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SILOXANES IN BIOGAS. ORIGIN, EFFECTS AND TREATMENTS. TECHNOLOGIES ON THE MARKET

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Abstract: Biogas from landfills and wastewater treatment plants (WWTP) is a raw material for the production of energy and new products. When it leaves the digester, biogas is a dirty gas with harmful components for its use (NH_3, siloxanes, halogenated hydrocarbons, BTEX, VOCs, H_2S, etc.). Among the components of greatest incidence, both in the energetic use of biogas and in its use for the production of biomethane, are the siloxanes due to the damage they cause, both in machines for the production of energy and in the technologies used for the production of biomethane. Several technologies for biogas cleaning are currently available on the market. The BTS-MPdry-Siloxa technology. It is a multipurpose technology based on the combination of operations developed by BGasTech for the removal of siloxanes present in biogas. The technology has two basic stages. A coarse removal stage and a refining stage that produces a raw material quality biogas with a high degree of cleanliness and low OPEX that guarantees the proper use of the biogas for any purpose
Keywords: Biogas, Siloxanes, Technologies, Cleaning, Machines, Biogas, Biogas, Siloxanes.

INTRODUCTION

Biogas from a technical point of view is a mixture of gases, both in its basic composition (CH_4, CO_2, H_2, O_2, N_2, etc.) and in its harmful components (NH_3, siloxanes, halogenated hydrocarbons, BTEX, VOCs, H_2S, etc.). Its composition is closely related to the type of material that undergoes the anaerobic digestion process, and to the technology used for its production, hence we can speak in general terms of two types of biogas.

Uncontrolled systems. Biogas from landfills, landfill sites, wetlands

Controlled systems. Urban wastewater treatment plant (WWTP) and anaerobic digestion plants (high organic load).

In general terms, it can be stated that the latter are characterized by a high concentration of H_2S, its main pollutant component, and in the case of WWTPs, the presence of siloxanes, while the former (landfills) are characterized by the appearance of siloxanes and high molecular weight hydrocarbons.

Siloxanes are man-made compounds and are used in many personal care and industrial products, such as cosmetics, foodstuffs, additives for plastics, cleaning products, etc.

A siloxane is an organosilicon functional group with the Si-O-Si bond. Examples are $[SiO(CH_{(3)}))_2]n$ (dimethylsiloxane) and $[SiO(C_{(6)}H_5)_{(2)}]n$ (diphenylsiloxane), where **n** is usually greater than 4.

Silicones. They are polymerized siloxanes (polysiloxanes).

As they are found in many industrial products and products used in society. Siloxanes can be found mainly in wastewater or municipal solid waste (MSW). When they enter the anaerobic digestion process, they are released as part of the volatile organic compounds present in the biogas generated.

These components cause damage to the machines and technologies used for their valorization, reducing their useful life due to the abrasive and deposition (incrustation) effect they produce on their internal parts, which leads to malfunction and breakage of parts and pieces and thus to an increase in operating costs due to repeated changes and replacement of oils and internal parts.

This paper presents the BTS-MPdry-Siloxa technology and its practical application in the case of the Butarque-Madrid WWTP as a technique for the removal of siloxanes in biogas.

DEVELOPMENT

ORIGIN OF SILOXANES

Siloxanes are a family of organic compounds consisting of linear or cyclic chains of silicon, oxygen and methyl groups. They are manufactured in a range of forms, including high and low viscosity fluids, rubbers, elastomers and resins, and are found in significant quantities in a wide and varied range of household products, such as detergents, shampoos, deodorants, toothpastes, cosmetics, among others.

Most of them volatilize quickly into the atmosphere and eventually degrade into carbon dioxide, silica and water. Some, however, end up in sewage and municipal waste solids and inevitably accumulate in landfills and wastewater treatment plants, where they are considered one of the most difficult pollutants to control.

These are organic compounds consisting of silicones, oxygen and methyl groups with structural unit $-(CH_3)_2SiO$, and molecular weight typically in the range 150 to 600. Their solubility in water decreases with increasing molecular weight and they can be volatile or non-volatile.

Figures 1, 2 and 3 show the structural unit and different types of siloxanes that appear.

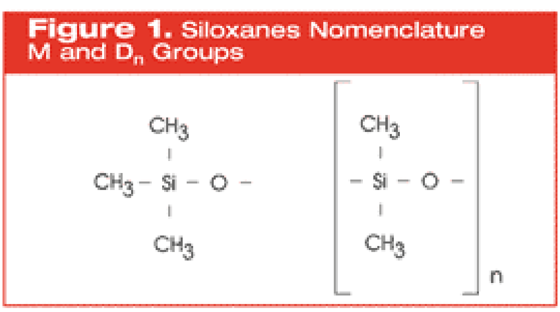

Figure 1. Structural unit of siloxanes.

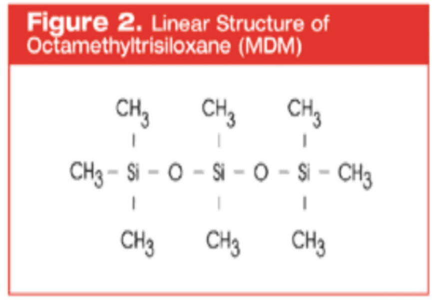

Figure 2. Straight chain siloxanes. Type L

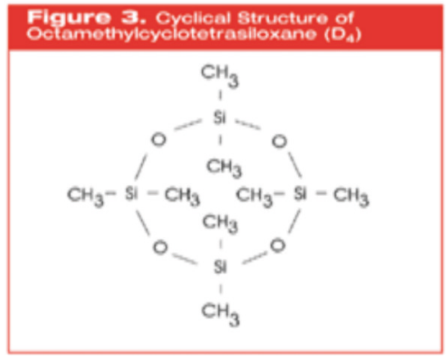

Figure 3. Cyclic chain siloxanes. Type D

EFFECT

Silicones, unlike sulfides, do not react with water to form acids; however, during combustion the siloxane molecules break down, releasing oxygen and silicon; the latter combines with other elements to form silicates, silica and other crystalline compounds that are deposited in the combustion chamber (mainly in the upper part of the liner), in the cylinder heads and on the faces of the valves.

These incrustations cause, on the one hand, wear by abrasion of different internal parts of the machines, and on the other hand, the loss of clearances between fixed and mobile internal parts of the machines. Figures 4, 5 and 6 show the fouling caused by siloxanes in different types of machines.

The permissible siloxane content in biogas for good engine performance should generally not exceed < 3 mg/Nm^3, although each machine manufacturer sets its own limits. A higher content will indicate possible silica deposition problems, and with it, the burning of exhaust valves and loss of lubrication oil.

Figures 4, 5 and 6 show the fouling produced by siloxanes in different types of machines.

Figure 4. Engine

Figure 5.Boiler

Figure 6. Turbina

TREATMENTS

Current technologies on the market for the elimination of these compounds (siloxanes) can be specific and combined. They usually apply one or two treatment techniques, among which the following can be mentioned.

1. Cooling. Up to 4 ºC., Subcooling (cooling down to -25 ºC).

2. Adsorption. Activated carbon, Regenerative thermal (membranes), Silicagel.

3. Washing with certain reagents. Methanol, Used lubricating oil.

4. Combination of techniques. BTS-MPdry-Siloxa.

BTS-MPdry-Siloxa. It is a multipurpose technology based on a combination of operations based on cooling, condensation, washing, drying and adsorption on activated carbon, which minimizes both energy and activated carbon consumption. The technology has two basic stages. One of coarse removal of contaminants including D-type siloxanes, hydrocarbons by cooling and conditioning of the biogas for entry into the refining/polishing stage by adsorption. Another is refining (removal of L- and D-type siloxanes) via adsorption on activated carbon. An important part of this technology is the scrubber-reclaimer that ensures, on the one hand, the conditioning of the biogas before entering the refining stage and, on the other hand, minimizes energy consumption in the biogas cooling process. Figures 7 and 8 show the BTS-MPdry-Siloxa technology developed for siloxane removal.

Figure 8. BTS-MPdry-Siloxa Technology

The technology has two ways of biogas cooling. One by heat transfer, thermal cooling, due to the energy exchange between the cooling medium provided by the refrigeration machine (water with glycol) and the biogas and the other by mechanical cooling, due to the sudden expansion that the biogas undergoes when it enters the condenser, which in turn facilitates greater efficiency, both in the condensation operation and in the elimination of the condensates formed.

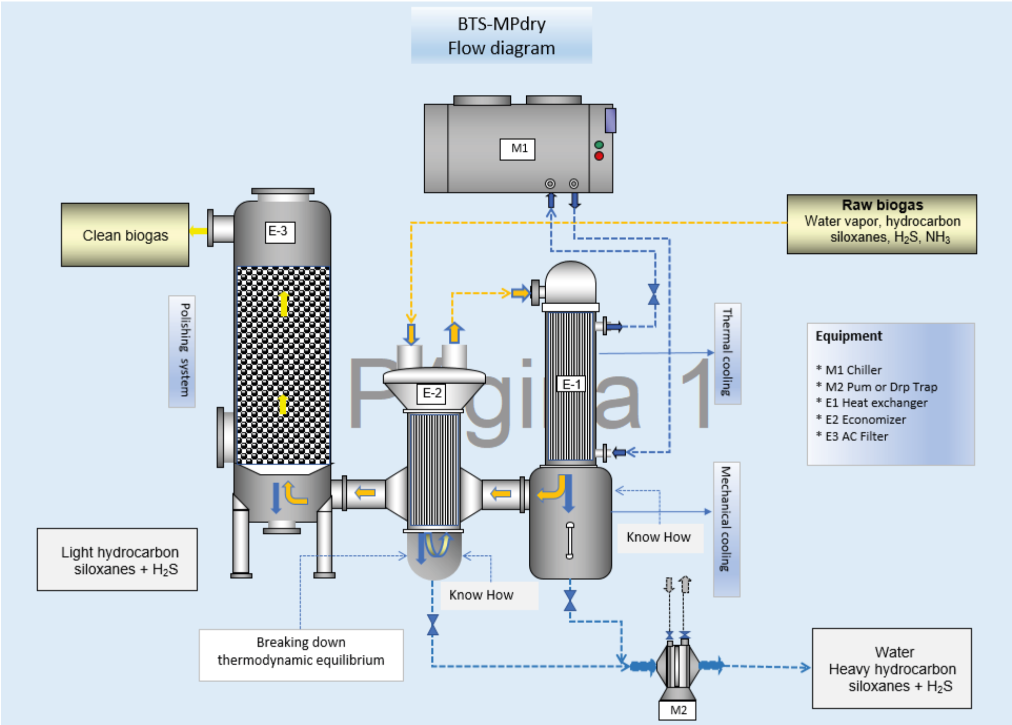

Figure 7. Flow diagram.

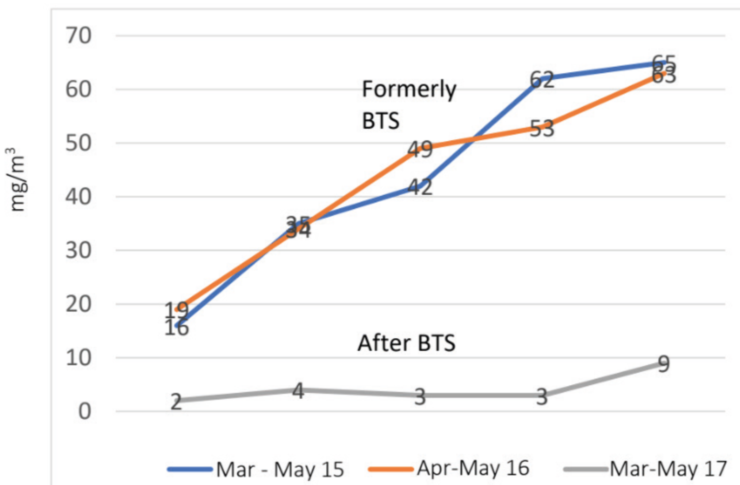

Figure 9. Behavior of silicon in engine oil before and after applying the BTS-MPdry technology.

CASE STUDY

This study was carried out at the Butarque WWTP in Madrid-Spain operated by Drace--Dragado.

The working conditions are as follows

1. Biogas flow rate = 1,300 Nm³/h.
2. Biogas technology inlet temperature = 38 ºC
3. Biogas pressure = 30 mbar.
4. Technology operating temperature = 2 ºC.
5. Objective. Reduction of the level of siloxanes in the biogas.

RESULTS

Table 1 shows the results achieved in siloxane removal and silicon reduction in the biogas stream before cogeneration engine input before and after applying the BTS-MPdry technology and the percentage of reduction achieved in both types of components.

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Siloxanes (mg/m³)	Silicon (mg/m³)
2016 without treatment	
1.99	0.75
2017 with treatment	
0.06	0.02
% reduction	
96,98	97,33

Table 1. Concentration of siloxanes and silicon in the biogas before and after applying the BTS-MPdry technology.

Figure 9 shows the behavior of the silicon concentration in the cogeneration engine oil before and after applying the BTS-MPdry-Siloxa technology.

CONCLUSIONS

The following conclusions can be drawn from the results of the application of the cleaning technology.

1. Optimal operation of machines used in biogas energy utilization (engines, turbines, boilers, etc.). Fulfillment of useful life time and more

2. Reduced maintenance costs (for spare parts, parts replacement and oil) of the machines involved in this type of energy recovery plant.

3. Long service life of the use of activated carbon (AC bed) as a biogas polishing system.

4. The overall reduction in OPEX of both the cleaning plant and the power generation plant due, on the one hand, to the reduction in process energy consumption and the increase in the useful life of the activated carbon and, on the other hand, due to the reduction of silicon in the motor oil.

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