Research progress of siloxane removal from biogas

Gao Ruiling, Cheng Shikun, Li Zifu*

(*School of Energy and Environmental Engineering, Beijing Key Laboratory of Resource-oriented Treatment of Industrial Pollutants,*
University of Science and Technology Beijing, Beijing 100083, China)

Abstract: Siloxanes in biogas are detrimental to engine, turbine, fuel cell, etc., thus it is necessary to remove siloxanes from biogas before biogas high-value utilization. At present, there are few domestic researches and related reports in view of siloxanes removal from biogas. This paper introduces the property of siloxanes as well as sampling and analysis method, and then presents the research progress of siloxanes removal from biogas. Three commercial technologies overseas are adsorption, absorption and cryogenic condensation. Among them, adsorption on activated carbon is the most widely used method. Other technologies, such as biological removal, catalytic processes, membranes, source controlling, etc. are under exploration and development. At last, this paper summarizes the advantages and disadvantages of siloxanes removal technologies as well as the applicability and analyzes the future research trend and emphasis. This paper could provide a reference in the field of biogas high-value utilization.

Keywords: biogas, purification, siloxane removal, activated carbon adsorption, physical and chemical absorption, biological removal

DOI: 10.3965/j.ijabe.20171001.3043

Citation: Gao R L, Cheng S K, Li Z F. Research progress of siloxane removal from biogas. Int J Agric & Biol Eng, 2017; 10(1): 30–39.

1 Introduction

As global energy and environmental issues have become increasingly prominent in recent years, biogas technology, a waste treatment which can also recover energy, has attracted worldwide attention. The International Energy Agency (IEA) will promote biogas technology in their development goals (IEA Bioenergy Task 37). Biogas technology has been fully recognized by the international community as an effective way to ease the international energy crisis and optimize the international energy supply structure.

The main components of biogas are CH_4 (50%-70%) and CO_2 (30%-40%)[1]; however, biogas also typically contains a few impurity gases, including water vapor, nitrogen, oxygen, hydrogen sulfide, mercaptan, siloxanes, and other hydrocarbons. Among these compounds, siloxanes have the strongest adverse effect on the utilization of biogas[2,3]. When biogas is used as fuel for electricity generation, the combustion of siloxanes contained in biogas will produce microcrystalline silica that have similar chemical and physical properties as glass and causes serious damage to generators, turbines, and fuel cells[4]. European and American practices revealed that the removal of siloxanes prior to the engine was a consensus in the sector, and studies in developing countries should be enhanced. Therefore, the removal of siloxanes in biogas technology and the research progress were summarized in this study.

2 Characteristics of siloxanes

The term siloxane refers to a subgroup of silicones containing Si–O bonds with an organic radical bound to Si and including methyl, ethy and other functional

---

Received date: 2016-09-15 **Accepted date:** 2016-12-07

Biographies: Gao Ruiling, PhD candidate, research interests: biogas technology, biomass energy, Email: gaoruiling1988@126.com; **Cheng Shikun,** PhD, lecturer, research interests: biogas technology, biomass energy, Email:chengshikun@ustb.edu.cn.

***Corresponding author: Li Zifu,** PhD, Professor, research interests: urban and domestic waste management. Mailing address: School of Energy and Environmental Engineering, University of Science and Technology Beijing, No. 30, Xueyuan Road, Haidian Distrct, Beijing 100083, China. Tel/Fax: +86-10-62334378; Email: zifuli@ustb.edu.cn.

organic groups. Siloxanes are widely used in various industrial processes because of their useful properties, including low flammability, low surface tension, water-repelling properties, high compressibility, high thermal stability, and the limited effect of temperature on these useful properties[5]. Siloxane is a volatile or semi-volatile compound containing methyl; it is also known as volatile methylsiloxane (VMS). The main compositions of siloxanes in biogas are shown in Table 1. Letters L and D refer to the linear and cyclic organic Si compounds, respectively, and the subsequent number refers to the number of Si atoms in the compounds.

Table 1 Names and physical properties of typical siloxane compounds in biogas

CAS No.	Full name and abbreviation	Formula	Boiling point/°C	Saturated vapor pressure at 25°C/Pa	Water solubility at 25°C/mg·L^{-1}
107-46-0	Hexamethyldisiloxane (L2)	$C_6H_{18}OSi_2$	106.9	5626.2	0.93
107-51-7	Octamethyltrisiloxane (L3)	$C_8H_{24}O_2Si_3$	153.0	445.0	0.034
141-62-8	Decamethyltetrasiloxane (L4)	$C_{10}H_{30}O_3Si_4$	194.0	50.0	0.00674
141-63-9	Dodecamethylpentasiloxane (L5)	$C_{12}H_{36}O_5Si_5$	232.0	9.0	0.000309
541-05-9	Hexamethylcyclopentasiloxane (D3)	$C_6H_{18}O_3Si_3$	135.2	471.0	1.56
556-67-2	Octamethylcyclotetrasiloxane (D4)	$C_8H_{24}O_4Si_4$	175.7	132.0	0.056
541-02-6	Decamethylcyclopentasiloxane (D5)	$C_{10}H_{30}O_5Si_5$	211.2	23.2	0.017
540-97-6	Dodecamethylcyclohexasiloxane (D6)	$C_{12}H_{36}O_6Si_6$	245.1	4.0	0.005

The raw materials of biogas fermentation are extensive, including livestock manure, crop residues, sewage sludge, and other organic waste. Landfill gas also belongs to the category. Siloxane content in biogas varies according to different feedstock. Usually, the siloxane content of biogas that originates from landfills (landfill biogas) or anaerobic sludge digestion in a sewage treatment plant (sewage-sludge biogas) is twice to three times higher than that of agricultural biogas[6-8]. Siloxane concentration in landfill and sewage-sludge biogas usually exceeds 50 mg/m^3, higher than the common required concentration limit (15 mg/m^3) of engine manufacturers[8-10], not to mention more stringent standards required by some European countries (Table 2). The main components of siloxanes in a landfill biogas are L2, L3, D4, and D5, according to the rank of content D4>L2>D5>L3, and the content of D4 accounts for approximately 60% of the total siloxanes. In sewage-sludge biogas, the contents of D4 and D5 are significantly higher than other siloxanes; they do not contain L2 and L3 because L2 and L3 are more likely to dissolve in water compared with D4 and D5[2,11,12]. Bletsou et al.[13] analyzed the siloxane migration process of a sewage treatment plant in Greece, the results showed that siloxane remained in sludge accounted for 68% of the total siloxane in initial wastewater, the rest of the siloxane mainly dissolved in the water and was discharged along with the treated water.

Table 2 Requirement of German thermoelectric unit on biogas composition

Parameter	Requirement
The CH_4 content/%	48-75
The sum of chlorine and fluorine/mg·m^{-3} CH_4	≤20
Hydrogen sulfide/mg·m^{-3}	≤250
Silicon/mg·m^{-3}	≤6
Other trace compounds/mg·m^{-3}	≤1
Maximum humidity/%	≤85
Maximum temperature/°C	≤30

3 Effect of siloxanes on biogas power equipment

European countries started the investigation and research of siloxanes early and have already formed a complete system of technology and application. The relevant industry or enterprise standards are formulated in their respective biogas power equipment industries (Table 2) to guarantee the biogas quality and extend equipment life[14].

This standard showed a stricter requirement for silicon content than hydrogen sulfide because the harm caused by silicon is fatal to the engine. Silicon exists in the form of siloxanes in biogas. In the process of combustion, silicon transforms into SO_2, which is referred to as quartz. The reaction process was shown in Equation (1):

$$((CH_3)_2SiO)_3 + 12\ O_2 \rightarrow 3\ SiO_2 + 6\ CO_2 + 9\ H_2O \quad (1)$$

This quartz can form a layer of covering film within a few hours, wear down the cylinder surface, and cover the spark plugs, valves and the turbo compressor. Moreover, this heat insulation layer and insulating layer can cause interference with various sensors[10]. This covering layer can lead to the cost of engine maintenance increasing by 5 to 10 times, and the maintenance intervals shortened from 40 000 h to 20 000 h.

The use of micro-turbines is common in European countries. The small exhaust quantity of the microturbine is an advantage, making it suitable for low-calorific-value gases such as CH_4. The microturbine is a solid device and can endure mechanical shock, but it is susceptible to siloxane damage[15]. The capability of microturbines to run normally for up to 30 years, without the interference of siloxanes, has been reported. In recent years, the siloxane content in biogas has increased. Resultantly, the frequency of equipment failure increased remarkably[2]. To deal with this condition, the microturbine company had modified the biogas quality standard. The maximum allowable siloxane concentration is 0.1 mg/m^3 in the actual execution. Presently, three companies, namely, Solar Turbines, Ingersoll Rand (IR) Microturbines and Capstone, require the siloxane concentration limit in biogas to be 0.10 mg/m^3, 0.06 mg/m^3 and 0.03 mg/m^3, respectively[14].

4 Sampling and analysis methods for siloxanes

4.1 Sampling methods

Precise scientific sampling methods are the basis of the follow-up test to ensure the accuracy of this study, because siloxanes are mostly volatile or semi-volatile compounds. Currently, no consensus has been reached for siloxane sampling methods. The simplest sampling method is the container direct sampling. The drawback of this approach is that volatile siloxanes easily condense on the walls. Other common methods include the use of activated carbon, silica gel or ion exchange resin for adsorption, followed by the use of organic solvents (carbon disulfide, benzene methanol, dichloromethane and hexyl hydride) for desorption[2].

Ajhar et al.[16] presented a sampling method using a PVF bag (brand name: Tedlar®). Two different types of Tedlar® bags are tested: one with a polypropylene valve control and the other with a stainless-steel valve control. Results showed that the PP valve bags perform better in the preservation of siloxanes, and siloxane content remained stable for 30 d.

4.2 Analysis methods

The importance of measuring siloxanes has increased with the growth of the biogas-to-energy market. Analysis of trace compounds is required to determine the need for a cleaning process prior to the combustion of biogas. The choice of a cost-efficient siloxane removal technology for engines, turbines and fuel cells relies on an accurate picture of the gas matrix to be treated. Presently, no standard method for the analysis of volatile siloxanes in a gaseous matrix exists[17-19]. Although several different analytical methods are available, accurate analysis remains challenging. The group of organosilicons contains many physically different compounds. The concentrations of individual compounds are often small. In addition, D3 and trimethylsilanol are chemically unstable compounds[20].

The most widely used method in the analysis of biogas trace compounds is the enrichment of solid sorbents or the absorption of gas sample in an organic liquid and the consequent analysis with GC-MS, GC-FID or GC-FPD. The total concentration of siloxanes absorbed into an organic solvent can be determined by atomic absorption spectrometry (AAS). The determination of total siloxanes is also performed by means of an atomic emission detector (GC/AED)[21]. An individual siloxane compound is usually identified with a GC/PID, a GC-MS, or AED. Methanol is often used as a solvent. Exact quantification is not possible because siloxane standards are not readily available in laboratories. Semi-quantification is then performed using the response factor of the detector to toluene. A risk exists that the result may be an underestimation of the true concentration of a compound, depending on the individual response of the detector to the compound in question. A major drawback of the laboratory analysis mentioned above is the time-consuming and laborious procedure, and the risk of sample losses owing to incomplete adsorption or absorption[22].

5 Technologies for removal of siloxanes from biogas

The removal of siloxanes in biogas is often combined with other impurity cleansing processes. In most biogas purification engineering processes, special measures for siloxane elimination are absent because siloxane can be reduced below the danger level simultaneously in the other process units (such as decarburization and desulfurization). However, with the biogas quality standards becoming stricter during its upgrading utilization, some companies specifically developed special technologies for the removal of siloxanes. Three kinds of technology, namely, adsorption, absorption and cryogenic condensation, presently have commercial applications[23]. Other techniques are also constantly being explored.

5.1 Adsorption

The most widely used adsorbent that reduces siloxane concentrations is activated carbon. The siloxane concentration has been reported to be reduced below 0.1 mg/m^3 in non-continuous operation[23,24]. In common units, activated carbon is used to reduce the siloxane content. However, the activated carbon is not regenerated in most cases because siloxanes are difficult to desorb from the material. Thus, these adsorbent beds should be replaced regularly, which increases the operation cost. In practical engineering, cheaper materials are sometimes also used, such as cocoa shell or bituminous coal[23]. Two beds are used in parallel to enable gas purification without interruption. During operation, one bed is adsorbing, while the parallel bed is being replaced or regenerated[10].

Several authors have shown that the use of different activated carbons (e.g., of varying source, BET surface, impregnation and microporous) strongly affects the siloxane adsorption capacity[25-29]. Other influencing factors are the siloxane species (e.g., the absorption rate of L2 is faster than that of D5), temperature, and relative humidity[30]. The activated carbon adsorption capacity of siloxanes is inversely proportional to the relative humidity of the biogas because active sites of the adsorbent will retain water vapor and other pollutants. Thus, adsorption on activated carbon is often combined with a pre-drying step[19]. A competitive adsorption of siloxanes and a variety of trace compounds must be considered because the biogas contains a broad range of compounds (H_2S, siloxanes, organics) with concentrations covering several orders of magnitude. The presence of relatively non-volatile, sulfur-containing, or halogenated compounds, for example, can significantly reduce the adsorption capacity toward siloxanes[31]. Activated carbon treatment systems reported by industry sources (e.g., Trecatti) can be costly because the spent carbon cannot be regenerated well, thus incurring high disposal costs[19]. Volatile organic compounds and H_2S concentration are high, especially for landfill biogas, and adsorbent will become saturated soon, which leads to a poor economic feasibility[32].

Other adsorbents used for the removal of gaseous siloxanes include molecular sieves and polymer beads[19]. Schweigkofler et al.[10] made a comparative study of adsorption materials using polymer beads, silica gel and activated carbon. In their tests, all the adsorbents exhibited large adsorption capacities for the siloxane D5. Silica gel seemed to be a promising and a highly cost-effective candidate for application in gas treatment because the gel can be used simultaneously for biogas drying. In addition, compared with activated carbon, silica gel performed better in regeneration. The desorption efficiency for silica gel can be up to 95% when heated to 250°C for 20 min. Montanari et al.[33] adopted silica gel and molecular sieves to remove L2 respectively and also found silica gel has a larger adsorption capacity.

5.2 Absorption

Absorption is the second major unit operation applied to siloxane removal. Physical and chemical absorption can be distinguished.

Theoretically, chemical absorption can completely remove siloxanes because the structure of siloxanes (Si–O bonds) can be destroyed by strong acids and bases[34]. However, only acidic liquid can be used because bases could react to form carbonates, which precipitate onto the equipment. Moreover, the reaction between strong bases and carbon dioxide in biogas can increase the consumption of bases. Schweigkofler et al.[10] studied siloxane (D5, L2) removal by gas-liquid extraction with different acids. Concentrated phosphoric acid (85%) was found to be ineffective in removing siloxanes, even at a temperature of 60°C. Elimination rates of only 44%-48% for D5 and 53%-60% for L2 were obtained. The application of 33% nitric acid at a temperature of 60°C led to siloxane elimination rates of 70%-75%. The removal effect is more significant when sulfuric acid is utilized. With an acid concentration close to 50%, siloxane elimination rates of more than 95% can be achieved[10]. However, the potential application of these chemical absorption agents is associated with safety and corrosion concerns. Therefore, technical and economic feasibility problems still exist in a wide range of applications[31].

Physical absorption includes absorbents such as water, an organic solvent, and mineral oil. The absorption in water (pH=7) was not successful because most siloxanes are hydrophobic. Nevertheless, the water absorption unit is a common preprocessing stage that ensures the treatment efficiency of subsequent units such that other water-soluble contaminants, including trimethylsilanol, could be removed[7]. A highly promising organic solvent for siloxane removal is Selexol^{TM} (dimethyl ethers of polyethylene glycol). Selexol^{TM} has been tested in a continuous pilot plant, and siloxane removal of 99% was reported by Wheless et al.[30] Huppmann et al.[35] used tetradecane as a collector liquid and achieved an elimination rate of 97% for D4. Stoddart et al.[36] reported an absorption system using a hydrocarbon oil as a solvent. Although the oil was primarily aimed at scrubbing halogenated organics, a 60% removal of siloxanes was achieved[36]. The absorption of siloxanes can be achieved using high-boiling organic solvents. Installations for siloxane absorption include both spray and packed columns (e.g., with Raschig rings). A disadvantage of this gas pretreatment method is siloxane desorption because the high volatile siloxanes (such as L2) are easily stripped from the solvent at elevated gas flow rates.

The main drawback of the physical absorption method is the difficulty of completely removing siloxane because the concentrations of siloxane in the landfill and sewage biogas can change over time. The decrease in siloxane concentration or increase in the gas flow rate will cause the desorption of high volatile siloxane (e.g., L2). This problem does not arise if the siloxanes are chemically removed because they are converted to compounds of low volatility[32].

5.3 Cryogenic condensation

When the temperature of biogas is decreased, a condensate is formed that contains part of the siloxanes that are present. Therefore, the removal of siloxanes is attained. The removal efficiency depends on the condensing temperature and the composition and concentration of siloxanes. A lower temperature can achieve a higher removal efficiency[23]. Schweigkofler et al.[10] studied the removal efficiency when the biogas was cooled to 5°C. Over 88% of the initial siloxane concentrations remained. Hagmann et al.[37] reported a cleanup efficiency for a range of volatile siloxanes of 25.9% when cooled down to –25°C and of 99.3% when frozen to –70°C. Rossol et al.[24] operated deep chillers to remove siloxanes from sewage-sludge biogas at a working temperature of –30°C, and reported elimination rates of 80%-90%.

The respective siloxane concentrations in the raw gas also play a decisive role in the removal efficiency achieved by cryogenic condensation. The maximum siloxane concentration at a certain temperature in an ideal gas mixture can be calculated according to its saturated partial pressure. Figure 1 shows the theoretically attainable siloxane concentrations at temperatures between 0°C and –70°C, and a total pressure of 1 bar. The more volatile the siloxane is, the more difficult it is to condense[3]. For D4, L4 and D5, the temperature should descend from –55°C to –70°C to reduce the concentration below the level of 1 mg/m^3. The reduction of the concentration of L2, D3 and L3 through cryogenic condensation is more difficult than those of D4, L4 and D5. The removal efficiency of siloxanes is usually higher in sewage-sludge biogas than landfill biogas because L2 mainly appears in the landfill biogas and sewage-sludge biogas contains more of D4 and D5.

This technology is usually applied in the condition of high gas flow and siloxane content and is used in conjunction with other processes e.g., adsorption, given that the cryogenic removal techniques require relatively high investment and operating costs. In the commercial application of cryogenic condensation process, the typical operating temperature is approximately –25°C[32].

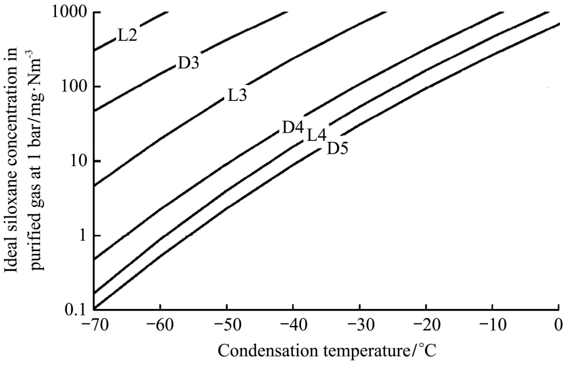

Figure 1 Siloxane concentrations at temperatures between 0°C and –70°C

5.4 Catalytic process

Alumina was shown to be a promising material for siloxane removal, based on a study by Finocchio et al.[27] The decomposition of D3 was tested at temperatures between 200°C and 400°C on the basic and acidic oxides CaO, MgO, alumina (Al_2O_3) and silica (SiO_2). Results indicated that CaO, MgO and silica showed the insignificant removal of D3. The alumina, which was exposed to a dry mixture of CO_2 and CH_4 and saturated with D3 at room temperature, showed an uptake of 24 wt.% at 250°C. The use of humidified gas caused a decline to 5 wt.%. However, at 400°C, D3 uptake re-increased to 31 wt.%.

Catalytic systems are unusual in terms of landfill sites. Although VOCs are usually destroyed by catalytic methods, a complex matrix such as landfill biogas makes their removal more challenging, because many minor components present in LFG act as poisons, even for non-noble metal oxides. Urban et al.[31] proposed a catalytic purification process combined with landfill gas use in molten carbonate fuel cells (MCFC). The catalytic process transforms harmful landfill gas minor compounds into products that can be easily removed from the gas stream by a subsequent adsorption step. The process consists of two catalysts. The first material is a commercially activated alumina that acts to remove high concentrations of volatile siloxanes, which have a deleterious effect on both a subsequent catalyst and a downstream MCFC. Alumina becomes deactivated over time and must be replaced periodically. The second material is a commercial V_2O_5–TiO_2 catalyst that possesses good activity for the oxidation/hydrolysis of organic and inorganic model compounds into a simpler compound class, ‘acid gases’ (HCl, HF and SO_2), which can be easily removed by absorption with, for example, alkalized alumina. The optimal process temperature was found to be in the range of 250°C-400°C[31].

5.5 Biological removal

Although siloxanes are reported to be relatively stable against biological degradation, some recent studies investigated the possibility of removing siloxanes by biological means.

Siloxane biodegradation has been investigated by Accettola et al.[38] to evaluate the possibility of using a biofiltration system to treat biogas. The experiment focused on the degradation of D4 in batch cultures and D3 in a bio-trickling filter by bacteria present in an activated sludge from a municipal wastewater plant and from a silicon-producing company. Results show that D4 can be biodegraded by a community of microorganisms. The dominating genus was identified as *Pseudomonas*, whereas other microorganisms found included *Rhodanobacter*, *Zooglea*, *Mesorhizobium* and *Xanthomonadacea.* Furthermore, dimethylsilanediol (DMSD), the degradation product of D4, has been found in bacterial cultures in a higher concentration than in the treatment of an air stream polluted with siloxane. Results showed a removal rate of 10%-20% of D3, whereas the same system in abiotic conditions reported zero removal.

Another study which focused on the siloxane removal efficiency of an anaerobic and aerobic bio-trickling filter was conducted on a lab-scale by Popat and Deshusses[39]. The D4 of roughly 45 mg/m^3 in test gas (humid air, i.e., oxygen-free synthetic gas in the anaerobic experiment) was the sole carbon and energy source. The efficacy of both aerobic and anaerobic bio-trickling filters was low. The removal of D4 in the aerobic bio-trickling filter followed a linear trend, reaching 43% at an empty bed residence time (EBRT) of 19.5 min. The anaerobic bio-trickling filter removed 15% of D4 at a residence time of 4 min, but no other EBRTs were tested. Aside from the very poor microbial degradability of D4, microorganisms adapt to D4 as the first carbon and energy source over a long time. Moreover, mass transfer limitations were revealed to play an important role in the low treatment performance. The maximum possible mass transfer rate of D4 in the bio-trickling filter was estimated between 30-100 mg/(m^3·h).

In 2013, Xu et al.[40] investigated the removal efficiency of activated sludge under anaerobic conditions. After 60 d processing, the removal rates of D3, D4, D5 and D6 were 3.0%, 44.4%, 62.8% and 18.1%, respectively. The result implies that siloxanes can be biodegradable, but the efficiency of biodegradation is very low.

5.6 Membrane separation

Membrane separation technology is another method used for siloxane removal, which implies the principle of selective siloxane permeation by solution and diffusion through the dense polymeric membrane material. The technology is still under experimental investigation[8]. Early trial tests were conducted by Albersen[41] in 1998 with a dense membrane characterized by silicon removal efficiencies above 80%. However, presumably owing to relatively high investment costs and moderate operating costs, the concept was not further pursued.

In recent years, Ajhar et al.[42] from the RWTH Aachen University have performed similar studies. They tested a series of elastomeric membrane tests to determine L2, L3, L4, D3, D4 and D5 permeability and selectivity toward CH_4 and found that commercially available polydimethylsiloxane (PDMS) membranes showed a better siloxane removal efficiency. Measurements of carbon dioxide as the sweep gas revealed siloxane permeability between roughly 9000 (L2) and 50 000 Barrer (D5) at 20°C. The ideal selectivity toward CO_2 was in the range of approximately four (L2) to 23 (D5) and toward CH_4 between 13 (L2) and 76 (D5). The permeability of all studied siloxanes decreased with rising temperatures. The stronger volatile the siloxane is, the more decrease is. Meanwhile, other problematic organic trace substances such as BTEX or halogenated hydrocarbons also showed high permeability in PDMS membranes.

The costs of a membrane process are directly linked to the power needed for compressors or vacuum pumps to establish a sufficiently high partial pressure difference across the membrane and induce target gas permeation, implying that the correct identification of a selective and permeable membrane determines the costs of such a process decisively[42,43]. In addition to the use of an appropriate membrane to improve the economic feasibility, the membrane separation process is particularly suitable for occasions when CH_4 has already been compressed. For example, the gas injection pipe network can significantly reduce the engineering investment and running costs[32].

6 Source controlling, equipment maintenance and online monitoring

In most cases, siloxanes are streamed down into the sewage treatment plant from dispersed sources, such as residential areas. On this occasion, the removal of siloxane can only be conducted after entering the biogas. However, when the discharge of pollutants contains considerable siloxanes, source controlling is of great significance. This condition means that the removal of siloxanes should be conducted prior to the organic waste anaerobic digestion before they volatilize into biogas. Source controlling is applied particularly for some industrial wastewater sites with high siloxane concentrations[32]. The destruction of siloxanes by peroxidation was studied by Appels et al.[44] Three peroxidation agents were used, and all achieved D4 and D5 elimination efficiencies between 40% and 50%. In the case of peroxidation by dimethyldioxirane (DMDO), 85% of D4 was eliminated[44]. Stripping is another way to remove siloxanes from sludge before digestion. Klingel et al.[45] have investigated the removal efficiency of L2 by stripping method at different temperatures, pH and different water contents of sludge on a lab-scale. The results showed that pH has little influence on the removal of L2 while the improvement of temperature and water content of sludge can speed up the removal efficiency. Ultrafiltration has also been reported to remove siloxanes from industrial wastewater by Rossol et al.[24] Ultrafiltration removes impurities according to the molecular weight, typical molecular weight that can be removed ranges 1000-100 000 g/mol. Thus, when the siloxane molecules are relatively small, they may be adsorbed and retained in the filter cake layer.

A separate siloxane removal unit need not be set up when the siloxane concentration is low, considering the economy of the engineering. Instead, the maintenance of several pieces of biogas utilization equipment (e.g., generators, turbines and fuel cells) becomes meaningful. An incident-oriented maintenance scheme could include more frequent oil changes, endoscopy inspection of the combustion chamber, and regular examinations of valves, spark plugs, and the turbo compressor[3]. Subjective judgment (such as listening to the noise and visual observation) and specific monitoring (such as oil and gas analysis) are also effective for routine maintenance. The choice of suitable engine oil seems particularly critical. The silicon content of the oil is disregarded as a general indicator of wear, because it may largely include amorphous SO_2 (particle size <1 μm), which is considered non-damaging to engine parts. The presence of crystalline SO_2 and high metal concentrations in the oil leads to damage.

The use of online monitoring of siloxane in the biogas industry is substantial. The combination of GC-PID and FT-IR proved to be a useful technique for biogas online determination. The main advantages were instant information acquisitions of the total gas matrix and variation in the concentrations. The equipment used is robust and can be used in difficult field conditions. The method also provided online data about the main gas components, which is useful for the control of biogas upgradation processes[22].

7 Cost of the removal of siloxane in biogas

The cost of removal of siloxanes depends on the processing capacity, processing technology, composition and concentration of siloxanes, and the quality requirements for the CH_4 combustion device[23]. Beese et al.[46] investigated a few projects in Europe, and statistics are shown in Table 3. Wheless et al.[47] had reported the construction and operation cost of two desilication devices in the landfill biogas in Calabasas and Waukesha, USA, as shown in Table 4. Wheless asserted that the cost of 0.3 cent/(kW·h) can be accepted and that 1.5 cent/(kW·h) was too high, but its corresponding siloxane concentration (34 mg/m^3) is representative.

Table 3 Cost of removal of siloxanes

Item	Biogas category	Construction investment/Euro	Operation cost /Euro·a^{-1}	Capital cost /Euro·m^{-3}	Maintenance cost /Euro·m^{-3}	Total cost /Euro·m^{-3}
Activated carbon adsorption	Sewage-sludge biogas	50 000	16 000	0.16	0.33	0.50
Graphite filter	Landfill biogas	120 000	227 000	0.19	0.16	0.35
Resin adsorption	Sewage-sludge biogas	125 000	24 500	0.26	0.40	0.70
	Landfill biogas	420 000	75 000	0.067	0.033	0.10
Condensation and adsorption	Sewage-sludge biogas	250 000	75 000	0.80	1.61	2.50
Cooling and adsorption	Landfill biogas	1 000 000	330 000	0.16	0.35	0.50

Note: The processing capacity of biogas desiliconizing equipment used for sewage-sludge biogas according to the 10 000 m^3/d, whereas for the landfill biogas, the processing capacity differs.

Table 4 Construction and operation cost of two desilication devices in the USA

Item	Calabasas	Waukesha
Equipment construction investment/cent·kW^{-1}	85	82
Siloxane concentration at device entry/mg·m^{-3}	2	34
Treatment costs using activated carbon/cent·(kW· h)$^{-1}$	0.3	1.5
Treatment costs using activated carbon/cent·m^{-3}	1.5	7.5

8 Conclusions

The siloxane content of the agricultural biogas is low. Therefore, daily maintenance is efficacious, and special siloxane removal equipment is unnecessary. Siloxane concentration in landfill and sewage-sludge biogas usually exceeds 50 mg/m^3, higher than the common required concentration limit of engine manufacturers. Thus, the removal of siloxanes prior to the engine is necessary.

Presently, the most common method of siloxane removal is the activated carbon adsorption combined with a preliminary drying unit for the sludge biogas. No general method has been identified for landfill gas, and the activated carbon adsorption method depends largely on other impurities contained in the gas. Different types of activated carbon can also make a difference. Silica gel and the alumina are also promising adsorbents. The removal of siloxanes is often combined with the removal of other impurity composition, especially volatile organic pollutants (VOC) and H_2S, given that most of the organic solvents are not selective.

Future research should be focused on the regeneration of the adsorbent properties and the adsorbent selectivity of siloxane. Although its application is limited, Selexol™ shows a good application prospect in the market. The selective membrane and catalyst are also future research hotspots. The efficiency of biological removal is currently low, and the future studies can be focused on the efficient microbial species and overcoming the mass transfer limitations.

Acknowledgments

The authors acknowledged the financial support by the Beijing Science and Technology Program (D141100001214003) , Fundamental Research Funds for the Central Universities (No. FRF-TP-15-045A1) and National Key Research and Development Plan (No. 2016YFE0115600).

[References]

[1] Ran Y, Cai P, Huang J H, Wang C, Tang X Y, Wang B. A review on research and application of biogas upgrading technologies in China and abroad. China Biogas, 2016; 34(5): 61–67. (in Chinese).

[2] Yao P, Boardman G D, Li E T. Research progress for removing siloxane from biogas by adsorption. Chemical Industry and Engineering Progress, 2016; 35(2): 604–611. (in Chinese)

[3] Ajhar M, Travesset M, Yüce S, Melin T. Siloxane removal from landfill and digester gas: A technology overview. Bioresource Technology, 2010; 101: 2913–2923.

[4] Rasi S, Läntelä J, Rintala J. Trace compounds affecting biogas energy utilisation: A review. Energy Conversion and Management, 2011; 52: 3369–3375.

[5] Zhang S L, Wu L H. The research progress of environmental distribution, behavior and effects of cyclic methylsiloxanes. Asian Journal of Ecotoxicology, 2016; 11(3): 72–85. (in Chinese)

[6] Cheng Y, Shoeib M, Ahrens L, Harner T, Ma J. Wastewater treatment plants and landfills emit volatile methyl siloxanes (VMSs) to the atmosphere: Investigations using a new passive air sampler. Environmental Pollution, 2011; 159: 2380–2386.

[7] Rasi S, Lantela J, Veijanen A, Rintala J. Landfill gas upgrading with countercurrent water wash. Waste Management, 2008; 28: 1528–1534.

[8] Zheng M, Wu W M, Chi L N, Wang C W. Distribution, migration and transformation of siloxanes in environment and its impact on biogas application. Acta Science Circumstantiae, 2015; 35(10): 3050–3056. (in Chinese)

[9] Surita S C, Tansel B. Emergence and fate of cyclic volatile polydimethylsiloxanes (D4, D5) in municipal waste stream: Release mechanisms, partitioning and persistence in air, water, solid and sediments. Science of the Total Environment, 2014; 468-469: 46–52.

[10] Schweigkofler M, Niessner R. Removal of siloxanes in biogases. Journal of Hazardous Materials, 2001; 83(3): 183–196.

[11] Liu N N, Shi Y L, Li W H, Xu L, Cai Y Q. Concentrations and distribution of synthetic musks and siloxanes in sewages sludge of wastewater treatment plants in China. Science of the Total Environment, 2014; 476-477: 65–72.

[12] Rasi S, Lehtinen J, Rintala J. Determination of organic silicon compounds in biogas from wastewater treatments plants, landfills, and co-digestion plants. Renewable Energy, 2010; 35: 2666–2673.

[13] Bletsou A A, Asimakopoulos A G, Stasinakis A S, Thomaidis N S, Kannan K. Mass loading and fate of liner and cyclic siloxanes in a wastewater treatment plant in Greece. Environmental Science and Technology, 2013; 47(4): 1824–1832.

[14] Cao Z R, Yang S S, Chen Y, Zheng X P. Features of siloxanes in biogas and its research advance in sewage treatment. Environmental Engineering, 2014; 32(8): 48–52.

[15] USEPA. Siloxane D5 in Drycleaning Applications. USA, Environmental Protection Agency, 2005.

[16] Ajhar M, Wens B, Stollenwerk K H, Spalding G, Yüce S, Melin T. Suitability of Tedlar® gas sampling bags for siloxane quantification in landfill gas. Talanta, 2010; 82: 92–98.

[17] Clark C, Zytner R G, Mcbean E. Analyzing volatile organic siloxanes in landfill biogas. Canadian Journal of Civil Engineering, 2012; 39: 667–673.

[18] Sharon C S, Berrin T. A multiphase analysis of partitioning and hazard index characteristics of siloxanes in biosolids. Ecotoxicology and Environmental Safety, 2014; 102: 79–83.

[19] Dewil R, Appel S L. Energy use of biogas hampered by the presence of siloxanes. Energy Convers. Manage., 2006; 47(13/14): 1711–1722.

[20] Grumping R, Mikolajczak D, Hirner A. Determination of trimethylsilanol in the environment by LT-GC/ICP-OES and GC-MS. Fresenius' Journal of Analytical Chemistry, 1998; 361: 133–139.

[21] Hayes H, Graening G, Saeed S, Kao S. A summary of available analytical methods for the determination of siloxanes in biogas. Presentation at SWANA LFG Symposium, Tampa, Florida, 2003.

[22] Arnold M, Kajolinna T. Development of on-line measurement techniques for siloxanes and other trace compounds in biogas. Waste Management, 2010; 30: 1011–1017.

[23] Yang S S, Chen Y, Huang Y, Cao Z R. Source of siloxane in biogas and its removal. China Water and Wastewater, 2013; 29(20): 19–21. (in Chinese).

[24] Rossol D, Schmelz K G, Hohmann R. Siloxane im Faulgas. KA-Abwasser Abfall, 2003; 8: 8.

[25] Matsui T, Imamura S. Removal of siloxane from digestion gas of sewage sludge. Bioresource Technology, 2010; 101: S29–S32.

[26] Boulinguiez B, Le Cloirec P. Biogas pre-upgrading by adsorption of trace compounds onto granular activated carbons and an activated carbon fiber cloth. Water Science and Technology, 2009; 59: 935–944.

[27] Finocchio E, Garuti G, Baldi M, Busca G. Decomposition of hexamethylcyclotrisiloxane over solid oxides. Chemosphere, 2008; 72, 1659–1663.

[28] Sangchul N, Wan N, Kang J H, Park J K, Namhoon L. Adsorption characteristics of siloxanes in landfill gas by the adsorption equilibrium test. Waste Management, 2013; 33: 2091–2098.

[29] Alba C C, Miguel A, Manuel S P, Maria J, Rafael G O. Biogas upgrading: optimal activated carbon properties for siloxanes removal. Environmental Science and Technology, 2014; 48: 7187–7195.

[30] Wheless E, Pierce J. Siloxanes in landfill and digester gas update. Proceedings of the 27th SWANA Landfill Gas Symposium. San Antonio, TX: Silver Springs, March 22–25, 2004.

[31] Urban W, Lohmann H, Gomez J I S. Catalytically upgraded landfill gas as a cost-effective alternative for fuel cells. Journal of Power Sources, 2009; 193: 359–366.

[32] Xu H P, Zhang X D, Jin F Q, Hua D L, Zhang J, Li Y. Progress on technology of siloxane removal from biogas. China Biogas, 2012; 30(6): 18–22. (in Chinese)

[33] Montanari T, Finocchio E, Bozzano I, Garuti G, Giordano A, Pistarino C, et al. Purification of landfill biogases from siloxanes by adsorption: a study of silica and 13X zeolite adsorbents on hexamethylcyclotirsiloxane separation. Chemical Engineering J., 2010; 165(3): 859–863.

[34] Ryckebosch E, Drouillon M, Vervaeren H. Techniques for transformation of biogas to biomethane. Biomass and Bioenergy, 2011; 35: 1633–1645.

[35] Huppmann R, Lohoff HW, Schroder H F. Cyclic siloxanes in the biological waste water treatment process-determination, quantification and possibilities of elimination. Fr J Anal Chem, 1996; 354: 66–71.

[36] Stoddart J, Zhu M, Staines J, Rothery E, Lewicki R. Experience with halogenated hydrocarbons removal from landfill gas. Proceedings Sardinia 1999, Seventh International Waste Management and Landfill Symposium, 1999; 2: 489–498.

[37] Hagmann, Hesse E, Hentschel P. Purification of biogas-removal of volatile silicones. Eight international waste management and landfill symposium. Sardinia: CISA, 2001: 641–644.

[38] Accettola F, Guebitz G M, Schoeftner R. Siloxane removal from biogas by biofiltration: biodegradation studies. Clean Technologies and Environmental Policy, 2008; 10: 211–218.

[39] Popat S C, Deshusses M A. Biological removal of siloxanes from landfill and digester gases: Opportunities and challenges. Environmental Science & Technology, 2008; 42(22): 8510–8515.

[40] Xu L, Shi Y L, Cai Y Q. Occurrence and fate of volatile siloxanes in a municipal wastewater treatment plant of Beijing, China. Water Research, 2013; 47(2): 715–724.

[41] Albertsen A. Silicium im Deponiegas- Risikominderung durch Vorbehandlung, 1998; pp.367–384.

[42] Ajhar M, Bannwarth S, Stollenwerk K, Spalding G, Yüce S, Wessling M, et al. Siloxane removal using silicone-rubber membranes. Separation and Purification Technology, 2012; 89: 234–244.

[43] Ajhar M, Melin T. Siloxane Removal with Gas Permeation Membranes. Desalination, 2006; 200: 234–235.

[44] Appels L, Baeyens J, Dewil R. Siloxane removal from biosolids by peroxidation. Energy Conversion and Management, 2008; 49: 2859–2864.

[45] Klingel M, Hahn H H, Hoffmann E. Ausgasungsverhalten von siloxan in der Klarschlammfaulung. Max-Buchner-Forschungsstiftung, 2002: 6.

[46] Beese J. Betriebsorptimierung der motorischen gasverwertung durch den einsatz von gasreinigungsanlagen. Presentation at Deponiegas 2007. F H Trier Saska: Si-loxa Engineering AG, 2007.

[47] Wheless G. Siloxanes in landfill gas and degester. SWANA Landfill Gas Symposium, USA, 2002.