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Shell Introduces a New Long Life Lubricant for Engines Burning Sour

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Part 1

Abstract

Shell Lubricants is introducing into the market, a new member to the Mysella range of Gas Engine Lubricants. The new product, currently named Shell Mysella S5 S, has been especially formulated for gas engines running on all types of biogas, including gas produced from biomass or manure, sewage gas and landfill gas.

In this paper Shell will present findings of the research that has been executed during its development. The paper describes the challenges that different qualities of biogas impose on the engine and the lubricating oil. It describes what properties a lubricating oil for biogas operation should ideally have, and different formulation routes to achieve these.

The performance of different candidate formulations is presented in the form of field trial results, where the focus is on:

1) Extension of oil life, by looking at the candidate's resistance to oxidation and its ability to neutralize acids from the combustion gas.
2) Improved engine protection, by minimizing deposit formation tendency and maximising engine cleanliness.

Finally this paper explains which candidate has been chosen to become the new Shell Mysella S5 S and how the performance of this oil will help the operator to reduce cost of operations.

1. Introduction

Organic material can be used as a source of combustible gas. In an oxygen free environment the organic material is digested by bacteria that produce a gas consisting of methane, CO2 and various trace constituents.

Many types of organic material can be used to produce gas, including organic waste. Most common examples are: gas from agricultural biomass, gas from livestock manure, gas from sewage cleaning sites, and gas from landfill sites. These types of gas are collectively called biogas. Biogas is a renewable fuel. Biogas can be suitably converted into electricity with the help of a gas engine. The gas engine has a relatively high single cycle efficiency, typically >40%, and a relatively low level of harmful exhaust gas emissions. The gas engine has proven to run reliably on different qualities of biogas, although with certain biogas qualities the engine requires more maintenance than the same engine running on natural gas.

The success of gas engines in biogas applications is illustrated by the large number of installations in operation already. In 2007 one of the leading suppliers of biogas engines, GEJenbacher, reported to have installed more than 1450 biogas systems in agricultural applications and 1300 systems in landfill gas applications, totalling more than 2200 MW of electrical capacity (ref 1). Several sources on the internet predict a large growth in the coming decades (ref 2, ref 3).

The lubricating oil in a gas engine burning biogas is often more stressed than the same oil in the same engine running on natural gas. The additional stress is caused by the trace contaminants present in the biogas. Dependent on the source of the biogas, it may contain acidic compounds. These compounds can corrode engine components if not neutralized by alkaline additives in the lubricating oil. Because of the consumption of these additives, the oil in a biogas engine needs to be more frequently changed than the oil in an engine burning natural gas.
Other contaminants such as siloxanes have a direct influence on deposit formation in the engine's combustion chamber. In order to control the total level of deposits, the lubricant's own contribution to deposit formation should be minimized. It is therefore beneficial if the lubricant is able to prevent formation of ash deposits as much as possible.

In order to serve the increasing market of biogas engine operators better, Shell Lubricants is introducing a new lubricating oil for biogas engines Shell Mysella S5 S.

This paper describes the challenges that different qualities of biogas impose on the engine and the lubricating oil. It describes what properties a lubricating oil for biogas operation should ideally have, and different formulation routes to achieve these. The paper will compare the performance of different candidate formulations, and explain how the new oil will help the operator to reduce cost of operations.

2. Challenges when operating an engine on biogas

Biogas from anaerobic digestion consists of methane (CH_4) and carbon dioxide (CO_2) and a number of trace compounds. There are three particular challenges related to the combustion of biogas in gas engines:

2.1. Presence of acidic compounds in the fuel gas

Biogas may contain acid producing species such as hydrogen sulphide (H_2S), hydrogen fluoride (HF) and hydrogen chloride (HCl). The H_2S is found in all types of biogas, but especially in biogas produced from agricultural material, manure and sewage, whereas HF and HCl are typically found in landfill gas.

After combustion and in combination with water these species can form sulphuric acid (H_2SO_4), hydrofluoric acid (HF) and hydrochloric acid (HCl). These are highly corrosive to engine components such as liners, piston rings, piston ring grooves and bearings, and must be neutralized by the lubricating oil before doing any harm. For this reason, the lubricating oil contains alkaline additives that will react with the acids when they get into contact with the oil film before they can reach metal surfaces. Because of this neutralization reaction, the alkaline additives in the oil are being consumed whilst the oil is in service, and the oil needs to be changed when the alkaline additives have been depleted.

The alkalinity reserve of a lubricating oil is represented by its base number (BN). Since every engine burns a small amount of lubricating oil, and since many types of alkaline additives are ash producing when burnt, they contribute to the formation of ash deposits in the combustion chamber. For this reason, the engine manufacturers (collectively called OEMs in this paper) limit the amount of ash producing additives in the lubricating oil. Most OEMs limit the ash to 0.6%, such oils are called low ash oils. Some OEMs allow oils with up to 1.0% ash, such oils are called medium ash oils.

Because of the limited amount of alkaline additives in the fresh lubricating oil, the achievable life time of a given oil is highly dependent on the amount of acidic species in the fuel gas.

2.2. Presence of siloxanes in the fuel gas

A siloxane is a (gaseous) hydrocarbon molecule with a silicon (Si) atom in it. Siloxanes are typically found in sewage gas and in landfill gas.

When combusted, the silicon atom is joined with oxygen atoms to form silicon dioxide (SiO_2), the chemical formula of sand and glass. The silicon dioxide is being formed in the combustion chamber, and deposited on the surfaces in the combustion chamber, such as the piston crown, the cylinder head flame bottom and the valve discs. An example of severedeposits originating from siloxanes is given in figure 1.

Figure 1. *Severe deposits originating from siloxanes on the piston crown.*

Potential consequences are:

- The deposits on piston crown and on the valve disc reduce the clearance between these components, and there is the risk that valve and piston crown touch each other.
- As a result of the deposits, the compression ratio increases, which can promote detonation (also called knocking).
- Because of the chemical composition, the deposits are very hard and abrasive. They also have a different coefficient of thermal expansion from metal. As a result of temperature changes, parts of the deposit layer will break off from the surface of piston and cylinder head. These parts may get trapped between ring and liner where they are ground and contribute to high wear rate of these components. This is demonstrated in figure 2.

Figure 2. *Abrasive wear caused by silicon dioxide deposits ground between rings and liner.*

2.3. Presence of other contaminants in the fuel gas

There can be other contaminants in the fuel gas, varying from ammonia (e.g. typically present in biogas from livestock manure) to arsenic. Ammonia can potentially attack the non-ferrous metals of the bearings.

2.4. Gas cleaning

Technologies have been introduced to remove contaminants from the biogas. Because these technologies are still relatively new, they are quite expensive to install and operate. Therefore the vast majority of the installations runs without such systems.

3. Factors limiting oil life in biogas engines

A finished lubricating oil consists of a base oil and selection of additives. Base oils exist in a large variety of qualities, ranging from refinery streams that have received basic treatment, to severely hydro treated streams to fully synthetic fluids. With the help of additives, the lubricating oil manufacturer tries to enhance, suppress or complement certain properties of the base oil. A finished lubricant is therefore a unique combination of base oil and carefully selected additives, designed to provide specific performance attributes that should help the end user to achieve best value for money.

When the oil is in service, its properties will change as a result of degradation processes. These are:

- Oxidation: this is the chemical reaction of the hydrocarbon molecules from the base oil with oxygen. As a result of this reaction weak acids are formed as well as polymerization products.
- Nitration: this is the chemical reaction of the hydrocarbon molecules from the base oil with nitrogen oxides (NOx). As a result of this reaction weak acids are formed as well as polymerization products.
- Reduction of alkalinity reserve, as indicated by a reduction of the base number (BN) of the oil. BN depletion is normally caused by the neutralization of the acidic products of the oxidation and nitration reactions. However if the fuel gas contains acidic species, which is often the case with biogas, then this will accelerate the depletion of BN.
- Increase of the concentration of acids in the oil. Although most acids formed by oxidation and nitration reactions are neutralized by the alkaline additives in the oil, some acids are so weak that they do not react with these additives. Because of their weakness, and as long as their concentration is not too high, these acids are not harmful to engine (bearing) metals either.

The total acid number (TAN) can be used as an indicator of acids in the oil, where one should realize that even a fresh oil will yield a TAN value when tested, even if there are no acids present at all. The concentration of acids is therefore best represented by the difference between the TAN of the used oil and the TAN of the fresh oil.

An additional measure is the ipH number that describes the strength of the acids accumulated in the lubricating oil.

- Increase of the viscosity of the oil. This is mainly caused by the polymerization products formed during the oxidation and nitration reactions.
- Increased level of contaminants in the oil, such as Si, water, soot, other insolubles, etc.

It is good practice to take regular oil samples. Analysis of these samples will then indicate oil condition, the rate of oil deterioration and will help to determine safe oil drain intervals. This is even more important in biogas applications as fuel quality can vary significantly over time.

Also oil analysis can detect premature wear processes in the engine, notably bearing wear, and cooling water leakage, and can therefore provide additional safety and peace of mind for the operator.

The criteria for oil rejection that Shell applies for this development project are:

- Oxidation by FTIR in abs/cm: maximum 20
- Nitration by FTIR in abs/cm: maximum 20
- BN (ASTM D2896) in mg KOH/g: minimum 50% of fresh oil BN
- TAN (ASTM D664) in mg KOH/g: maximum 3 increase over fresh oil TAN
- iPh (GE-Jenbacher method): minimum 4
- Viscosity at 100 °C in mm2/s: SAE40: min 12.0 or max 17.5

A discussion about allowable levels of contaminants is beyond the scope of this paper. But there is one exception: silicon (Si). Accumulation of Si in the lube oil is always seen at plants where siloxanes are present in the fuel gas. Sometimes customers use Si as a criterion for oil drain. Several customers have seen a correlation between Si in oil and engine wear rate. This is correct: the correlation is there, but it is not a causal correlation. Both are a consequence of high siloxanes in the fuel.

If the oil filtering arrangements in the plant are correct, so that particles are being removed, any Si reported in the lube oil is in principle harmless. Although some OEMs limit Si in used oil to 300 ppm, others explicitly state that the Si content of used oil has no limit (ref 4).

4. Lubricating oil formulation routes

Based on the above, Shell Lubricants have defined the following targets for the newly developed lubricant for gas engines burning biogas:

- Suitable for biogas from any source, including biomass, manure, sewage and landfill.
- Able to handle the contaminants that these different types of biogas may contain.
- Ash content to be compliant with latest OEM requirements.
- Significantly longer oil life than internal and external benchmarks, where the internal benchmark is Shell Mysella MA.
- Highest level of engine protection at given fuel quality.
- Suitable for use in engines equipped with exhaust gas catalyst.

The lubricants technology team at Shell's Marine and Power Innovation Centre in Hamburg has been tasked with formulating the new oil. The following approach has been used to develop a series of candidate formulations:

- Retardation of oxidation and nitration processes. Slower oxidation directly contributes to longer oil life. In addition however, less BN will be required to neutralize the acids that are the result of the oxidation/nitration reactions, and more BN will be available to neutralise acidic compounds from the fuel gas. This also contributes to longer oil life.
- As high as possible BN, in order to maximize the alkalinity reserve of the oil and extend oil life on gases that contain acidic species.
- Minimise the contribution of oil to deposit formation, by limiting the ash producing additives to 0.6% and by applying a base oil and additive combination that is highly resistant to oxidation and carbonization.

For this reason the candidate oils have been formulated with severely processed Grp II base oils. This has also been recognized by one of the leading OEMs who explicitly prefers Grp II based lubricants for their engines running on biogas (ref 5).

In this paper we will compare three of the candidate formulations, each of them based on a distinctly different additive technology. Table 1 provides the main characteristics of these three formulations and of the internal benchmark Shell Mysella MA (Oil E):

	Benchmark oil	Oil C	Oil D	Oil E
Base oil	Grp I	Grp II	Grp II	Grp II
BN	8.5	7.1	8.8	5.3
Sulphated ash	0.9%	0.50%	0.50%	0.57%

Table 1. *Main characteristics of three candidate oils compared with internal benchmark.*

From these characteristics, Oil D looks most attractive because of its high BN in combination with low ash. The table also shows that the BN in Oil C and Oil D is provided by additives that produce less ash than the BN additives in Oil E.

5. Experience in the field

Following laboratory bench tests and in-house engine tests, the candidate oils have been tested in the field. Trial engine was a GE-Jenbacher J312 GSC21 installed on a landfill site.
The installation was not equipped with fuel gas cleaning, but the fuel acidity was relatively mild. An exhaust gas cleaning catalyst was installed. Details of the installation are given in Appendix 1.

Figure 3. *Test site.*

5.1. Comparison of oil life of the candidate oils

The results of the oil analysis results are presented in appendix 2. The two most important charts are replicated here in figure 4 and 5, and show the oxidation and BN trends of the three candidate oils.

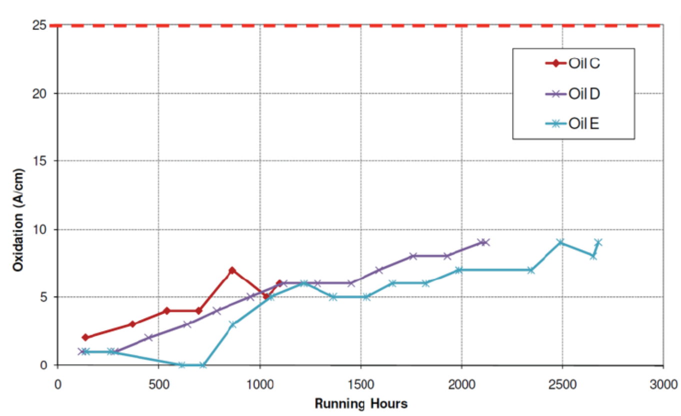

Figure 4. *Oxidation trends of three candidate oils.*

The rate of oil oxidation, which is leading over the nitration in this lean burn engine, is very similar for the three candidate oils. Even after 2000 running hours the oxidation is below 10, which proves the excellent oxidative stability of the candidates.

__PART 2__ in the next edition of Lube Magazine, February 2015