of methane in column reactor 1

In day 4, the % methane removal found in Port 4 from the bottom was 100. This could have been due to some initial block in the gas reaching the top Ports. There was a steady increase in the percentage change of methane in Port 1 up to 54 days and it went as high as 67% in day 44. Then it remained in 60s until 56 days and started dropping from then. The Port showed a lowest of about 18% removal on 76th day. The percentage change reached about 24% at the end of 90 days. This likely meant there were some methane generation at the bottom portion of the column reactor after about 54 days.

The percentage change of methane in Port 2 started out around 50% and increased steadily up to 54 days to about 85%. After a slight drop in percentage change, the Port 2 stabilized to a percentage of around 71 by 76 days. Port 3 and Port 4 followed a close path and were showing a high percentage change of methane. Both Port 3 and Port 4 started with a high percentage change of about 70% and increased steadily until day 54 to about 93%. There was a drop of % removal in both the ports. Port 3 dropped to 88% and Port 4 dropped to 80% on 66th day. After that, both the ports showed an increase in % removal of methane and Port 4 achieved 100 % removal of methane on 76th day and stabilized. Port 3 achieved a 93% removal of methane on the 76th day and stabilized in and around that number from then on. The analysis of gas samples from the Tedlar bag installed on column reactor 1 showed an average percentage change of 91%.

It is to be noted that in about 17 days, the Port 4 of the column reactor had achieved the removal efficiency of around 78%, equal to that of the removal efficiency showcased by the batch reactor that contained grass which was monitored for 90 days.

4.5.2 Column reactor 2 – Grass duplicate

The column reactor 1 was filled with grass as the biocover material to serve as a duplicate for column reactor 1. The percentage change obtained from bottom (Port 1) to top (Port 4) of the reactor varied over the time as shown in Figure 4.3.

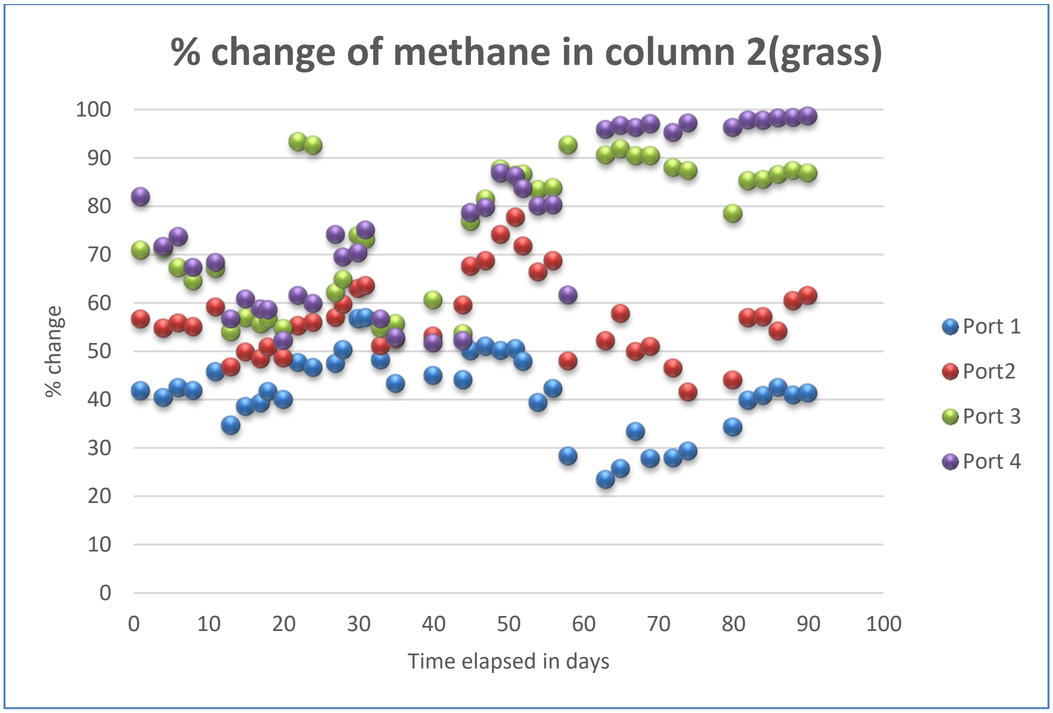

Figure 4.3: Percentage change of methane in column reactor 2

The starting percentage change on Port 1 was as same as the column 1 and it increased with a few drops intermittently to 57% by 30 days and started dropping from there. Port 1 achieved a least percentage change of 23% on 63rd day again increased its potential to 44% of removal by 82nd day and stabilized around 44% of removal of methane. Comparing with column reactor 1, Port 1 of column reactor 2 achieved the highest possible and least possible methane removal earlier. Column reactor 1 was getting stabilized on methane removal percentage by 90 days and column reactor 2 had already stabilized by 82nd day. Port 2 started with a percentage change of 60 like column reactor 1 but went through a decrease in percentage change until up to 48% until 20 days. After that the percentage change increased up to 54 days to a maximum of 72%. The percentage change of methane again dropped from there until 74 days and increased back to 62 percent by the end of 90 days monitor time.

Port 3 and Port 4 followed the same trend in percentage change except for the change in percentages. Port 3 started with 70 % removal and Port 4 started with an 80% removal like column reactor 1. Both the Ports showed a steady decrease from there until 20th day, where Port 3 decreased to 50% and Port 4 to 52%. From there percentage change of Port 3 increased to 92.6% by 58th day and stabilized to around 85% by the end of monitoring time. Port 4 on the other hand, showed intermittent drops in between the steady increase and reached 95% removal by 63 days. Then it stabilized to around 97% in the time until 90 days. All the four Ports in this column had a noise in percentage change until 44 days and picked up to a relatively stable condition from there. This could be because of the moisture content of the grass being different from that of the column reactor 1. The analysis of gas samples from the Tedlar bag installed on column reactor 2 showed an average percentage change of 92.3%

4.5.3 Column reactor 3 – Grass, biosolids, fly ash

The column reactor 1 was filled with 70% grass, 9% biosolids and 1% fly ash as the biocover material. This was the design mix that showed the highest percentage change of methane in the batch reactors. The percentage change obtained from bottom (Port 1) to top (Port 4) of the reactor varied over the time as shown in Figure 4.4.

The percentage change of methane in the Port 1 of column 3 started at 3.6% at day 1 and increased up to 43.2% until 32 days. Then there was a decrease in the percentage change until 66 days and it dropped up to 2.5%. Then there was again an increase in percentage change until 76 days and it went up to 15.6%. The percentage change was seen to stabilize for Port 1 around 10% at the end of 90 days' time frame. Port 2, which started with a 100 % removal of methane, dropped to 80% by day 8 and followed the trend shown by Port 1, except for the number in percentage change. The least percentage change shown by Port 2 in this reactor was 53.3% on day 56. The % removal went up to 90% after that and stabilized around 70% after that.

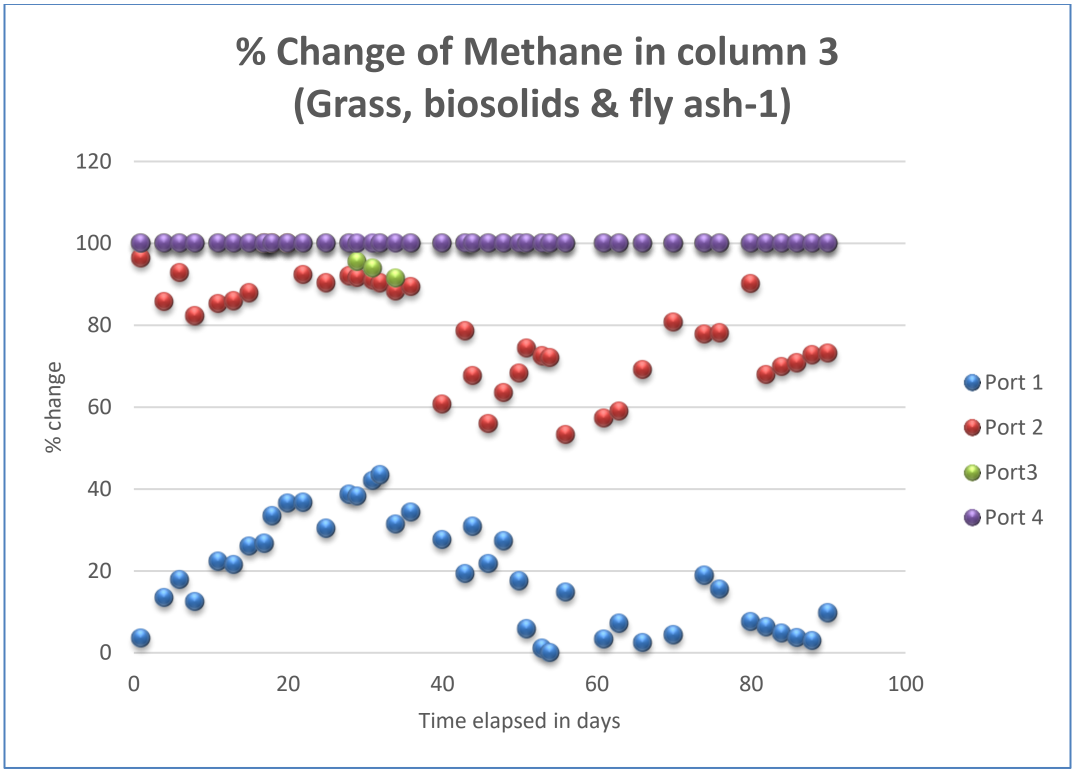

Figure 4.4: Percentage change of methane in column reactor 3

Port 3 and Port 4 were showing a percentage change of methane close to 100 from the starting of the reactor. However, Port 3 showed a slight drop in the percentage oxidation from day 29 to day 34 where the number dropped to 91.5 and got stabilized back to 100% after that. The analysis of gas samples from the Tedlar bag installed on column reactor 3 showed an average percentage change of 96.8%. In the batch reactors, the same mix of grass, biosolids and fly ash showed an 82% removal of methane. However, in the column reactor of the same mix, we could achieve up to 100 % removal.

4.5.4 Column 4 - Grass, biosolids, and fly ash duplicate

The column reactor 1 was filled with 70% grass, 9%biosolids and 1%fly ash as the biocover material and served as a duplicate for column 3. The percentage change obtained from bottom (Port 1) to top (Port 4) of the reactor varied over the time as shown in Figure 4.5.

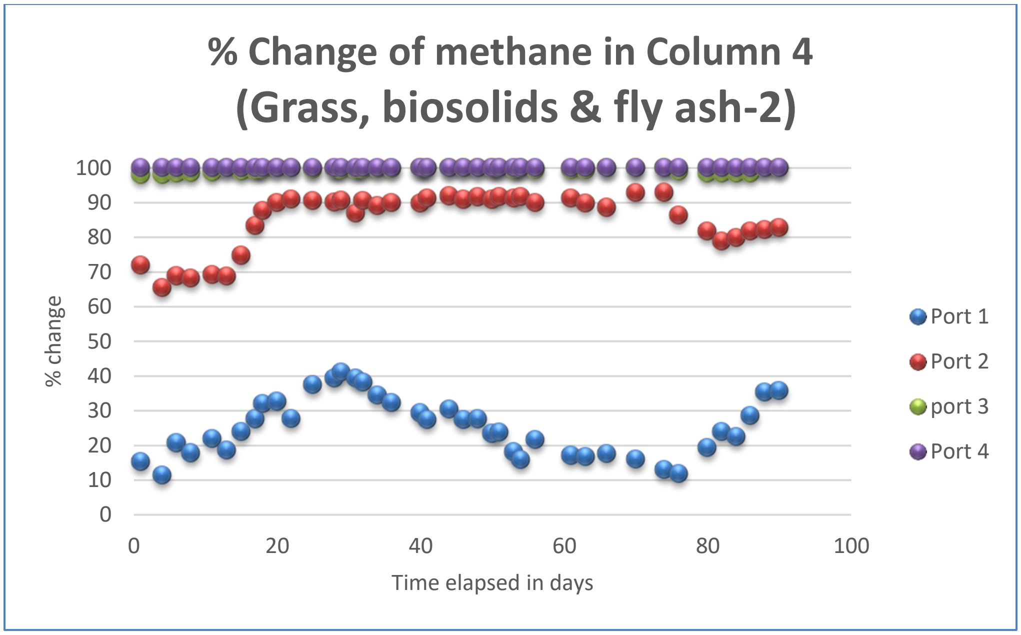

Figure 4.5: Percentage change of methane in column reactor 3

The Port 1 of column 4 started with a percentage change of around 15% and increased steadily to 41% by day 31 which was the same trend shown by column 3. Then the percentage change decreased steadily up to 11.9 % by 76th day and increased from there. Port 1 stabilized in its percentage change at about 35% by the end of the monitoring period. There was a significant difference in percentage change of methane in Port 1 of column 3 and column 4. This could be attributed to the age of the grass clippings, its source and moisture content. The moisture content of column 3 was 64.8% by weight whereas for column 4 was 56.1% by weight.

Port 2 started with a percentage change of about 70 % and increased to about 90% from 13th day to 20th day. It was a stable 90% removal until 74 days and the percentage change dropped from there to about 80% by day 82 and stabilized. Port 3 and 4 on the other hand were showing a constant 100 % removal from the first day to the last day of the monitoring period. Port 3, although it had a slight noise initially, stabilized at 100% by about 11 days. The uniformity of column 3 and column 4 is that in both of them, the Ports 3 and Port 4 were showing 100 % removal. Although the Port 2 showed a significant difference in percentage change of the two column reactors, it was compensated by the biocover materials between Port 1 and Port 3. The analysis of gas samples from the Tedlar bag installed on column reactor 4 showed an average percentage change of 97.9%.

4.5.5 Column 5 – Additional control -Compost

Fresh yard waste compost was analyzed as a biocover material for comparison of performance between the biocover from fresh grass and a compost in removing methane emissions. The percentage change obtained from bottom (Port 1) to top (Port 4) of the reactor varied over time as shown in Figure 4.6.

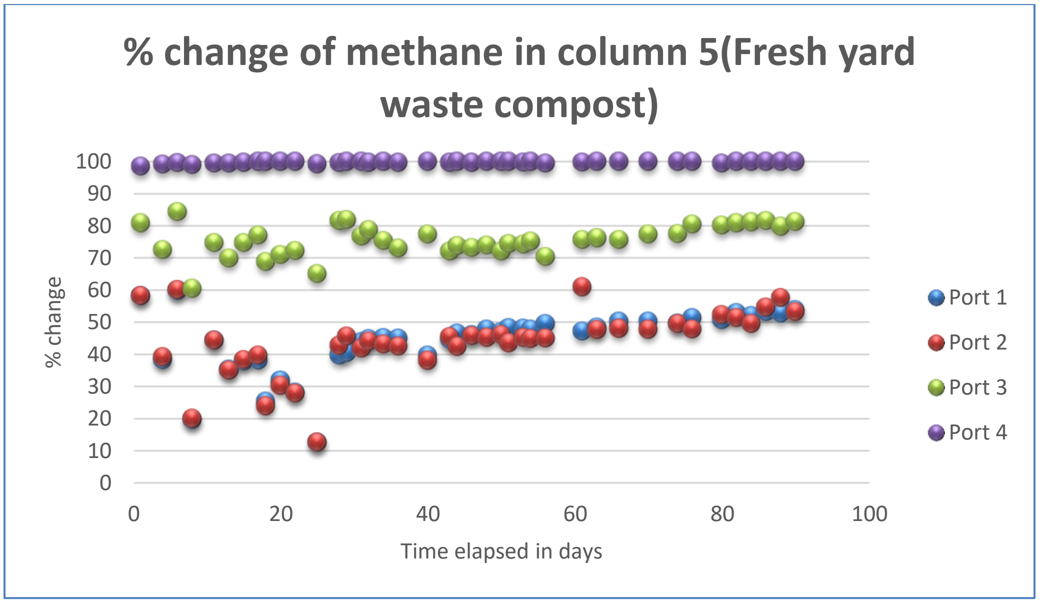

Figure 4.6: Percentage change of methane in column reactor 5

The percentage change of methane in Port 1 and post 2 of fresh yard waste compost reactor started with day 1 at about 60 %. It decreased up to 30% for Port 1 and 10 % percent for Port 2 by about 25 days from the start of the monitoring period. However, for both the Ports 1 and 2, the percentage methane removal increased and stabilized around 50 % after that. The 3rd Port started with a percentage methane removal of 80 and decreased up to 65% by 25 days. Then the removal increased and stabilized to 80% by 76 days. The 4th Port showed a constant removal of 100% from the beginning to end of the monitoring period. The analysis of gas samples from the Tedlar bag installed on column reactor 5 showed an average percentage change of 95.8%.

4.5.6 Biocover Performance Index

Biocover performance indices of the 5 columns were calculated based on the performance measured on the column from Port 1 to Port 4 over 90 days of monitoring period. Table 4.7 shows the mean, maximum, minimum and standard deviation of the biocover performance index showcased by each column.

Table 4.7: Biocover performance index of column reactors

	Column 1	**Column 2**	**Column 3**	**Column 4**	**Column 5**
Mean BPI (µg/g/hr)	19.7	21.9	40.3	46.3	29.0
Maximum BPI(µg/g/hr)	40.5	38.4	66.2	67.8	39.8
Minimum BPI(µg/g/hr)	9.1	13.2	21.7	20.7	15.6
Standard deviation	10.5	6.6	12.7	10.8	3.5

For columns 1 and 2 which contained grass as biocover material, the mean BPI and maximum BPI were not substantially different. However, the minimum BPI varied by 4 units, which caused a huge difference in the standard deviation. For columns 3 and 4, the mean BPI, maximum, minimum and standard deviation were close. The mean BPI of column 5 falls in between the BPI of column 3 and 4. The biocover performance index does not vary significantly if uncomposted yard waste is used instead of composted waste. The variation of biocover performance index with respect to time is shown in Figure 4.7.

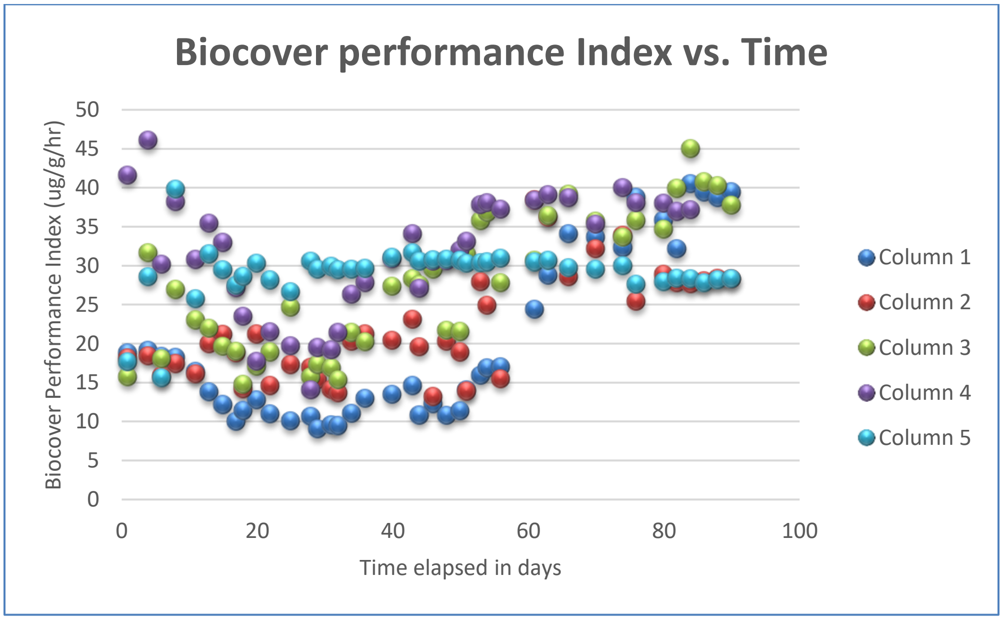

Figure 4.7: Variation of Biocover performance index with time

From the plot, we can see that the biocover performance index of the column reactors 1, 2, 3 and 4 decreases from the initial values until about 30 days and increases and stabilizes by about 65-70 days. However, the performance index of the column reactor 5 which has compost stabilizes by 25 days.

The biocover performance index is not provided in any of the literature that talks about column experiments on biocovers. However, assuming a density of 1.3 kg/l (from this study), the BPI of biocovers in literature could be compared with the biocovers in this study. The maximum BPI observed from the literature is 30.65 μg/g/hr for yard waste (Haubrichs and Widmann, 2006) and the minimum is 1.52 µg/g/hr (Scheutz et al., 2009). The mean BPI of all the biocovers observed in the literature would be around 10.5 µ/g/hr.

4.5.6 Temperature variation in column reactors over time

Temperature in the columns measured varied over the monitoring period as shown in Figure 4.8. For column 1, there was a steady increase in temperature from 28.7 ° C to 31.9 ° C. For column 2 the temperature inside the reactor reduced initially from 29.1 to 27.5 and increased gradually to 31.4 ° C. Both these columns showed an increase in temperature probably due to microbial activity. For reactor 3, the temperature showed a decrease from 30.5 ° C to 28.1° C. The grass clippings collected for reactor 3 already had masses that had started to decay, although were not used for the reactor. These grass clippings were more than a week old too. Hence, they might be at the starting point of decay which might have caused elevated temperatures initially. Later, the materials settled and there were gaps allowing air flow around the probe wire, which may have caused the lower temperature range.

For column reactor 4, temperature of the column showed an increase from 27.1° C to 31.4° C gradually. In this reactor fresh grass clippings were used, and the microbial reaction might have been slow compared to the third reactor. For reactor 5, temperature inside the column decreased from 31.1° C and remained constant around 30.1 ° C. Composts are relatively stable biocover, compared to the other 4 and hence the microbial activity due to decaying of materials would not be present here. This might have caused the temperature of the reactor to be stable near 30° C.

Overall, the temperature variation in all the columns were not substantially high so as to conclude the microbial activity. This was because, the columns were not insulated for temperatures and were controlled by environmental factors.

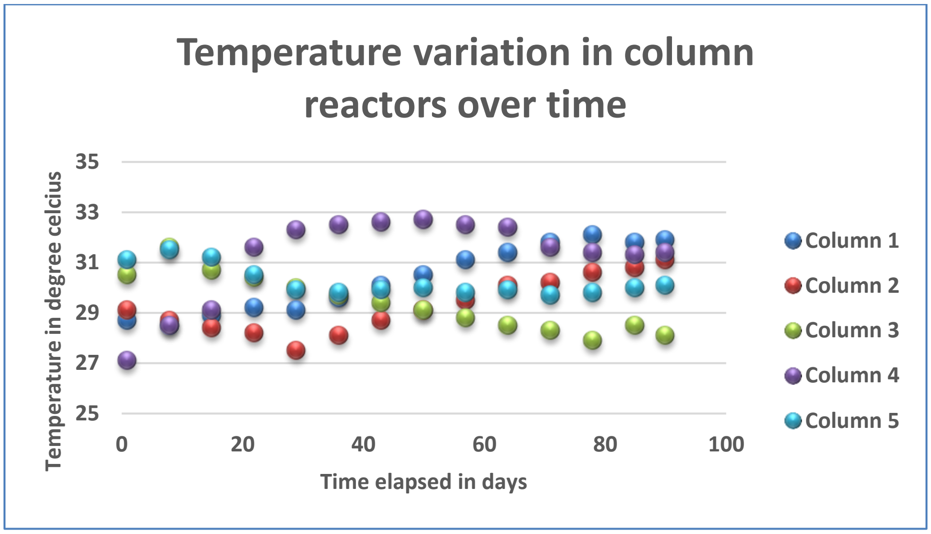

Figure 4.8: Temperature variation in column reactors over time.

4.5.7 Variation of moisture content over time

The moisture content of the column reactors varied over the time as shown in Figure 4.9. In all five column reactors, the moisture content seemed to increase steadily over the time.

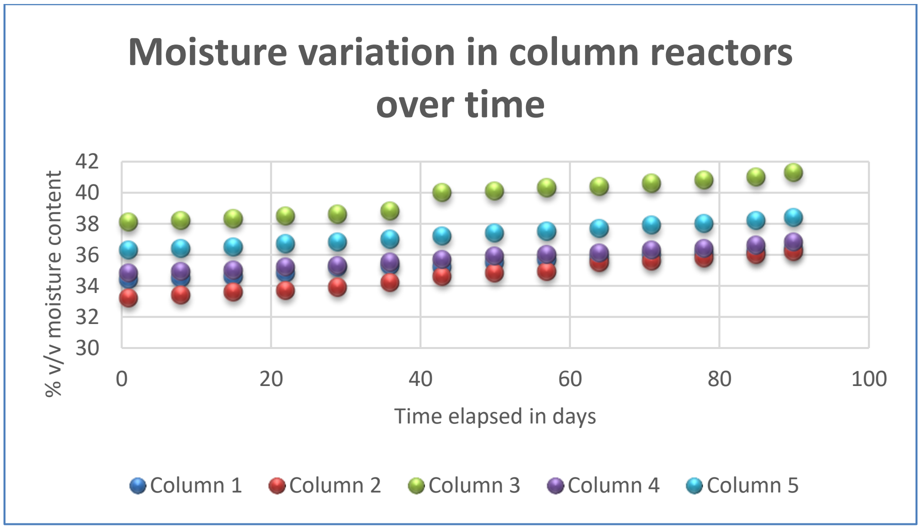

Figure 4.9: Moisture variation in column reactors

4.6 Total Organic Carbon analysis results

Higher organic content provides a favorable condition for biocovers to perform well (Huber-Humer, 2009). The total organic content was tested for fresh materials which was used to build the reactors as well as the biocover materials from each reactor. The results obtained are provided in Table 4.8.

Table 4.8: Analysis of total organic content in column reactor materials

Sample ID	**Carbon % w/w**	**Hydrogen % w/w**	**Nitrogen % w/w**	**Inorganic C % w/w**	**Organic C* % w/w**
Grass (column 1)	43.08	6.03	1.92	0.03	43.05
Grass (column 2)	43.53	6.26	1.89	0.02	43.51
Grass, biosolids & fly ash (column 3)	10.87	1.48	1.22	0.38	10.49
Grass, biosolids & fly ash (column 4)	17.06	2.38	1.46	0.37	16.69
Compost (column.5)	25.25	2.77	2.08	0.62	24.63
Grass (fresh)	45.82	6.05	2.14	0.08	45.74
Biosolids (fresh)	41.70	3.27	2.96	2.55	39.15

*By difference

The total organic content recommended by Huber-Humer is >7% on a dry weight basis. In all the reactors it was greater than 7%. The interesting point to note is that the total organic content of the column reactors 1 and 2 that had only grass, did not change significantly after 90 days period. Whereas, the reactors 3 and 4 which had biosolids and fly ash along with grass, the TOC had reduced substantially. This could be because of the presence of a variety of microorganisms in the reactors due to the presence of biosolids in them.

4.7 Observations while dismantling the column reactors

Column reactor 1 had a pinkish growth around the base of the column. It could be possibly an anaerobic fungus since the bottom part of all the column reactors were anaerobic. All other column reactors had a white pigmented mold growth at the bottom of the reactors. There were also signs of settlement of materials in column reactors 3 and 4. Column reactor 3 had settled about 2.5 inches whereas column reactor 4 had settled about an inch. The samples were collected from each column reactor for microbial analysis and were preserved in deep freezers.

4.8 LEAF test results on fly ash

LEAF test performed on the fly ash used in the column reactors revealed the leaching characteristics of heavy metals present in the fly ash. The maximum leaching concentration observed are shown in Table 4.9.

Table 4.9: Maximum heavy metal leaching during LEAF test on fly ash

Heavy metal	**Maximum leached (mg/l)**	**Maximum permissible in drinking water (mg/l)**
Ag	44.40742	0.1
Al	0.002444	0.05 to 0.2
As	15.9996	0.006
Ba	0.000533	2
Be	0.001467	0.004
Cd	0.502654	0.005
Co	0.12413	
Cr	0.502654	0.1
Cu	0.52532	1.3

Heavy metal	Maximum leached	Maximum permissible in drinking water
Mn	0.005067	0.05
Mo	0.0028	
Ni	0.002667	
Pb	0.018	0.015
Sb	0.001067	0.01
Se	0.0004	0.05
Th	0.000267	
Tl	0.157329	0.002
U	0.037199	0.03
V	0.157329	
Zn	0.037199	5

The physical characteristics such as pH, conductivity and oxidation reduction potential also varied significantly with change in Liquid-solids fraction. The change of these parameters for different L/S fraction is shown in Table 4.10.

It was seen that silver, arsenic, cadmium, chromium and thallium exceeded the permissible level in drinking water. Greater exposure to silver causes Liver, kidney damage; irritation of eyes, skin, respiratory, intestinal tract; changes in blood cells. Higher exposure to arsenic causes skin damage or problems with circulatory system; possible increased risk of cancer. Cadmium causes kidney disease, and chromium causes allergic dermatitis. Exposure to thallium causes hair loss; changes in blood; kidney, intestine, or liver problems. The pH of the eluate decreased from first to the ninth interval, which means the impurity in the eluate was decreasing. Conductivity decreased over the time and ORP increased over the time, both of which meant the contaminant leaching was decreasing over the time.

Table 4.10: Physical characteristics of leached eluate during LEAF test

Interval label	Fraction L/S (ml/g-dry)	Fraction volume (ml)	pH	Conductivity (ms/cm)	ORP (mV)
T01	0.2	160	12.43	3.78	-43.1
T02	0.3	240	12.47	1.99	-35.8
T03	0.5	400	12.5	3.17	-30.3
T04	0.5	400	12.38	2.21	-25.7
T05	0.5	400	12.29	2.05	-17.3
T06	2.5	2000	12.01	1.578	0
T07	0.5	400	12.22	1.59	-1.6
T08	4.5	3600	11.95	0.951	23
T09	0.5	400	11.85	0.904	29.7

4.9 Microbial Analysis

The exposure of the agrose gel in UV light was read using software pertaining to the UV light reader, which yielded pictures as shown in Figures 4.9 and 4.10

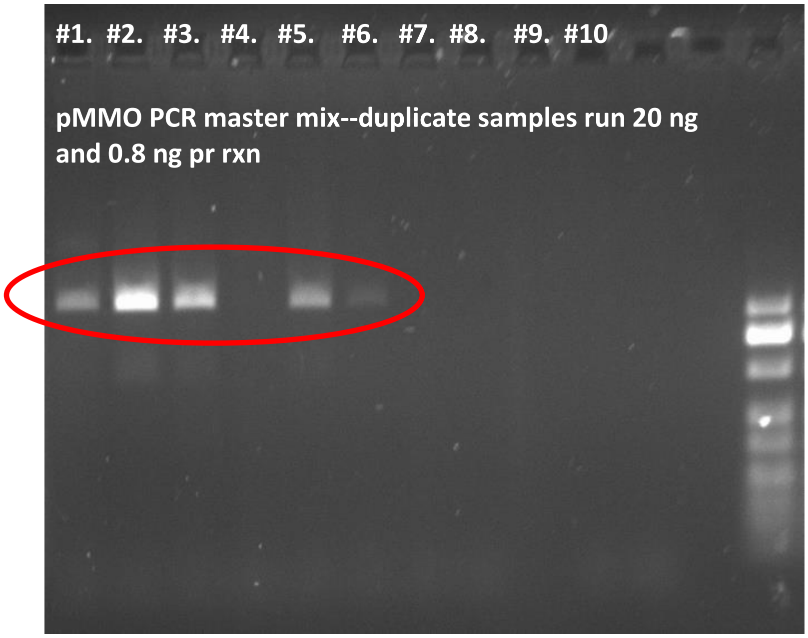

Figure 4.9: Gel picture showing positive bands for A 189- A682 primer

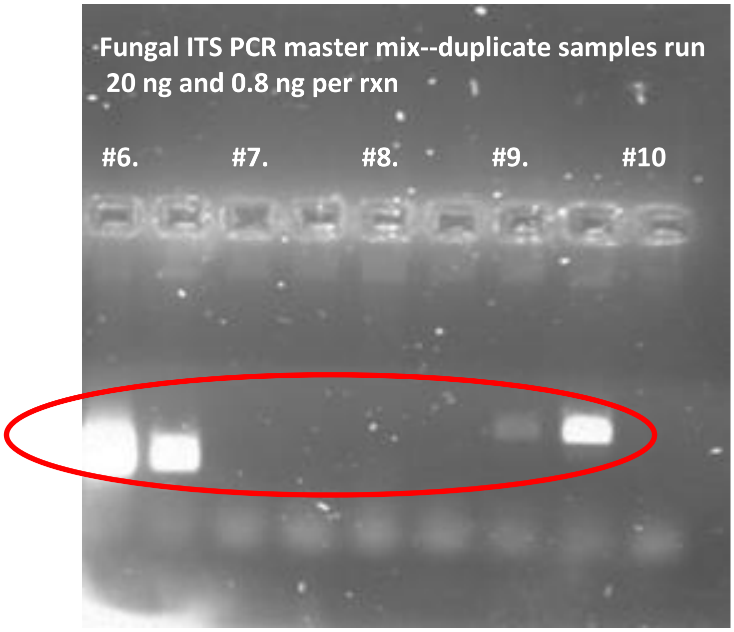

Figure 4.10: Gel picture showing positive band for ITS primer

From Figure 4.9, we see evidence of pMMO PCR amplification products in columns 1-5, indicating the presence of the pMMO gene, which is found in methanotrophs and hence confirming the presence of methanotrophs. Of the PCR reactions showing the pMMO bands, we had enough material to obtain a preliminary identification of pMMO in Columns 1, 2, 3 and 5. Column 4 had weaker PCR signals, but it was also our lowest DNA yields, so it is not surprising that we did not see robust PCR bands. A BLAST performed on the sequence obtained confirmed methalocystics and type 2 methanotrophs.

For the ITS assay (Figure 4.10), the yeast positive control was confirmed as Saccharomyces cerevisiae, validating the ITS PCR. Unfortunately, but not unexpectedly, the Column 6 ITS sequencing reaction appears to contain mixed sequences. Using the two sequence regions with the lowest amount of mixed signal, we putatively identified Scedosporium, possibly S. minutisporum.

4.10 Life cycle Inventory

As stated in the literature review, biocovers, typically used in landfills are majorly composts. Composts acts as a good biocover. However, there is a cost involved in the production of compost. Apart from that, there are also greenhouse emissions during the production stage of compost (Boldrin et al., 2009). Although composting is theoretically an aerobic process, in actually, anaerobic pockets form, which generate methane. Typically, the GHG emissions from a closed compost facility during production are lower than that of an open composting facility. Methane generation, in particular, varies from 0.03 to 6.8 kg per ton of wet weight for open composting and from 0.2 to 1.8 kg per ton of wet weight for closed composting. In landfills, the incoming green waste is normally composted, and mostly it is a static pile/windrow composting which is an open type composting. This mainly solves the economic factor involved to a great extent since the labor required and machinery maintenance is lower. This section compares the life cycle inventory of methane for composts and un-composted yard waste as biocover.

The life cycle inventory for a compost biocover and uncomposted biocover is given in Table 4.9. This analysis is based on values of methane production different types of yard waste composts from the literature and from the results obtained in this research study.

Methane emissions involved in raw material accumulation, that is yard waste collection, will be the same for both compost and un-composted category, and are cancelled out and not included in this comparison. The methane emissions during production of compost varies from 0.03 to 6.8 kg of methane per ton of wet weight composted. However, there are no methane emissions associated with production of un-composted material, since the yard waste (grass clippings) is directly used as biocover. The fresh green compost were able to oxidize 22.7 kg of methane per wet weight of compost and aged green compost could oxidize 17.02 kg. Comparatively, the un-composted grass clippings and its combination with biosolids and fly ash could oxidize more than twice that value, i.e 47.26

kg, and 93.52 kg respectively per wet weight of the waste. Leaf compost oxidizes almost equivalent methane as oxidized by un-composted grass clippings.

Table 4.9: Life cycle inventory of methane for compost and un-composted biocover

Life Cycle Phase	Composted materials (per ton wet weight)					Un-composted materials (per ton wet weight)		References
	Leaf compost	Garden compost	Fresh green compost	Aged green compost	Yard waste compost (this study)	Grass clippings (this study)	Grass, Biosolids & fly ash (this study)	
Raw material accum-ulation	-	-	-	-	-	-	-	
Produc-tion of material	0.03 to 6.8 kg	0.03 to 6.8 kg	0.03 to 6.8 kg	0.03 to 6.8 kg	0.03 to 6.8 kg	0	0	(Boldrin et al., 2009)
Use as biocover	(-) 45.4kg	(-) 5.67 kg	(-)22.7 kg	(-)17.02 kg	(-)62.75 kg	(-)47.26 kg	(-)93.52 kg	(Scheutz et al., 2009) , (Wilhusen et al., 2004), (Yazdani, 2010)
End of cycle	-	-	-	-	-	-	-	
TOTAL	- 45.37 to – 38.6	-5.64 to 1.1	-22.67 to -15.9	-16.99 to -10.22	-62.72 to -55.95	-47.26	-93.52	

From the literature review, we can find the efficiency of various types of yard waste compost in oxidizing methane in terms of g/m^2/day. Assuming a bulk density of 1.3 kg/l for the composts (equivalent to that obtained in this study for yard waste compost), a depth of application of 2 feet for the biocovers, for a span of 3 months, the mass of methane removed by the biocovers in kg per ton of wet weight can be calculated. Table 4.9 gives the calculated biocover efficiency in removing methane mass in kg per ton of wet weight of biocover.

Overall, we can see that the carbon foot print for the un-composted biocovers are lower than the composted ones, even though the methane removal by the yard waste compost is fairly good as un-composted yard waste. The use of yard waste as a biocover proved 62.75 kg of methane removal per ton of compost in this study. As per literature, the methane removal reported for yard waste compost is 66.2 kg per ton of compost. (Haubrichs and Widmann, 2006). It is still less than the methane removal by un-composted grass clippings, biosolids and fly ash mixture. Total carbon foot print by yard waste compost is from -62.72 to -55.95, whereas, it is -68 kg/ton wet weight for un-composted grass, biosolids and fly ash mixture. This is because there is no methane generated as in composting during the un-composted grass clippings being used as biocover directly.

Chapter 5

Conclusions and Recommendations

Biocovers have been globally playing a very important role in enhancing methane oxidation. Traditional biocovers implemented are various types of composts, materials such as wood ships, saw dust, mulch, and waste water sludge, which can support the growth of methanotrophs. Composts are biocovers that are most widely used. Production of composts, although being theoretically aerobic, generates methane in anaerobic pockets inside them and is a time-consuming and money involved process. This research focused on developing a more sustainable biocover from un-composted yard waste and other materials.

5.1 Summary and Conclusions

Major findings from this research are:

1. Yard waste by itself possess the physical and chemical characteristics to serve as a biocover; except for the bulk density, which can be achieved by mixing with bulking agents such as biosolids and fly ash. A compaction test on grass clippings at its natural moisture content showed that it can achieve the bulk density recommended for biocovers.

2. Fly ash by itself did not show any oxidation due to absence of microbes. Also, the availability of biologically available carbon is not known. The combinations of fly ash and biosolids were producing methane probably due to the fly ash encapsulating the biosolid particles and creating an anaerobic condition.

3. In batch tests, leaves, grass clippings, leaves with grass clippings, and combinations of grass clippings with biosolids demonstrated a better biocover performance indeces of 79 % methane removal (2.25 µg/g/hr), 76.8 % methane removal (2.1 µg/g/hr), and 81.5% methane removal (2.3 µg/g/hr) respectively, compared to biosolids by itself with 3.36 % methane removal (0.095 µg/g/hr), biosolids combined with fly ash having -9.89 % methane removal (-0.25 µg/g/hr), fly ash by itself 0% with methane removal(0 µg/g/hr), and leaves combined with biosolids with 0.25 % methane removal(0.01 µg/g/hr).

4. A factorial design of batch experiments showed that the ratios of grass: biosolids: fly ash giving the highest methane oxidation were 70:21:9, 70: 27:3, and 80:18:2, with methane removal of 81.8% (2.3 µg/g/hr), 79% (2.2 µg/g/hr) and 79.8% (2.3 µg/g/hr)(respectively. From adsorption study, it was found that, there was adsorption in grass, leaves, biosolids and fly ash that contributed to 4.38%, 6.8%, 3.78% and 2.4% methane removal, respectively. Methane generation study on these materials revealed that there was methane generation by grass (1.08 %), biosolids (1.9 %) and leaves (1.3 %).

5. From the column reactor experiment, we learned that the un-composted grass clippings and its combination with biosolids and fly ash works well as a biocover, with slightly more efficiency in methane removal than the compost biocover. The average biocover performance index for grass, biosolids and fly ash mixture from column experiment was 30.28 µg/g/hr with 100% methane removal in the top

layers. The average biocover performance index for yard waste compost from the column experiment study was 29.04 µg/g/hr with 100% removal of methane in the top layers. Also, there were evident settlements in heights of the materials in the grass/biosolids/fly ash columns, which meant the microbial activity was more for the grass-biosolids-fly ash combinations. This is a positive factor for temporary covers since the landfill volume used will be less and waste can directly be placed on this cover in real time condition.

6. The average biocover performance index of column reactors 3 and 4 which is 30.28 µg/g/hr was almost equal to that of the biocover performance of compost 29.04 µg/g/hr in this study. However, it is greater than the biocover performance index reported for leaves compost from the literature which is 21.01 µg/g/hr. This is fairly equal to the biocover performance index of grass clippings reactor in this study.

7. From the LEAF test on fly ash it was found that the leaching of heavy metals arsenic, thalium, cadmiu, chromium, and silver were beyond the permissible limit. Hence fly ash should not be considered for the biocover, without a mechanism to prevent leaching. Even otherwise, the grass-biosolids mixture passes the density criteria for biocovers after compaction. Hence fly ash is not mandatory in this cover since it doesn’t contribute to methane removal.

8. From the life cycle inventory of the composted biocovers vs. un-composted biocovers, it was observed that the overall carbon foot print for the un-composted biocovers is less compared to the composted biocovers. The carbon footprint for composted biocovers varied from 1.1 kg of methane to -62.72 kg of methane emissions per ton of wet weight of compost used as biocover. The carbon foot print for un-composted grass clippings and grass clippings with biosolids and fly ash was -47.26 kg of methane emissions and -68.04 kg of methane emissions respectively per ton of wet weight of material used.

9. The microbial analysis done on samples from the column tests revealed high presence of Type 2 methanotrophs and Methylobacter bacteria. The addition of biosolids helped in increasing the microbial colonies in the biocover. There were also presence of fungi putatively identified as S.minutosporium, which are fungi known to oxidize hydrocarbons.

5.2 Recommendations for future study:

1. The grass collected in fall and spring showed differences in their properties such as moisture content, bulk density etc. It would be beneficial to study the seasonal variation of yard waste characteristics and their effect on methane removal.

2. The LEAF test on fly ash showed leaching of potentially harmful heavy metals greater than permissible limits. Hence it is advisable to conduct additional batch tests to determine the optimal grass/biosolids mixture ratio, without fly ash, conduct additional column tests and field tests on the optimal mix.

3. In the column experiments, the reactors attained a stable methane removal by 75-80 days. It is beneficial to run these reactors for at least a year to understand its behavior in longer run. H_2S emissions from the column reactors are another potential area to be explored during this period.

4. It would be worth to study the impact of methane flux on the grass and biosolids biocovers since it may not be a steady methane flux in ideal case

5. From the batch reactors, leaves were competing almost equal to the grass clippings. However, the bulk density of leaves could not be achieved around the

recommended values for biocovers even after compaction. A similar type of study on leaves as biocovers, with techniques to improve its bulk density would help to solve a lot of yard waste volume issues in the landfills.

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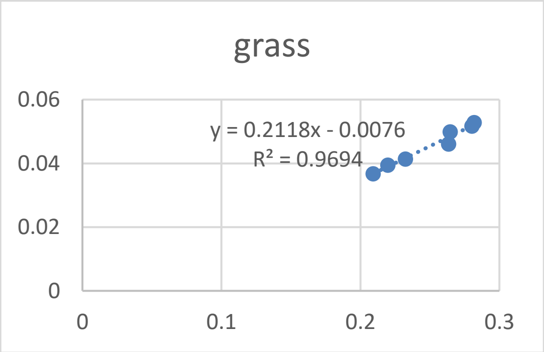
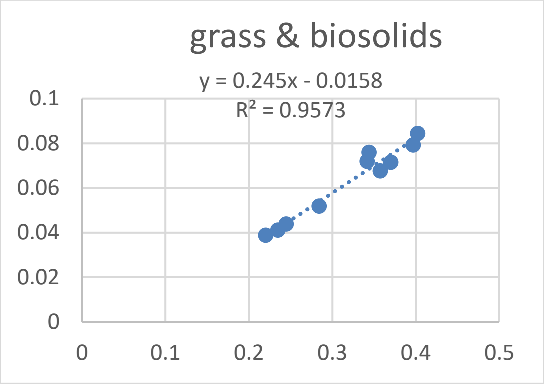
Appendix 1

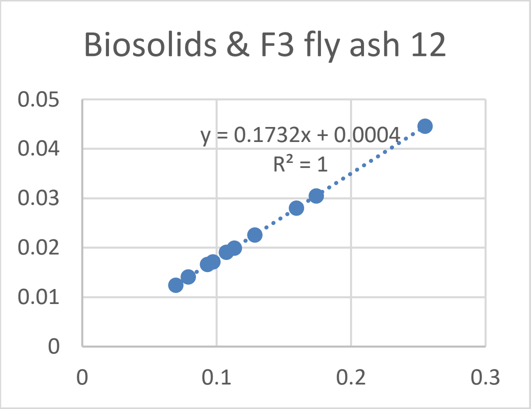
Batch test 1 data

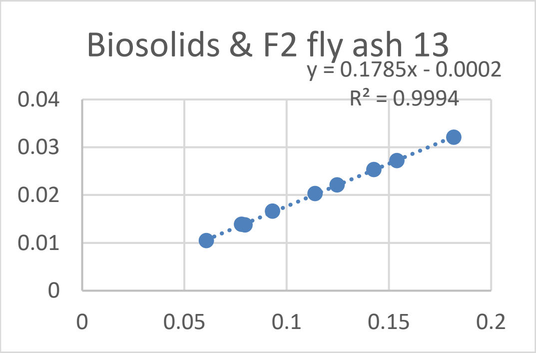
Cover Material	Days	% molar conc. CH_4	$(A_o\text{-}A_t)/t$ %moles/day	$(\ln(A_o/A_t))/t$
Grass	0	5.85		
	1	5.587	0.263	0.0461
	1.5	5.536	0.209	0.0368
	2	5.385	0.232	0.0414
	2.5	5.300	0.220	0.0395
	3	5.009	0.280	0.0517
	3.5	4.863	0.282	0.0528
	4	4.791	0.265	0.0499
Grass & biosolids	1	5.615	0.235	0.0410
	1.5	5.520	0.220	0.0388
	2	5.360	0.245	0.0437
	2.5	5.139	0.284	0.0518
	3	4.777	0.358	0.0675
	3.5	4.554	0.370	0.0715
	4	4.261	0.397	0.0792
	5	3.837	0.403	0.0843

	6	3.799	0.342	0.0720
	7	3.440	0.344	0.0759
Biosolids	1	5.790	0.0600	0.0103
	1.5	5.760	0.0599	0.0103
	2	5.735	0.0576	0.00994
	2.5	5.706	0.0574	0.00994
	3	5.685	0.0551	0.00956
	3.5	5.643	0.0590	0.0103
	4	5.544	0.0765	0.0134
	5	5.536	0.0629	0.0110
	6	5.486	0.0607	0.0107
	7	5.469	0.0545	0.00963
Biosolids & Fly ash 12	1	5.595	0.255	0.0446
	1.5	5.589	0.174	0.0304
	2	5.532	0.159	0.0280
	2.5	5.529	0.128	0.0226
	3	5.511	0.113	0.0199
	3.5	5.510	0.0972	0.0171
	4	5.422	0.1071	0.0190
	5	5.385	0.0930	0.0166
	6	5.377	0.0788	0.0140
	7	5.364	0.0695	0.0124
		5.294		
Biosolids & Fly ash F2 13	1	5.770	0.0797	0.0137
	1.5	5.759	0.0608	0.010473834
	2	5.486	0.1818	0.032081005
	2.5	5.465	0.1539	0.027220915
	3	5.422	0.1427	0.025335744
	3.5	5.414	0.1246	0.022137686
	4	5.394	0.1140	0.020280252
	5	5.384	0.0931	0.0165901
	6	5.382	0.0780	0.013891754




grass & biosolids
y = 0.245x - 0.0158
R² = 0.9573
0.1
0.08
0.06
0.04
0.02
0
0
0.1
0.2
0.3
0.4
0.5


Biosolids & F3 fly ash 12
y = 0.1732x + 0.0004
R² = 1
0.05
0.04
0.03
0.02
0.01
0
0
0.1
0.2
0.3


Biosolids & F2 fly ash 13
y = 0.1785x - 0.0002
R² = 0.9994
0.04
0.03
0.02
0.01
0
0
0.05
0.1
0.15
0.2

Batch test 2

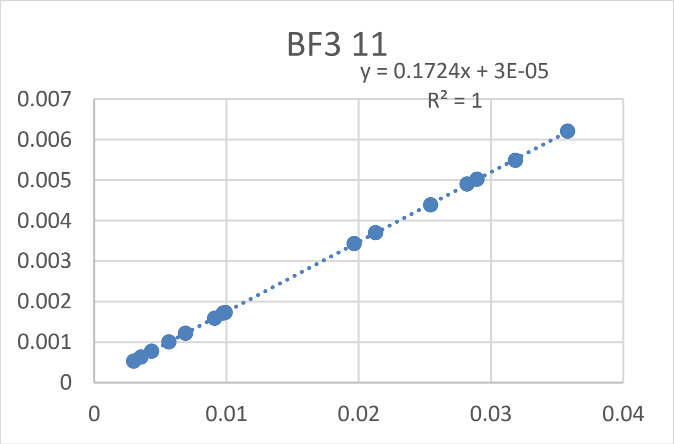
Material	No: hours	% molar concentration of methane	$(A_o-A_t)/t$ %moles/day	$(\ln(A_o/A_t))/t$
BF3 11	1	5.788	0.032	0.005
	2	5.769	0.025	0.004
	3	5.713	0.036	0.006
	4	5.704	0.029	0.005
	5	5.679	0.028	0.005
	7	5.671	0.021	0.004
	9	5.643	0.020	0.003
	20	5.638	0.009	0.002
	24	5.582	0.010	0.002
	28	5.547	0.010	0.002
	48	5.488	0.007	0.001
	72	5.414	0.006	0.001
	96	5.403	0.004	0.001
	120	5.394	0.004	0.001
	144	5.391	0.003	0.001
BF310		5.819	0.001	0.000
		5.815	0.002	0.000
		5.814	0.002	0.000
		5.801	0.005	0.001
		5.801	0.004	0.001
		5.777	0.006	0.001
		5.779	0.005	0.001
		5.746	0.004	0.001
		5.743	0.003	0.001
		5.740	0.003	0.000
		5.710	0.002	0.000
		5.695	0.002	0.000
		5.684	0.001	0.000
		5.681	0.001	0.000
		5.680	0.001	0.000
BF3 9	1	5.726	0.094	0.016
	2	5.706	0.072	0.010
	3	5.701	0.050	0.007
	4	5.690	0.040	0.006
	5	5.687	0.033	0.005
	7	5.679	0.025	0.004

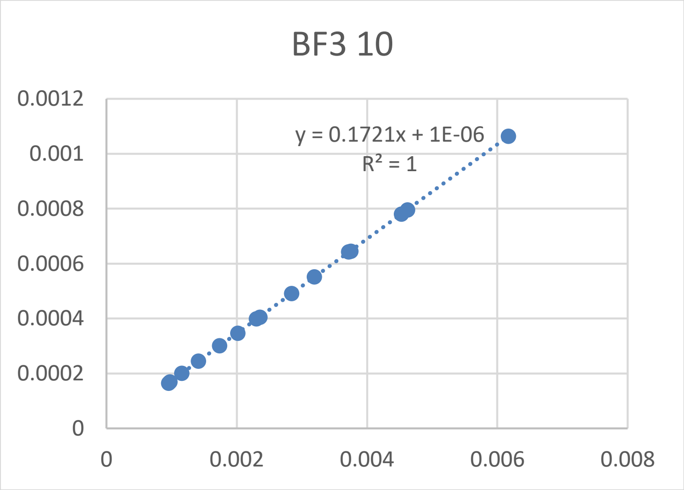
	9	5.677	0.020	0.003
	20	5.659	0.010	0.001
	24	5.653	0.008	0.001
	28	5.636	0.008	0.001
	48	5.630	0.005	0.001
	72	5.600	0.003	0.001
	96	5.583	0.003	0.000
	120	5.571	0.002	0.000
	144	5.569	0.002	0.000
BF3 8	7	5.7201	0.019	0.002
	9	5.673	0.020	0.003
	20	5.671	0.009	0.001
	24	5.665	0.008	0.001
	28	5.662	0.007	0.001
	48	5.660	0.004	0.001
	72	5.659	0.003	0.000
BF2 13	2	5.714	0.068	0.009
	3	5.678	0.057	0.008
	4	5.647	0.051	0.008
	5	5.610	0.048	0.007
	7	5.563	0.041	0.006
	9	5.516	0.037	0.006
	20	5.506	0.017	0.003
	24	5.490	0.015	0.002
	28	5.483	0.013	0.002
	48	5.479	0.008	0.001
	72	5.474	0.005	0.001
	96	5.452	0.004	0.001
	120	5.444	0.003	0.001
	144	5.441	0.003	0.000
FB2 14	1	5.732	0.118	0.015
	2	5.730	0.060	0.008
	3	5.622	0.076	0.012
	4	5.618	0.058	0.009
	5	5.617	0.047	0.007
	7	5.616	0.033	0.005
	9	5.512	0.038	0.006
	20	5.511	0.017	0.003
	24	5.503	0.014	0.002
	28	5.498	0.013	0.002

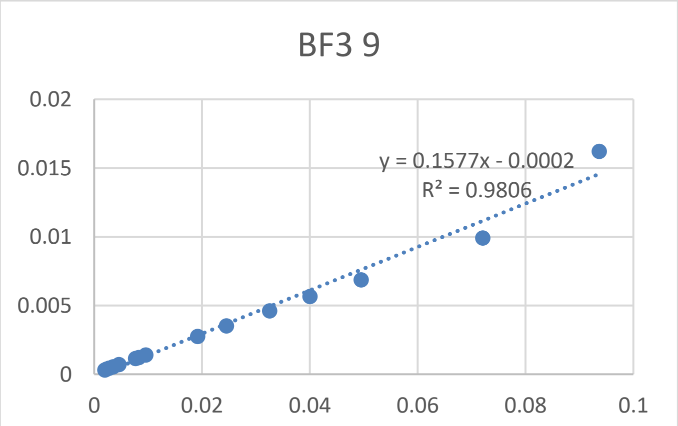
	48	5.491	0.007	0.001
	72	5.489	0.005	0.001
	96	5.487	0.004	0.001
BF2 15	2	5.769	0.040	0.004
	3	5.757	0.031	0.004
	4	5.745	0.026	0.003
	5	5.739	0.022	0.003
	7	5.722	0.018	0.002
	9	5.674	0.020	0.003
	20	5.655	0.010	0.001
	24	5.437	0.017	0.003
	28	5.422	0.015	0.003
	48	5.404	0.009	0.002
	72	5.399	0.006	0.001
	96	5.395	0.005	0.001
BF2 16	2	5.713	0.069	0.009
	3	5.693	0.052	0.007
	4	5.691	0.040	0.006
	5	5.674	0.035	0.005
	7	5.658	0.027	0.004
	9	5.631	0.024	0.004
	20	5.614	0.012	0.002
	24	5.594	0.011	0.002
	28	5.572	0.010	0.002
	48	5.562	0.006	0.001
	72	5.552	0.004	0.001
	96	5.514	0.003	0.001
	120	5.505	0.003	0.000
	144	5.504	0.002	0.000
LB 14	3	5.709	0.047	0.006
	4	5.688	0.041	0.006
	5	5.658	0.038	0.006
	7	5.652	0.028	0.004
	9	5.618	0.026	0.004
	20	5.592	0.013	0.002
	24	5.587	0.011	0.002
	28	5.549	0.011	0.002
	48	5.506	0.007	0.001
	72	5.482	0.005	0.001
	96	5.257	0.006	0.001

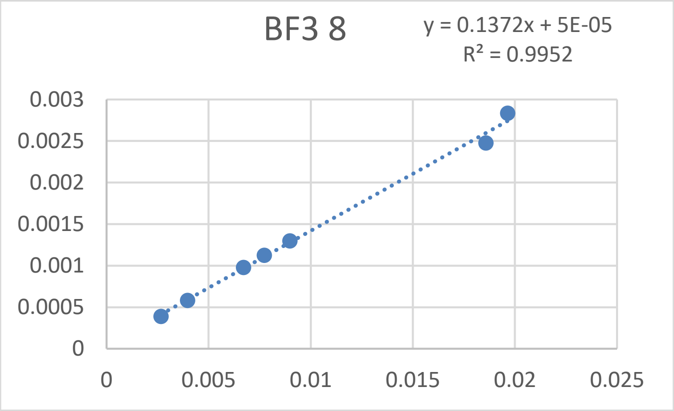
	120	5.218	0.005	0.001
LB 15	3	5.735	0.038	0.005
	4	5.722	0.032	0.004
	5	5.704	0.029	0.004
	7	5.692	0.023	0.003
	9	5.674	0.020	0.003
	20	5.662	0.009	0.001
	24	5.640	0.009	0.001
	28	5.628	0.008	0.001
	48	5.623	0.005	0.001
	72	5.513	0.005	0.001
	96	5.421	0.004	0.001
	120	5.418	0.004	0.001
Leaves	3	5.228	0.207	0.036
	4	5.218	0.158	0.027
	5	5.210	0.128	0.022
	7	5.202	0.093	0.016
	9	5.186	0.074	0.013
	20	4.596	0.063	0.012
	24	4.454	0.058	0.011
	28	3.993	0.066	0.013
	48	3.778	0.043	0.009
	72	3.624	0.031	0.007
	96	3.570	0.024	0.005
	120	3.467	0.020	0.004
LB 16	3.5	5.473	0.108	0.018
	4	5.423	0.107	0.018
	4.5	5.423	0.095	0.016
	12	5.386	0.039	0.006
	24	5.382	0.019	0.003
	36	5.368	0.013	0.002
	48	5.335	0.011	0.002
	72	5.221	0.009	0.002
	96	5.186	0.007	0.001
	120	5.154	0.006	0.001
	144	5.097	0.005	0.001
	168	5.052	0.005	0.001
	192	4.836	0.005	0.001
LB 17	36	5.421	0.012	0.002
	48	5.421	0.009	0.001

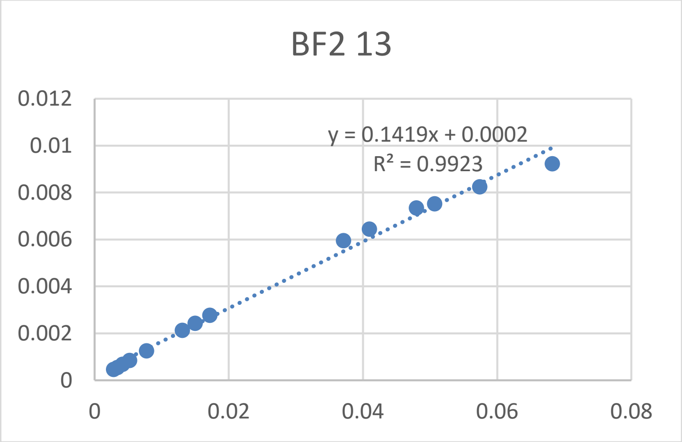
	72	5.361	0.007	0.001
	96	5.340	0.005	0.001
	120	5.300	0.005	0.001
	144	5.268	0.004	0.001
	168	5.265	0.003	0.001
	192	5.174	0.004	0.001

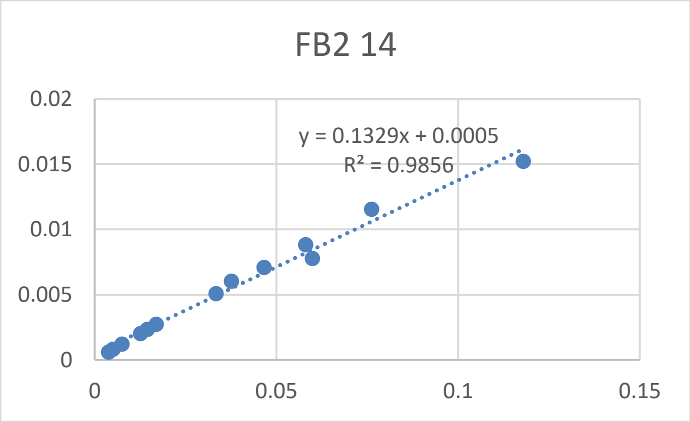


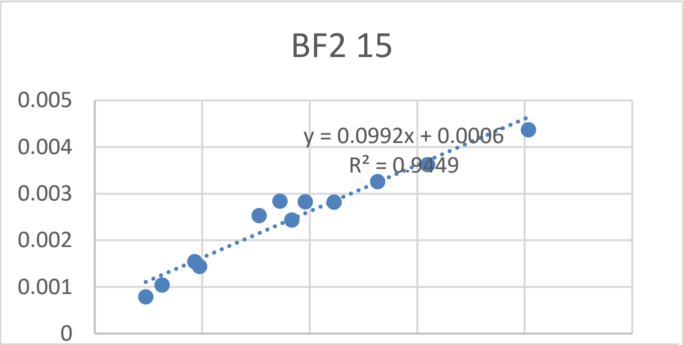


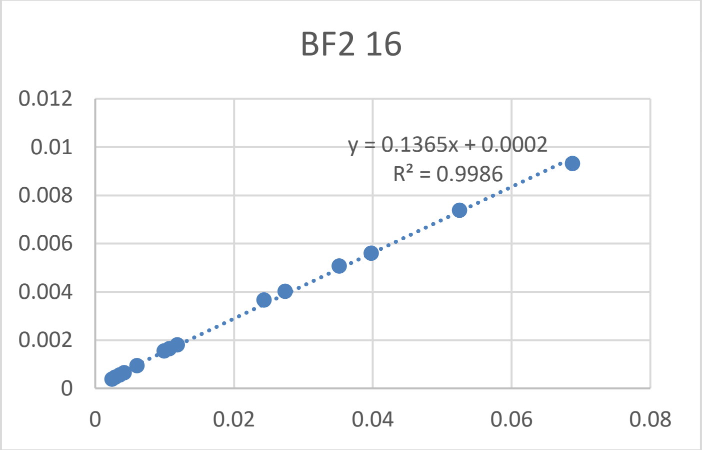


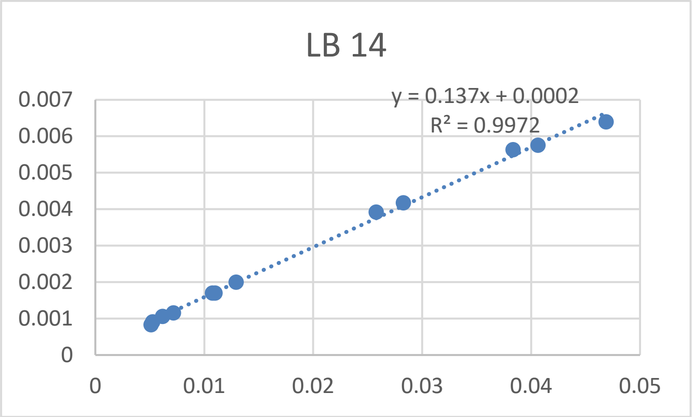

BF3 8
y = 0.1372x + 5E-05
R² = 0.9952
0.003
0.0025
0.002
0.0015
0.001
0.0005
0
0
0.005
0.01
0.015
0.02
0.025

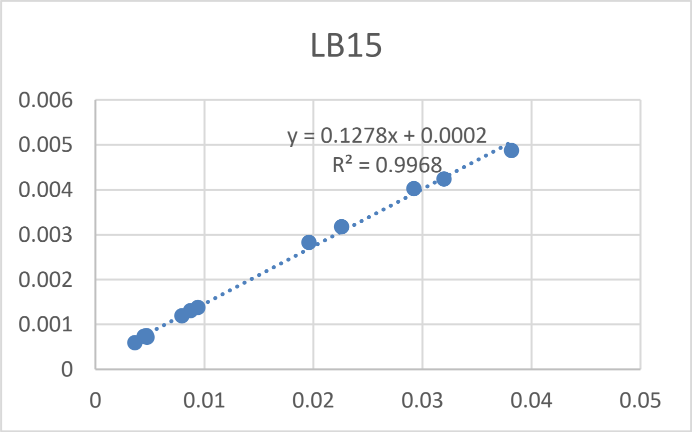

BF2 13
y = 0.1419x + 0.0002
R² = 0.9923
0.012
0.01
0.008
0.006
0.004
0.002
0
0
0.02
0.04
0.06
0.08

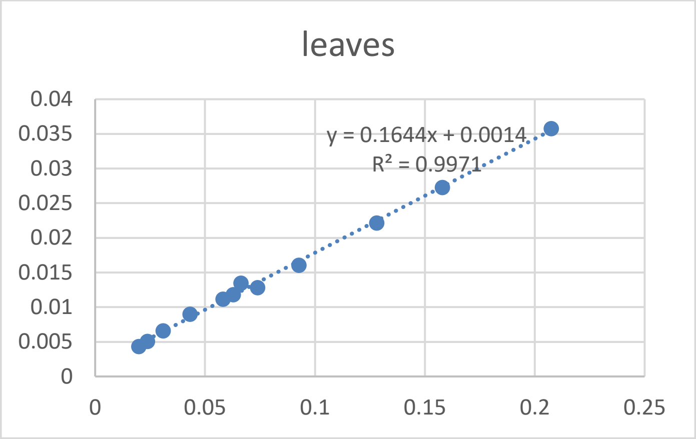

FB2 14
y = 0.1329x + 0.0005
R² = 0.9856
0.02
0.015
0.01
0.005
0
0
0.05
0.1
0.15

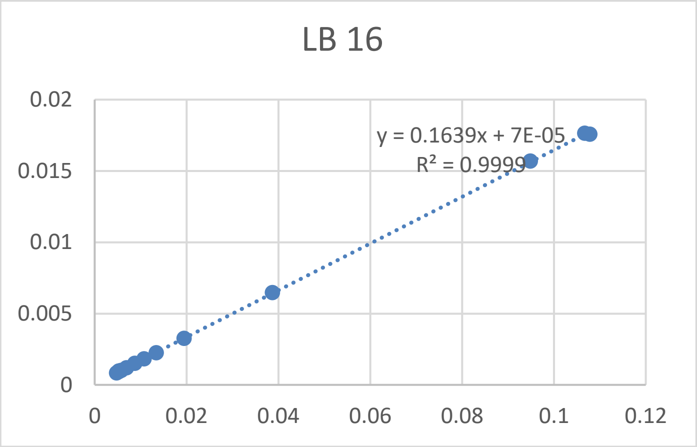

BF2 15
0.005
0.004
0.003
0.002
0.001
0
y = 0.0992x + 0.0006
R² = 0.9449

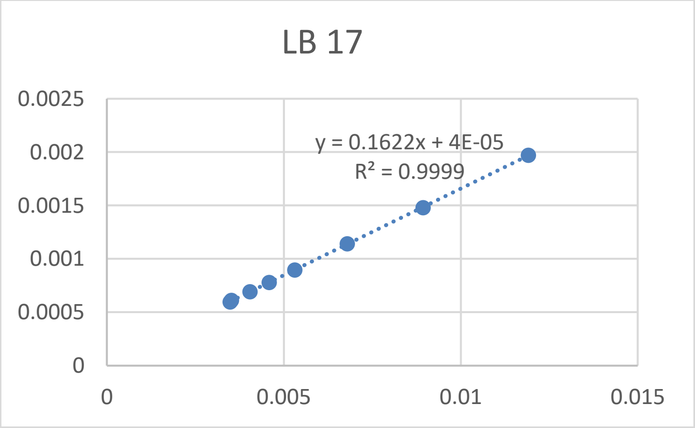

BF2 16
0.012
0.01
0.008
0.006
0.004
0.002
0
0
0.02
0.04
0.06
0.08
y = 0.1365x + 0.0002
R² = 0.9986


LB 14
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
0
0.01
0.02
0.03
0.04
0.05
y = 0.137x + 0.0002
R² = 0.9972


LB15
0.006
0.005
0.004
0.003
0.002
0.001
0
0
0.01
0.02
0.03
0.04
0.05
y = 0.1278x + 0.0002
R² = 0.9968


leaves
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.05
0.1
0.15
0.2
0.25
y = 0.1644x + 0.0014
R² = 0.9971


LB 16
0.02
0.015
0.01
0.005
0
0
0.02
0.04
0.06
0.08
0.1
0.12
y = 0.1639x + 7E-05
R² = 0.9999


LB 17
0.0025
0.002
0.0015
0.001
0.0005
0
0
0.005
0.01
0.015
y = 0.1622x + 4E-05
R² = 0.9999

Batch Test 3

Material	No: hours	%molar concentration of methane	(Ao-At)/t	(ln(Ao/At))/t
1	1	3.566	0.334	0.090
6		3.532	0.061	0.017
8		3.506	0.049	0.013
12		3.318	0.049	0.013
24		3.244	0.027	0.008
48		3.224	0.014	0.004
72		3.177	0.010	0.003
96		2.946	0.010	0.003
120		2.903	0.008	0.002
1	2	3.713	0.187	0.049
6		3.681	0.037	0.010
8		3.637	0.033	0.009
12		3.615	0.024	0.006
24		3.572	0.014	0.004
48		3.562	0.007	0.002
72		3.442	0.006	0.002
96		3.375	0.005	0.002
120		3.235	0.006	0.002
144		3.225	0.005	0.001
0.5	3	3.599	0.602	0.161
1		3.571	0.329	0.088
6		3.536	0.061	0.016
8		3.473	0.053	0.014
12		3.432	0.039	0.011
24		3.341	0.023	0.006
48		3.225	0.014	0.004
72		3.225	0.009	0.003
0.5	4	3.609	0.582	0.155

1		3.606	0.294	0.078
6		3.584	0.053	0.014
8		3.553	0.043	0.012
12		3.542	0.030	0.008
24		3.366	0.022	0.006
48		3.225	0.014	0.004
72		3.222	0.009	0.003
0.5	5	3.690	0.420	0.111
1		3.654	0.246	0.065
6		3.598	0.050	0.013
8		3.574	0.041	0.011
12		3.573	0.027	0.007
24		3.485	0.017	0.005
48		3.411	0.010	0.003
72		3.225	0.009	0.003
0.5	6	3.892	0.017	0.004
1		3.543	0.357	0.096
6		3.528	0.062	0.017
8		3.527	0.047	0.013
12		3.507	0.033	0.009
24		3.504	0.016	0.004
48		3.449	0.009	0.003
72		3.439	0.006	0.002
96		3.414	0.005	0.001
0.5	7	3.852	0.096	0.025
1		3.698	0.202	0.053
6		3.621	0.046	0.012
8		3.611	0.036	0.010
12		3.611	0.024	0.006
24		3.610	0.012	0.003
48		3.589	0.006	0.002
72		3.562	0.005	0.001
96		3.528	0.004	0.001
0.5		3.818	0.163	0.042
1	8	3.684	0.216	0.057
6		3.655	0.041	0.011
8		3.549	0.044	0.012
12		3.519	0.032	0.009
24		3.513	0.016	0.004
48		3.495	0.008	0.002

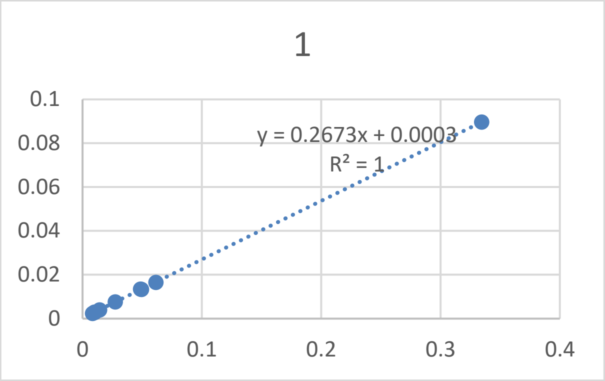
72		3.468	0.006	0.002
96		3.457	0.005	0.001
0.5	9	3.669	0.462	0.122
1		3.646	0.254	0.067
6		3.580	0.053	0.014
8		3.571	0.041	0.011
12		3.568	0.028	0.007
24		3.552	0.015	0.004
48		3.500	0.008	0.002
72		3.337	0.008	0.002
96		3.327	0.006	0.002
120		3.317	0.005	0.001
1	10	3.852	0.048	0.012
6		3.658	0.040	0.011
8		3.646	0.032	0.008
12		3.645	0.021	0.006
24		3.588	0.013	0.003
48		3.577	0.007	0.002
72		3.565	0.005	0.001
96		3.528	0.004	0.001
1	11	3.653	0.247	0.066
6		3.651	0.041	0.011
8		3.603	0.037	0.010
12		3.560	0.028	0.008
24		3.531	0.015	0.004
48		3.519	0.008	0.002
1	12	5.105	0.095	0.018
6		4.944	0.043	0.008
8		4.787	0.052	0.010
12		4.562	0.053	0.011
24		4.250	0.040	0.008
48		3.787	0.029	0.007
72		3.631	0.022	0.005
96		3.588	0.017	0.004
120		3.580	0.013	0.003
144		3.548	0.011	0.003
168		3.534	0.010	0.002
192		3.530	0.009	0.002
0.5	13	4.164	2.073	0.445
1		4.061	1.139	0.247

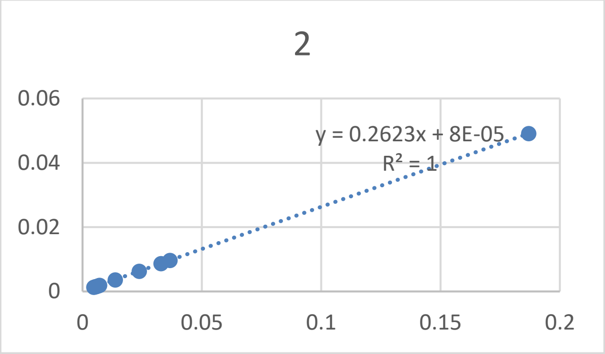
6		4.051	0.191	0.042
8		3.837	0.170	0.038
12		3.505	0.141	0.033
24		3.480	0.072	0.017
48		3.468	0.036	0.008
72		3.451	0.024	0.006
96		3.422	0.019	0.004
120		3.418	0.015	0.003
1	14	3.753	1.447	0.326
6		3.731	0.245	0.055
8		3.711	0.186	0.042
12		3.667	0.128	0.029
24		3.635	0.065	0.015
48		3.611	0.033	0.008
72		3.225	0.027	0.007
1	15	3.467	1.733	0.405
2.5		3.444	0.702	0.165
6		3.443	0.293	0.069
8		3.392	0.226	0.053
12		3.355	0.154	0.037
24		3.281	0.080	0.019
48		3.225	0.041	0.010
1	16	5.000	0.200	0.039
2.5		4.060	0.456	0.099
6		3.808	0.232	0.052
8		3.717	0.185	0.042
12		3.646	0.130	0.030
24		3.645	0.065	0.015
48		3.636	0.033	0.007
72		3.618	0.022	0.005
1	17	4.447	0.753	0.156
2.5		3.723	0.591	0.134
6		3.601	0.267	0.061
8		3.544	0.207	0.048
12		3.537	0.139	0.032
24		3.532	0.069	0.016
48		3.387	0.038	0.009
72		3.299	0.026	0.006
96		3.225	0.021	0.005
1	18	5.185	0.015	0.003

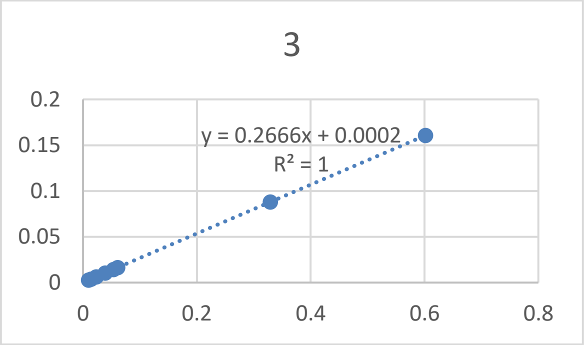
2.5		4.959	0.096	0.019
6		3.849	0.225	0.050
8		3.778	0.178	0.040
12		3.720	0.123	0.028
24		3.590	0.067	0.015
48		3.225	0.041	0.010
72		2.413	0.039	0.011
96		2.220	0.031	0.009
1	19	5.080	0.120	0.023
6		4.715	0.081	0.016
8		4.695	0.063	0.013
12		4.036	0.097	0.021
24		3.860	0.056	0.012
48		3.560	0.034	0.008
72		3.553	0.023	0.005
96		3.547	0.017	0.004
120		3.541	0.014	0.003
144		3.532	0.012	0.003
168		3.532	0.010	0.002
192		3.225	0.010	0.002
1	20	4.771	0.429	0.086
6		4.650	0.092	0.019
8		4.616	0.073	0.015
12		4.241	0.080	0.017
24		4.179	0.043	0.009
48		3.652	0.032	0.007
72		3.609	0.022	0.005
96		3.515	0.018	0.004
120		3.489	0.014	0.003
144		3.489	0.012	0.003
168		3.469	0.010	0.002
192		3.461	0.009	0.002
1	21	5.195	0.005	0.001
6		4.364	0.139	0.029
8		4.247	0.119	0.025
12		4.022	0.098	0.021
24		3.987	0.051	0.011
48		3.800	0.029	0.007
72		3.749	0.020	0.005
96		3.677	0.016	0.004

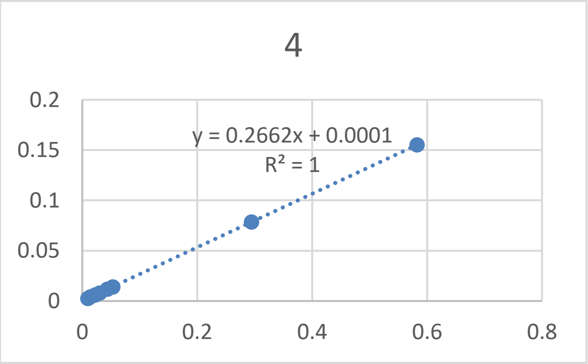
120		3.675	0.013	0.003
144		3.636	0.011	0.002
168		3.225	0.012	0.003
192		3.225	0.010	0.002
1		4.137	1.063	0.229
6		3.905	0.216	0.048
8		3.609	0.199	0.046
12		3.482	0.143	0.033
24		3.467	0.072	0.017
48		3.428	0.037	0.009
72		3.405	0.025	0.006
96		3.353	0.019	0.005
1		5.134	0.066	0.013
6		4.759	0.074	0.015
8		4.464	0.092	0.019
12		4.063	0.095	0.021
24		3.711	0.062	0.014
48		3.679	0.032	0.007
72		3.613	0.022	0.005
96		3.582	0.017	0.004
120		3.538	0.014	0.003
144		3.225	0.014	0.003
1		5.077	0.123	0.024
6		4.469	0.122	0.025
8		4.042	0.145	0.031
12		3.648	0.129	0.030
24		3.608	0.066	0.015
48		3.577	0.034	0.008
72		3.567	0.023	0.005
96		3.537	0.017	0.004
120		3.489	0.014	0.003
144		3.225	0.014	0.003
1		5.172	0.028	0.005
6		4.895	0.051	0.010
8		4.434	0.096	0.020
12		3.900	0.108	0.024
24		3.671	0.064	0.015
48		3.523	0.035	0.008
72		3.498	0.024	0.006
96		3.458	0.018	0.004

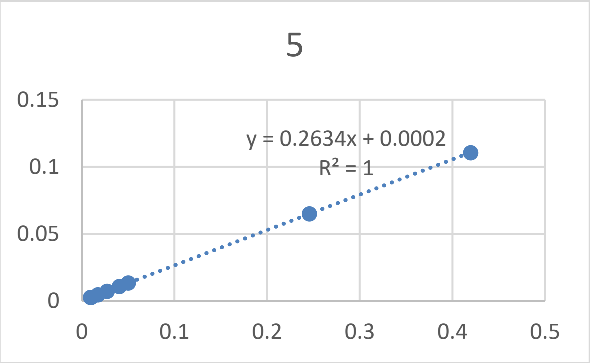
120		3.458	0.015	0.003
144		3.457	0.012	0.003

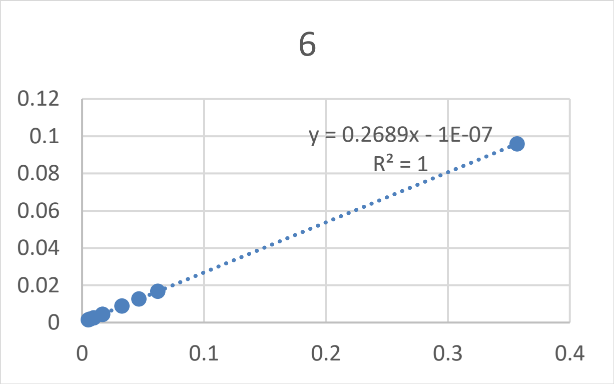

1
0.1
0.08
0.06
0.04
0.02
0
0
0.1
0.2
0.3
0.4
y = 0.2673x + 0.0003
R² = 1

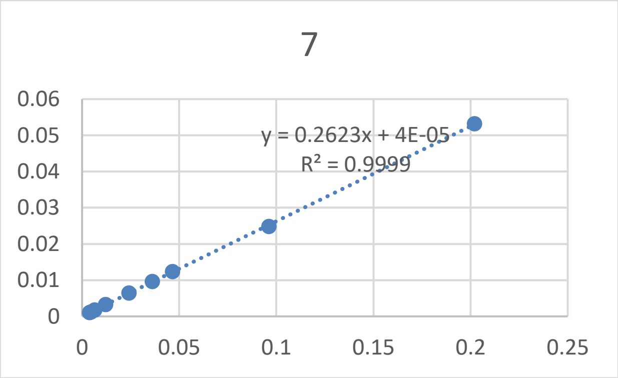

2
0.06
0.04
0.02
0
0
0.05
0.1
0.15
0.2
y = 0.2623x + 8E-05
R² = 1

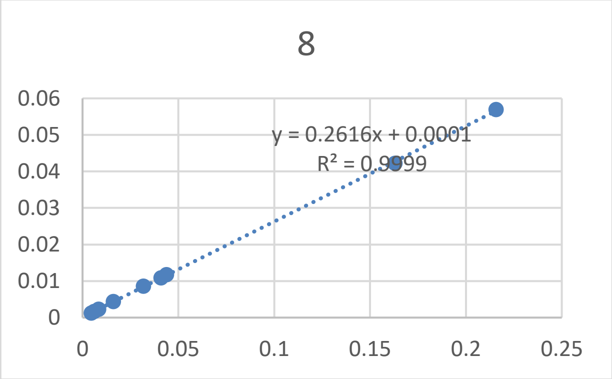

3
0.2
0.15
0.1
0.05
0
0
0.2
0.4
0.6
0.8
y = 0.2666x + 0.0002
R² = 1

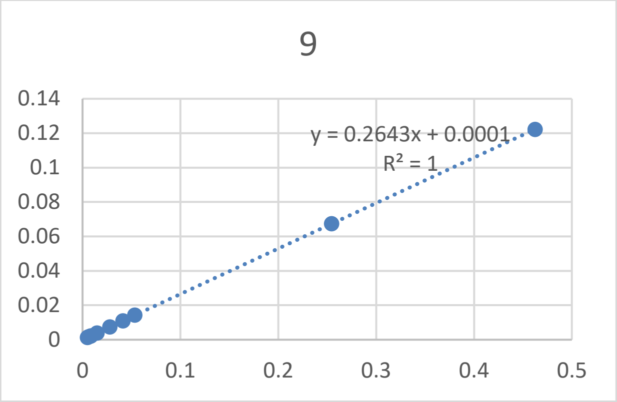

4
0.2
0.15
0.1
0.05
0
0
0.2
0.4
0.6
0.8
y = 0.2662x + 0.0001
R² = 1

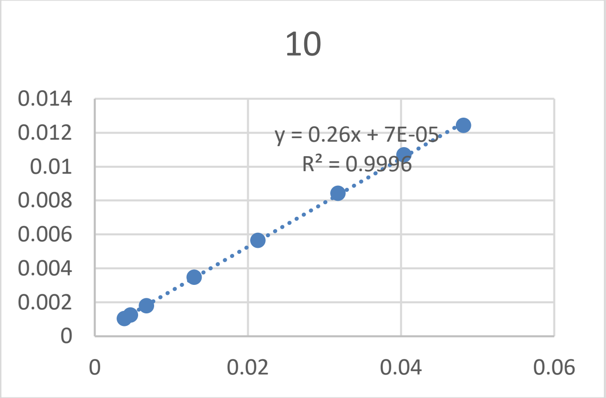

5
0.15
0.1
0.05
0
0
0.1
0.2
0.3
0.4
0.5
y = 0.2634x + 0.0002
R² = 1

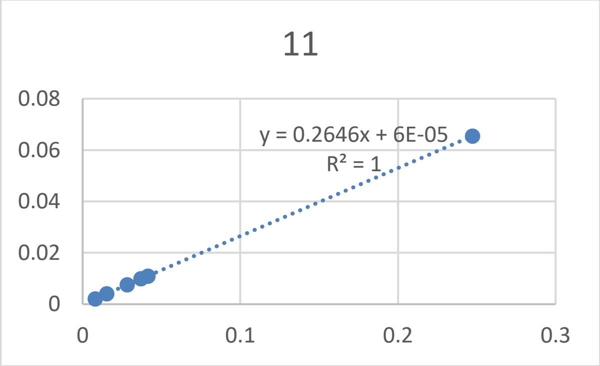

6
0.12
0.1
0.08
0.06
0.04
0.02
0
0
0.1
0.2
0.3
0.4
y = 0.2689x - 1E-07
R² = 1

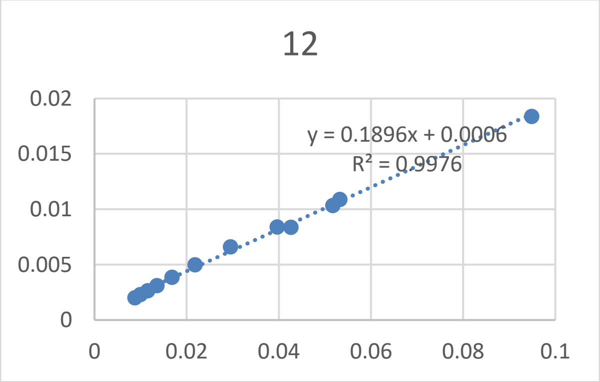

7
0.06
0.05
0.04
0.03
0.02
0.01
0
0
0.05
0.1
0.15
0.2
0.25
y = 0.2623x + 4E-05
R² = 0.9999

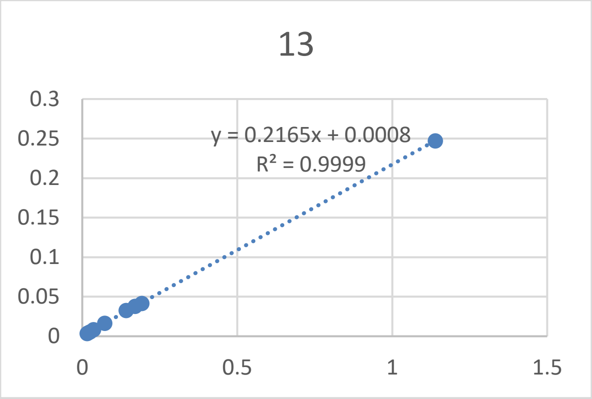

8
0.06
0.05
0.04
0.03
0.02
0.01
0
0
0.05
0.1
0.15
0.2
0.25
y = 0.2616x + 0.0001
R² = 0.9999

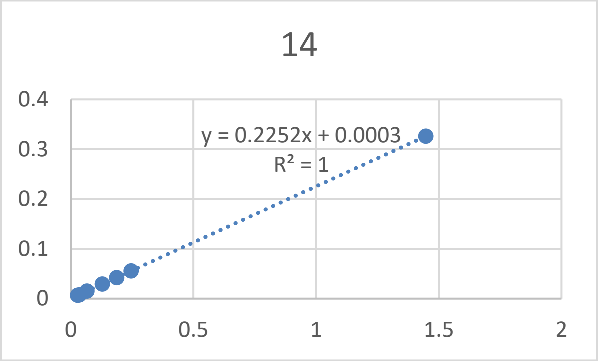

9
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0
0.1
0.2
0.3
0.4
0.5
y = 0.2643x + 0.0001
R² = 1

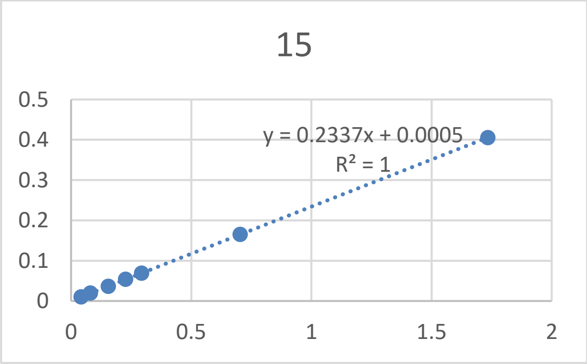

10
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
0
0.02
0.04
0.06
y = 0.26x + 7E-05
R² = 0.9996

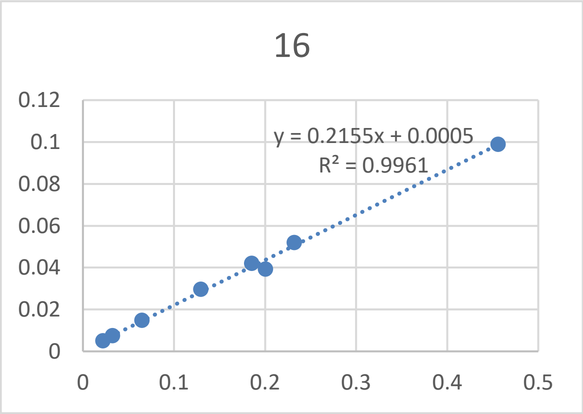

11
0.08
0.06
0.04
0.02
0
0
0.1
0.2
0.3
y = 0.2646x + 6E-05
R² = 1

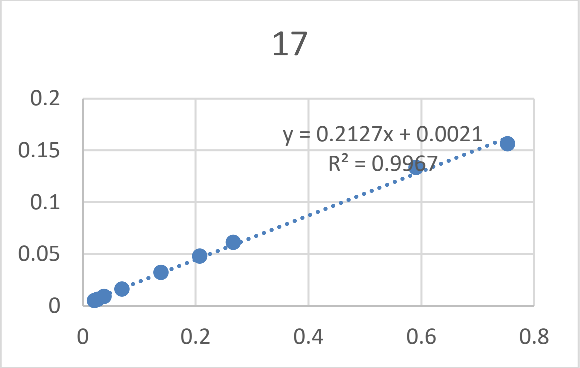

12
0.02
0.015
0.01
0.005
0
0
0.02
0.04
0.06
0.08
0.1
y = 0.1896x + 0.0006
R² = 0.9976

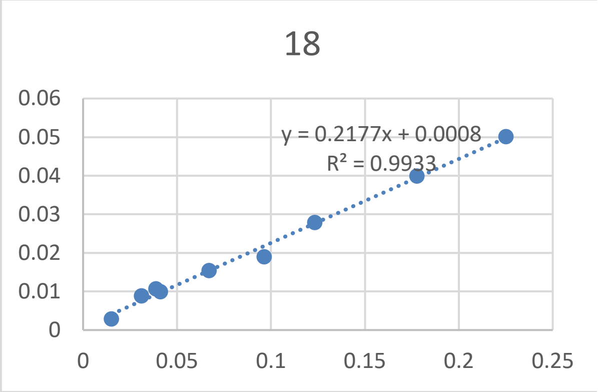

13
0.3
0.25
0.2
0.15
0.1
0.05
0
0
0.5
1
1.5
y = 0.2165x + 0.0008
R² = 0.9999

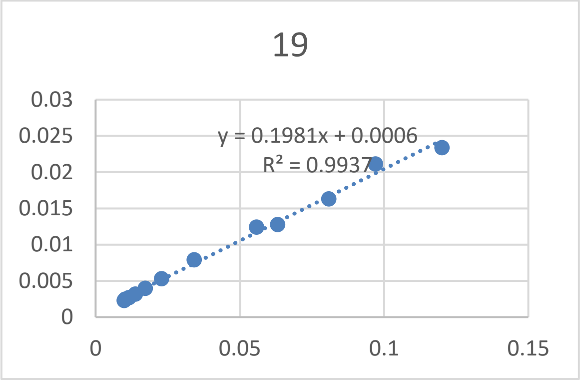

14
0.4
0.3
0.2
0.1
0
0
0.5
1
1.5
2
y = 0.2252x + 0.0003
R² = 1

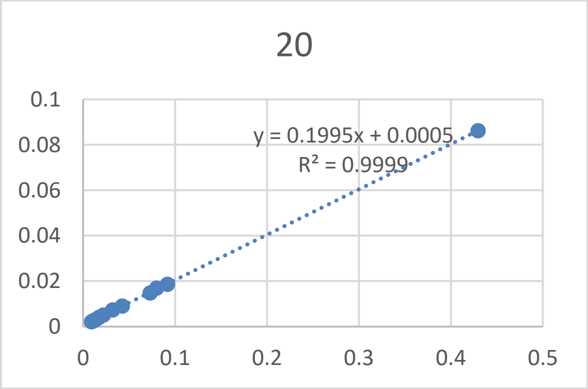

15
0.5
0.4
0.3
0.2
0.1
0
0
0.5
1
1.5
2
y = 0.2337x + 0.0005
R² = 1

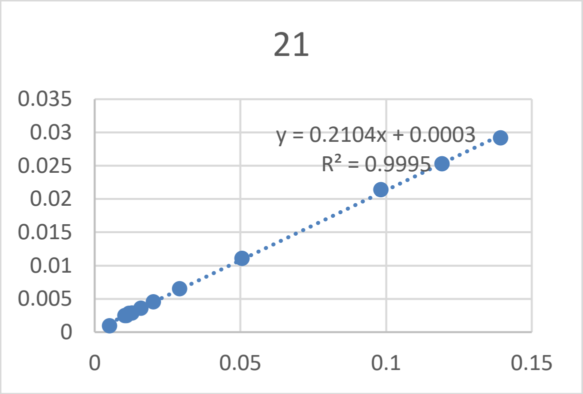

16
0.12
0.1
0.08
0.06
0.04
0.02
0
0
0.1
0.2
0.3
0.4
0.5
y = 0.2155x + 0.0005
R² = 0.9961

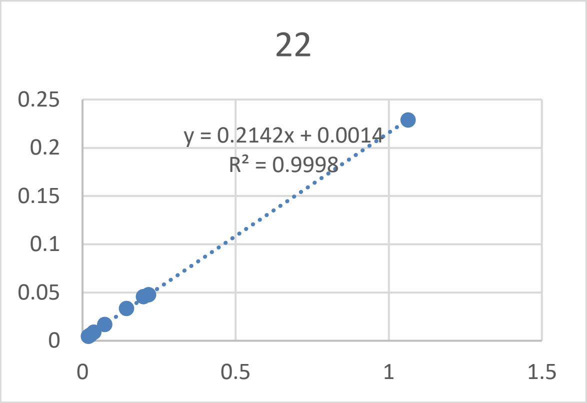

17
0.2
0.15
0.1
0.05
0
0
0.2
0.4
0.6
0.8
y = 0.2127x + 0.0021
R² = 0.9967

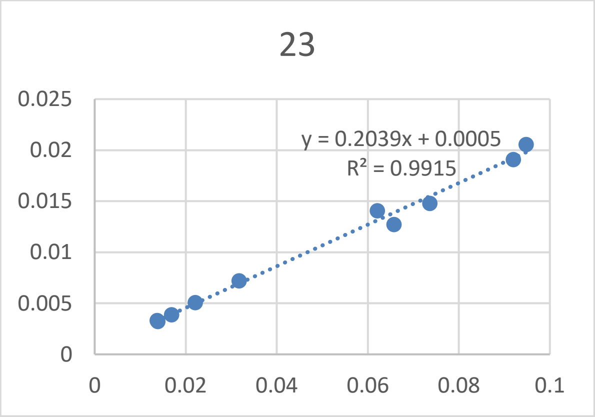

18
0.06
0.05
0.04
0.03
0.02
0.01
0
0
0.05
0.1
0.15
0.2
0.25
y = 0.2177x + 0.0008
R² = 0.9933

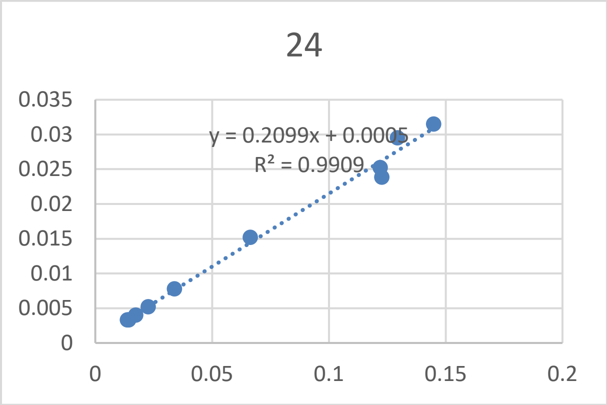

19
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.05
0.1
0.15
y = 0.1981x + 0.0006
R² = 0.9937

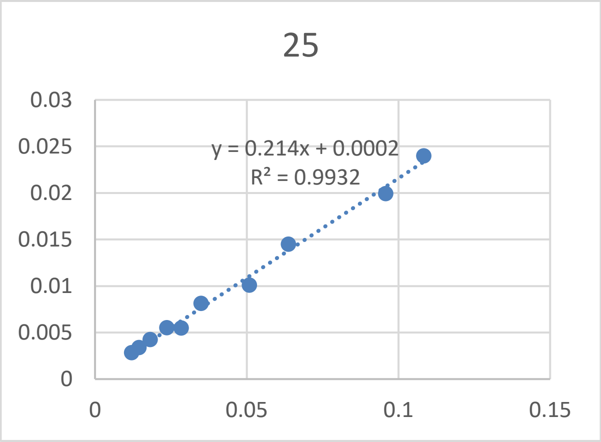

20
0.1
0.08
0.06
0.04
0.02
0
0
0.1
0.2
0.3
0.4
0.5
y = 0.1995x + 0.0005
R² = 0.9999


21
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.05
0.1
0.15
y = 0.2104x + 0.0003
R² = 0.9995


22
0.25
0.2
0.15
0.1
0.05
0
0
0.5
1
1.5
y = 0.2142x + 0.0014
R² = 0.9998


23
0.025
0.02
0.015
0.01
0.005
0
0
0.02
0.04
0.06
0.08
0.1
y = 0.2039x + 0.0005
R² = 0.9915


24
y = 0.2099x + 0.0005
R² = 0.9909
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.05
0.1
0.15
0.2


25
y = 0.214x + 0.0002
R² = 0.9932
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.05
0.1
0.15

Appendix 3

Column reactors data: Column 1 – port 1

Date	Number of days	Area CH4	Area CO2	Area O2	%methane removal	BPI (ug/g/hr)
6/8/2018	2	1426.894	4716.748	6297.743	41.24691603	18.81863699
6/11/2017	4	1455.827	4406.323	6834.626	37.52385187	19.1108744
6/13/2018	6	1433.935	4414.557	7132.36	40.05430093	18.31367627
6/15/2018	8	1425.769	4279.093	8523.279	38.98030963	18.21132514
6/18/2018	11	1324.039	4152.962	9342.159	45.88611008	16.3882082
6/20/2018	13	1114.624	3651.671	9261.845	47.58718108	13.80693406
6/22/2018	15	1019.849	3861.021	10851.38	54.63746945	12.1582662
6/24/2018	17	830.795	3396.441	19498.21	57.27532244	10.01454223
6/25/2018	18	985.266	3935.105	10476.31	58.12482958	11.36457124
6/27/2018	20	1108.520	3841.661	9410.417	55.83610175	12.77676474
6/29/2018	22	997.705	3967.712	9067.779	61.99349168	10.95803268
7/2/2018	25	919.278	3826.655	11340.88	63.37955085	10.06230336
7/5/2018	28	1006.248	4074.345	16184.01	64.1624521	10.63936874
7/6/2018	29	912.502	3862.454	11660.9	67.01399682	9.050908016
7/8/2016	31	965.536	3755.105	10976.31	66.61887632	9.567055343
7/9/2016	32	1012.849	3641.061	10652.38	66.11372181	9.424939832
7/11/2018	34	1188.816	3926.346	9090.479	63.6610071	11.05399943
7/13/2018	36	1324.860	4209.964	9939.533	60.98961516	12.93473131
7/17/2018	40	1280.892	4297.34	14279.98	60.52594139	13.46225257
7/20/2018	43	1331.367	4326.594	11428.8	59.16008413	14.60085986
7/21/2018	44	970.076	4139.094	9363.107	67.01283634	10.79104384
7/23/2018	46	1093.189	3566.761	21235.51	59.63511864	12.21911335
7/25/2018	48	916.642	3587.07	7435.649	63.98747935	10.76886516
7/27/2018	50	920.780	3939.413	10261.11	64.89158332	11.33118518
7/28/2018	51	1132.673	4206.484	14046.18	60.60560803	14.06191612
7/30/2018	53	1128.429	4223.449	9716.326	56.79740353	15.87770206
8/1/2018	54	1150.870	4359.781	7323.065	55.81589061	16.82277438
8/3/2018	56	1119.715	4900.365	7688.579	59.32786371	17.02188058
8/8/2018	61	1306.254	4125.88	8684.59	41.87237356	24.41474624
8/10/2018	63	1289.248	4158.158	10289.21	35.45749167	28.74390029
8/13/2018	66	1209.457	4138.792	12587.16	27.61127814	34.05873016
8/17/2018	70	1189.824	4208.614	8106.825	29.13281331	33.58828894
8/21/2018	74	1371.852	4314.117	8247.052	34.60580007	32.27239649
8/23/2018	76	1098.834	3647.079	9057.459	18.31100456	38.74149591
8/27/2018	80	761.954	3807.337	10821.77	24.10782252	35.82560656
8/29/2018	82	1138.490	4216.25	9325.12	33.77527604	32.13915731
8/31/2018	84	1149.347	4317.136	10345.2	24.21527486	40.52581611

9/2/2018	86	1118.352	4892.196	7721.478	31.2445222	39.43226473
9/4/2018	88	1265.421	4268.253	11985.45	25.87895291	38.69923756
9/6/2018	90	1289.78	4218.116	10921.45	24.43256144	39.44418705

Column 1 – port 2

Date	Area CH4	Area CO2	Area O2	%methane removal
6/8/2018	891.7022	4399.711	6272.7	56.41188
6/11/2017	907.3102	3973	12032.64	52.20876
6/13/2018	835.5658	3631	19880.15	53.46838
6/15/2018	878.7344	3723	27787.15	52.55345
6/18/2018	878.7344	3723	27787.15	56.91082
6/20/2018	632.9173	3039	25987.17	60.98666
6/22/2018	597.942	3392	16620.93	67.25418
6/24/2018	450.7222	3037	20158.54	71.69962
6/25/2018	428.0464	2982	26816.87	73.63898
6/27/2018	500.0781	2991	20076.98	71.79099
6/29/2018	439.2726	3155	29652.97	77.003
7/2/2018	423.247	3163	34737.98	77.80407
7/5/2018	369.4152	2920	31031.62	79.886
7/6/2018	346.628	3032	31829.01	82.55121
7/8/2016	412.6587	3078	32478.13	81.08205
7/9/2016	425.4586	2925	29754.28	80.7246
7/11/2018	184.8363	1575	40843.56	84.15474
7/13/2018	375.9208	3127	18720.78	83.05662
7/17/2018	309.4643	3301	28498.62	85.64004
7/20/2018	331.5558	3228	27213.83	84.22052
7/21/2018	168.7993	2734.946	22105.2	90.11162
7/23/2018	366.3348	3323.835	20245.79	83.33033
7/25/2018	84.8898	84.8898	41360.72	7.563025
7/27/2018	73.0878	2732.057	33266.5	95.24208
7/28/2018	287.5366	3260.45	31266.91	85.12778
7/30/2018	255.1371	3246.924	26065.69	85.00811
8/1/2018	229.2816	3120.252	30694.17	85.3679
8/3/2018	690.6134	3598.51	26409.7	64.68947
8/8/2018	322.4342	3181.561	29392.96	76.81091
8/10/2018	309.2458	3084.487	30821.29	73.29917
8/13/2018	260.4776	3123.862	27936.57	72.13755

8/17/2018	200.2813	3082.836	19014.96	77.60229
8/21/2018	268.7528	3171.28	24785.35	77.07376
8/23/2018	164.1745	2792.966	31465.03	76.25689
8/27/2018	21.0506	1018.865	30386.89	88.12369
8/29/2018	255.318	3071.412	28413.52	73.55086
8/31/2018	271.247	3112.531	27316.49	74.45081
9/2/2018	300.012	3512.98	29317.48	70.99631
9/4/2018	310.349	3519.441	30431.22	70.19279
9/6/2018	318.619	3741.28	30193.42	71.06542

Column 1- port 3

Date	Area CH4	Area CO2	Area O2	%methane removal
6/8/2018	396.0444	2902.224	18977.75	68.4018
6/11/2017	0	2684	25027.43	100
6/13/2018	373.2931	2136	28440.51	62.56702
6/15/2018	274.7124	1533	40771.51	61.79004
6/18/2018	348.9378	2033	37889.1	66.70738
6/20/2018	282.4744	1830	25896.66	70.73183
6/22/2018	205.4874	1860	28989.68	78.14275
6/24/2018	136.2639	1652	28079.34	83.95239
6/25/2018	126.392	1706	28439.61	86.43203
6/27/2018	142.5046	1716	26102.29	85.61967
6/29/2018	111.308	1756	28990.24	88.8323
7/2/2018	20.5131	366	42142.99	87.61657
7/5/2018	67.4347	1160	37239.73	90.72898
7/6/2018	78.8826	1566	27077.25	92.44741
7/8/2016	91.385	1956	29890.27	93.37533
7/9/2016	115.9542	2264	25953.76	92.7596
7/11/2018	79.2412	1326	30370.95	91.20041
7/13/2018	100.3522	1631	28153.16	90.3396
7/17/2018	68.497	1637	28911.21	93.25863
7/20/2018	78.4154	1587	27713.24	92.00563
7/21/2018	31.474	1416	28626.92	96.39973
7/23/2018	42.0931	838.9082	23517.37	91.73249
7/25/2018	13.1692	391.1321	42495.57	94.04839
7/27/2018	9.4351	1281.622	40430.69	98.6677
7/28/2018	52.5792	1512.954	38887.91	93.08026
7/30/2018	41.1762	1445.701	29264.16	94.06252

8/1/2018	36.8109	1436.496	40124.81	94.43366
8/3/2018	208.6597	1761.913	39124.9	76.35095
8/8/2018	59.775	1421.255	27277.32	89.67632
8/10/2018	53.2568	1532.549	30248.13	89.86081
8/13/2018	42.2465	1396.33	39535.79	88.90539
8/17/2018	27.2366	1386.606	39583.95	92.65413
8/21/2018	38.4905	1390.997	36927.9	91.88786
8/23/2018	19.2238	1152.011	28432.85	92.63343
8/27/2018	2.7946	698.4526	30629.49	97.5844
8/29/2018	20.023	1125.421	29483.12	93.68249
8/31/2018	33.425	1496.321	28432.44	92.76357
9/2/2018	31.432	1365.41	27654.1	91.25567
9/4/2018	35.193	1402.114	29312.63	90.50317
9/6/2018	30.658	1475.22	30403.01	92.07216

Column 1 – port 4

Date	Area CH4	Area CO2	Area O2	%methane removal	BPI
6/8/2018	93.6398	885.1837	27700.96	74.60305	20.53558306
6/11/2017	101.869	702	33106.18	66.74389	18.37223449
6/13/2018	80.044	532	31280.13	66.90554	18.41672986
6/15/2018	79.4446	444	31840.6	61.85493	17.02647518
6/18/2018	57.4236	337	44501.94	66.92935	18.42328442
6/20/2018	49.7733	314	31926	70.07636	19.28954652
6/22/2018	35.4114	317	33011.32	77.95264	21.45760602
6/24/2018	20.9276	244	32680.55	83.35157	22.94374298
6/25/2018	19.0838	256	32349.41	85.39604	23.50651243
6/27/2018	23.4502	296	31118.43	86.25205	23.7421404
6/29/2018	17.0532	297	43513.3	89.82099	24.72454384
7/2/2018	14.8727	274	42478.22	87.96852	24.21462393
7/5/2018	1.2873	35	20834.62	93.96638	25.86562445
7/6/2018	8.518	181	31935.64	92.42067	25.44014529
7/8/2016	9.1786	210	30487.21	93.80235	25.8204721
7/9/2016	11.2487	229	31257.49	93.03967	25.61053278
7/11/2018	13.4224	219	33542.79	90.99558	25.04786783
7/13/2018	14.6776	228	33798.15	89.8938	24.74458719
7/17/2018	8.8101	204	43260.78	92.81286	25.54809958
7/20/2018	10.6984	198	38940.45	91.29828	25.13119165
7/21/2018	4.3227	169.7718	36955.11	95.75532	26.35805492
7/23/2018	10.6286	195.2442	43001.3	91.06171	25.06607176
7/25/2018	4.387	108.4898	44492.46	92.89462	25.57060585

7/27/2018	1.0428	104.5852	31809.08	98.19979	27.03093286
7/28/2018	10.5688	200.8581	45236.26	89.70606	24.69290929
7/30/2018	4.1043	124.1377	35347.3	93.14036	25.63825053
8/1/2018	3.2614	113.1565	44311.11	93.76097	25.80908243
8/3/2018	5.9752	54.7124	32698.74	76.77299	21.13289085
8/8/2018	5.3	124.5876	33236.13	89.56408	24.65382564
8/10/2018	5.128	119.248	33158.18	87.60226	24.11380788
8/13/2018	5.9736	109.1008	31618.3	80.78519	22.23730841
8/17/2018	2.4373	116.9984	44391.95	92.22666	25.38674036
8/21/2018	3.5622	99.1572	31724.69	89.59411	24.66209353
8/23/2018	0	7.9966	25556.71	100	27.52646637
8/27/2018	0	23.2105	33047.05	100	27.52646637
8/29/2018	1.1728	29.1788	31046.65	86.27382	23.74813327
8/31/2018	0.923	38.149	32178.21	92.18566	25.37545426
9/2/2018	0	57.649	28347.14	100	27.52646637
9/4/2018	1.021	87.413	29138.28	95.46556	26.2782957
9/6/2018	1.016	100.048	21083.11	96.04591	26.43804493

Column 2 – port 1

Date	Area CH4	Area CO2	Area O2	%methane removal	BPI
6/8/2018	1300.753	4360.247	9542.981	38.17102	2.67384E-05
6/11/2018	1341.336	4348.033	9784.413	36.72979	6.79663E-06
6/13/2018	1197.209	3900.847	19989.87	38.77489	3.89203E-06
6/15/2018	1309.025	4210.503	11940.31	38.22543	3.20985E-06
6/18/2018	1256.555	3924.319	15557.09	37.78281	2.15847E-06
6/20/2018	1561.747	3745.502	11862.44	37.11191	2.26863E-06
6/22/2018	1727.485	4324.768	8720.039	40.90343	2.08331E-06
6/24/2018	1537.813	3911.64	9860.95	41.5634	1.63477E-06
6/25/2018	1217.387	3120.212	30969.28	34.43552	1.16034E-06
6/27/2018	1817.707	4158.343	8664.121	29.33233	1.56316E-06
6/29/2018	1318.416	3466.801	19462.87	42.71186	9.77154E-07
7/2/2018	1562.873	4005.706	14708.52	45.91578	1.06458E-06
7/5/2018	1609.908	3987.191	16571.48	41.54818	9.24107E-07
7/6/2018	1551.383	3921.669	16687.29	46.41191	8.08119E-07
7/8/2016	1428.348	4026.549	18256.75	52.19701	6.93508E-07
7/9/2016	1468.482	3927.188	17348.13	50.10736	6.50197E-07
7/11/2018	2172.681	4553.363	15485.51	38.51667	9.0578E-07
7/13/2018	2160.457	4207.159	16342.3	29.93804	8.93709E-07
7/17/2018	1947.618	4224.194	11730.42	36.88668	7.53751E-07
7/18/2018	2588.917	4831.773	11701.96	22.73117	9.99589E-07
7/20/2018	2103.109	4665.065	12250.92	32.93541	7.76483E-07
7/21/2018	1755.066	4448.265	6365.848	41.19605	6.41467E-07
7/23/2018	1170.882	3070.479	26626.45	37.21164	4.13448E-07
7/25/2018	1728.465	4613.173	11880.06	36.20728	6.11231E-07

7/27/2018	1517.853	4196.872	10698.64	35.2079	5.46629E-07
7/28/2018	1116.207	2884.209	23384.24	32.20663	3.9387E-07
7/30/2018	1979.747	4689.089	10356.8	22.45116	7.62326E-07
8/1/2018	1697.676	4493.44	10559.03	24.57427	6.56576E-07
8/3/2018	1014.756	2028.655	28133.68	3.682634	3.93232E-07
8/8/2018	2042.379	4523.821	8650.465	-9.25282	8.98091E-07
8/10/2018	1620.599	4476.03	7926.479	-6.8263	8.20326E-07
8/13/2018	1516.521	4173.185	11838.51	19.32559	6.25816E-07
8/17/2018	1518.361	4155.661	15491.88	9.764264	6.85343E-07
8/21/2018	1799.621	4389.84	11080.58	3.250757	6.91415E-07
8/23/2018	1199.941	3395.399	20649.98	22.24016	5.04105E-07
8/27/2018	1752.986	4310.703	10345.9	16.8461	5.27569E-07

Column 2 – Port 2

Date	Area CH4	Area CO2	Area O2	%methane removal
6/8/2018	741.1076	3682.777	17956.12	53.62704
6/11/2017	697.0742	3271	21899.57	51.55301
6/13/2018	691.3322	3212	24014.55	52.73769
6/15/2018	695.6168	3161	30543.36	51.93168
6/18/2018	714.0015	3236	30888.14	52.53777
6/20/2018	1012.189	3240	29411.69	48.84783
6/22/2018	1033.223	3422	17178.64	51.85928
6/24/2018	1114.547	3562	17884.27	50.54081
6/25/2018	939.56	3046	29033.82	44.33904
6/27/2018	1115.174	3164	17990.1	38.83626
6/29/2018	991.186	3208	3208.287	50.81715
7/2/2018	934.3527	3083	30064.48	55.28477
				#DIV/0!
7/5/2018	941.8452	3033	22583.81	51.79769
7/6/2018	944.6456	3127	33471.01	56.30856
7/8/2016	948.3589	3246	35264.59	58.89237
7/9/2016	1088.266	3584	39546.28	57.49639
7/11/2018	1543.372	3495	32129.23	41.76066
7/13/2018	1311.499	3244	21368.68	40.40479

7/16/2018	gc not working			#VALUE!
7/17/2018	1253.636	3372	18576.82	45.79571
7/18/2018	1496.315	3714	29246.24	35.73714
7/20/2018	1066.112	3621	18303.78	50.43653
7/21/2018	800.1251	3482	18332.87	60.95751
7/23/2018	775.2178	3550	17700.54	58.47436
7/25/2018	440.5368	2623	28493.16	65.29518
7/27/2018	450.8532	3268	26050.81	69.08938
7/28/2018	473.1273	2614	34186.37	61.31582
7/30/2018	724.7819	3693	24667.4	54.51153
8/1/2018	600.2233	3470.923	25157.18	56.60115
8/3/2018	582.9264	1850.476	39082.73	26.18086
8/8/2018	612.7604	2677.291	34367.22	24.19824
8/10/2018	543.2134	3308.735	18034.82	31.58854
8/13/2018	541.9666	3151.178	27966.63	35.13804
8/17/2018	514.1608	3068.629	18802.68	33.09715
8/21/2018	713.0576	3159.16	29122.4	21.58875
8/23/2018	517.7614	3040.223	28520.34	32.37044
8/27/2018	665.6122	3136.471	29364.51	-2.9637

Column 2- port 3

Date	Area CH4	Area CO2	Area O2	%methane removal
6/8/2018	354.2734	2857.816	20635.24	68.64121
6/11/2017	365.988	2997	33814.82	69.03284
6/13/2018	316.5658	2126	32836.71	64.73909
6/15/2018	329.42	2013	37284.83	61.91001
6/18/2018	281.7283	1662	39532.72	61.41395
6/20/2018	378.0157	1468	38976.1	55.86308
6/22/2018	338.0166	1365	39628.82	58.73914
6/24/2018	326.5868	1271	32139.59	57.49519
6/25/2018	324.4333	1240	40673.22	50.71472
6/27/2018	387.8106	1298	28325.1	45.60941
6/29/2018	1.4985	40	41045.88	92.46361
7/2/2018	1.16	28	25982.76	92.463
				#DIV/0!
7/5/2018	317.043	1197	41718.19	57.36116
7/6/2018	307.4854	1203	43317.18	61.73731
7/8/2016	317.4125	1645	46257.98	70.82396
7/9/2016	309.1856	1455	45386.93	68.22217
7/11/2018	517.3992	1295	42587.4	45.80967

7/13/2018	399.731	1079	30989.7	43.98616
7/16/2018	gc not working			#VALUE!
7/17/2018	372.0236	1247	30887.92	54.05255
7/18/2018	443.428	1267	30413.75	41.72993
7/20/2018	269.8619	1199	40586.36	59.77007
7/21/2018	175.698	1127	29295.97	71.74356
7/23/2018	140.035	1168	31834.4	74.8446
7/25/2018	92.6418	1253	40291.93	83.07915
7/27/2018	86.4644	1080	40957.82	80.82258
7/28/2018	100.8779	1282	39761.99	81.11649
7/30/2018	107.6974	1221	31154.64	76.63878
8/1/2018	93.591	1138.956	41136.77	76.72733
8/3/2018	21.8425	101.6962	31679.07	42.97146
8/8/2018	174.466	1106.56	39893.99	40.8014
8/10/2018	125.464	1102.255	41258.13	47.01069
8/13/2018	120.594	1124.879	39287.37	53.94325
8/17/2018	106.7184	994.4573	39091.4	51.29284
8/21/2018	163.2589	1001.031	39813.08	36.42812
8/23/2018	110.5128	962.4461	29617.32	48.75698
8/27/2018	154.4313	1007.221	40322.88	13.2105

Column 2 – Port 4

Date	Area CH4	Area CO2	Area O2	%methane removal
6/8/2018	17.3084	238.833	45115.01	80.39046
6/11/2017	36.3841	303.0454	47668.69	69.47827
6/13/2018	27.5696	239.175	32394.04	71.57073
6/15/2018	22.8512	153.8724	44515.24	64.81531
6/18/2018	13.2792	82.0404	29291.72	62.83111
6/20/2018	17.426	73.2014	45147.04	58.49605
6/22/2018	13.2146	60.098	45812.57	62.48559
6/24/2018	13.277	56.6694	44656.98	60.51324
6/25/2018	14.3436	57.9869	44548.39	52.76515
6/27/2018	16.9522	52.9658	29837.58	42.84957
6/29/2018	14.9958	58.7737	34089.56	57.56475
7/2/2018	13.7423	50.9717	43808.33	59.21968
				#DIV/0!
7/5/2018	13.0512	77.5271	45918.59	70.62376
7/6/2018	20.2104	93.7638	45040.44	66.74632
7/8/2016	18.4878	82.7804	36948.95	66.98046
7/9/2016	17.2418	88.4759	40578.35	70.4706
7/11/2018	20.5486	54.4487	44238.34	48.03148

7/13/2018	15.5546	39	35157.27	40.78105
7/16/2018	gc not working			#VALUE!
7/17/2018	18.014	47	34246.33	44.25413
7/18/2018	16.356	45	33908.68	39.90478
7/20/2018	9.5778	40	32067.51	57.96595
7/21/2018	4.8746	34	33294.12	73.92709
7/23/2018	4.9591	37	43335.9	72.56985
7/25/2018	3.3271	42	44675.9	81.86371
7/27/2018	2.969	37	32869.47	80.58956
7/28/2018	3.2659	33	31954.87	77.00261
7/30/2018	3.7967	35	34959.13	72.18063
8/1/2018	3.3953	33.3272	33969.65	71.92978
8/3/2018	4.2113	19.0166	33117.04	41.71618
8/8/2018	5.507	35.3542	44105.55	41.30507
8/10/2018	4.125	33.248	39578.87	43.58731
8/13/2018	4.7018	31.7902	38449.87	41.56819
8/17/2018	3.8432	32.3094	36449.16	47.40026
8/21/2018	5.9779	31.5579	32871.79	29.76747
8/23/2018	3.7326	33.7526	32736.03	50.17708
8/27/2018	5.786	39.4092	32891.78	15.3341

Column 3 – port 1

Date	Area CH4	Area CO2	Area O2	%methane removal	BPI
6/8/2018	1115.29	1647.68	25022.14	-0.76035	2.32351E-05
6/11/2018	2240.44	4043.753	18679.8	9.225441	1.1669E-05
6/13/2018	1333.11	2520.453	22727.89	13.61573	4.436E-06
6/15/2018	1990.52	3368.638	35048.87	8.142265	4.96766E-06
6/18/2018	1777.91	3024.522	23604.99	9.349901	3.08664E-06
6/20/2018	1693.86	2832.724	35062.36	20.64495	2.48831E-06
6/22/2018	1590.26	2791.351	25454	25.14124	1.9326E-06
6/24/2018	1534.90	2737.72	24109.78	25.89059	1.64588E-06
6/25/2018	2241.11	2467.755	43597.33	-6.33184	2.16157E-06
6/27/2018	1451.17	2682.162	25845.76	19.30999	1.2597E-06
6/29/2018	1689.54	2976.376	25892.83	25.06375	1.26662E-06
7/2/2018	2207.29	3376.287	40804.06	23.37502	1.4562E-06
7/5/2018	1482.42	2591.665	41717.27	26.18323	8.27246E-07
7/6/2018	1729.04	2833.094	37859.61	27.82334	8.81079E-07

7/8/2016	1687.75	3017.813	40128.13	33.76317	8.03419E-07
7/9/2016	1628.18	2837.589	43157.72	32.44736	7.06673E-07
7/11/2018	2275.68	2993.522	27361.46	17.15339	9.29607E-07
7/13/2018	2047.25	3025.945	25820.27	16.93204	8.29327E-07
7/17/2018	2581.45	522.736	40277.1	-66.3205	1.00838E-06
7/18/2018	2263.34	3747.526	31467.17	16.98305	9.00891E-07
7/20/2018	2558.35	1529.898	29048.11	-30.3454	9.70951E-07
7/21/2018	2461.46	3378.965	31013.83	13.06242	9.22657E-07
7/23/2018	2611.77	3575.735	38875.19	6.58152	9.46294E-07
7/25/2018	1843.12	2220.806	41464.5	-1.83632	6.66636E-07
7/27/2018	1725.36	1280.904	29710.93	-28.1805	6.35029E-07
7/28/2018	2521.59	1474.24	27989.27	-38.7691	9.09888E-07
7/30/2018	2531.09	1524.369	39686.76	-42.7037	9.94924E-07
8/1/2018	2524.58	1539.276	27981.31	-44.879	1.01457E-06
8/3/2018	1816.98	2187.076	37102.47	-21.3488	7.32288E-07
8/8/2018	1631.61	1917.999	26688.02	-25.9633	7.4299E-07
8/10/2018	1628.19	1965.178	28345.13	-32.6084	8.525E-07
8/13/2018	1386.99	1373.628	41213.8	-47.6145	8.75626E-07
8/17/2018	1263.68	1299.407	40062.4	-46.1494	7.52193E-07
8/21/2018	1428.04	2302.577	34339.03	-21.5835	6.70065E-07
8/23/2018	1014.01	2044.048	34890.08	-22.5774	6.94905E-07
8/27/2018	737.22	786.4555	31271.63	-59.9111	6.39947E-07

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Date	Area CH4	Area CO2	Area O2	%methane removal
6/8/2018	4.2946	324.566	26025	96.10771
6/11/2018	9.753	174	44892.59	84.52125
6/13/2018	4.3168	152	38413.48	92.17943

6/15/2018	5.074	69	30952.88	80.82761
6/18/2018	4.5764	62	33729.53	81.12308
6/20/2018	4.1264	59	43672.1	85.71871
6/22/2018	1.4375	23	33915.76	87.66038
6/24/2018	0	20	33767.84	100
6/25/2018	0	21	44243.81	100
6/27/2018	0	21	32188.33	100
6/29/2018	269.5714	551	42995.48	31.88161
7/2/2018	380.8518	609	42182.87	25.46905
7/4/2018				#DIV/0!
7/5/2018	316.435	588	44057.8	28.96496
7/6/2018	335.6938	564	43737.42	28.96131
7/8/2016	347.6748	538	44286.15	27.25303
7/9/2016	360.1824	525	45519.33	24.21645
7/11/2018	460.0216	572	32424.79	14.41456
7/13/2018	393.1522	506	43010.65	10.16812
7/16/2018	gc error			#VALUE!
7/17/2018	56.8694	180	33600.09	51.90553
7/18/2018	60.5748	190	32825.57	45.54718
7/20/2018	63.1207	213	32143.53	50.1174
7/21/2018	54.1358	203	38972.58	56.12861
7/23/2018	74.2772	231	34761.08	44.34067
7/25/2018	86.4208	266	44302.11	42.20773
7/27/2018	84.3994	233	43379.71	35.17925
7/28/2018	60.3382	214	31746.26	45.59156
7/30/2018	61.7576	228	33762.67	42.25839
8/1/2018	62.1045	234.0985	43479.51	40.33633
8/3/2018	128.4278	376.6258	31389.1	22.45314
8/8/2018	80.78	327.9725	43487.77	33.99417
8/10/2018	82.574	334.2886	44385.13	26.05107
8/13/2018	83.1758	430.1882	41493.87	29.90604
8/17/2018	51.2101	451.8681	31434.13	51.94462
8/21/2018	63.4005	557.7454	40125.92	55.74115
8/23/2018	36.5064	437.846	29165.92	57.9657
8/27/2018	23.2554	410.8104	31748.96	61.17495

Column 3 – port 3

Date	Area CH4	Area CO2	Area O2	%methane removal
6/8/2018	0	53.6079	31632.06	100
6/11/2018	0	53	43904.89	100
6/13/2018	0	31	28579.8	100

6/15/2018	0	46	32183.28	100
6/18/2018	0	38	32787.82	100
6/20/2018	0	33	32797.95	100
6/22/2018	0	35	33686.5	100
6/24/2018	0	31	43782.82	100
6/25/2018	0	31	31317.37	100
6/27/2018	0	29	31658.56	100
6/29/2018	0	13	34237.65	100
7/2/2018	0	13	39187.99	100
7/4/2018				#DIV/0!
7/5/2018	0	38	45009.15	100
7/6/2018	1.577	50	46039.19	94.35767
7/8/2016	1.457	34	36546.42	92.68007
7/9/2016	0	34	41249.12	100
7/11/2018	2.4029	37	44174.75	88.63716
7/13/2018	0	14	36072.26	100
7/16/2018	gc error			#VALUE!
7/17/2018	0	22	33897.23	100
7/18/2018	0	26	33177.92	100
7/20/2018	0	27	33527.16	100
7/21/208	0	25	32413.36	100
7/23/2018	0	26	35344.75	100
7/25/2018	0	25	43732.12	100
7/27/2018	0	24	44114.4	100
7/28/2018	0	21	32033.59	100
7/30/2018	0	24	34648.83	100
8/1/2018	0	15.5424	33668.59	100
8/3/2018	0	23.4942	32776.52	100
8/8/2018	0	26.88	33078.79	100
8/10/2018	0	51.403	31511.75	100
8/13/2018	0	22.6538	43336.63	100
8/17/2018	0	24.2782	32686.69	100
8/21/2018	0	21.5868	43424.28	100
8/23/2018	0	20.3786	32054.47	100
8/27/2018	0	21.4901	32894.63	100

Column 3 – port 4

Date	Area CH4	Area CO2	Area O2	%methane removal
6/8/2018	0	17.5716	37325.19	100
6/11/2018	0	35	45572.76	100
6/13/2018				#DIV/0!

6/15/2018	0	13	44378.17	100
6/18/2018	0	11	32769.34	100
6/20/2018	0	11	44220.28	100
6/22/2018	0	11	33764.97	100
6/24/2018	0	10	32694.14	100
6/25/2018	0	10	31840.78	100
6/27/2018	0	10	32228.81	100
6/29/2018	0	12	33021.34	100
7/2/2018	0	11	44211.49	100
7/4/2018				#DIV/0!
7/5/2018	0	26	45480.7	100
7/6/2018	0	16	45384.54	100
7/8/2016	0	15	43258.35	100
7/9/2016	0	14	44962.29	100
7/11/2018	0	11	44600.99	100
7/13/2018	0	9	34214.22	100
7/16/2018	gc error			#VALUE!
7/17/2018	0	14	34267.83	100
7/18/2018	0	9	33671.41	100
7/20/2018	0	10	33456.16	100
7/21/2018	0	9	33580.99	100
7/23/2018	0	10	35170.24	100
7/25/2018	0	13	33525.82	100
7/27/2018	0	14	32186.92	100
7/28/2018	0	9	44188.97	100
7/30/2018	0	9	34574.65	100
8/1/2018	0	9	33507.84	100
8/3/2018	0	8.628	43044.89	100
8/8/2018	0	11.6402	43451.48	100
8/10/2018	0	14.278	43512.25	100
8/13/2018	0	12.5787	44128.64	100
8/17/2018	0	9.452	32857.34	100
8/21/2018	0	9.3228	32844.62	100
8/23/2018	0	9.6784	32800.91	100
8/27/2018	0	10.5641	32932.97	100

Column 4 – port 1

Date	Area CH4	Area CO2	Area O2	%methane Removal	BPI
6/8/2018	2946.8548	3011.4642	23853.3634	-18.9568	6.13928E-05
6/11/2018	3266.4324	3080.0186	35310.4700	-22.8033	1.70127E-05

6/13/2018	2228.5470	2436.0420	23491.4700	-13.6091	7.41559E-06
6/15/2018	2820.5885	2905.7006	34959.7000	-16.5064	7.03923E-06
6/18/2018	2379.3112	2554.4516	25377.7400	-13.5533	4.13075E-06
6/20/2018	2736.9102	2742.9601	23057.6200	-4.65175	4.02057E-06
6/22/2018	2667.1616	2853.5081	34444.6400	0.93718	3.24134E-06
6/24/2018	2198.4372	2545.6442	32926.2200	4.888442	2.35739E-06
6/25/2018	1997.2487	2427.1723	33475.4500	-1.40927	1.92636E-06
6/27/2018	1506.4422	1856.9202	36541.1400	-0.69874	1.30768E-06
6/29/2018	1921.4580	2014.6521	35871.5200	-0.33525	1.44049E-06
7/2/2018	1760.5729	2298.7536	33396.4600	15.76838	1.16149E-06
7/5/2018	1327.9856	1713.7088	41006.4200	11.57409	7.41063E-07
7/6/2018	1945.6982	2478.5065	36014.9000	15.85324	9.91486E-07
7/8/2016	1918.3672	2345.2342	33926.4200	15.99193	9.13201E-07
7/11/2018	2793.9066	2862.4771	35207.0200	4.824611	1.1413E-06
7/13/2018	2814.5839	2888.8739	32398.2800	-1.13684	1.14017E-06
7/17/2018	2915.1208	3001.6962	23738.1100	1.463209	1.13872E-06
7/18/2018	3081.4174	3181.7478	23981.4200	-6.45238	1.22651E-06
7/20/2018	2959.7060	3060.2401	23018.8600	-3.95167	1.12327E-06
7/21/2018	2421.3186	2699.6794	32755.8700	2.736993	9.07612E-07
7/23/2018	2704.9850	2847.2080	32676.5700	-6.54459	9.80067E-07
7/25/2018	2606.2352	2870.0724	33848.1000	-6.32719	9.42649E-07
7/27/2018	2562.8336	2736.2542	30057.2600	-10.755	9.43265E-07
7/28/2018	2652.4351	2858.7684	33823.4600	-10.2884	9.57101E-07
7/30/2018	2678.2494	2897.5401	26186.1300	-16.1945	1.05277E-06
8/1/2018	2586.4100	2783.3027	34021.4600	-19.6528	1.03942E-06
8/3/2018	3164.7276	3071.4552	22321.4700	-19.0923	9.81128E-07
8/8/2018	2716.9462	2879.2056	34025.7300	-17.2003	9.27919E-07

8/10/2018	2768.2451	2912.2897	34033.1900	-17.5533	9.15425E-07
8/13/2018	2741.4682	2940.1339	33613.9800	-13.0837	8.65362E-07
8/17/2018	2307.0842	2588.7422	33823.3500	-14.7907	7.43852E-07
8/21/2018	2614.2866	2756.4536	33234.9900	-21.2967	7.97338E-07
8/23/2018	2308.8844	2564.8114	33715.9200	-14.5572	7.38404E-07
8/27/2018	2691.0538	33210.1300		-12.1495	7.00795E-07

Column 4 – port 2

Date	Area CH4	Area CO2	Area O2	%methane removal
6/8/2018	380.3624	3216.619	11300.8	69.8696
6/11/2018	499.16	3290.96	13787.05	62.93116
6/13/2018	422.24	3012.11	9054.92	66.45747
6/15/2018	455.09	3171.09	14967.87	65.79613
6/18/2018	509.84	3260.53	6756.37	63.86484
6/20/2018	365.11	2296.06	12368.89	70.22468
6/22/2018	403.26	3096.67	22758.47	75.94248
6/24/2018	225.46	2748.85	23538.39	84.14156
6/25/2018	55.59	828.48	28938.89	84.5229
6/27/2018	122.92	2282.35	17068.64	87.38503
6/29/2018	104.50	2065.55	32340.62	89.86094
7/2/2018	99.77	1883.37	33615.32	90.41718
7/3/2018				#DIV/0!
7/5/2018	60.87	970.79	41400.06	87.94714
7/6/2018	186.18	2963.56	21156.15	89.01333
7/8/2016	217.29	2419.37	31482.67	85.26692
7/9/2016	199.27	2942.79	28357.16	88.64503
7/11/2018	236.64	3034.69	10764.53	86.47372
7/13/2018	207.62	3019.44	9493.74	86.53279
7/16/2018	gc error			#VALUE!
7/17/2018	198.80	3182.64	11398.61	88.24156
7/18/2018	202.00	3136.48	11138.07	85.92967
7/20/2018	132.14	2333.57	32003.37	88.08161
7/21/2018	145.34	2823.44	16541.30	89.69275
7/23/2018	174.71	3019.73	11487.75	87.01629

7/25/2018	154.38	3052.47	11530.16	88.1077
7/27/2018	145.81	2776.70	31229.57	86.98951
7/28/2018	135.55	2859.78	12293.82	88.18196
7/30/2018	130.47	2950.44	12629.80	87.55923
8/1/2018	120.8726	2848.033	14882.65	87.26346
8/3/2018	81.6762	1630.184	35949.77	82.97468
8/8/2018	43.354	1224.243	29445.7	86.77174
8/10/2018	45.2485	1288.125	30578.14	84.59932
8/13/2018	86.527	2631.72	18094.01	83.19146
8/17/2018	43.5375	2138.921	31379.31	89.24979
8/21/2018	49.9293	2087.874	31368.09	88.71755
8/23/2018	72.2194	2266.696	32474.03	81.54021
8/27/2018	72.892	2223.394	31132.84	75.51452

Column 4 – port 3

Date	Area CH4	Area CO2	Area O2	%methane removal
6/8/2018	18.9383	2689.013	12661.26	97.90923
6/11/2018	18.37	2582.07	26559.79	97.88832
6/13/2018	13.57	2377.09	23495.75	98.37255
6/15/2018	11.91	2288.47	23108.84	98.51527
6/18/2018	9.73	1962.20	19867.53	98.61107
6/20/2018	0.00	35.00	27634.23	100
6/22/2018	7.50	1869.81	15024.25	99.16157
6/24/2018	4.85	1806.55	20415.60	99.43813
6/25/2018	3.19	1684.48	19380.41	99.52724
6/27/2018	0.00	48.54	11454.52	100
6/29/2018	0.00	51.87	15478.68	100
7/2/2018	1.62	852.14	12884.42	99.64011
				#DIV/0!
7/5/2018	1.40	930.99	16113.74	99.69341
7/6/2018	2.80	959.49	16580.83	99.46155
7/8/2016	2.18	820.07	19955.69	99.52972
7/9/2016	1.86	893.48	15398.49	99.6302
7/11/2018	1.40	919.55	14347.19	99.71622
7/13/2018	1.15	987.39	13275.68	99.75656
7/16/2018	gc error			#VALUE!
7/17/2018	0.00	903.64	12837.21	100
7/18/2018	0.00	938.95	14514.89	100
7/20/2018	0.00	879.40	12490.75	100
7/21/2018	0.00	876.76	11596.19	100
7/23/2018	0.00	547.97	15699.04	100

7/25/2018	0.00	774.29	14435.66	100
7/27/2018	0.00	724.14	12627.82	100
7/28/2018	0.00	893.95	19013.37	100
7/30/2018	1.89	1082.30	38643.95	99.47853
8/1/2018	0.00	326.29	33536.26	100
8/3/2018	1.7976	987.3742	28639.46	99.32606
8/8/2018	1.273	863.8514	28897.63	99.41228
8/10/2018	1.4334	886.6017	29077.48	99.23499
8/13/2018	0	754.3794	29945.13	100
8/17/2018	0	566.8288	29910.64	100
8/21/2018	0	568.7198	42280.29	100
8/23/2018	1.145	586.6068	28398.97	98.76182
8/27/2018	1.0458	432.6104	31146.66	97.96357

Column 4 – Port 4

Date	Area CH4	Area CO2	Area O2	%methane removal
6/8/2018	0	291.2407	36440.71	100
6/11/2018	0	204.1536	44245.08	100
6/13/2018	0	217.2996	43870.13	100
6/15/2018	0	169.7698	44513.7	100
6/18/2018	0	213.8999	43861.53	100
6/20/2018	0	167.4594	43656.63	100
6/22/2018	0	156.008	33623.7	100
6/24/2018	0	131.4668	32677.9	100
6/25/2018	0	118.881	30437.02	100
6/27/2018	0	93.7734	32072.57	100
6/29/2018	0	119.6762	32567.28	100
7/2/2018	0	106.3328	43239.76	100
				#DIV/0!
7/5/2018	0	125.7645	44664.98	100
7/6/2018	0	111.3127	44619.56	100
7/8/2016	0	118.956	43587.16	100
7/9/2016	0	115.8568	43178.52	100
7/11/2018	0	112.911	32526.66	100
7/13/2018	0	109.7564	34759.9	100
7/16/2018	gc error			#VALUE!
7/17/2018	0	109.3282	33793.21	100
7/18/2018	0	111.0736	33721.71	100
7/20/2018	0	102.861	32715.24	100
7/21/2018	0	96.7011	43160.68	100
7/23/2018	0	98.6629	43534.02	100

7/25/2018	0	90.7737	30745.76	100
7/27/2018	0	89.2823	31499.2	100
7/28/2018	0	83.3982	43309.88	100
7/30/2018	0	82.0846	32978.64	100
8/1/2018	0	75.8208	32740.44	100
8/3/2018	0	86.2382	33066.94	100
8/8/2018	0	75.3414	32718.73	100
8/10/2018	0	75.5975	31233.56	100
8/13/2018	0	76.518	31524.49	100
8/17/2018	0	50.9774	32921.7	100
8/21/2018	0	52.7663	32265.54	100
8/23/2018	0	54.2502	32130.82	100
8/27/2018	0	59.8714	32234.57	100

Column 5 – Port 1

Date	Area CH4	Area CO2	Area O2	%methane removal	BPI
6/8/2018	6271.959	6549.365	5597.668	27.01749	2.60232E-05
6/11/2018	6076.933	6235	12092.93	1.284894	1.05369E-05
6/13/2018	5523.171	6048	12059.4	29.20327	3.83218E-06
6/15/2018	5288.614	5774	8979.704	-18.8828	7.33876E-06
6/18/2018	5469.63	6010	12154.96	4.704294	3.45046E-06
6/20/2018	5351.681	5915	13462.29	-6.14581	3.5715E-06
6/22/2018	5011.031	5885	8377.015	-3.1175	2.89901E-06
6/24/2018	4671.756	5529	11724.13	-2.73256	2.3855E-06
6/25/2018	3473.324	4313	20762.89	-16.9879	2.34503E-06
6/27/2018	4291.302	4914	11017.29	-13.4197	2.23505E-06
6/29/2018	3415.813	4197	20766.83	-17.5042	1.88689E-06
7/2/2018	2263.951	2870	27374.8	-32.7046	1.57075E-06
7/5/2018	5200.717	5913	14290.55	-4.73272	1.61166E-06
7/6/2016	5024.348	5829	14902.27	-3.72707	1.50394E-06
7/8/2016	5077.516	5973	15580.71	-3.0329	1.4218E-06
7/9/2016	5009.647	6037	13854.6	-1.82756	1.3585E-06
7/11/2018	6276.671	6089	11531.4	-1.52052	1.282E-06
7/13/2018	6301.928	6106	11230.95	-1.57988	1.21509E-06
7/17/2018	5276.251	5619	19144.92	-7.9959	1.14502E-06
7/18/2018	6385.979	6353	10860.33	-0.26157	1.08164E-06
7/20/2018	6724.808	6455	12039.27	-2.04569	1.0855E-06
7/21/2018	6485.836	6302	12299.96	-1.43932	1.02365E-06
7/23/2018	6533.503	6283	10399.36	-1.95231	9.85994E-07
7/25/2018	6545.253	6565	10698.59	0.153334	9.46941E-07
7/27/2018	6524.563	6222	9066.926	-2.37457	9.06189E-07

7/28/2018	6435.638	6335	13261.17	-0.788	8.76312E-07
7/30/2018	6452.488	6322	10925.07	-1.01934	8.45259E-07
8/1/2018	6470.877	6290	10289.87	-1.41893	8.3216E-07
8/3/2018	7309.435	6700.012	10381.42	0.915169	8.15009E-07
8/8/2018	6470.842	6208.506	10580.62	-2.069	7.36516E-07
8/10/2018	6509.809	6434.794	10363.12	-0.57951	7.17572E-07
8/13/2018	6316.413	6170.643	11419.37	-1.16737	6.64606E-07
8/17/2018	6275.658	6153.382	8759.298	-0.9838	6.22585E-07
8/21/2018	6368.237	6120.014	10158.03	-1.98765	5.9762E-07
8/23/2018	5863.788	5913.804	7294.042	0.424671	5.35799E-07
8/27/2018	5932.915	5891.231	8946.271	-0.35253	5.1473E-07

Column 5 – port 2

Date	Area CH4	Area CO2	Area O2	%methane removal
6/4/2018	3871.61	4029.241	23832.62	26.86114
6/11/2018	3314.686	3475	33197.26	2.362017
6/13/2018	3359.718	3710	34790.88	29.59112
6/15/2018	2971.243	3275	34485.43	-18.428
6/18/2018	3182.994	3497	32835.12	4.702405
6/20/2018	2968.383	3270	21903.47	-6.31531
6/22/2018	2709.617	3221	30521.03	-2.5076
6/24/2018	2503.888	3072	32465.16	-0.94038
6/25/2018	2485.039	2998	21731.28	-18.388
6/27/2018	2631.397	2897	21620.45	-15.3436
6/29/2018	2466.057	3012	21574.85	-17.7971
7/2/2018	2538.947	3221	31343.4	-32.6688
7/5/2018	2113.486	2590	29563.79	-0.98586
7/6/2016	2604.616	3203	33798.5	-0.8128
7/8/2016	2563.951	2870	29374.8	-5.51067
7/9/2016	2623.937	3097	32462.16	-2.8665
7/11/2018	3935.545	3634	21896.86	-3.97925
7/13/2018	4065.344	3700	32730.55	-4.70322
7/16/2018	gc error			#VALUE!
7/17/2018	3836.509	3796	32133.38	-11.6396
7/18/2018	4022.994	3808	31117.03	-2.75117
7/20/2018	4778.725	4201	32233.81	-6.43939
7/21/2018	4112.17	3799	31691.67	-3.96443
7/23/2018	4201.558	3831	30580.56	-4.60824

7/25/2018	4251.268	3966	21397.8	-3.46853
7/27/2018	4066.16	3551	32007.02	-6.75945
7/28/2018	4024.845	3659	32154.26	-4.76681
7/30/2018	4299.904	3882	32027.95	-5.10832
8/1/2018	4141.412	3761.341	32985.65	-4.80935
8/3/2018	5387.025	4313.064	32334.85	14.32484
8/8/2018	4086.675	3727.517	22501.62	-4.59623
8/10/2018	4209.675	3876.826	32197.57	-4.11611
8/13/2018	4074.573	3729.303	32149.22	-4.42434
8/17/2018	4124.533	3735.078	22433.48	-4.95514
8/21/2018	4417.739	3831.046	31669.64	-7.11248
8/23/2018	3584.471	3500.267	26422.57	-1.18853
8/27/2018	3637.28	3465.988	24115.69	-2.41145

Column 5 – Port 3

Date	Area CH4	Area CO2	Area O2	%methane removal
6/8/2018	1787.792	4652.707	4149.33	62.52913
6/11/2018	1411.35	4068		48.48928
6/13/2018	814.8871	2638	38386.75	68.72672
6/15/2018	1280.938	3819	3819.295	30.156
6/18/2018	1437.251	4204	11009.99	49.04205
6/20/2018	1396.779	4177	9282.947	41.04472
6/22/2018	1124.157	4107	11729.31	49.01825
6/24/2018	908.3533	3707	15269.46	53.10182
6/25/2018	925.7646	3710	14015.46	39.2064
6/27/2018	897.2345	3129	18941.19	39.84818
6/29/2018	930.8651	3979	16896.24	41.90375
7/2/2018	810.0681	3764	15908.71	30.03334
				#DIV/0!
7/5/2018	220.8701	1069	42190.03	58.94417
7/6/2016	857.1638	3943	24212.82	57.26866
7/8/2016	831.768	2912	23557.35	47.37439
7/9/2016	910.0681	3504	19908.71	50.98066
7/11/2018	480.1538	1252	31214.07	44.56769
7/13/2018	1825.684	4298	9539.685	40.37194
7/16/2018	gc error			#VALUE!
7/17/2018	1654.632	4385	8811.799	35.90349
7/18/2018	173.9726	485	28651.9	47.18751
7/20/2018	1796.252	3945	18521.5	37.42705
7/21/2018	1959.047	4480	10166.65	39.1483

7/23/2018	2022.154	4494	10840.38	37.93718
7/25/2018	2110.294	4850	6820.238	39.36269
7/27/2018	1995.892	4239	10325.83	35.97597
7/28/2018	1938.673	4544	9602.088	40.19245
7/30/2018	1960.259	4567	11472.03	39.94072
8/1/2018	1868.174	4537	8461.146	41.66984
8/3/2018	2682.363	4984.706	9817.219	34.74304
8/8/2018	1928.82	4497.062	10392.44	39.96715
8/10/2018	1930.795	4630.733	10344.73	41.14801
8/13/2018	1883.115	4388.982	10145.96	39.95262
8/17/2018	1842.216	4415.376	10049.66	41.12061
8/21/2018	1785.059	4314.265	10320.9	41.46699
8/23/2018	1507.223	4269.686	10796.32	47.81905
8/27/2018	1500.855	4184.14	10455.39	47.19943

Column 5 : Port 4

Date	Area CH4	Area CO2	Area O2	%methane removal
6/8/2018	26.383	993.8628	26263.77	96.86443
6/11/2018	7.678	761.0232	29507.5	98.00234
6/13/2018	4.8318	727.1198	42147.25	99.20575
6/15/2018	4.7033	671.6913	41410.49	97.78413
6/18/2018	4.0981	714.6684	31201.61	98.85969
6/20/2018	3.0053	673.9298	41385.55	98.89134
6/22/2018	1.5381	668.526	30921.77	99.42647
6/24/2018	0	543.1156	31140.92	100
6/25/2018	0	293.8363	32535.49	100
6/27/2018	0	525.7872	29329.36	100
6/29/2018	0	548.5932	30727.25	100
7/2/2018	2.07	545.624	41604.99	98.12091
7/5/2018	2.1309	533.5606	44449.73	99.00653
7/6/2016	0	523.9808	43002.56	100
7/8/2016	0	529.9327	42105.25	100
7/9/2016	1.66	538.624	40804.99	99.23247
7/11/2018	0	687.454	30865.86	100
7/13/2018	2.8884	709.3044	31366.8	99.18887
7/16/2018	gc error			#VALUE!
7/17/2018	0	611.591	32878.55	100
7/18/2018	0	638.6578	30395.14	100
7/20/2018	3.4212	752.5644	30031.3	99.0949
7/21/2018	0	676.1886	31909.61	100

	Temperature in deg C					Moisture content (%v/v)				
	column1	column 2	column 3	column 4	column 5	column1	column 2	column 3	column 4	column 5
1	28.7	29.1	30.5	27.1	31.1	34.4	33.2	38.1	34.8	36.3
8	28.5	28.7	31.6	28.5	31.5	34.5	33.4	38.2	34.9	36.4
15	28.9	28.4	30.7	29.1	31.2	34.6	33.6	38.3	35	36.5
22	29.2	28.2	30.4	31.6	30.5	34.8	33.7	38.5	35.2	36.7
29	29.1	27.5	30	32.3	29.9	35.2	33.9	38.6	35.3	36.8
36	29.6	28.1	29.7	32.5	29.8	35.3	34.2	38.8	35.5	37
43	30.1	28.7	29.4	32.6	29.9	35.2	34.6	40	35.7	37.2
50	30.5	29.1	29.1	32.7	30	35.5	34.8	40.1	35.9	37.4
57	31.1	29.5	28.8	32.5	29.8	35.7	34.9	40.3	36	37.5
64	31.4	30.1	28.5	32.4	29.9	35.8	35.5	40.4	36.1	37.7
71	31.8	30.2	28.3	31.6	29.7	36	35.6	40.6	36.3	37.9
78	32.1	30.6	27.9	31.4	29.8	36.1	35.8	40.8	36.4	38
85	31.8	30.8	28.5	31.3	30	36.2	36	41	36.6	38.2
90	31.9	31.1	28.1	31.4	30.1	36.4	36.2	41.3	36.8	38.4

7/23/2018	2.277	680.3774	40458.46	99.3329
7/25/2018	0	734.3147	40878.76	100
7/27/2018	0	525.6152	32374.91	100
7/28/2018	0	605.995	29602.48	100
7/30/2018	1.4748	603.445	41305.78	99.5124
8/1/2018	0	590.2552	41603.25	100
8/3/2018	6.9579	778.959	29661.78	98.40501
8/8/2018	1.2859	558.3231	42680.47	99.54043
8/10/2018	0	570.7124	29750.08	100
8/13/2018	0	486.4402	31838.32	100
8/17/2018	0	490.8554	41600.84	100
8/21/2018	0	493.873	30659.34	100
8/23/2018	0	397.127	41719.2	100
8/27/2018	3.2253	374.3341	42600.11	98.2915

Appendix 3

Temperature and moisture data of column reactor

Appendix 4

LEAF test : Heavy metal raw results

Cumulative L/S fraction	Ag (mg/l)	Al(mg/l)	As(mg/l)	Ba(mg/l)	Be (mg/l)	Cd (mg/l)	Co (mg/l)	Cr (mg/l)
0.2	44.40742	0.001778	13.27287	0.000533	0.001467	0.058665	0	0.058665
0.5	42.39894	0.0004	15.9996	0.0004	0.000533	0.048665	0.12413	0.048665
1	31.69254	0.000267	15.2438	0.000267	0.0004	0.069998	0.043466	0.069998
1.5	27.33265	0.000711	9.444208	0.0004	0.000267	0.374657	0.118797	0.374657
2	19.86617	0.001022	5.59986	0.0004	0.000267	0.502654	0.019333	0.502654
4.5	13.22634	0.000889	3.893236	0.000267	0.000267	0.405323	0.028666	0.405323
5	10.99973	0.0012	3.351027	0.000267	0.000267	0.283993	0.051065	0.283993
9.5	5.933185	0.001333	1.511073	0.000133	0	0.363991	0.043866	0.363991
10	4.279893	0.002444	0.995531	0.000133	0	0.355991	0.023066	0.355991

Cumulative L/S fraction	Cu (mg/l)	Mn (mg/l)	Mo (mg/l)	Ni (mg/l)	Pb (mg/l)	Sb (mg/l)	Se (mg/l)	Th (mg/l)
0.2	0.275993	0	0.000533	0.002133	0.008666	0.001067	0.0004	0.000267
0.5	0.241327	0.004533	0.0028	0.001467	0.007333	0.000133	0.000133	0
1	0.353991	0.004	0.001333	0.001467	0.009333	0.000133	0.000133	0
1.5	0.52532	0.004133	0.0028	0.002533	0.018	0	0	0
2	0.469322	0.004	0.000933	0.002667	0.018	0	0.000133	0
4.5	0.325325	0.004	0.000667	0.002533	0.0152	0	0	0
5	0.218661	0.003467	0.001867	0.002533	0.012	0	0	0

9.5	0.162663	0.005067	0.0008	0.002267	0.010666	0	0.000133	0
10	0.107997	0.0032	0.000267	0.002667	0.010666	0	0.000133	0

Cumulative L/S fraction	Tl (mg/l)	U (mg/l)	V (mg/l)	Zn (mg/l)
0.2	0.0088	0	0.0088	-0.0656

0.5	0.005733	0.037199	0.005733	0.037199
1	0.008	0.0176	0.008	0.0176
1.5	0.031066	0.025466	0.031066	0.025466
2	0.059065	0.011333	0.059065	0.011333
4.5	0.085731	0.010933	0.085731	0.010933
5	0.072665	0.0104	0.072665	0.0104
9.5	0.126397	0	0.126397	0
10	0.157329	0	0.157329	0