INTRODUCTION

All biogas, whether from a landfill or an anaerobic digester, contains a class of trace organic compounds referred to as siloxanes. These siloxanes are generally grouped as volatile methylsiloxanes (VMSs) and linear poly dimethylsiloxanes (PDMs). The sources of the siloxanes in biogases are numerous, and increasing. For example, in the search for improved environmental cleaners, volatile methylsiloxane solvents have value because they are aroma-free, widely available from natural sources and are exempt from current VOC regulations. Other uses of siloxanes include: carrying agents in skin cream and stick deodorants, as well as shampoos, cosmetics, detergents, ink, lubricants, and adhesives. A solid antiperspirant may contain as much as 50% siloxanes (by weight).

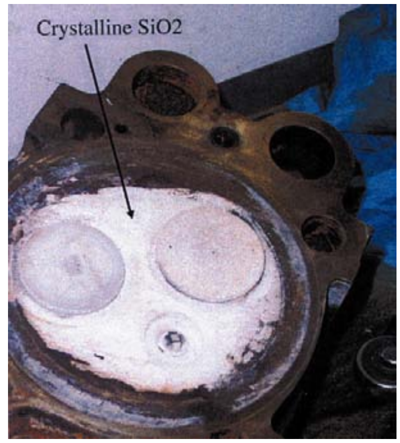
As a consequence of their widespread and growing use, siloxanes are becoming increasingly prevalent in landfills and wastewater. In wastewater, hydrophobic siloxanes accumulate in the sewage sludge and under anaerobic digestion transfer to the biogas. Similarly, siloxanes in the anaerobic environment of a landfill, also transfer to the biogas.

Siloxane Behavior

Siloxanes have high vapor pressures and high Henry's Law constants, resulting in low water solubility's (See Table 1). As a result, siloxanes have an affinity for the vapor phase, and are easily transported in biogas.

Siloxane Compound	Abbreviation	Molecular Weight (g/mol)	Boiling Point (°F)	Melting Point (°F)	Vapor Pressure (kPa)
Hexamethylcyclotrisiloxane $C_{12}H_{18}O_3Si_3$	D3	222.46	273	147	1.14 @ 25 °C 1.83 @ 25 °C
Octamethylcyclotetrasiloxane $C_8H_{24}O_4Si_4$	D4	296.61	347	63	0.13 @ 25 °C
Decamethylcyclopentasiloxane $C_{10}H_3O_5Si_5$	D5	370.77	410	-47	0.05 @ 25 °C 0.02 @ 25 °C
Dodecamethylcyclohexasiloxane $C_{10}H_{36}O_6Si_6$	D6	445.00	473	26.6	0.003 @ 25 °C
Hexamethyldisiloxane $C_6H_{18}Si_2O$	L2	162.4	212	-88.6	4.12 @ 25 °C
Octmethyltrisiloxane $C_8H_{24}Si_3O_2$	L3	236.5	307	-115.6	0.52 @ 25 °C
Decamethyltetrasiloxane $C_{10}H_{30}Si_4O_3$	L4	310.7	381	-90.4	0.073 @ 25 °C
Dodecamethylpentasiloxane $C_{12}H_{36}Si_5O_4$	L5	384.8	446	-113.8	0.009 @ 25 °C

The major siloxane issue facing biogas users is the fact that the high molecular weight volatile compounds convert to silicon oxides during combustion and form amorphous silica ash. These silicon oxides deposit firmly on cylinder heads, valves, and pistons of engines. The hard silicon residues abrade and rapidly wear gas engine surfaces. Because



silicone oxide also acts as a thermal insulator, it contributes to the overheating of the engine parts. Typically, for internal combustion engines, the slip liners become abraded and the piston crowns become worn. Problems include up to 75% reduction in engine head life, valve plugging, and spark plug fouling. Furthermore, siloxanes also have a deleterious effect on engine emissions control devices such as SCRs and catalytic oxidation (which are now required in some states such as California).

Impact on Warrantees

We are seeing a growing trend: Manufacturers of engines and turbines are qualifying their warrantees with stringent limits on siloxanes in the fuel supply. Whereas limits were between 5 to 35 mg/m^3, now, we are seeing limits stipulated under 5 mg/m^3. Additionally, some manufacturers have been decreasing the limits for silicon in the engine oil (i.e., 1 mg/L in the oil).

Siloxane Removal

The good news is that siloxanes can be removed from biogas; doing so cost effectively is the challenge. Venture has developed a siloxanes removal system for biogas. Depending on the specification, biogas matrix and budget, either a single stage or a two stage system configuration can be used. For optimum removal efficiency (<100 ppbv), Venture incorporates selective adsorption using a variety of media, followed by activated carbon adsorption. Selective adsorption upstream of carbon does several things: 1) it economically removes moisture from the raw landfill gas that competes for activated carbon surface area, 2) it removes a significant portion of the siloxanes (99%+ removals of total siloxanes, or <1mg/m^3)), and 3) it reduces the size of the activated carbon system.

Siloxane Measurement & Control

Most adsorption processes are regenerated on-site with heat, including Venture's siloxane removal system. Currently, the regeneration sequences are time-based (controlled by PLC) and are initially set based on empirically derived siloxane breakthrough curves that are generated during the testing and study phase (or predicted using our ChemCAD process model). These regeneration time sequences are often set conservatively (hours before anticipated breakthrough of the siloxanes) in order to assure protection of the downstream unit operations.

The most widely used method for siloxane analysis of biogas is done via grab samples and off-site analysis using gas chromatography / mass spectrometry (GC/MS). A major drawback of the laboratory analyses is the time consuming and laborious procedure.

That is all about to change. For the past 6 months, Venture has been working on the development of an on-line, real-time siloxane monitoring device. This new device (based on GC and GC/MS) will be able to be used for determining siloxane levels in treated biogas with digital output to a plant PLC. In this manner, the siloxane monitoring system will also function as a process controller. By providing instantaneous and continuous siloxane measurements at the adsorber outlet and sending those results to a PLC, the sequence of regeneration (and even its duration) can be controlled based on concentration rather than time. This will save considerable energy costs. It will also be used as a predictive maintenance tool for media replacements.

Field testing and verification of the new monitoring system is on-going. Full commercial availability and use is expected in July 2009. To learn more about these exciting developments, please contact Mr. Dave Moniot at 412-231-5890, ext. 301. Or, visit Venture's Web site at http://www.ventureengr.com/blog and read the post titled: Siloxane Removal System – Venture Engineering Announces New Offering to Landfill and Digester Gas Customers.

Regenerative Selective Adsorption System - Siloxanes