Waste Management 34 (2014) 2271–2277

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Differences in volatile methyl siloxane (VMS) profiles in biogas from landfills and anaerobic digesters and energetics of VMS transformations

Berrin Tansel *, Sharon C. Surita

Department of Civil and Environmental Engineering, Florida International University, College of Engineering and Computing, 10155 West Flagler Street, Miami, FL 33174, United States

ARTICLE INFO

Article history:
Received 16 February 2014
Accepted 26 July 2014
Available online 23 August 2014

Keywords:
Siloxanes
Biogas
Volatile methyl siloxanes
Anaerobic decomposition
Electron acceptor
Waste to energy

ABSTRACT

The objectives of this study were to compare the types and levels of volatile methyl siloxanes (VMS) present in biogas generated in the anaerobic digesters and landfills, evaluate the energetics of siloxane transformations under anaerobic conditions, compare the conditions in anaerobic digesters and municipal solid waste (MSW) landfills which result in differences in siloxane compositions. Biogas samples were collected at the South District Wastewater Treatment Plant and South Dade Landfill in Miami, Florida. In the digester gas, D4 and D5 comprised the bulk of total siloxanes (62% and 27%, respectively) whereas in the landfill gas, the bulk of siloxanes were trimethylsilanol (TMSOH) (58%) followed by D4 (17%). Presence of high levels of TMSOH in the landfill gas indicates that methane utilization may be a possible reaction mechanism for TMSOH formation. The free energy change for transformation of D5 and D4 to TMSOH either by hydrogen or methane utilization are thermodynamically favorable. Either hydrogen or methane should be present at relatively high concentrations for TMSOH formation which explains the high levels present in the landfill gas. The high bond energy and bond distance of the Si–O bond, in view of the atomic sizes of Si and O atoms, indicate that Si atoms can provide a barrier, making it difficult to break the Si–O bonds especially for molecules with specific geometric configurations such as D4 and D5 where oxygen atoms are positioned inside the frame formed by the large Si atoms which are surrounded by the methyl groups.

1. Introduction

Use of siloxanes in consumer products has been increasing due to their excellent water repelling (antimicrobial) characteristics. Siloxanes are used in a range of products (i.e., personal care products which include shampoos, creams, and make up, sunblock; exterior coatings for buildings, wood, textile, paper; electronics) which end up in the wastewater or landfills, eventually affecting the biogas quality. Use of silicon based coatings has been increasing due to their performance for corrosion prevention and mildew formation. In the recent years, volatile methyl siloxanes have been a concern for utilization of biogas for energy generation due to presence of siloxanes (Beech, 2004; Sevimoglu and Tansel, 2013a; Surita and Tansel, 2014a).

Siloxanes have a chemical structure of silicon and oxygen atoms, alternating in position with hydrocarbon groups attached to the silicon side chain. Siloxanes can be in linear configuration (designated as L), cyclic form (designated as D), or tetrahedral formation with organic groups. Some commonly found siloxanes in the environment (i.e., biogas, sludge, wastewater, air) include cyclosiloxanes are hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6). Cyclosiloxanes are typically formed during depolymerization or reversion reactions (Badjagbo et al., 2010; Rasi et al., 2010; Sevimoglu and Tansel, 2013b; Surita and Tansel, 2014a,b; Tansel and Surita, 2014).

At landfills and anaerobic digesters, initially there are high amounts of easily biodegradable substrates, therefore, suitable conditions exists for active decomposition with assimilatory pathways by taking nutrients into the cell for biosynthesis with high energy yields. However, as the availability of easily biodegradable materials decline, the rate limiting steps shift depending on the available microbial populations and their metabolic rates that can utilize alternative electron acceptors. At landfills and anaerobic digesters the metabolic pathways shift from assimilatory to dissimilatory mechanisms by bacteria that are able to utilize substrates other than oxygen as electrons acceptors for energy generation. Secondary electron acceptors such as nitrate, nitrite, ferric iron, sulfate, carbon dioxide can provide the necessary elec-

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* Corresponding author. Tel.: +1 (305) 348 2928.
E-mail address: tanselb@fiu.edu (B. Tansel).

http://dx.doi.org/10.1016/j.wasman.2014.07.025
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tron transfer mechanisms some of which can be accomplished through relatively slow biotransformation processes (Thauer et al., 1977; Reineke, 2001; Valentine, 2002).

Volatile methyl siloxanes (VMS) have been detected in both landfill gas and biogas from anaerobic digesters at wastewater treatment plants (Surita and Tansel, 2014b). This indicates that siloxane based compounds are utilized under anaerobic conditions as electron acceptors along with the organic matter (Caldwell et al., 2008; Moran et al., 2008). However, there are significant differences between the types and levels of siloxanes present in the biogas from landfills and anaerobic digesters. Objectives of this study were to compare the VMS profiles and levels in the biogas from the anaerobic digesters and landfills, evaluate the energetics of anaerobic siloxane transformations, and analyze the differences in anaerobic conditions present in digesters and municipal solid waste (MSW) landfills which result in differences in siloxane profiles in the biogas.

2. Methodology

2.1. Biogas sampling

Biogas sampling was conducted at the South District Wastewater Treatment Plant (SDWWTP) and South Dade Landfill (SDLF). Four biogas samples were collected (2 from the landfill and 2 from the anaerobic digester. The SDWWTP uses grit removal, biological treatment, neutralization and disinfection (both chemical and physical) processes with the sludge being sent to the anaerobic digesters for stabilization. The SDLF is a 300-acre Class I landfill that accepts a variety of waste including household waste, shredded tires, animal carcasses, construction and demolition debris, asbestos (with authorization from the Department of Regulatory and Economic Resources), and yard waste.

The gas sample at the SDLF was collected from the manifold prior to flare. Biogas from the anaerobic digester at the SDWWTP was collected just before the anaerobic digester gas enters the scrubber. For sampling, sorbent tubes were used at a flow rate of 0.2 l per minute. Sample time was 30 min to obtain a total gas volume of 6 l. The siloxane analyses were performed by utilizing thermal desorption for extraction and gas chromatography–mass spectrometry (GC–MS) to identify and quantify siloxane compounds in the gas samples.

Siloxane compounds analyzed included trimethylsilanol (TMSOH), hexamethyldisiloxane (L2), hexamethylcyclotrisiloxane (D3), octamethyltrisiloxane (L3), octamethylcyclotetrasiloxane (D4), decamethyltetrasiloxane (L4), decamethylcyclopentasiloxane (D5), dodecamethylpentasiloxane (L5) and dodecamethylsiloxane (D6). Of these, all of the compounds were found within the anaerobic digester with the exception of L2, L4 and L5, which are all linear compounds. In the SDLF, all of the compounds were encountered with the exception of L4 and L5.

2.2. Free energy estimations

The Gibb's free energy is defined as the driving force for a system to reach a chemical equilibrium. The energy comes from the enthalpy and entropy of reaction in the system, and ΔG can be defines as follows:

$$\Delta G = \Delta H - T\Delta S \tag{1}$$

where ΔG is the free energy, ΔH is the change in enthalpy, T is the temperature, and ΔS is the change in entropy of the system. If temperature is constant and ΔS is small, then:

$$\Delta G = \Delta H \tag{2}$$

The change in free energy can be estimated by the following equation:

$$\Delta G = \sum G_p - \sum G_r \tag{3}$$

where G_p is the free energy of products and G_r is the free energy of reactants. If ΔG is negative, the forward reaction or process will occur spontaneously. If ΔG is positive, the reverse reaction will occur spontaneously. If ΔG is zero, the reaction is at equilibrium.

Bond enthalpy is the energy required to break a chemical bond. It is usually expressed in units of kJ mol^{-1}, measured at 298 K. The exact bond enthalpy of a particular chemical bond depends upon the molecular environment in which the bond exists. The enthalpy change during a reaction can be estimated by the following equation:

$$\Delta H = \sum \Delta H(\text{bonds broken}) - \sum \Delta H(\text{bonds formed}) \tag{4}$$

The free energies of the siloxanes were estimated from the bond energies provided by Wilbraham et al. (2008). Similarly, the free energy changes for the examples siloxane transformation reactions were estimated from the bond energies of the products and reactants using Eq. (3).

It should be noted that ΔG depends on temperature, pressure, and the initial concentrations of reactants and products. Most biological reactions taking place in aqueous conditions are also affected by the pH of solution. When the concentrations of reactants and products are variable, ΔG can be estimated by the following equation:

$$\Delta G = \Delta G^{\circ} + RT\ \ln(C_p/C_r) \tag{5}$$

where ΔG° is the value of the change in free energy under the standard conditions (i.e., 298 K, 1 atm pressure, pH 7.0 if in water, and initial concentrations of 1 M for all reactants and products except protons, which are kept at pH 7.0), R is the universal gas constant, T is temperature, and C_p and C_r are the initial concentrations of the products and reactants. When the concentration of the reactants is significantly higher than the products (i.e., $C_p/C_r < 1$), ln (C_p/C_r) is negative (hence, ΔG is likely to be negative if ΔG° small or negative). However, as the concentration of products increase, the reaction approaches chemical equilibrium (i.e., ΔG approaches zero).

3. Results and discussion

3.1. Siloxane levels in biogas from landfills and anaerobic digesters

Table 1 presents the VMSs detected and concentrations present in the digester and landfill gas. The siloxanes detected in the biogas from the anaerobic digester included D4, D5, D3, L3, TMSOH, and D6; while the siloxanes in the biogas from the MSW landfill included TMSOH, D4, D5, L2, D3, L3, and D6 in the order of decreasing concentration. In the digester gas, D4 and D5 comprised the majority of the total siloxanes (62% and 28%, respectively) whereas in the landfill gas TMSOH (58%) followed by D4 (17%) were present at the highest concentrations.

D4 was the most prevalent cyclic siloxane in the biogas from both the MSW landfill and anaerobic digester. D5 is the second most prevalent cyclic siloxane in biogas from both the MSW landfill and anaerobic digester. In the landfill gas, significantly high levels of TMSOH were present, while in the biogas samples from the anaerobic digester TMSOH levels were very low (7250 $\mu g/m^3$ in landfill gas vs 75 $\mu g/m^3$ in digester gas). High levels of TMSOH in the landfill indicates that the anaerobic reactions for siloxanes may follow different mechanisms. High levels of TMSOH in the landfill gas indicate anaerobic conditions with higher reduction potential which may be due to higher levels of H^+ or H_2 or higher