



Preliminary investigation to characterize deposits forming during combustion of biogas from anaerobic digesters and landfills



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ABSTRACT

The objectives of this study were to compare composition and morphological characteristics of the deposits forming in engines operated with biogas from anaerobic digesters and from landfills. Engine deposit samples were collected from biogas to energy facilities in Florida, USA. The deposit samples were analyzed by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Similarities and differences between the deposit samples collected from the engines operated with biogas from anaerobic digesters and biogas from landfills were analyzed in terms of chemical composition and morphology. The sample obtained from the anaerobic digester gas did not contain potassium while calcium and zinc were present at a higher ratio. Relatively high levels of carbon were present in the crystalline deposits forming during the combustion of biogas. C:O:Si ratios were about 5:7:1 in the deposits obtained from the engines operated with biogas from the anaerobic digesters and 2:3.5:1 in the deposits from the engines operated with landfill gas. In general, the silicon content from deposits found in facilities utilizing biogas from anaerobic digesters was lower than those operated with landfills gas. The difference was made up with higher phosphorus, sulfur and calcium content in the deposits from the engines operated with digester gas.

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1. Introduction

The increasing demand for energy and dependency on fossil fuels has created opportunities for renewable energy sources. Regions with high potential for bioenergy production (i.e., from waste materials) have implemented programs and facilities to utilize the bioenergy [4]. It has been estimated that by the year 2050, half of the world energy demand in developing countries will stem from improved biomass energy [7]. The United States accounts for the consumption of approximately 19 percent of the world's energy but only accounts for a population of 4.5 percent of the world. Approximately 84 percent of the energy supply comes from fossil fuels [3]. According to the International Energy Agency (IEA), biogas provides an estimated the gross electricity generation of 9281 GWh and heat production of 999 TJ [15]. Additionally gross electricity generation from municipal waste and industrial wastes was estimated at 16,900 and 5500 GWh. Gross heat production for these facilities was estimated at 11,700 and 3800 TJ, respectively.

Biogas is generated from landfills and wastewater treatment plants (WWTPs) during the step-wise degradation process when microorganisms decompose the organic material under anaerobic conditions [7]. The gas produced is typically used as fuel for energy production, pumps and boilers [34]. Although utilization of biogas is more costly than energy derived from fossil fuels, the reuse of biogas eliminates much of the greenhouse gas emissions from landfills and can be further upgraded for pipeline use. The potential energy of biomass from waste in the United States has been estimated to be 1.5 EJ/yr for the municipal solid waste industry, 0.8 EJ/yr for sewage sludge bio-solids, and 0.4 EJ/yr for industrial waste biodegradation [6]. In 2005, Demirbas et al. [8] reported the top five of ten bio-electricity producers to be USA (30.7%), Germany (7.33%), Brazil (7.31%), Japan (5.13%) and Finland (4.85%). The composition of biogas is variable, but ranges between 40 and 60 percent methane, 40 to 55 percent carbon dioxide and the remainder consists of trace compounds such as nitrogen, oxygen, halogenated compounds, hydrogen sulphide and siloxanes.

Siloxanes in the wastewater stream originate from discarded consumer products (i.e. cosmetics, cleaning products, deodorants, and hair/skin care products, landfill leachate). Landfill origins can be traced to a multitude of consumer products including paper,

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construction debris, treated woods, and wastewater treatment sludge. With the increase of siloxanes found in consumer products, concentrations of siloxane compounds are intensifying in the waste stream. It was projected that the world demand for silicone has increased by 6.3 percent per year [27,35]. Siloxanes typically sorb onto solids due to their low solubilities or volatilize due to their inherent vapor pressures. Table 1 provides mean siloxane concentrations found at different locations. Fig. 1 provides the levels of the volatile methyl siloxanes in biogas from landfills and wastewater facilities which take only municipal discharges.

The comparison of the types and levels of siloxanes in biogas shows that volatile methyl siloxanes (VMS) presents in landfill gas are primarily TMSOH, D4 and D5 as well as small concentrations of L2 and L3. The VMS in biogas from anaerobic digesters are mainly D5, D4 and D3. It is interesting to note that the landfill conditions promote formation of TMSOH and D4 is present at higher concentrations than D5. On the other hand, in the biogas forming in anaerobic digesters, D5 levels are significantly higher than those for D4. Lack of significant levels of linear siloxanes (L2–L4) and TMSOH in the biogas from anaerobic digesters in comparison to those in the biogas from landfills indicate that the reduction potential in the anaerobic digesters are significantly lower in comparison to those present in the landfills or formation of TMSOH, L2 and L3 occur through slow reduction processes. Siloxanes are released from the solid phase (biomass) during anaerobic decomposition processes which result in release of the bound siloxanes through volatilizing when temperatures reach 60 °C [21]. When biogas is combusted, the siloxanes are oxidized leaving white deposits on heated metal surfaces. Siloxane combustion yields silicon dioxide (SiO₂) or silicates, which is visible on engine

components, pistons, cylinder heads, turbine blades, and spark plugs among others [24,37]. Deposits formed, contain mostly SiO₂ or silicates; however may contain calcium, zinc, phosphorus, sulfur and other trace elements.

Deposits on spark plugs often cause premature engine failure, excessive fouling of heated surfaces, misfiring and noise. Pistons with excessive deposit accumulation may limit the expansion of piston rings thereby leading to higher oil consumption. When siloxane present in gas phase are burned, they form nanoparticles which accumulate when proper maintenance technologies and procedures are not employed [25,29,31]. Additional compounds present in engine deposits include metals in solid form ([9,20,14]) (i.e., calcium, copper, sodium, sulfur and zinc) [25,36].

At energy facilities operated with biogas, the presence of VMSs reduce the engine performance and increase maintenance activities. Operation and maintenance costs can become increasingly high due to silicate deposition [1]. No state, federal or regional mandates have been implemented for siloxane quantification and control; however several methodologies for sampling and analytical procedures have been developed [2,17,23,28]. Consequently, manufacturers have adapted equipment warranties for inclusion of deficiency due to these deposits.

Objectives of this study were to compare the composition of deposits forming in engines operated with biogas from anaerobic digesters and biogas from landfills. In the literature review conducted by the authors, no additional studies have aimed to specifically characterize siloxane deposits. Engine deposit samples were collected from the facilities in Florida, USA. The morphological characteristics and elemental composition of the deposit samples were analyzed by scanning electron microscopy (SEM) which was

Table 1
Siloxane concentrations (mg/m³) in landfill gas and biogas at different locations.

Facility	Concentration of Si containing compounds (mg/m ³)									
	TMSOH	L2	L3	L4	L5	D3	D4	D5	D6	
LF-1 ^a	–	6.07	0.32	–	NR	0.49	12.53	4.73	NR	
LF-2 ^b	6.08	1.65	0.03	0.04	–	0.42	7.70	1.26	–	
LF-3 ^c	0.30	0.33	0.01	–	–	0.10	0.67	0.30	–	
LF-4 ^d	–	0.34	–	–	–	0.58	2.80	1.26	–	
LF-5 ^{e,o}	35.7	–	–	–	NR	2.80	29.1	11.80	1.50	
LF-6 ^f	10.10	0.10	–	–	NR	0.10	3.60	6.40	0.40	
LF-7 ^g	6.70	0.10	–	–	NR	0.50	11.80	6.00	0.50	
LF-8 ^h	12.70	1.50	–	–	NR	0.40	5.00	0.90	–	
LF-9 ^j	7.25	0.72	0.10	–	NR	0.52	2.16	–	0.09	
Averageⁿ	7.19	1.35	0.12	0.04	0.00	0.39	5.78	2.98	0.33	
WW-1 ^a	–	0.02	0.02	–	–	0.04	0.93	6.03	–	
WW-2 ^b	0.11	0.05	0.03	0.10	–	0.25	6.12	9.05	–	
WW-3 ^c	0.04	0.01	0.20	0.04	–	0.04	0.45	0.69	–	
WW-4 ⁱ	–	–	–	–	NR	1.60	0.50	5.30	0.10	
WW-5 ^{k,o}	–	3.40	–	0.70	NR	–	8.10	340.7	8.70	
WW-6 ^l	–	–	–	–	NR	2.80	0.90	11.90	0.20	
WW-7 ^{m,o}	–	–	–	–	NR	0.10	1.00	48.40	2.50	
WW-9 ^j	0.08	0.05	0.05	0.29	1.80	0.26	0.05	4.15	0.09	
Averageⁿ	0.08	0.03	0.08	0.14	0.05	0.83	1.49	6.19	0.13	

^a Asten, Austria [39].

^b Germany [39].

^c Finland [39].

^d Canada [39].

^e Poland [32].

^f Poland – Woj. Podlaskie [32].

^g Germany-Baden-Wuerttemberg [32].

^h Germany-Sachsen-Anhalt [32].

^j Germany-Niedersachsen [32].

ⁱ Miami (this study).

^k Germany-Hessen [32].

^l Germany-Hessen [32].

^m Poland-Woj. Pomorskie [32].

ⁿ Facilities which accept only municipal was.

^o Not included in the average.

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