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Title: Analysis of damage caused by siloxanes in stationary reciprocating internal combustion engines operating with landfill gas

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Abstract: Failures in reciprocating internal combustion engines operating with landfill gas are not uncommon. In general, damage is located in the combustion chamber surfaces and in the ring grooves, where a layer of non-volatile combustion products is deposited. These deposits attached to the surfaces reduce heat transfer and increase inner temperature, which produces a knocking phenomena damaging the crank bearings and fusing of the piston head material. Lubrication problems also appear due to the formation of a layer of soft paste silicone deposits in the rings grooves, which increases friction losses and accelerates wear on cylinder and rings.

In this paper, some typical examples of damaged engines are presented. The deposits found were analysed using Scanning Electron Microscope and Energy Dispersive X-ray Spectroscopy (SEM-EDX). Additionally, the engine oil used was also analysed by Infra-Red Spectrometry (IR) and the results were compared with known organo-compounds. A method to detect incipient failure caused by organo-compounds contained in landfill gas is introduced.

Silica appears in the layers covering the combustion chamber, as well as silicone compound in the top cylinder zone, piston and ring grooves. Damage is associated with siloxanes (organo-silicon compounds) contained in the landfill gas, which decompose in the combustion chamber, generating silicic acid and formaldehyde under the high temperature conditions throughout the combustion processes.

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As suggested by the editor a throughout revision of the paper has been carried out and the comments of the reviewer has been 100 % included in the current version of the manuscript. All changes on the original version of the manuscript appear in red in the current version.

The reviewer commented the first half of manuscript, but his recommendations have been extended to the whole manuscript.

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The new Research Highlights according the magazine rules has been uploaded.

Yours sincerely

Jesus Alvarez-Florez

Highlights

The main types of damage found in ICE using landfill gas have been studied

Combustion of fuel with siloxanes produces two types of residues

Residues attach to combustion chamber surfaces reducing the heat transfer

Residues also attach to piston ring grooves causing lubrication problems

A method to prevent damage based in engine oil IR analysis is presented

“Analysis of damage caused by siloxanes in stationary reciprocating internal combustion engines operating with landfill gas”

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ABSTRACT

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1. Introduction

Reciprocating internal combustion engines (RICE) are used in some power plants to transform the chemical energy contained in gas fuels into mechanical energy for running electrical generators with acceptable brake specific fuel consumption and reliability, and also providing useful heat for application in other industrial processes, thus increasing the overall efficiency of the cogeneration plant. Depending on the kind of fuel used, RICE can be classified into two groups, one operating under the Diesel concept and another operating under the Otto concept. Engines used in landfill plants are of the Otto type. Their designs have been changing for the last 20 years to adapt to the characteristics of the new gas fuels.

Landfill gas (LG), natural gas (NG), low heating value gases and natural gas-hydrogen mixtures are the new fuels commonly used in these types of power plants. The composition of these new

gas fuels fluctuates due to different reasons [1]. Consequently the RICE used require capacity to operate with the variations in the chemical composition of these new fuels [2].

A typical landfill gas power plant is composed of many extraction wells with pipes which merge into a common gas collector. The gas of this collector is cleaned and pumped to be used as fuel in RICE, or burned in a torch. The landfill gas is a major source of air pollution if it is allowed to escape to the atmosphere; the methane contained within is a powerful greenhouse gas, according to the Intergovernmental Panel on Climate Change (IPCC), the methane global-warming potential (GWP) index, in reference to carbon dioxide, is 34 times more over 100 years [3], although its lifetime is 12.4 years. Today, the mandatory Directive 2009/28/EC in Europe is aimed at a share of 20% of energy produced from renewable sources in 2020. Accordingly, US regulations set a target of 25% for the energy generated from renewable sources in 2025.

The landfill gas, obtained basically in Municipal Solid Wastes (MSW), is generated during the anaerobic decomposition of organic substances. The MSW contains about 150-250 kg of organic carbon per ton of waste, which is converted to landfill gas by micro-organisms via anaerobic processes. The landfill gas generated, with 40-60% methane, has an average heating value of 17765kJ/Nm^3 . With an energy conversion efficiency of 34% the electric energy produced is of 2.5kWh/Nm^3 approximately [4].

The main factors that affect landfill gas quantities generated are: Waste composition, humidity content, temperature, age of landfill, and others [5]. The gas production starts one to two years after the waste is deposited in the landfill and lasts 15-25 years. The continuously decreasing gas volume can be compensated by the disposal of additional waste during this period. As an example, Table 1 shows the variation in the main components of a typical landfill gas.

Component	Composition (by volume)
Methane (CH_4)	40-60%
Carbon dioxide (CO_2)	35-50%
Nitrogen (N_2) / Sulphur / NMOCs	5-25%
Oxygen (O_2)	0-3%
Water vapour	Saturated

Table 1.- Range of the main landfill gas components, including Non-Methane Organic Compounds (NMOCs)

However the gas obtained is not clean and contains other minor components such as hydrogen sulphide, organic silicon compounds (siloxanes) and others, that can be dangerous when found in the landfill gas used as fuel [6,7]. Siloxane compounds decompose under high temperature levels in the combustion chamber [8,9], and the landfill gas must be analysed because a small quantity of siloxanes can cause severe damage to the engines when deposited over a longer period [10,11]. Consequently some engine manufacturers recommend siloxane limits in landfill gas in order to ensure the maintenance operations are not dependent on the siloxane levels [12].

When landfill gas is used as fuel, the engine design and the operating parameters are established according to the Otto concept. The efficiency and reliability of engines in these power plants are

important issues. For good efficiency the compression ratio has to be as high as possible, but not too high, in order to keep combustion knocking under control. Consequently, in landfill gas engines, if the compression ratio is too high the knock combustion mode can appear, in the same way as in engines using natural gas and hydrogen mixtures [13,14].

Landfill gas engines are Diesel engines that have been adapted with a thermodynamic cycle changed from the Diesel to the Otto concept. This requires important changes in all aspects, in the mechanical design, in the hardware and software of the control systems, in the oil engine and lubrication system, in the cooling system, and other subsystems. For safe operation of the engine, the regulation and control systems need to be intelligent in order to adapt the engine to possible fluctuations in the fuel characteristics and in the chemical composition. Neural networks, genetic algorithms, fuzzy logic and other mathematic procedures can be used for that purpose [15]. These changes have been improved thanks to the maintenance process and the analysis of failures. This information has been very important in order to adapt step by step the design and the engine operation conditions according to the gas fuel used.

The combustion chamber is designed to improve the thermodynamic efficiency. It operates with a lean mixture fuel/air ratio and it has a special ignition system because the mixture, at the moment of ignition, is heterogeneously distributed, from stoichiometric between spark plug electrodes to very poor on the combustion chamber end. The engine also has a high turbulent pre-chamber on the piston head as well as pipes with a geometry designed to generate turbulence. In order to stabilize the output power it may be necessary to introduce some devices with the aim of adjusting the fuel/air ratio mixture and the gas flow rate as used in biomass and other low heating value gases power plants. This device can compensate the variations of the mixture with time.

When the combustion chamber is covered with a layer of silicates, heat transfer is reduced and the consequences over time are:

- Increase of combustion knocking mode conditions.
- Possible heating of surface with incandescent points producing ignition without control.
- Fused material on piston head as a consequence to the two points indicated previously.
- Mechanical problems in the cylinders, as a result of silica layer detachment, causing longitudinal scratches.

2. Main types of damage

Damage appears basically in the combustion chamber parts, and in the crankshaft and connecting rod bearings of the reciprocating mechanism, as is shown in Figure 1. The most typical types of damage are introduced and discussed in the next paragraphs in which an engine of 16 cylinders in V and 56.30 litres of swept volume are analysed using information obtained during the inspection process in the maintenance period.

Figures 2 to 4 correspond to the engine damaged by siloxanes, in which several kinds of symptoms were presented before the corrective maintenance operation, such as increased consumptions of fuel and oil, increased exhaust gas temperature, mechanical problems from exhaust valve crack, instability above certain power output caused by spark plugs, and others.

In this engine, each cylinder has a bore of 160 mm, a stroke of 175 mm and the compression ratio is 11.7:1. The engine has capacity to operate with lean burn (λ 1.6) and landfill gas fuel of 4500 - 5500 kcal/nm³, producing an electrical power output of 985 kW at 1200 rpm.

Figure 1.- Sketch of a RICE with indication of the damaged parts typically damaged by combustion of landfill gas.

In Figure 2, a typical cylinder head with damage can be observed; layers of solid deposits are formed on the combustion chamber surface, around the plate valves. All cylinder head surfaces appear covered with a deposit layer, including plate valves, the Figure 2 was taken after manipulation by samples extraction process, and so some zones appear, in the photo, without deposit layer. The deposit thickness was 0.1 to 0.3 mm and its texture was extremely brittle and, in consequence, broken easily off the surface.

Figure 2.- Picture of typical RICE head cylinder with dirty surface

In Figure 3, a cylinder with damage is shown. Soft paste like deposits is deposited on the top of the cylinder, on the expansion side, along 80 mm in diameter direction and 100 mm along the length axis liner approximately. Scratched zones can also be observed in the same expansion side liner surface.

Figure 3.- Cylinder liner with soft paste and scratches along the liner.

In Figure 4, the state of the piston surface and of its piston rings blocked by the soft paste deposits in ring grooves can be observed. Some fused material from the self-piston on the piston head can also be seen. Under these conditions, the engine operates without the rings movement in the grooves, causing bad lubrication conditions, consequently the temperature rises in the piston head, increasing the size of the piston until it causes contact with the cylinder surface, producing the scratches.

If the engine works under these conditions it is possible that a local bad combustion process will appear in the combustion chamber (Knocking), causing a very high temperature rise in the zone, leading to the fusion of the material.

Figure 4.- Dirty piston with soft paste deposits and damage on the head by fused material.

In Figure 5 a piston from other stationary engine is shown, in which serious damage can be seen in the piston head, due to the long term bad combustion with knocking, as well as fused material from the piston head and re-solidified between the piston and the cylinder surface. If the engine is running under these conditions, serious damage can be produced in other parts of the engine, like the crankshaft bearings.

Figure 5.- Piston with large fused areas in the piston head and with piston rings blocked.

If in the landfill gas used there are insufficiently filtered silica particles, strong erosion on the rotor blades of the compressor appears, as can be seen in Figure 6. The most affected part is the tip of the blades in front of the diffuser channel, where the maximum flow velocity is achieved.

Figure 6.- Rotor blades of the compressor with severe erosion damage.

3. Analytical procedure used to determine the damage origin.

In order to determine the origin of the deposits appearing in the internal surfaces of the engine, several samples of deposits have been extracted, by scraping-off from the damaged parts and analysed by Scanning Electron Microscope and Energy Dispersive X-ray Spectroscopy (SEM-EDX) using a Jeol (JSM-5610, Japan). Additionally, the engine oil used has also been analysed using Infra-Red Spectrometry in which the chemical structure was characterized with a Perking Elmer Fourier Transform Infrared (FTIR) using optical Perking Elmer software. The line scan spectra were based on 32 scans and a resolution of 4 cm^{-1} .

a. Damage in cylinder head

All 16 cylinder heads presented the same deposits, and in order to understand the origin of the damage caused by deposits it is shown in the Figure 2, small samples were extracted as shown in Figure 2. The samples were taken from one of the cylinder heads of the combustion chamber, near to the spark plug zone.

Analysing the material that appeared in the combustion chamber surface using SEM-EDX, silica compounds were found. In Table 2 the results of the analysis can be observed. The theoretical O/Si mass rate in the silicates unit $(\text{SiO}_4)^{4-}$ is of 2.278; analysing the O/Si ratios indicated in table 2 obtained from the samples analysis, it can be concluded that the silica layer on the cylinder head surface is an orthosilicate form.

Sample	O	Si	S	Ca	Fe	Ratio O/Si
A	35.90	21.38	4.36	7.76	23.96	1.67
B	45.34	19.44	8.43	14.93	8.16	2.33
C	45.37	18.42	5.36	10.72	1.56	2.46

Table 2.- Weight percentage of the elements contained in the sample of the deposit appeared on the cylinder head.

b. Damage in cylinder liner, pistons and piston rings

The roughness of the cylinder surface is very important for the lubrication process between piston and cylinder because it retains the oil, but if the soft paste deposits are present, lubrication is made impossible, because the oil engine is not present on the cylinder surface. The axial movement of piston rings inside their grooves is also very important in order to pump oil to this point of the engine, but if the soft paste deposits are present, the lubrication processes are worse.

The samples of soft paste deposits were taken from the piston near to the 3rd ring, the deposits observed in the cylinder liner, pistons and pistons ring grooves are the same.

In Figure 7 it can be seen, 25 times magnified, how the soft paste deposit occupies, in the left image area, an important part of the surface instead of oil. The results of the analysis indicating the chemical elements detected and quantified by EDX are shown in table 3.

Soft deposit samples were extracted from the 3rd piston ring groove zone for SEM-EDX analysis. To determine the composition of this soft paste deposit, different combinations of the components obtained are analysed: First the O/Si ratios are considered (Table 3). Because the theoretical mass rate in the silicon dioxide SiO_2 , is 1.14, this soft paste deposit would be silicon dioxide. However the texture of this deposit is not the same.

Refining the analysis, if O/Si/C ratios are considered, as shown in table 4, we could consider the possibility that the analysed sample may contain the methylsiloxane unit $[(\text{Me}_2\text{SiO})_x]$ as a base compound of the new silicone deposit form.

Fig. 7.- Soft paste accumulated in the piston rings zone (left) in SEM image magnified 25 times.

Sample	C	O	Si	S	Ca	Fe	Ratio O/Si
General	6.78	15.82	13.29	4.79	7.58	43.03	1.19
Local	14.61	18.04	22.88	11.31	18.71	6.23	0.79

Table 3.- Weight percentage of the elements contained in the soft paste extracted from upper part of cylinder surface.

Sample	O/Si Ratio	O/C Ratio	Si/C Ratio
General	1.19	2.33	1.96
Local	0.79	1.23	1.56
methylsiloxane unit [(Me ₂ SiO) _x]	1.14	1.14	1

Table 4.- Mass ratios O/Si, O/C, Si/C from weight percentage of elements in soft paste sample extracted from the cylinder surface, present on the piston surface and also in the piston ring grooves, and compared with theoretical ratios to the methylsiloxane unit [(Me₂SiO)_x].

The discrepancies between O/Si, O/C and Si/C ratios in the sample in comparison with methyl siloxane unit can be explained as the oil components contributing in deposit formation. Hence, carbon in the deposit can also originate from the oil, not only from siloxane.

Concluding, the results of the analysis deposits are that the solid layer that appeared on the combustion chamber surfaces is an orthosilicate, and the soft paste deposits on the cylinder, the piston surfaces and the piston ring grooves can be a silicone deposit, but another more accurate method of chemical analysis should be applied in order to confirm this first approach. Hence both deposits located inside the engine are probably formed by silica atoms.

4. Discussion

Only in the landfill gas used as fuel, silica atoms can appear in combination with other elements; the most common organosilicon compounds in landfill gas are siloxanes.

Table 5 shows the landfill gas compounds detected in one installation operating without new siloxane removal technologies [20], [21] and [22], and in which the gas is only cleaned with the dehumidifiers, the cyclones, the particle filters at different points and also with cooling-heating processes.

Name	Formula	PM (g/mol)	% Si in weigh	Measure compound in landfill gas mg/m3
Hexametil-di-siloxano (L2)	$C_6H_{18}OSi_2$	162.2	34.7%	2.05-6.80
Hexametil-ciclo-tri-siloxano (D3)	$C_6H_{18}O_3Si_3$	222.3	37.9 %	0-1.90
Octometil-ciclo-tetra-siloxano (D4)	$C_8H_{24}O_4Si_4$	296.4	37.9 %	10-17
Decametil-ciclo-penta-siloxano (D5)	$C_{10}H_{30}O_5Si_5$	444.6	37.9 %	2.40-3.01

Table 5: Compounds in landfill gas measured and some its properties.

It is possible to verify that the Octa-methyl-cyclo-tetra-siloxane (D4) is the most important compound contained in the landfill gas used. This organosilicon-compound was the cause of damage in the engine components presented.

Origin of the Siloxanes found in fuel and their decomposition in the combustion chamber.

The “Siloxane” word expresses a chemical compound molecules group and the word origin is the sum of the syllables **Sil**(icon), **Ox**(igen) and (Meth)**ane**. The siloxanes can be classified into two main groups, depending on the structure formed by the unit $[(Me_2SiO)_x]$:

- Molecules with linear structure (L2÷L4)
- Molecules with cyclic structure (D3÷D6)

The D4 (Octa-methyl-cyclo-tetra-siloxane) is much used in different applications such as a base product in cosmetic, and in the manufacture of silicones. One example is the polydimethyl-siloxane (PDMS) which is the silicone type most used in industrial and domestic applications [16]. The main characteristics of the D4 in normal conditions are: a molecular weight of 296.6 g/mol; a density in liquid state of 0.956 kg/l; a fusion temperature of 17-18 °C; and a gasification temperature of 175-176 °C. In Figure 8 the molecule structure is shown.

Fig. 8.- Octa-methyl-cyclo-tetra-siloxane (D4), $C_8H_{24}O_4Si_4$, (OCMTS)

The anaerobic decomposition of the silicones existing in the landfill produce Siloxanes as the OMCTS (the most common), the Dimethyl Silanediol $CH_3)_2-Si-(OH)_2$ (DMSD) and other organo-silicon-compounds. Only volatile siloxanes are detected in the landfill biogas; the non-volatile siloxanes exist but cannot be taken into account because their vapour pressure is very low [16]. This is the main reason why the siloxanes appear in landfill gas in different quantities. Actually it is very important to measure the siloxane quantities correctly, using the adequate procedures [17-19], so that the best reduction processes can be established. Several technologies to clean the gas like adsorption, absorption, deep chilling, biological removal, catalytic processes, membranes, or other methods can be used [20,21].

The siloxanes are decomposed during the combustion process inside the engine in which the temperature rise is around 3000 °C and the combustion chamber pressure rise is around 15 MPa; under these conditions two new and aggressive products appeared:

- Formaldehyde (CH_2O)
- Orthosilicic acid (H_4SiO_4) which is the most common silicic acid generated [8,9].

All the mentioned problems were basically originated by the formaldehyde chemical activity. Above -19.5°C formaldehyde is a very chemically active gas. It is a polymerizer of methane and engine oil, producing the soft paste that appeared inside the engine. The second compound mentioned, resulting from the combustion process, is silicic acid, which it is solid under 1704°C and it is very reactive, like formaldehyde. It is possible to form silicates with different shapes and structures, in solid the deposits form as solid layers appearing on the combustion chamber surfaces.

As has been indicated, siloxanes should be removed or reduced to avoid problems and damage in the engine.

The most-used new siloxane removal technologies are: the adsorption on fixed bed, the adsorption on a fluidized bed and the absorption and gas chilling. Other less-developed methods, like the biological methods, the catalytic processes and cleaning by membranes [20-22] are also appearing on the market.

Action of the Siloxanes inside the engine

The solid deposits on the combustion chamber surfaces are the result of the thermal decomposition of the siloxanes contained in fuel. Orthosilicic acid (H_4SiO_4) can be produced during the combustion process.

Under the high temperature of the combustion chamber, chemical reactions between some fuel components and some engine fluids may occur. For instance, the engine oil present in the combustion chamber surfaces can interact in the top of the cylinder with the siloxanes thermal decomposition compounds (formaldehyde and orthosilicic acid), producing deposits. These soft pastes also appear on the piston surface and in the piston ring grooves.

It can be confirmed that soft paste is due to the chemical reaction of the formaldehyde acting with the engine oil or with methane contained in fuel. The conclusion regarding the soft paste appearing inside the engine is that it is a silicone form, polymerized by formaldehyde chemical action with either the methane contained in fuel, with the engine oil or with both together.

Siloxane decomposition inside the combustion chamber under high temperature affects the engine oil, consequently the analysis of the engine oil can be an interesting method to recognize the contamination level of the engine and correlate it with the potential damage.

5 Engine oil IR analysis as a siloxane detection method.

The presence of siloxanes in fuel can be assessed by a detailed analysis of the paraffinic engine oil taking into account the following procedure: first, comparing the engine oil before and after working in the engine; second, comparing the engine oil used with another engine oil based on silicone compound. In Figure 9, the results of the new and used engine oil analysis using infrared absorption spectrophotometry method (IR) can be seen. The two absorbance spectra of both oils can be observed; the main components of the spectra are in the 3000-2500 cm^{-1} band and in the 1500-1300 cm^{-1} band wave numbers. Within these bands the spectral structure is very similar; however there are significant differences outside them, especially in the 1300-1000 cm^{-1} band.

Fig. 9: Comparison between infrared absorption spectra corresponding to the engine oil without use inside the engine, and paraffinic mineral base unused oil sample

In order to clarify these differences, the absorption spectra of the used oil are compared with the Silopren E 3078. The Silopren E 3078 is an additive compound based on silicone. It can be seen in Figure 10 how different the Silopren E 3078 spectra are in comparison with the engine oil used in the engine, except in the 1090 - 1020 cm^{-1} band. The main component of the Silopren E 3078 is the $[(\text{CH}_3)_2\text{SiO}]_x$ which is characterized by two strong bands in different spectral positions of 1090 and 1020 cm^{-1} with similar absorbance amplitude [23-25]. Therefore it can be concluded that the mineral engine oil used was contaminated with the organ-silicon compound with a polydimethyl siloxane structure $[(\text{CH}_3)_2\text{SiO}]_x$.

Fig. 10: Peaks detected corresponding to cyclic tetramers compounds $[(\text{CH}_3)_2\text{SiO}]_x$

4 Conclusions

In stationary Reciprocating Internal Combustion Engines (RICE) operating with landfill gas in power plants some failures can occur due to the organo-silicon compounds (L_n and D_n) contained in this fuel.

The types of failures detected in these power plants are located in:

- The combustion chamber surface temperature increases as a consequence of silica layer deposits on all the surfaces, favouring the knocking or ignition without control and fused material from the piston head if the engine works for a long time.
- The roughness of the cylinder is occupied by the soft paste deposits instead of the engine oil, if the engine works under these conditions the cylinder-piston lubrication is worse, causing scratches on the cylinder surfaces or even seizure.

- The piston rings are immobilized because the soft paste deposits detected are inside the grooves, so the engine oil does not reach the liner and consequently the engine can seize.

The analysis of failures in several engines shows damage in different elements of the engine always as a consequence of the two kinds of deposits detected:

- Solid thin layers deposits in the combustion chamber on all the surfaces.
- Soft paste deposits located in the top of the cylinder and pistons as well as in the piston ring grooves.

Samples have been extracted from the damaged parts and analysed by Scanning Electron Microscope and Energy Dispersive X-ray Spectroscopy (SEM-EDX). Additionally, the engine oil used has been analysed using Infra-Red Spectrometry (IR). The results of the analysis determine that the silica layer on combustion chamber surfaces is an orthosilicate form, and the soft paste deposit is, probably, a new silicone form.

The analysis of the landfill gas shows siloxanes, basically D4, and these decompose inside the combustion chamber under high temperature into formaldehyde and silicic acid. These components are very active, especially the formaldehyde, and react with:

- The engine oil present on the cylinder and piston surfaces, and
- The methane contained in the landfill gas inside the combustion chamber.

The siloxanes present in the landfill gas need to be removed or reduced under certain levels, but for more safety monitoring the engine oil absorption spectra between 1090 and 1020 cm^{-1} can be used as a tool to predict possible damage.

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