

ENHANCING METHANE OXIDATION IN LANDFILL COVER USING BREWERY SPENT GRAIN AS BIOCOVER

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ABSTRACT Landfill gas (LFG) is a potent greenhouse gas (GHG) generated by anaerobic degradation of decomposable municipal solid wastes (MSW). LFG contains (50-60%) of methane (CH₄) and (40-50%) carbon dioxide (CO₂). If a landfill is neither aerated nor equipped with gas capture systems, the LFG emissions, mainly CH₄, in the cover soil is best reduced by using a biocover. Biocovers normally act as a biofilter to reduce emissions by improving the biological oxidation of CH₄ to CO₂. In this study, the optimal ratio for a biocover using mixture of brewery spent grain (BSG) and compost made out of grass and cow manure is determined. Thereafter, column experiments were carried out to investigate the best height level of the biocover. Batch incubation experiments were conducted for screening the best ratio of BSG to compost. A mixing ratio from 10% to 100% BSG to compost with 10% increment was tested. The best ratio of BSG to compost was 7:3. This ratio was later tested with different parameters such as pH, moisture content and temperature. Overall, the optimum biocover performance was at pH 6, moisture content of 66% (v/v) and temperature of 40°C. The column experiments showed that 100% CH₄ oxidation occurred fastest at the height of 50cm.

(Keywords: Greenhouse gas, methane oxidation, biocover, brewery spent grain, compost)

INTRODUCTION

Climate change mitigation efforts to date have been mainly concerned with reducing emissions of CO₂. However, recent research has drawn interest to the importance of CH₄, the second most abundant GHG after CO₂. CH₄ is 25 times more potent than CO₂ in trapping heat in the atmosphere [1]. In a report by USEPA [2], the five main sources of CH₄ are identified as agriculture, coal mines, landfills, oil and natural gas systems and waste water. Globally landfills account for 12% of CH₄ emission [2] while in Malaysia it is about 47% of the total CH₄ emission [3]. Emissions of CH₄ from landfills are due to anaerobic decomposition of organic material stemming from MSW.

In Malaysia, 30,000 tonnes of MSW are disposed of in landfills and dumpsites each day [4]. Over the past 10 years, the generation of MSW has increased more than 91% with the urban population being the main waste generators and it accounts for an average of 1.3-7.5 L/kg/year of CH₄ released into the atmosphere [5]. Since the landfills are small and do not have extensive gas collection system, an alternative method is used to mitigate the CH₄ emission. One such method is by introducing a

biocover to the cover soil at landfills which possess the capacity of CH₄ oxidation to CO₂.

The objective of this study is to design a suitable biocover material using organic wastes that are capable of oxidizing CH₄ into CO₂. Also studied is the thickness level of the biocover material that is needed for maximum CH₄ oxidation.

MATERIAL AND METHODS

Compost

Compost pile of grass clippings and cow manure with a ratio of 75 to 25 was made following the heap method [6],[7]. The ratio was chosen to optimize conditions within the pile in terms of nutrition, oxygen, moisture content, pH and temperature levels so that an ideal rate of microbial activity is achieved. Daily mixing of the compost pile was done to maintain the aeration and optimum composting for 10 days and thereafter the mixing was done on alternate days. The moisture content was maintained between 40 to 70% throughout the composting period by adding sufficient water when required. The ASTM Standard D2216 (2005) was used to determine the moisture content of the compost by oven drying 5g of compost overnight at

105°C and expressed as the mass ratio of water content to wet compost. The pH was measured using the indoor Metler Toledo pH meter. Daily temperature readings were taken using a laboratory thermometer until a stable temperature profile was recorded. The compost pile took 2 to 3 days to increase beyond mesophilic (10-40°C) temperatures and reach the thermophilic (41-70°C) stage of composting. Later it decreased to ambient level.

Brewery Spent Grain

Brewery spent grain (BSG) is a by-product of the brewery industry, representing about 85% of the total by-product generated [8]. It is an organic waste from barley and other cereal malts used in the production of beer [9]. In Malaysia, BSG is available throughout the year and its main application is for animal feed because of the high protein and fibre content (20-70% respectively by dry weight) [8]. However, it is under-utilized with approximately 15% sold for feedstock while the balance discarded to landfills [10]. In this study, fresh BSG was obtained from Carlsberg Brewery Malaysia Berhad and used immediately. The pH, temperature and moisture content were determined using the same methods used for compost.

Batch incubation experiments

Batch incubation experiments were carried out using Wheaton bottles. Mixture of BSG and compost ranging from 10 to 100% ratio of BSG to compost with a 10% increase was prepared in 150ml bottles in triplicates. Each bottle with 20g of substrate (compost and BSG) was sealed with a septa and aluminium seal to ensure air tight. Then 18ml of air was withdrawn from the headspace of each Wheaton bottle using an airtight syringe and replaced with 6ml of CH₄ gas (99.9% purity) and 12ml of O₂ gas (99.98% purity). This amount provided a mixing ratio of approximately 4% of CH₄ (v/v) and 8% O₂ (v/v) required for substrate saturation and determination of maximum CH₄ oxidation rate [11]. O₂ gas in the headspace maintains an aerobic condition within the bottles during the experiments. The concentrations of CH₄, O₂ and CO₂ in the headspace were measured daily using the Shimadzu 8A Gas Chromatography (GC) equipment to quantify the CH₄ oxidation rate for the different ratios. The procedures were repeated for other tested ratio under different factor of pH, moisture content and temperature.

The influence of moisture content

The influence of moisture content on CH₄ oxidation was tested using different percentages of moisture content. The original moisture content of the mixture was about 66% and it was used as a control setup. Moisture content is lowered by oven drying the mixture while it is increased by adding deionised water to the mixture. Moisture content of 50% to 80% was tested using triplicate bottles.

The influence of pH

The influence of pH on CH₄ oxidation was tested by modifying the pH of mixture ranging from pH4 to pH8. Sulphuric acid was added to lower the pH level while nitric acid was used to increase the pH level. The original pH 6 of the mixture was used as the control. Each pH was done in triplicate and headspace gas was analysed using GC. The analysis was carried out until the CH₄ concentration becomes zero or reaches a plateau.

The influence of temperature

The influence of temperature on CH₄ oxidation was tested between 25°C to 55°C with 5°C increase. Triplicates samples were incubated in different temperature setting and analysed until the CH₄ concentration becomes zero or reaches a plateau. The original temperature 30°C was used as a controlled experiment.

Column experiments

The column experiments represented an advanced step for evaluating the CH₄ oxidation of biocover material of certain thickness or height. The best BSG to compost ratio and with the optimum parameters from the batch incubation experiments were chosen for the column experiment. The columns were prepared in duplicates and the experiment was repeated twice. Columns of one- m height were fabricated using 10mm thick PVC with an internal diameter of 0.15m. Sampling ports at 0.1m interval enable gas sampling at different heights. The biocover material i.e. the best BSG to compost ratio was placed inside the columns and the top of the column was sealed with a 5mm thick plexiglass to ensure air-tight. Similar to the batch incubation experiment approximately 4% of CH₄ (v/v) and 8% O₂ (v/v) was introduced into the column using a Dwyer Rate-Master flow meter.

Later, the gas samples at each port were analysed using GC.

RESULTS AND DISCUSSION

Material properties

Table 1: The physiochemical properties of the compost and fresh BSG used for batch incubation and column experiments

Test Parameter	Test Method	Compost	Fresh Brewery Spent Grain
Moisture content (%)	ASTM 2004	62.17 ± 0.14 % (v/v)	70.58 ± 0.14 % (v/v)
pH	ASTM 2004	6.33 ± 0.12	4.41 ± 0.12
Organic matter (%)	ASTM 830-97	63.6 %	73.6 %
Total carbon (%)	ASTM 777-87 (96)	20.3 %	40.1 %
Total nitrogen (%)	ASTM E778-87	1.20 %	1.07 %
Carbon: Nitrogen ratio	USEPA 3050B	17:1	38:1

The moisture content, organic matter, pH and C and N ratio are important parameters for materials used. Both materials used in this study have moisture content above 60% which has the ability to retain water to sustain the microbial population for CH₄ oxidation [12]. Compost with neutral to slightly acidic pH optimized the CH₄ oxidation [13] but the acidic pH of raw BSG is not favourable. Nutrient rich soil increases the CH₄ oxidation rate. Carbon is used a source of energy for growth of microbes while nitrogen is used for synthesis of cellular material, amino acids and proteins [14]. Therefore, the organic matter and C:N ratio enhanced CH₄ oxidation and both materials used in this experiment are in the optimal range.

The physiochemical properties of compost and BSG are given in **Table 1**. All material properties were measured by following the methods prescribed in ASTM and USEPA standards.

BSG to compost ratio

Figure 1 shows the CH₄ oxidation among the different ratios of BSG to compost from the batch incubator experiment. The BSG to compost ratio of 7:3 had the highest percentage of CH₄ oxidation of 64.5% while 100% had the lowest CH₄ oxidation (5.7%). The poor performance of the 100% BSG was attributed to inactive microbes in BSG which hindered CH₄ oxidation. The compost added to BSG provides the mixtures with either microbes or nutrients for the microbes in BSG for CH₄ oxidation. This is an indicative that methanotrophic activity is present and could be accelerated with the addition of compost but only at suitable amount. This is evident in the ratios of 1:9 and 9:1 BSG to compost. Thus, the best ratio was chosen for further investigation with different parameter such as pH, moisture content and temperature.

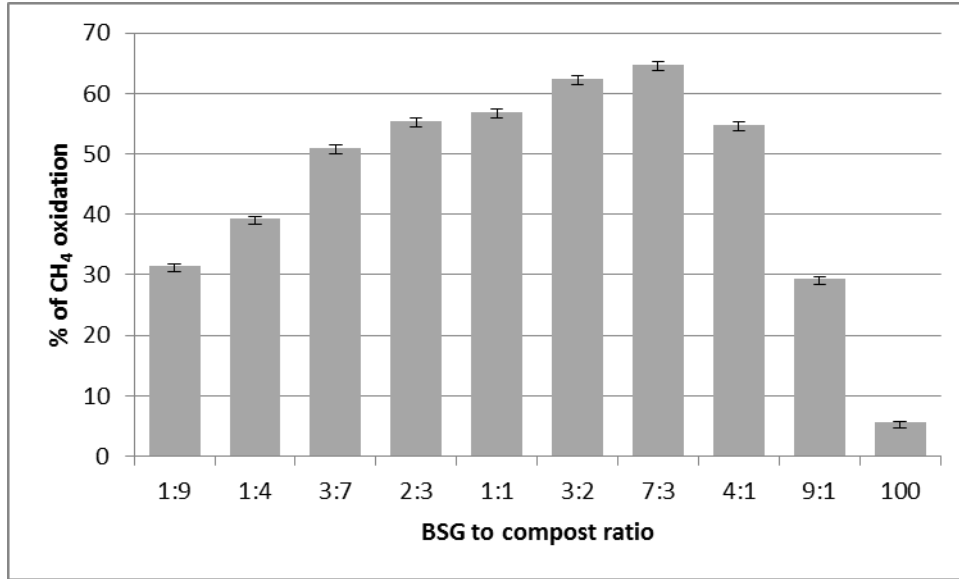


Figure 1: Percentage of CH₄ oxidation at different BSG to compost ratio.

Moisture content, pH and temperature response experiments

Figure 2 shows the influence of moisture content, pH and temperature on CH₄ oxidation by the 7:3 BSG to compost ratio. The shaded bar in each chart represents the control experiment. In Figure 2(a), the control showed the highest percentage of CH₄ oxidation (more than 60%) indicating that the suitable moisture content for optimum CH₄ oxidation for this ratio. At 80% moisture content, the percentage CH₄ of oxidation is the lowest (<10%). This suggested that very high moisture (>70%) does not sustain microbial population for CH₄ oxidation. Previous

studies have also shown that extreme conditions related to moisture content can limit O₂ diffusion [15] or cause physiological stress to the microbes [16],[17]. In landfill condition the biocovers tend to oxidize more CH₄ than the laboratory scale experiment. But high moisture content has a potent risk of producing CH₄ [18] due to the high methanogenesis activity.

In Figure 2(b) the optimum pH was evaluated. Very acidic pH has a low percentage (below 40%) of CH₄ oxidation while neutral to slightly alkaline pH gave higher CH₄ oxidation (40%). Studies by

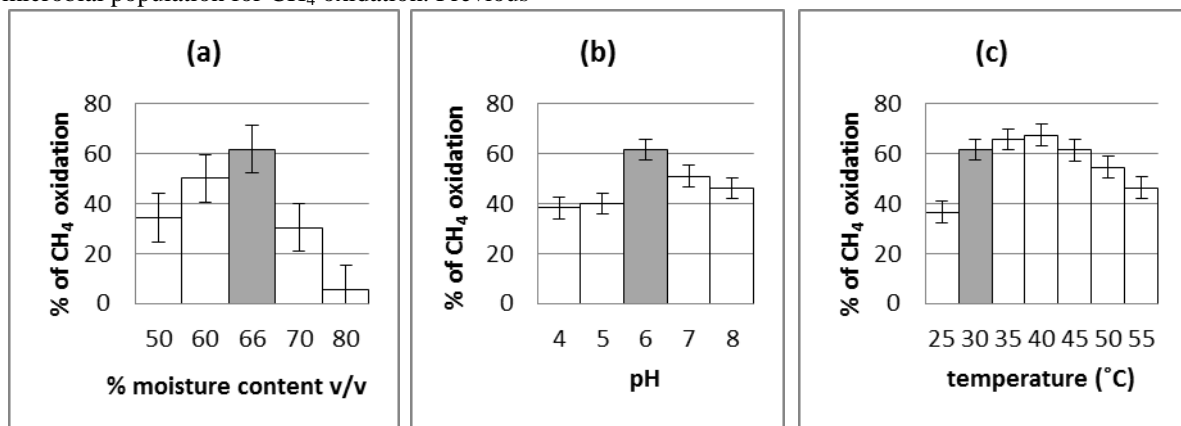


Figure 2: Influence of (a) moisture content, (b) pH and (c) temperature on CH₄ oxidation

previous researches show that optimal pH ranges from pH 6.6 to 8.1 [19] and again it depends on the methanotrophs present in the material used. Figure 2(c), shows that the optimum

temperature ranged from 30 to 45°C with more than 60% of CH₄ oxidation. Similar studies by Perez, [19] depict that CH₄ oxidation occurs at range of temperatures and certain temperatures

favour certain type of methanotrophs. In this study, the highest percentage of CH₄ oxidation was obtained at 40°C.

Column Experiment

The best BSG to compost ratio, optimum moisture content, pH and temperature from the batch incubation experiments were chosen for the column experiments. While the optimum moisture content and pH were of the original material used, only the temperature was adjusted to the optimum level of 40°C for the column experiments. Columns were put in incubators with 40°C throughout the study period. CH₄ and O₂ were introduced through the bottom valve of the columns to simulate the condition in landfills where methane is released below the biocover material [20].

Figure 3 presents the results from the column experiments on CH₄ oxidation efficiency at different biocover thickness level. The error bars indicates the standard deviations from the

experiments conducted. Day 0 represents the day CH₄ gas is introduced to the column. Initial analysis with GC shows that the CH₄ concentration is highest at 10cm and fluctuates at the other height levels. This could be because the CH₄ gas has not fully diffused throughout the column.

In Day 1, a more homogenous concentration of CH₄ is obtained after much diffusion of the gas within the column. Between Day 2 to Day 4 (histograms not shown here), CH₄ oxidation was observed at all level of height. On Day 5, as shown in **Figure 3**, CH₄ concentration at 50cm decreased to zero indicating 100% CH₄ oxidation. While on Day 6 (also histograms not shown here) 100% CH₄ oxidation was observed at all level of height. This concludes that within 5 days this biocover material (mixture of BSG and compost) is able to fully oxidize CH₄ at 50cm height.

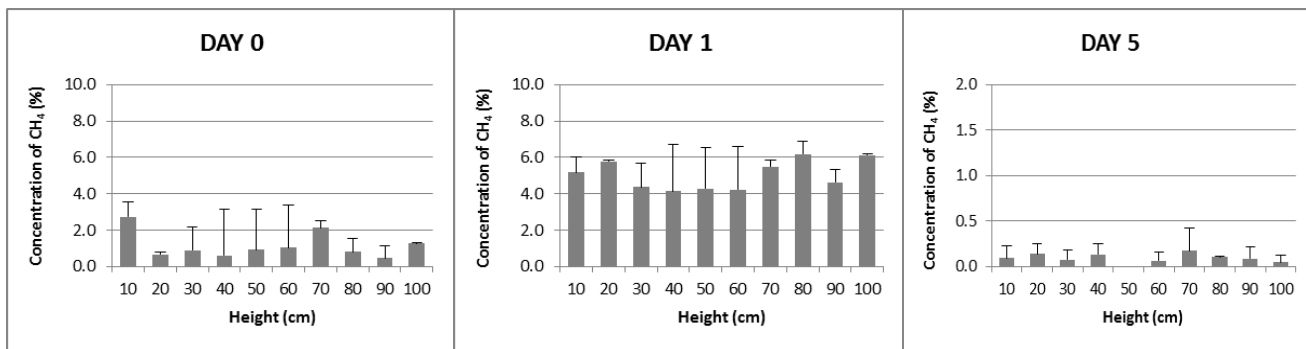


Figure 3: CH₄ concentration in percentage for Day 0, Day 1 and Day 5 of column experiment.

In batch incubation experiments the maximum CH₄ oxidation was about 64.48% in 14 days while in column experiments 100% CH₄ oxidation was achieved between 5 to 6 days. A reason suggested for this difference, is the amount of material used for the batch incubation experiment is insufficient (20g) compared to the total material in the column which is about 10kg to 13 kg. Therefore, the amount of material in batch incubation experiments has attained a saturation level in oxidizing CH₄.

CONCLUSION

The optimal ratio of BSG to compost as the biocover material is 7:3 with optimum parameters were moisture content of 66%, pH of 6 and temperature of 40°C. The column experiments showed complete 100% CH₄

oxidation on day 5 at 50cm height and day 6 for the others. The results also show that both batch incubation experiments and column experiments enhanced CH₄ oxidation. However, the batch incubation experiments does not show 100% CH₄ oxidation compared to that of column experiments.

ACKNOWLEDGEMENT

The authors thank all individuals directly or indirectly involved in this project for their academic and technical support. We thank the University of Malaya's RG143/11SUS and PPP (PV009/2012A) for providing the necessary funding for realizing the project. We also thank Carlsberg Brewery (M) Berhad for their contribution.

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