APPLICATION NOTES

No. WED6/93

Information from the Application Engineers at Waukesha Engine/Waukesha Power Systems

EFFECTS OF GASEOUS SILICON COMPOUNDS IN THE FUEL OF SPARK–IGNITED ENGINES

INTRODUCTION

Landfill and digester gas fuels are composed primarily of methane (CH_4) and carbon dioxide (CO_2). In addition to these two components, there are usually small concentrations of "trace" gases, some of which can cause major problems within an engine.

For example, digester gas frequently contains hydrogen sulfide (H_2S). Small concentrations of hydrogen sulfide can ultimately create enough sulfuric acid in the lube oil to cause catastrophic engine bearing failure.

Similarly, landfill gas typically contains trace amounts of halogenated hydrocarbons. The chlorines and flourines within these compounds can also cause catastrophic bearing failure within a very short period of engine operation.

While both hydrogen sulfide and halogenated hydrocarbons have been identified and recognized for some time now, there is now another trace gas beginning to show itself as a potential nuisance within bio–gas fuels: gaseous silicon compounds, also known as "siloxanes".

SILOXANES

The name siloxane is derived from **sil**icon + **ox**ygen + methane. It refers to compounds containing alternate silicon and oxygen atoms in either a linear or cyclic arrangement, usually with two organic (carbon + hydrogen) groups attached to each silicon. Two examples of siloxanes are shown in Figure 1.

These substances are also known as polysiloxanes, organosiloxanes, organosilicons, or silicones. For simplicity, the term "siloxane" will be used throughout this Application Note when referring to this family of compounds.

Siloxanes are used quite heavily in "down–the–drain" products such as shampoos, deodorants, cosmetics, and medicine. These siloxanes enter a wastewater treatment plant as part of the liquid influent, then change to a gas during the digester process.

Siloxane compounds are also used in lubricants, hydraulic fluids, inks, paper, polishes, and water–proofing agents. In conjunction with sub–microscopic particles of sand (silicon dioxide), it is obvious that an engine operating on landfill gas can also ingest considerable amounts of silicon–based compounds.

SILOXANES IN THE COMBUSTION CHAMBER

Unlike hydrogen sulfide or halogenated hydrocarbons, siloxanes will not react with water to create an acid in the fuel system or lube oil. Rather, the problems with siloxanes involve the formation of deposits within an engine's combustion chambers.

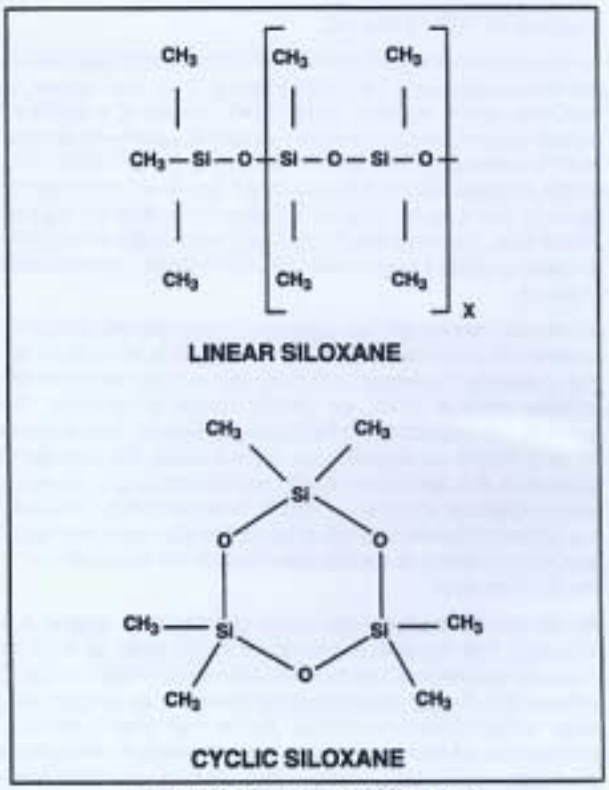

Figure 1. Examples of Siloxanes

During combustion in a gaseous–fueled engine, the high temperatures and pressures in the combustion chamber cause the siloxane molecule to "come apart". The carbon + hydrogen organic group is then free to burn, leaving behind the individual silicon and oxygen atoms. These two elements are highly unstable on their own, and will thus combine to form silicon dioxide (SiO_2), also known as "silica" or "sand".

If the siloxane concentration in the fuel is great enough, the silicon dioxide can form significant deposits on cylinder heads, exhaust valves, spark plugs, and gas admission valves. These deposits generally take on a fine, white, powdery appearance, but have also been seen as either a glaze–like coating or a ceramic–like coating.

Experience has shown that lean–burn engines tend to have more difficulties with deposit formation than stoichiometric ("rich–burn") engines. This is due to the more intricate fuel system componentry typical to lean–burn engines. These difficulties generally occur in the small–diameter passage ways and/or

close-tolerance componentry, which are more susceptible to blockage from accumulated silica deposits.

The presence of excess oxygen in the combustion chamber of a lean burn engine may actually promote the formation of silica deposits, as there is an excess oxygen supply for the silicon to react with to form SiO_2.

Siloxane-related deposits can also be found downstream of the combustion chamber, especially in exhaust manifolds and the exhaust heat recovery unit (if equipped). Catalytic converters have also been found to be masked by silicon dioxide deposits.

Because of the numerous trace gases found in bio-gas fuels, sites experiencing chronic deposit-related problems should have a laboratory analysis conducted on the deposit to determine the major constituents (silicon, iron oxide, ash, sulfur, etc.).

SILICON IN THE LUBE OIL

Some of the silicon dioxide formed in the combustion chamber will get into the lube oil via the blow-by gases. Thus, it is common to have high levels of silicon in the used lube oil of a landfill or digester gas engine. These silicon levels will typically range from 10 to 50 ppm, sometimes reaching as high as 100 ppm depending on the concentration of siloxane in the fuel and the number of hours on the lube oil. Experience has shown that this type of silicon does not cause accelerated wear rates within the engine, as these particles are extremely fine and relatively non-abrasive in nature.

It should be noted that while siloxane-derived silicons in the lube oil generally do not cause accelerated wear rates, the same is not true of silicons originating from other sources (i.e., sand and dirt entering through faulty air intake/filtration equipment). For example: although 20 ppm of siloxane-derived silicon in the lube oil of a landfill or digester gas engine would be considered acceptable, this same level caused by ingested sand or dirt would cause significant abrasive damage to oil-wetted parts. Therefore, it is important that the lube oil analysis monitor both wear metals and silicon levels to insure that the silicons in the lube oil are not of the abrasive type.

As bio-gas fuels often have many obscure trace gases, it is advisable that engines operating on these types of fuels be regularly monitored for combustion chamber condition, so as to prevent any deposit-related engine damage (i.e., cylinder liner wear, valve recession/deposits, piston ring groove deposits, prechamber deposits, etc.). Likewise, oil-wetted components (bearings, camshafts, gears, etc.) should be periodically examined for any signs of accelerated abrasive wear or acid attack. This monitoring should continue until it is apparent that siloxanes or other contaminants in the fuel are within reasonable levels.

MEASURING SILOXANE CONTENT IN A FUEL

In the past, measurement for silicon-bearing compounds in a gas involved only two specific siloxane compounds: octamethyl-cyclotetrasiloxane (or "OMC") and decamethyl-cyclopenta-siloxane (or "DMC"). Recent advancements have been made in an attempt to measure all silicon-bearing compounds in a gas.

In simple terms, the present measurement of siloxane is conducted by passing a specified volume of bio-gas fuel through either a condenser or adsorbing desiccant. The liquid condensate or desiccant is then sent to a laboratory to be analyzed for silicon content. In reality, this measurement is complex and awkward. Efforts are now underway to greatly improve the sampling, shipping, and lab analysis techniques for total silicon measurement.

Experience has shown that the siloxane concentration of a bio-gas fuel can fluctuate significantly from day to day. Therefore, several samplings may be required to establish an average level.

Specific details regarding the methods, costs, and guidelines relative to quantitative analysis of total silicon compounds are rapidly changing. Contact the Waukesha Application Engineering Department for updated information regarding the measurement of siloxane content in a fuel.

RECOMMENDATIONS WHEN FUEL CONTAINS SILOXANE

1. Field surveys have shown that sites utilizing refrigeration dryers have less fuel-related problems than those without these devices. A properly sized refrigeration dryer will condense most of the water out of a bio-gas fuel, simultaneously removing some of the siloxanes, H_2S, and halogenated hydrocarbons along with the water. For this reason, the use of a refrigeration dryer sized to produce a fuel pressure-dewpoint below 40° F (4° C) is required for all landfill, digester, and other bio-gas fuel applications.
2. For lean-burn engines with pre-chamber fuel systems, the use of commercial quality natural gas as the prechamber fuel will reduce the likelihood of silicon deposits on the prechamber components.

SUMMARY

Siloxane compounds are undesirable trace gases often found in landfill and digester fuels. Their presence is detectable through both fuel and lube oil analysis. Although the effects of siloxanes on lube oil quality are not as severe as those caused by hydrogen sulfide or halogenated hydrocarbons, problems due to silicon deposits formed in the combustion chamber may require fuel treatment such as refrigeration dehydration or commercial quality natural gas fueled prechamber systems.

For further information regarding the operation of Waukesha Engines on bio-gas fuels, see the latest version of the following literature:

Landfill Gas Fuel Treatment Systems, Application Note WED 10/90, Waukesha Engine Division Technical Data Book.

Guidelines for Landfill Gas Use in Waukesha Gas Engines, SDBC 1100.

Gaseous Fuel Specification, S-7884-C, Waukesha Engine Division Technical Data Book.

Engine Lubrication Oil Recommendations, S-1015Y, Waukesha Engine Division Technical Data Book.

Operating with Alternate Fuels, Waukesha Maintainer, Volume 14, Issue 2, 1992.

Jon Jeffords
Application Engineer

Waukesha

WAUKESHA ENGINE DIVISION
DRESSER INDUSTRIES, INC.
WAUKESHA, WISCONSIN 53188

APPLICATION NOTES