



CH₄ CAN BE WORTH SO MUCH MORE

THE ROLE OF OIL ANALYSIS IN GAS ENGINE RELIABILITY (PART 2)

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In Technical Bulletin 60, we looked at the various laboratory techniques used to detect abnormal wear and contaminants in gas engine oils and the relevance thereof.

In this final instalment, we will look at what oil analysis can measure in terms of the third function of oil analysis, which is to detect oil degradation.

Oil is the lifeblood of any mechanical system and as such has many functions to perform. These functions can be categorised into four fundamental groups: reduction of wear, removal of contaminants, removal of heat and acting as a structural material. All these functions are negatively impacted if the oil physically or chemically degrades.



A Jenbacher JMS312 GS-BL engine powered by biogas derived from the anaerobic digestion of fruit waste. Courtesy of Clark Energy

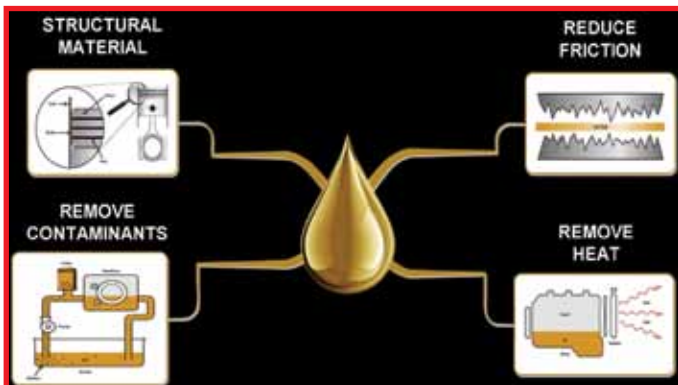
As already mentioned, gas engine oils need to withstand the various levels of oil degradation caused by the gas fuel combustion process. This is even more important in applications where fuel quality can vary significantly over time, such as gas engines running on biogas.

Due to these variations in fuel quality, it is vitally important that oil samples be taken regularly to assess the oil's condition, rate of deterioration and ultimately determine the optimal oil drain intervals.

The most widely used and OEM-requested laboratory techniques for detecting oil degradation will be discussed below.

KV (KINEMATIC VISCOSITY)

Kinematic viscosity is defined as a fluid's resistance to flow under gravity, at a specified temperature and this in turn determines the thickness of the oil film that prevents contact between metal surfaces. KV is measured in centistokes (cSt) and is typically reported at 40°C (KV40) and 100°C (KV100) for gas engine oil analysis.



The main functions of a lubricant

All the functions that an oil has to perform, as listed at the beginning of this Technical Bulletin, are negatively impacted if the viscosity of the oil falls outside of the intended viscosity range i.e. too high or too low. If the viscosity is not correct for the load, the oil film cannot be adequately established at the friction point. Heat and contamination are not carried away at the proper rates, and the oil cannot sufficiently protect the component. A lubricant with the improper viscosity will lead to overheating, accelerated wear, and ultimately failure of the component. It is for this reason that viscosity is considered the most important physical property of a lubricant.

The viscosity readings obtained are compared with the viscosity specifications of the new oil as defined by

the lubricant manufacturer. Trending of viscosity data is important as deviations from the norm may indicate base oil degradation, additive depletion or the use of an incorrect lubricant.

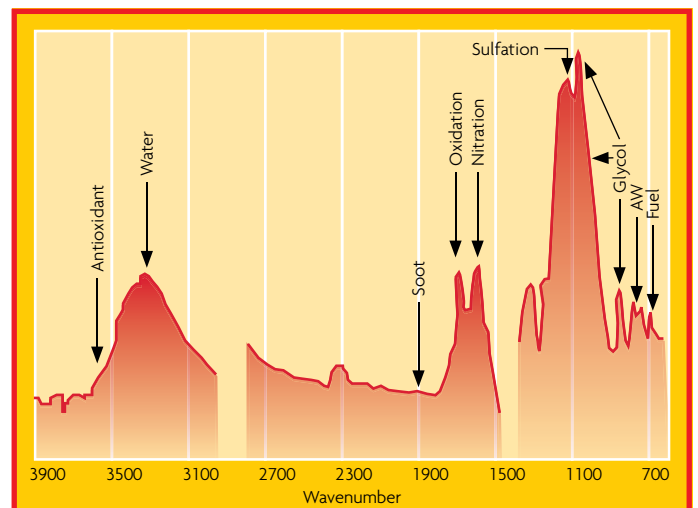
When the oil's viscosity increases, it is usually due to the presence of insoluble polymerisation products formed as a result of oxidation or nitration, high operating temperatures, the presence of water, the presence of other oxidation catalysts or the addition of an incorrect lubricant.

Decreases in oil viscosity are attributed to degradation of the viscosity index improver (VII) additive in multigrade oils or due to the use of an incorrect lubricant during refilling and topping-up procedures. As gas engines burn gaseous fuel, there is no risk of a reduced viscosity as a result of fuel dilution. This of course does not apply to dual fuel applications where both gas and diesel can be utilised as a fuel source.

VI (VISCOSITY INDEX)

The VI characterises the effect of temperature on an oil's viscosity and is of particular importance in applications where operating temperatures vary significantly. The VI can change when the lubricant degrades (chemically "breaks down") or degradation by-products accumulate. The kinematic viscosities at 40°C and 100°C are used to calculate the viscosity index. In layman's terms, the higher the viscosity index value, the less the viscosity changes with a change in temperature.

FTIR (FOURIER TRANSFORM INFRARED)



FTIR spectrum showing oxidation and nitration peaks. Courtesy of Noria Corporation

FTIR analysis is a technique used to detect base oil degradation. Oxidation and nitration are modes of oil degradation measured by FTIR.

FTIR produces an infrared (IR) spectrum that is often referred to as the 'fingerprint' of the oil as it contains specific features of the chemical composition of the oil. The IR spectrum can be used to identify types of additives, trend oxidation and nitration by-products that could form as a result of high operating temperatures and thermal degradation. The FTIR can also be utilised as a screening test for glycol, fuel and water contamination.

The technique is based on the principle that infrared "light" is absorbed in very specific ways by different structures in organic molecules. Consequently, the FTIR is capable of detecting and identifying specific molecular structures even in a complex mixture like used engine oil.

OXIDATION

Oxidation is the reaction of oxygen with the hydrocarbon molecules in the engine oil. The rate of oxidation increases exponentially as temperature rises and with the presence of metallic contaminants. An increase of 10 degrees Celsius in the temperature of the oil effectively doubles the rate of oxidation. Iron- and copper-containing alloys in the engine act as catalysts for oxidation. Oxidation is typically the main contributor to sludge and varnish formation in gas engine oils.

Oxidation by-products form lacquer deposits, corrode metal parts and thicken the oil beyond its ability to lubricate efficiently. Most lubricants contain additives that inhibit the oxidation process but these additives are sacrificial in nature.

NITRATION

Nitration is a form of oil degradation that occurs when the oil reacts with gaseous nitrogen oxides (NOx) created during the combustion process in gas engines.

Nitration products, formed during combustion, are introduced into the oil via blow-by gases which leak past the compression rings and into the oil reservoir. These products, which are more commonly found in natural gas engine oils, are highly acidic, create deposits and also accelerate oil oxidation.

As a result, natural gas engine oils are designed to withstand various levels of oil degradation caused by the gas fuel

combustion process, which results in the accumulation of nitrogen oxides.

Since the rate of formation of NOx increases exponentially with temperature, gas engines can generate NOx concentrations high enough to cause severe nitration of the engine oil.

The rate of nitrogen oxides formed during combustion is also influenced by ambient air temperatures, spark timing, air-to-fuel ratio, engine load and oil temperature, to name a few.

If the oil is exposed to severe nitration conditions, the nitration products formed in the oil will cause the viscosity, acidity and insolubles to increase. This includes varnish in hot areas of the engine, and sludge in cooler areas of the engine which may lead to ring sticking and filter plugging, respectively.

The usefulness of FTIR in determining oxidation is dependent on the base oil used to formulate the lubricant. Synthetic lubricants often contain ester compounds which have a significant peak in the infrared spectra area where the oxidation level for mineral oils is measured.

For this reason it is important to not view FTIR results in isolation but instead to trend these results and view them in conjunction with other oil-related parameters like viscosity, TAN (Total Acid Number), TBN (Total Base Number) and ipH (Initial pH). Evaluating these parameters holistically will yield a more accurate assessment of the oil's condition and ability to withstand further degradation.

TBN (TOTAL BASE NUMBER)

One of the many functions an engine oil has to perform is to ensure appropriate corrosion protection for the engine's components. This is accomplished by blending alkaline additives into the oil which neutralise acids that are formed during the combustion process. These alkaline additives, like all additives, are sacrificial in nature, which means that as a result of this neutralisation reaction, the alkaline additives in the oil are being consumed.

The TBN is a measure of the oil's alkaline reserve and a decrease in the TBN would be an indication of additive depletion; in other words TBN measures the oil's ability to counteract acids.

The oil in an engine running on landfill gas is often more



TBN ASTM test methods

stressed than the same oil in an engine burning natural gas. The additional stress is caused by trace contaminants in the gas. Biogas – which includes landfill gas and sewage gas – contains corrosive hydrogen sulphide, which places more stress on the oil in terms of its ability to neutralise acids.

Hydrogen fluoride and hydrogen chloride are also typically found in landfill gas. After combustion and in the presence of water, these compounds can form sulphuric acid, hydrofluoric acid or hydrochloric acid, all of which are highly corrosive to engine components such as liners, piston rings, piston ring grooves and bearings. It is for this reason that monitoring the TBN is particularly important in biogas applications.

The TBN is also an essential element in establishing the optimal oil drain intervals since it indicates whether the additives are still capable of providing sufficient engine protection. Most gas engine manufacturers require the oil to be drained when its TBN reaches one-half or one-third its original value.

The American Society for Testing and Materials (ASTM) defines two methods for determining the TBN of an oil and it would be prudent to note that while these two test methods are, in essence, designed to measure the same thing, they do not necessarily yield the same results.

ASTM D2896 requires the use of a very strong acid (perchloric acid) for the test procedure. Perchloric acid will react with the TBN additives as well as weak bases and wear metals. It is for this reason that it is more commonly used for new oils. When ASTM D2896 is used to assess the TBN of a used oil, the wear metals and weak bases present in the oil will elevate the reading, resulting in an overestimation of the TBN.

As a result of this, many commercial oil analysis laboratories, in accordance with the ASTM, use ASTM D4739 to determine the TBN of used engine oils. In this method hydrochloric acid is used to neutralise the base components present in the oil, resulting in a more realistic assessment of the oil.

As per ASTM International ASTM D4739 – 11 (Book of Standards, Volume: 05.02) points 5.3.1, 5.3.2 and 5.3.4:

- 5.3.1 “...When the base number of the new oil is required as an expression of its manufactured quality, Test Method D2896 is preferred...”
- 5.3.2 “When the base number of in-service oil is required ASTM D4739 is preferred...”
- 5.3.4 “In ASTM Interlaboratory Crosscheck Programs for both new and used lubricants, historically Test Method D2896 gives a higher value for base number.”

TAN (TOTAL ACID NUMBER)

The TAN is a quantitative measure of acidic compounds in the oil that are generated as a consequence of oxidation and the formation of acidic degradation by-products as a result of burning natural and landfill gas.

The TAN is a measure of both weak and strong, organic and inorganic acids within the oil.

What should be noted, however, is that even an unused engine oil will yield a TAN value when tested, as a result of the inherent acidic properties that certain engine oil additives possess. As a result of this, the concentration of acids is best represented by the difference between the TAN of the used oil and that of the fresh oil.

The TAN of the new oil will vary based on the base oil and additive package. As the TAN value of the oil

increases, viscosity rises and the lubricating potential of the oil is compromised, ultimately leading to increased wear.

Very much like the TBN, TAN is also used as an indicator of oil serviceability. TAN is often used to establish optimum oil drain intervals for many types of industrial oils, particularly those used in gas engines, as an increased TAN is viewed as an indicator of nitration, oxidation and contamination.

NOW FOR THE NEW KID ON THE BLOCK, IPH (INITIAL PH)

TAN provides an indication of acid concentration, but not acid strength. As such, it cannot always be relied upon to provide a reliable indication of the corrosion potential of an oil.

To overcome this drawback, a new internationally applicable standard for determining the ipH of an oil

was adopted in June 2014 by the ASTM.

This new method is believed to provide an absolute measurement of the corrosive potential of used oil and subsequent over-base additives depletion.

The ipH value is considered an important parameter along with the TAN and TBN value, particularly for the evaluation of engine oils in biogas and landfill gas applications as it represents the strong acids in the oil which directly cause corrosion of engine components.

While TAN and TBN provide information on the overall content of acidic or alkaline compounds respectively, the ipH value allows the acidity to be qualitatively assessed.

This method can even be used to detect minor quantities of strong corrosive acids in oil, even if the TAN has not yet increased significantly.



The RULER instrument is operated here by senior laboratory technician Sheila Naidoo

RULER (REMAINING USEFUL LIFE EVALUATION ROUTINE)

A change in TBN, TAN or ipH is usually a lagging indicator of oxidation. Despite the validity of all of these measurements, the fact remains that they all reveal damage to the base oil after it has occurred. A preferable scenario would be to evaluate the oil's ability to resist further oxidation by measuring the anti-oxidant additive reserves, in essence, its remaining useful life. Oil oxidation is a series of chemical reactions both initiated and propagated by reactive chemicals (free-radicals) within the oil. As the oil degrades, a sequence of events occurs, each of which can be measured with oil analysis. At first, the anti-oxidant additive package depletes and then the base oil oxidises. The anti-oxidant additive is sacrificial – it is there to protect the base oil from oxidation. The most common antioxidant additives found in gas engine oils are phenolic inhibitors, aromatic amines and metal-containing additives like zinc-dialkyl-dithiophosphate.

RULER is a proactive technique used for measuring anti-oxidant depletion rates and calculating the remaining useful life of the oil. Working in the proactive domain, maintenance staff can perform a partial drain and fill or top-treat the oil to replenish the anti-oxidant concentration to avoid base oil degradation. Likewise,

for planning and scheduling purposes, RULER monitoring provides management with a significant forewarning of impending oil failure (assuming no intervention affects the chemistry of the oil), which allows the possibility of such a failure to be handled in a way that cost and impact on the organisation are minimised. It is for this reason that RULER analysis is ideally suited to monitoring gas engine oil degradation caused by exposure to elevated temperatures and oxidation. The rate of anti-oxidant depletion versus time (anti-oxidant depletion trend) can be monitored and used to predict the right oil change intervals.

The successful utilisation of gas engines for power generation will be dependent on several factors, some of which can be controlled and some of which cannot. The type and quality of maintenance practices employed by gas engine manufacturers or operators is a factor that can be controlled and condition monitoring techniques, like oil analysis, can facilitate the effective maintenance of gas engines and ultimately support the utilisation of this emerging form of power generation not only in South Africa but in the world.

The truth is that CH₄ can be worth so much more, and when managed properly, it does not have to cost the earth.

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