MICROPHILOX
Energy recovery from Landfill’s Biogas by the use of MICROturbines and biological removal of hydrogen sulPHIde and siLOXanes


(1) CESPA G.R., Departamento Técnico, Av. Catedral 6-8, 08002 Barcelona. E-mail: ferran.relea, e.jimenez, e.gonzalez, jaume.cabrre, a.ayats}@cespa.es
(2) PROFACTOR GmbH, A-4407 Steyr-Gleink Austria/Im Stadtgut A2, E-mail: marianne.haberbauer@profactor.at
(3) IQS-PEINUSA, Via Augusta 390 08017 Barcelona, E-mail: francesc.broto, lluis.comellas, cristina.ribas, gemma.gotor, eusebi.roig, nuria.vallmitjana}@iqs.url.edu

High energetic potential of landfill biogas makes it an interesting energy source, whose valorisation makes possible obtaining electricity and heat, at the same time that contributes to energy diversification and reduction of green house effect.

Nowadays, landfill gas recovery presents several difficulties which are mainly related to energy recovery equipments, biogas quality and present methodologies for contaminant detection in biogas. Within this framework, arises in 2005 the MICROPHILOX project (www.microphilox.com) that has been developed by Cespa, Profactor, Institut Químic de Sarrià (IQS) and Promotora de Enlace Industria Universidad, S.A. (PEINUSA) and which has counted with financial contribution from the LIFE-Environment programme from the European Commission. This project contributes with important technological innovations as the use of microturbines for biogas recovery, an innovative biological biogas upgrading system and the development of a methodology with proved repeatability for siloxane analysis.

INTRODUCTION

MICROTURBINES IN LANDFILLS

Nowadays, the most developed and used technology for landfill gas energy recovery is CHP engines. Nevertheless, they are only technical and economically feasible when generated power is over 600 kW and when biogas has a methane content of at least 40%. This means that today biogas recovery is only carried out in those exploitations with high biogas flow and methane content, being excluded small landfills and those who are in its initial or final exploitation stage. In these cases, biogas is being flared with the consequent lose of an important renewable energy source.

Microturbines characteristics

In view of these problems, microturbines are presented as an attractive technological alternative to CHP engines thanks to two of their main characteristics:

- They are modular elements with unitary capacities between 30 and 200 kW that can be connected in series and therefore are suitable for any installation size.
They allow operation with low calorific fuels, what in the case of biogas means a minimum methane content of 30-35%, lower than the 40% required by a CHP engines.

Microturbines are equipments very similar to conventional turbines. Their operation consists of: air is sucked and filtrated and then it is compressed. Next, air is leaded to a heat exchanger where part of exhaust gases energy is absorbed. The reason is to raise its temperature previous entrance in the combustion chamber what allows increasing the efficiency of the combustion process, being this the main difference with turbines. Once air is in the combustion chamber, biogas is injected and mixture is ignited. Unlike alternative engines, turbines need a biogas pressure between 3 and 7 bar, enough to be injected in the combustion chamber. Hot gases coming from the combustion are expanded in the turbine blades, turning the axel where the generator and the compressor are assembled. Exhaust gases are then leaded to the heat exchanger. The turning of the generator produces a high frequency electric current, so it is necessary the incorporation of an inverter to obtain a 50 Hz three-phase current.

From a mechanical point of view, as microturbines have only one moving part they require less maintenance than CHP engines. Moreover, as the have air bearings, operational costs are reduced since they don’t need lubricants. In relation to air emissions, microturbines present less CO₂ and NOx emissions than CHP engines.

**Potential applications of microturbines**

With stated characteristics, microturbines seem a very interesting option, especially suitable for those landfills where biogas parameters are not appropriate for the installation of an energy recovery plant with CHP engines, either due to low biogas flow or due to low methane content, as for example would be the case of small landfills or those who are in its initial or final life stage, or even, exploitations where there is a high biogas production that is being used in cogeneration engines, but where there is a biogas surplus that the engines cannot consume and that is then flared.
BIOGAS UPGRADE

Viability of a biogas energy recovery plant can be put into risk due to the presence in the biogas flow of trace elements, like sulphuric acid or siloxanes, which produce severe damages to recovery equipments increasing maintenance costs and reducing the efficiency of the whole system to the point of making operation unviable.

There are several biogas upgrading technologies, but the one most used is activated carbon due to its simplicity of operation and high efficiency and despite of its high cost and the drawback of the formation of a final waste that must be properly managed. Lately, biological upgrading methods have achieved great improvements and nowadays they achieve similar efficiencies than physical-chemical methods. By this way, biological filters for biogas depuration would allow reducing operating costs, either by the complete replacement of the activated carbon filter or as a pre-treatment of this filter, with the subsequent increase of activated carbon replacement periods.

Biotechnological methods for biogas upgrading

Biotechnological systems use microorganisms to degrade biogas contaminants. In particular, *Thiobacillus sp* is the bacterium used for the removal of sulphuric acid from biogas and *Pseudomonas fluorescens* for the removal of siloxanes.

Among the different biotechnological upgrading methods, biofilters, bioscrubbers and biotrickling filters are the most important. Among them, biotrickling filters have some advantages in comparison with the other technologies, as for example that they don’t present medium acidification problems.

![Figure 4. Biological methods for biogas upgrading](image-url)
SILOXANE CAPTURE AND ANALYSIS

Presence in biogas of trace concentrations of siloxanes means a serious problem for its energy recovery since combustion of these compounds causes a substance with characteristics similar to those of glass, causing severe damage to equipment, so manufacturers set maximum concentration of siloxane in biogas. For this reason, and also to evaluate upgrading process efficiencies, it is important to know which quantity of siloxanes is contained in our biogas. Nevertheless, application of different capture and analysis methods of siloxanes in biogas occurred in a non acceptable variation in obtained results and therefore a reliable and repeatable method for the determination of these compounds in biogas is needed.

THE MICROPHILOX PROJECT

The MICROPHILOX project tries to develop a technological alternative for present landfill gas energy recovery problems. Stated solution, which is schemed in Figure 5, consists on the technical and economical demonstration of two 30 kWe microturbines for electricity and heat generation from biogas, together with the development of a prototype for the biological removal of H₂S and siloxanes. With the aim of knowing the efficiency of the biological biogas cleaning system, a reliable and repeatable methodology for siloxane capture and analysis has been obtained.

Figure 5. Scheme of the technical solution of the project

Each of the project partners has been responsible of one of the different technical parts of the Project, CESPA has been in charge of the microturbine application, while PROFACTOR has developed biofilters and IQS-PEINUSA has obtained a method for siloxane detection in biogas. Partner’s know-how has been a key point for the whole system integration.

BIOGAS ENERGY RECOVERY WITH MICROTURBINES PLANT

Available biogas in Orís landfill in the beginning of the project allowed us to use two microturbines Capstone C30 of 30 kW each. Designed energy recovery plant consists of four parts (Figure 6): degasification station, treatment unit, microturbines and exhaust gases recovery system. The design was thought so that all produced power was consumed in the landfill installations.

According manufacturer technical specifications, biogas that arrives to the microturbines must be free of water and must have a maximum concentration of siloxanes of 5 ppb. For this reason it is necessary to condition biogas in the treatment unit, where water is withdrawn by means of a chilling process and for the removal of siloxanes an activated carbon filter is used, due to no industrial equipment for biological removal of siloxanes is available in market. Then a compressor is used to raise biogas pressure up to 5 bar.

With the aim of increasing energetic efficiency of the process, it was decided to use heat from exhaust gases in a drying plant for leachate treatment existing in the landfill (CLONIC project LIFE03).
Operational parameters

Operational follow up of the energy recovery plant with microturbines has allowed evaluating some operational parameters and comparing them to those of a plant with CHP engines:

- Microturbines availability has been around 90%, similar to the one which is obtained with cogeneration engines.
- We have demonstrated the operation of microturbines with a minimum methane content of 31%, improving concentration required by engines, which is of 40%.
- Average generated power has been 52 kWe.
- Maintenance costs have been of 0.029 €/kWh, less than 5% higher than those had in a 1 MWe CHP engine plant, but it's necessary to bear in mind that operation costs are easier to optimize for higher output powers.

Biogas and microturbine exhaust gases follow-up

During the project a periodic follow-up of landfill biogas has been carried out in order to control those parameters that could affect energy recovery equipments, as for example, methane content, sulphuric acid and siloxanes. The first two compounds haven't caused any trouble during the project, but siloxane concentration was always over the limit established by the microturbine manufacturer, and besides, their concentration increased in 5 times the values used for the design of the plant. This fact obliged us to replace the 250 L activated carbon filter initially installed by a 1 m³ vessel with the aim of reducing activated carbon changes.

In relation to microturbine exhaust gases, it was also carried out a follow-up of the concentrations of carbon monoxide (CO), nitrogen oxides (NOx) and sulfur oxides (SO₂) in order to know if emissions are under those limits regulated by environmental legislation.

Nowadays, it doesn't exist, neither in Spain nor in Catalunya, any directive that regulates emission limits for combustion systems using biogas as fuel, so it must prevail what it is stated in the environmental authorisation. Nevertheless, due the lack of reference values for these limits, data used as reference are values stated by Annex I, Section 2.1. about gas turbines in the Real Decreto 319/1998 of 15 December about emission limits for combustion industrial installations with power under 50 MWt and cogeneration installations. These limits, all of them referred to 15% O₂, are 450 mgNOₓ/Nm³ for NOₓ, 100 mgCO/Nm³ for CO, 300 mgSO₂ for SO₂. If we compare these limits with microturbine emissions, it can be observed that...
all parameters are below the maximum allowed, but CO₂, what on the other hand is the consequence of using biogas instead of natural gas, which doesn’t contain CO₂.

Table 1. Comparison of microturbine emissions with environmental legislation and with CHP engines emissions

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<tr>
<th></th>
<th>CO</th>
<th>NOₓ</th>
<th>SO₂</th>
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<tr>
<td></td>
<td>(mg/Nm³)</td>
<td>(mg/Nm³)</td>
<td>(mg/Nm³)</td>
</tr>
<tr>
<td>Real</td>
<td>5% O₂</td>
<td>15% O₂</td>
<td>5% O₂</td>
</tr>
<tr>
<td>MICROTURBINE</td>
<td>135</td>
<td>561</td>
<td>209</td>
</tr>
<tr>
<td>1 MW CHP ENGINE</td>
<td>995</td>
<td>995</td>
<td>261</td>
</tr>
<tr>
<td>DECRET 319/1998</td>
<td>100</td>
<td>450</td>
<td>300</td>
</tr>
<tr>
<td>(Turbines: 1&lt;P&lt;1MW, natural gas)</td>
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<tr>
<td>TA LUFT</td>
<td>1,000</td>
<td>500</td>
<td>350</td>
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A deeper study of European environmental regulations, showed that German environmental legislation “Technische Anleitung zur Reinhaltung der Luft” takes into account biogas as a fuel in cogeneration plants, but with engines as combustion technology. When microturbine emissions are compared with this regulation, it can be observed in table 1 that limits are accomplished.

Microturbine emissions have been also compared with those of a cogeneration engine. Results are shown in table 1, where it can be seen that microturbines reduce CO emissions in 44% lower and NOₓ emissions in 83%.

**BIOGAS BIOLOGICAL CLEANING SYSTEM (BBCS)**

Due to advantages of biotrickling filter for biogas cleaning, PROFACTOR technological centre has designed and built, in the MICROPHILOX project framework, a prototype for biological biogas cleaning (BBCS) for the removal of sulphide acid and siloxane based in this technology with the following objectives:

- H₂S concentration at the system outlet < 10 ppmv
- 50% reduction of siloxanes independently of siloxane concentration in inlet biogas.

Since the project started using results obtained in previous laboratory tests, it was needed to carry up an upscaling and eventually two prototypes with maximum flows of 15 m³/h for H₂S and 2 m³/h for siloxanes were obtained.

The developed system was installed in a standard container of 2,44x9,09x2,89 m³ (HxLxW) and consisted of two biotrickling filters connected in series (Figure 9). Desulfuration takes place in the first column, while in the second column biogas siloxanes are removed. Microorganisms in charge of contaminant degradation are fed with oxygen and with an NPK aqueous solution which contains necessary nutrients for the metabolic reaction. In the case of the H₂S biofilter, oxygen is added to the nutrient solution by a bubble column, being this the main technological innovation of the system. For siloxane biofilter microorganisms, oxygen is directly injected to the biogas flow. Values for pH were fixed between 5 and 6 and it is regulated through the addition of NaOH, which is stored in an annexed vessel.

All the system has been designed to work in an autonomous way thanks to the connection of the equipment to a PLC and to the control software developed that also allows remote operation of the BBCS.
The biological biogas cleaning system was in operation in the Orís landfill for nine months. During this period, both biofilters were studied. H$_2$S removal efficiencies reached values up to 95% and it was demonstrated that in order to maintain these values a stable biogas flow is necessary, avoiding, as far as possible, biogas or electricity cuts.

On the other hand, the removal goal for siloxane biological cleaning couldn’t be achieved, being much different of those results initially obtained in laboratory tests. Reasons that led to these bad results can be attributed to the following reasons:

- Short residence times of biogas in the biofilter
- Different compounds in the landfill gas are possibly easier biological degradable than siloxanes.
- Low solubility in water of siloxanes.

With the aim of improving initial results, some laboratory tests were carried out using tensioactives, but when they were applied to the Orís biofilter, again results were not what was expected and it was no possible to increase water solubility of siloxanes and therefore cleaning efficiencies weren’t improved.

In relation to siloxane biological biofilter, studies will continue in order to improve the prototype operation, since laboratory tests showed good results in biological siloxane degradation.
METHODOLOGY FOR THE ANALYSIS AND CAPTURE OF SILOXANES

The participation of IQS and PEINUSA in the MICROPHILOX project has consisted in the development of a study of present methods for capture and analyses of siloxanes in landfill biogas, with the objective of obtaining an appropriate sampling and analysis methodology, both for simple and continuous testing.

The first part of the work was an exhaustive bibliographic research to identify different existing analysis techniques for the determination of siloxane concentration in air samples with the aim of evaluating which was the most appropriate for the study of the evolution of siloxane concentration in landfill biogas samples.

In a second stage, tests were carried out to evaluate the different siloxane capture methods previously detected: tedlar bags, liquid solvents (hexane and acetone) or solid adsorbents as activated carbon, graphite, divinylbenzene-stirene polymers and tenax. Obtained results allowed concluding that the use of solid adsorbents was the most effective and simplest method. Therefore, siloxane sampling would consist of retaining siloxanes in solid adsorbents using activated carbon tubes.

Once siloxanes have been concentrated in the activated carbon tubes, procedure involves desorption using hexane and an analysis by means of chromatographic methods. Different tests were carried out using two different techniques: HRGC-FID and HRGC-MS in SCAN and SIM mode and combining SCAN and SIM. HRGC-MS (SCAN/SIM) technique allowed obtaining necessary selectivity for the detection of siloxane in a complex biogas matrix. For the estimation of the concentration of siloxane in this kind of samples it was concluded that HRGC-MS(SIM) analysis was enough precise and exact.
In order to optimize and validate developed analyses procedures, solutions of siloxanes in hexane, laboratory prepared synthetic siloxane samples in air and biogas samples from three different landfills were used. Once the procedure for siloxane sampling and qualitative and quantitative analysis was developed and validated, then IQS-PEINUSA proceeded to analyse real biogas samples obtained from three different landfills located in: Orís, Palautordera and Hostalets de Pierola. The objective was to determine the variability of siloxane concentration in different landfills and to complete the validation of the developed procedure with samples of different origins. Chromatographic profiles from the three localizations were very similar and showed a total of 80 peaks in SCAN mode. When analysed in SIM mode, once free of interferences, they allowed to identify and quantify peaks corresponding to the five siloxanes which are present in biogas. The total siloxane content in biogas from Orís landfill was between 8 and 12 mg/m³.

The siloxane content in the biogas from the three analysed landfill changed in one magnitude order between 8 and 80 mg/m³. The D4 compound proportion was about 50% of the total siloxane content. L2 compound represents between 27% and 32% of the total, and the sum of D3 and D5 represents between 12 and 19% of the total. L3 represents about 2% of the global content. L4 and L5 were only detected in one of the landfills, in particular in the one which showed more siloxane concentration.

The last phase of the project consisted on the definition and implementation of a continuous system for siloxane control. In the initial project planning, it was thought that this system would be based in mass spectrophotometry technique. This method coupled to a gas chromatograph is what is normally used in laboratories. This is a sensible and selective method, but at the same time expensive and complex. These are some of the reasons why the installation in a landfill of an on-line system for an exhaustive and continuous follow-up of siloxane concentration in biogas is so complicated.
ECONOMICAL ENVIRONMENTAL STUDY

In order to evaluate economical and environmental costs or revenues of the technology developed in the MICROPHILOX project it has been carried out a study where four different scenarios were analysed:

- **Scenario 1**: represents the situation in the Orís landfill before the project, where all biogas was flared.
- **Scenario 2**: part of the landfill biogas is used in two Capstone C30 microturbines, but without a previous upgrading system. This case, on one hand, represents those exploitations where due to optimum quality of biogas it is not necessary to upgrade it, and on the other hand, the analysis of this scenario wants to evaluate what is more favorable, biogas cleaning or using it without upgrading but with higher maintenance costs.
- **Scenario 3**: represents the situation that we have had in Oris during the project, using an activated carbon filter for the biogas cleaning previous to the entrance of fuel in the microturbines.
- **Scenario 4**: it is the technical solution proposed in the MICROPHILOX project, where the activated carbon filter is replaced by a biofilter for \( \text{H}_2\text{S} \) and siloxane removal. This is a theoretical situation due to the fact that nowadays, developed biofilter is a prototype and therefore used data for the economic-environmental study was obtained from the extrapolation of the project results.

Table 2. Economical Environmental costs for the different scenario analysed

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<tr>
<th>Impact</th>
<th>Scenario 1</th>
<th>Scenario 2</th>
<th>Scenario 3</th>
<th>Scenario 4</th>
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<tbody>
<tr>
<td>Benefit</td>
<td>- 7509 €</td>
<td>13 685 €</td>
<td>21 694 €</td>
<td>21 827 €</td>
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The most important conclusion from this study is that, in spite of the fact that private benefits could be rather small or even negative when biogas is used for energy generation, good results are clearly achieved regarding environmental issues, when biogas is used for energy generation. That is to say in Scenarios 2, 3 and 4. Comparisons between these three cases indicate that best results are obtained for scenarios where biogas is upgraded before its use in microturbines. In particular, highest benefits are obtained for Scenario 4, where biofilter is used. This implies that when an industrial biological biofilter is installed, scale economies are expected to appear (that is, reductions in costs linked to the size of the plant). The main reason is that investment costs could be reduced, and therefore final benefits should increase.

Rather bad results are obtained for Scenario 1, where all biogas is flared. This scenario represents the minimum exigencies that are demanded in regulations. So, although infrastructure costs are higher when biogas recovery equipments are considered, net benefits improve.

CONCLUSIONS

The MICROPHILOX project allowed to demonstrate that microturbines are a feasible technology for the generation of power and heat from landfill biogas, being the best alternative for the energy recovery in landfills with low biogas flow or with biogas with low methane content.

In relation to biogas upgrading, developed prototypes reached cleaning efficiencies up to 95% in the \( \text{H}_2\text{S} \) removal process. Nevertheless, it is necessary to continue the analysis of siloxane biofilters, since obtained efficiencies didn’t achieve expected results.

Another result of the project was the obtention of a reliable and repeatable methodology for the capture and analyses of siloxanes in landfill biogas consisting of an adsorption using activated tubes, desorption with hexane and HGRC-MS (SIM/SCAN) analysis procedure.

The technological interest as well as the technical quality of this process were acknowledged with several prizes, in a national and international framework, as the ones granted by Garrigues Medio Ambiente y Expansión to the most brilliant enterprise initiative 2006 in the category of Innovation, development and application of best technologies, the Energy Globe Award 2006 and the prize Bionergia Silver 2008 granted by ATEGRUS.