

Fluid Maintenance and Dissolved Gas Analysis for Ester-based Transformer Liquids

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Introduction

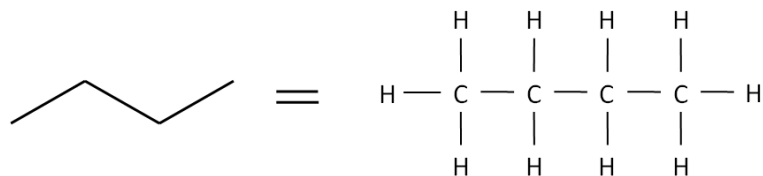
These days the use of ester-based transformer fluids as an alternative to mineral oil is on the increase. The environmental and fire benefits of these fluids are being realised by more and more users, which has led to esters being used in a wide range of transformers, even up to the 400kV transmission level. These larger power transformers are closely monitored to ensure their correct operation; this includes fluid testing, such as dissolved gas analysis.

There are some fundamental chemical differences between mineral oil and ester-based fluids and it is important for asset operators to understand how to monitor and maintain these liquids. This paper aims to give an overview of the key chemical differences between mineral oil and esters and advice on how these differences affect the correct maintenance of ester fluids, as well as providing a review of the ongoing research into the area of dissolved gas analysis

Chemistry of Fluids

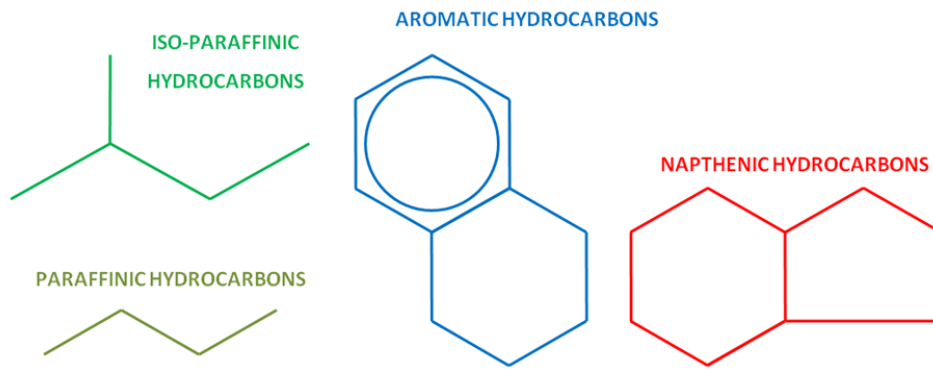
It is useful for non-chemists working within the electrical industry to know a little about chemistry in order to understand the differences between mineral oil and esters, which in turn have an influence on maintenance and DGA. To start with there is a short hand notation used by chemists to describe the molecular structure of substances. Figure 1 illustrates how this shorthand can be expanded into a longer form, showing the carbon and hydrogen elements and their bonds.

Figure 1 - Chemist's shorthand



Utilising this knowledge of chemical shorthand it is then possible to interpret the chemical structure of mineral oil, as shown in Figure 2. Mineral oil is essentially a mixture of hydrocarbon structures, being termed either paraffinic, iso-paraffinic or naphthenic depending on the dominant constituents. Oils with a high aromatic content tend to be used for cable and capacitor applications where gas absorption is important. For transformer applications aromatic content is kept lower, as this gives a good balance of properties. Polycyclic aromatic content, where multiple aromatic rings are bonded together, is kept well below 3% for health and safety reasons.

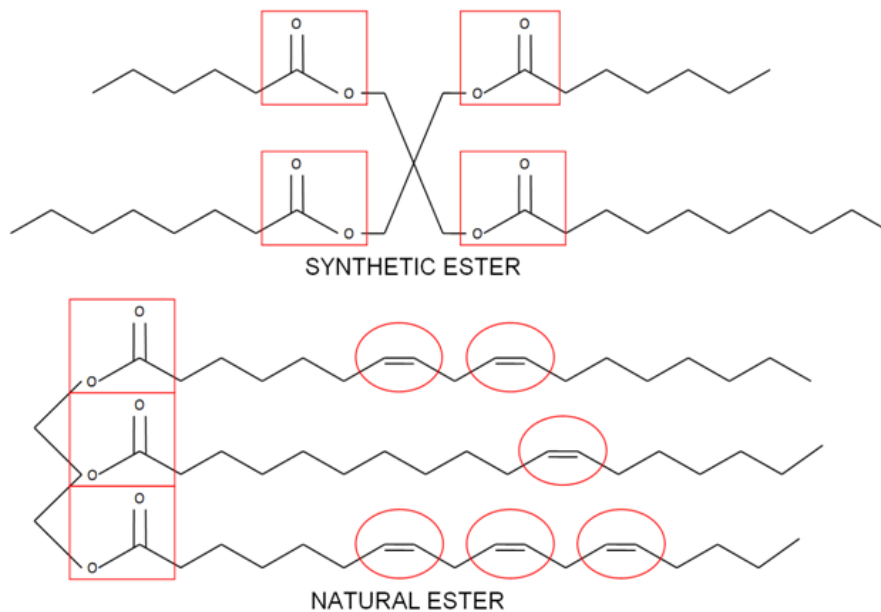
Figure 2 - Typical mineral oil structures



Within mineral oil there will be some small quantities of polar molecules, such as acids and ketones. These are removed during the manufacturing process, but will increase as the fluid ages. The presence of these polar molecular structures has a direct influence on parameters such as water solubility, tan delta and interfacial tension. Consequently, these parameters are monitored for mineral oil, but as will be discussed later they are less relevant to esters, as these fluids contain polar structures in their molecular structure.

Using the same shorthand notation it is possible to now look at the chemical structures of natural ester, otherwise known as triglycerides, and synthetic esters of the type typically used in transformers, shown in Figure 3.

Figure 3 - Typical chemical structure of ester molecules



There are some similarities with mineral oil, as esters can be largely composed of hydrocarbon chains. However, there are fundamental differences and it is important to focus on these areas to understand how to handle the different fluids and interpret laboratory data. The parts of the molecule structure in the square boxes are the ester linkages. In the case of the natural ester, the circled areas show the unsaturated carbon-carbon double bonds. The ester linkages are what give esters dielectric fluids some of their benefits, and also in the case of the double carbon-carbon bonds, some weakness.

The ester linkage is somewhat polar and this leads to attributes such as much higher water solubility, higher tan delta and lower volume resistivity, when compared to mineral oil. It also means that some parameters routinely monitored for mineral oil are less useful in assessing the condition of esters. For example there is no proven link between interfacial tension value and fluid condition in esters, despite this being a commonly used measurement for mineral oil.

It is the unsaturated double carbon-carbon bonds in natural ester that lead to a lower level of oxidation resistance, when compared to other fluids. Depending on the base seed oil the amount and type of unsaturated content will vary. Carbon chains with one double bond are known as mono-unsaturated, two double bonds di-unsaturated and three double bonds poly-unsaturated. Fluids with pre-dominantly mono-unsaturated content are known as high-oleic. Table 1 shows the proportions of unsaturated content for three common seed oils, of the type used in transformer fluids.

Table 1 - Fatty acid composition of natural esters [1]

Base Oil Type	Saturated	Mono- Unsaturated	Di- Unsaturated	Poly- Unsaturated
Soya Bean Oil	15	24	54	7
Canola Oil	6	62	22	10
High Oleic Sunflower	9	82	9	<1

These unsaturated links in the molecular structure are open to attack from oxygen and this will lead to increased viscosity and in the worst case polymerisation of the fluid into a solid. For this reason natural esters are only recommended for sealed equipment, without free access to oxygen from the air. As will be discussed later the unsaturated content of natural ester can also have an impact on DGA.

Water Interaction

The ester linkage is responsible for the very different interaction with water that ester fluids have when compared to mineral oil. This part of the molecular structure is somewhat polar, as is water. This leads to the possibility for water molecules to be attracted to esters, in an interaction known as hydrogen bonding. This gives esters a much higher moisture saturation limit and allows far higher dissolved water content without a detrimental impact on dielectric strength. In fact in electrical terms there is a strong link between relative water content of a fluid, as a percentage of the saturation limit, and the breakdown voltage. A fluid which has a relative water content of up to 20% will have good dielectric strength, as shown in Figure 4 and taking this 20% value as a maintenance limit it can be seen that the acceptable ppm water content for esters would be much higher than for mineral oil.

Figure 4 - Breakdown voltage vs. relative saturation for a number of fluids [2]

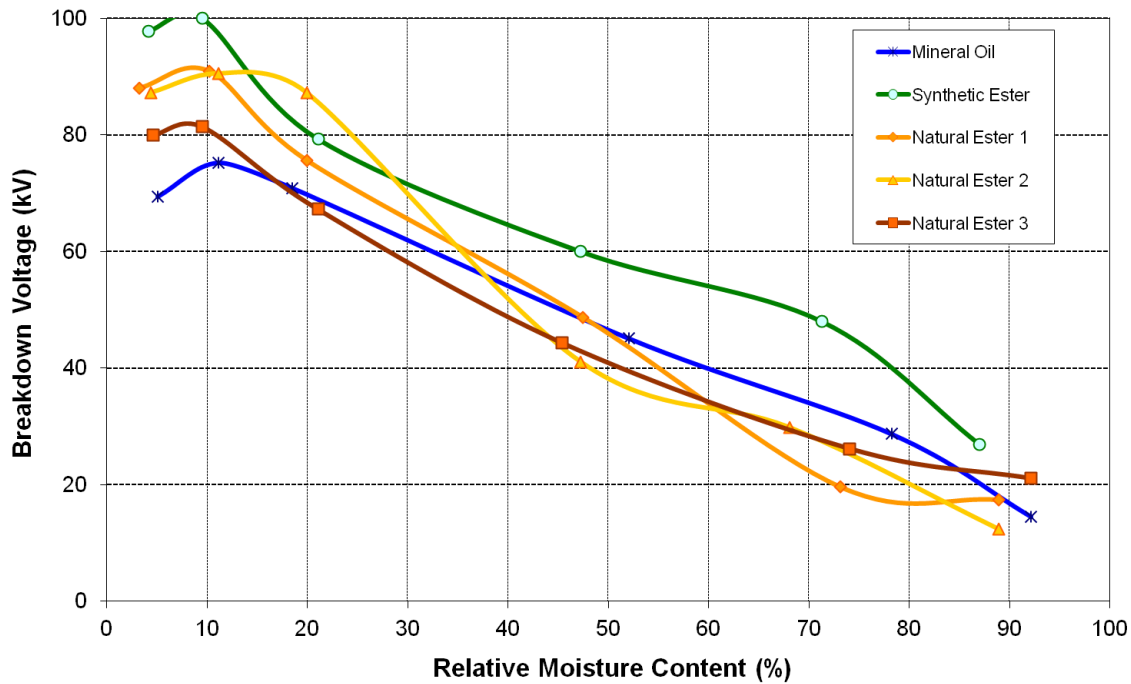


Table 2 - Water content in ppm at 20% relative humidity

Fluid Type	ppm value at 20% saturation	
	20°C	60°C
Mineral Oil	11	49
Natural Ester	218	379
Synthetic Ester	540	963

The IEEE C57.147 maintenance guide for natural esters[4] suggests that the relative water content of the fluid be maintained at the same level as mineral oil. In this case the ppm value limit can be calculated once the saturation limit is known, based on the fluid temperature. The IEC 61203 maintenance standard for synthetic ester[5] stipulates that in use water contents should be below 400ppm; however users have in the past stipulated higher acceptable values, based on the very high moisture saturation limit of this type of fluid.

Volume Resistivity

Another property closely related to the polar nature of the ester linkage is the DC volume resistivity of the fluid. Ester fluids have a DC volume resistivity which is typically an order of magnitude lower than that of mineral oil. This in itself does not affect the fluid's ability to operate as an effective AC dielectric, but what users will notice is that measurements of insulation resistance on a transformer filled with ester will be lower than would be expected for mineral oil. The magnitude of difference will depend on factors such as the volume of paper insulation and the dielectric structure.

Acid Limits

The type of acids produced by ester fluids when they age are somewhat different to those produced by mineral oil. These acids predominantly have longer chain lengths, meaning they have higher numbers of carbon atoms linked together. This in turn means that these acids are less water soluble than the shorter chain acids produced by mineral oil. Research has shown that these longer chain acids are less harmful to cellulose paper, which is a major limiter for transformer lifetime.[5] This phenomenon leads the IEC to propose that a higher level of acid can be accepted in esters during

operation than in mineral oil. Table 3 shows the acid content limits for the different fluids, with the relevant standards.

Table 3 - Acid content limits for in service fluid [5],[7]

Fluid Type	Mineral Oil	Synthetic Ester
Standard	IEC 60422	IEC 61203
In Service Acid Limit mg KOH/g	0.3	2.0

Dissolved Gas Analysis

DGA is one of the key methods used to monitor transformers in operation, to ensure that they are free from electrical and thermal faults. The rules and interpretation methods for DGA in mineral oil have been established over many years, using a large amount of data from transformers in the field. Since there is currently a lack of field based data for esters, especially from failed transformers, a large amount of laboratory work has been carried out directly comparing the behaviour of esters with mineral oil. These studies have shown that in the case of DGA there are differences between synthetic esters and natural esters. It has also become apparent that different natural esters will require adjustments in interpretation depending on the base vegetable oil used in their manufacture. This will make it important to ensure traceability and brings into question the validity of mixing different types of natural esters when applying methods such as DGA.

As discussed earlier, there are similarities between the chemical structure of esters and mineral oil, ie they both contain hydrocarbon chains. This means that the gasses esters produce during electrical and thermal faults are the same as for mineral oil, but the quantities and relative amounts are slightly different. The differences in the molecular structure do impact on the DGA for the different fluid types, mainly due to the ester linkage and the unsaturated bonding in natural esters.

DGA principles

Faults are typically broken down in four different categories when interpreting DGA results.

1. Partial discharge
2. Discharges of low energy
3. Discharges of high energy - arcing
4. Thermal faults

Category four for thermal faults is also subdivided into three temperature zones as follows

1. Thermal fault <300°C
2. Thermal fault 300°C – 700°C
3. Thermal fault >700°C

A lot of the advice provided for DGA with mineral oil still holds true with esters. It is best to look at trends of results, rather than one off measurements and if possible fleets of transformers should be compared to each other. All transformers will give some sort of normal gassing pattern; this could be anything from producing no gas at all, to having low levels of gas which accumulate over the lifetime of the unit. Having a number of units to compare simplifies DGA interpretation since it allows the user to look for outliers, which indicate faulty operation. High levels of gassing should always be investigated, especially for the gasses that indicate high temperature or high energy faults, such as acetylene.

Laboratory work has shown that the key gasses for each type of fault will also still broadly hold true for esters, as shown in Table 4. The ratios of the gasses will be different however and require adjustment to interpretation methods.

Table 4 - Key DGA gasses

Fault Category	Key Gasses
Partial Discharge	Hydrogen
Discharges of Low Energy	Hydrogen, Methane
Discharges of High Energy	Acetylene
Thermal Fault	Methane, Ethane, Ethylene

The key areas where esters really differ are in the interpretation of thermal fault temperature, the presence of carbon oxides and stray gassing of ethane. The solubility of gasses in esters is also somewhat different to mineral oil and the differences need to be taken into account for certain measurement methods.

Gas Solubility

The laboratory methods used for extracting and quantifying the different types of DGA gases with mineral oils are still valid for use with ester fluids. If using headspace methods of DGA it is also important to understand that gasses dissolve into esters in different proportions than in mineral oil. Solubility coefficients give an indication of how much gas can be dissolved into a liquid at normal atmospheric pressure. These have been evaluated by the Cigré WG32 group for DGA in alternative fluids; the results are shown in Table 5.

Table 5 - Gas solubility/partition coefficients at 20°C [8]

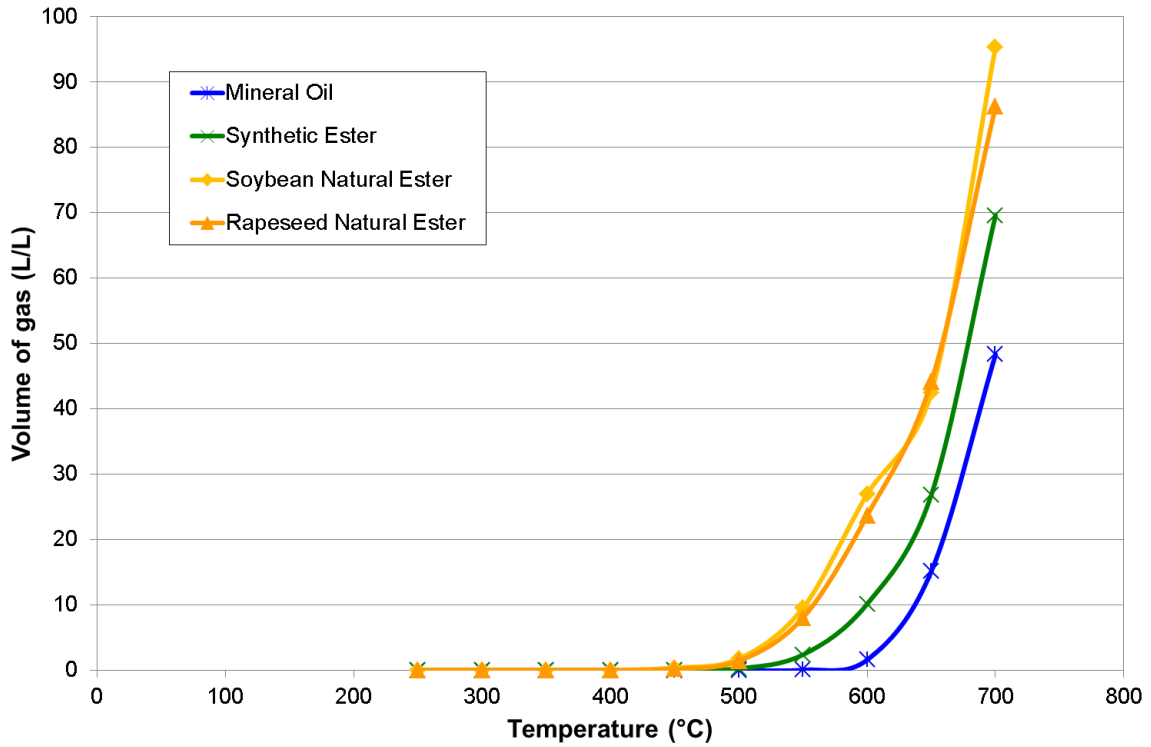
Gas Name	Gas Symbol	Mineral Oil	Synthetic Ester	Natural Ester
Nitrogen	N ₂	0.091	0.091	0.074
Oxygen	O ₂	0.172	0.152	0.134
Hydrogen	H ₂	0.0504	0.0479	0.0471
Methane	CH ₄	0.423	0.378	0.341
Ethane	C ₂ H ₆	2.88	2.20	2.14
Ethylene	C ₂ H ₄	1.81	1.85	1.67
Acetylene	C ₂ H ₂	1.25	4.26	2.58
Carbon Monoxide	CO	0.125	0.130	0.108
Carbon Dioxide	CO ₂	1.10	2.08	1.54

There are some differences in the solubility of gasses with esters, most notably acetylene and carbon dioxide, this means that if these gasses are produced during a fault larger quantities will be dissolved into the liquid. Even though these coefficients have been evaluated by the CIGRE working group WG32 they recommend using the calibration method in section 7.5.5.1 of IEC 60567 for head space measurement as this is believed to be the most reliable method.

Thermal Fault Interpretation

As part of the work to create the IEEE guidance for ester DGA, gas production under thermal stress was compared for synthetic ester, two different natural esters and mineral oil.[1][3] One ester was of the high-oleic type, which has a low level of poly-unsaturated content. The other natural ester was from a soyabean base, this natural ester has a higher level of di and polyunsaturated content. In this study the high temperature was applied for a period of eight hours and the total amount of gas evolved was calculated. The chart in figure 5 shows a comparison of the total gas for the three fluid types.

Figure 5 - Gas volume vs. temperature for mineral oil, synthetic ester and natural esters



It can be seen that the natural ester fluids started to produce significant volumes of gas at a lower temperature than synthetic ester and mineral oil. This was then followed by the synthetic ester, with mineral oil requiring the highest temperature. With the esters the predominant dissolved gas in the temperature range 400-600°C were carbon oxides, so these may need to be monitored more closely to give indication of faults that are below 600°C. Since these gasses are also produced by the normal ageing of cellulose insulation further work is needed to evaluate a method for this.

The work of the Cigré group looking at DGA in alternative fluids also concluded that the mixture of gasses is somewhat different in esters during thermal faults, leading to the need to modify the Duval triangle boundaries for esters. The updated Duval triangles for MIDEL 7131 synthetic ester, BIOTEMP natural ester and FR3 natural ester are shown in figures 6 and 7. [8]

Figure 6 - Modified Duval triangle for synthetic ester

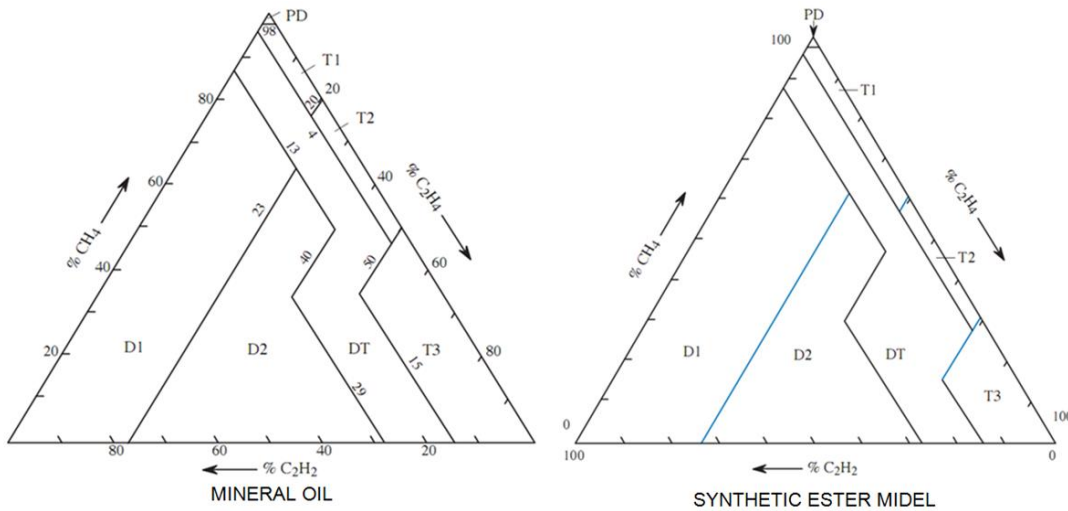
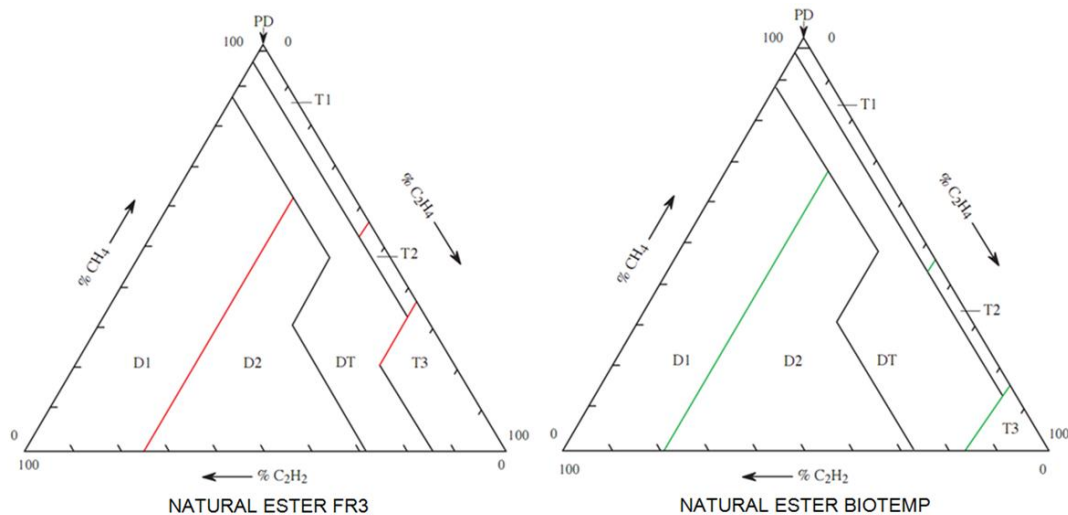


Figure 7 – Modified Duval triangles for natural esters

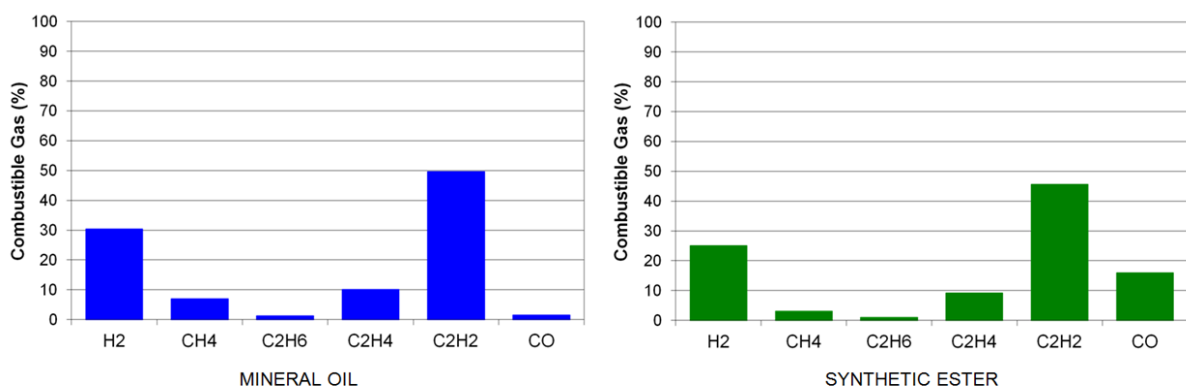


It is worth noting that the triangle for BIOTEMP, a high oleic oil, is somewhat different to FR3, despite these both being natural esters. This indicates that the base oil has an impact on the interpretation for this group of fluids. To take account of this difference the IEEE working group currently producing DGA guidance for ester fluids have proposed to split natural esters into two categories, high-oleic and low-oleic.

Carbon Oxides

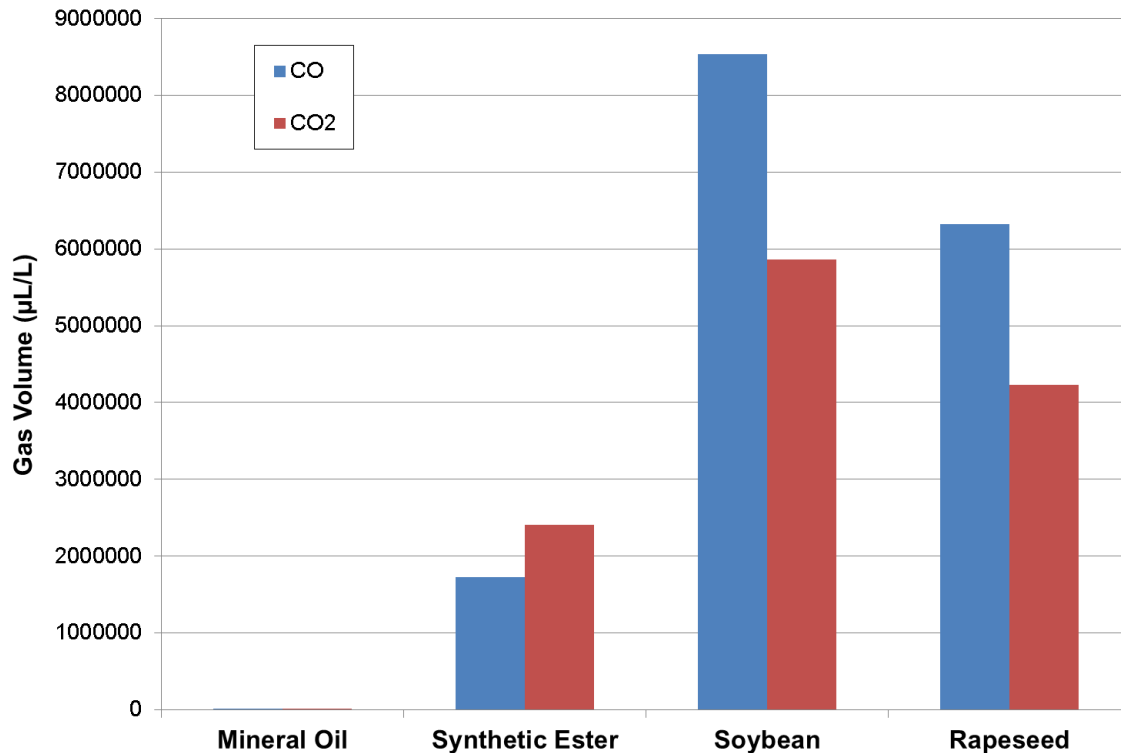
In mineral oil DGA the presence of high levels of carbon oxides is usually an indication of the involvement of cellulose paper in a fault. The ratio of CO to CO₂ is also used to try and interpret whether paper is involved when a thermal or electrical fault is indicated by other gasses. In esters this is somewhat complicated as several researchers have found that carbon oxides will form under electrical and thermal faults, even when no paper is present. An example of this is given in Figure 8, comparing synthetic ester and mineral oil under arcing conditions where the gas pattern is very similar, apart from the higher level of CO.

Figure 8 - Comparison of dissolved gas under fluid breakdown conditions



As mentioned previously studies with natural and synthetic esters which subjected the liquids to 600°C for 8 hours have also shown much higher levels of CO and CO₂ than mineral oil under the same conditions, as shown in Figure 9.[10][3] In this case the measured values of dissolved CO and CO₂ for mineral oil are so much lower they do not appear visible on the chart. The other point of note is that with natural ester fluids the level of CO is higher than the level of CO₂ and this is the reverse for mineral oil and synthetic ester. This means that the use of the CO₂/CO ratio may be less valid for natural ester fluids than for mineral oil when determining if a fault involves cellulose.

Figure 9 - Comparison of carbon oxide production under thermal stress



Looking back to the chemical structure of esters it is possible to see how carbon oxides are formed with these fluids, even in the absence of cellulose paper. The ester linkage contains oxygen atoms, not present in the mineral oil structure. In simple terms high energies can break the bonds between the carbon and oxygen atoms, allowing the recombination into carbon oxides, normally associated with paper degradation in mineral oil. This means that care needs to be taken when looking at carbon oxide numbers in ester DGA to infer whether paper is involved in a fault and it is unlikely that this will be a reliable indicator for paper involvement.

Stray Gassing in Different Natural Esters

It has been well reported that natural esters can produce ethane at moderate temperatures below 250°C, which may occur in localised hot spots and possibly during factory testing. This does not happen in either mineral oil or synthetic ester fluids and is thought to be related to the unsaturated content in the base oil.

This stray gassing phenomenon has been further investigated by researchers who have discovered that the type of base oil can have an influence on the amount of ethane produced. The results of one experiment comparing dissolved gas after a period of one day at an elevated temperature in the presence of oxygen. Table 6 shows the results from one experiment which exposed different seed oils to an elevated temperature over a period of one day. It is interesting to note that the level of ethane is significantly higher in the natural esters which have a higher polyunsaturated content. [10]

Table 6 - DGA results for various oils

	HO Sunflower	Peanut	Soybean	Flaxseed
Polyunsaturated Content	0.2%	0.2%	7%	53%
H2	357	282	316	708
CH4	21	10	10	17
C2H6	4	26	563	2371
C2H4	8	16	7	16
C2H2	0	0	0	0
CO	203	389	408	977
CO2	876	2232	1330	3212

The inference from this data is that low-oleic oils are likely to produce higher levels of stray gassing than high oleic oils. This does not mean that the oils which have higher unsaturated content are less preferable, it just means that it is useful to know the oil base type when evaluating DGA data, especially when high levels of ethane are indicated.

Conclusion

The use of mineral oil in the electrical industry is well established and the uses of methods such as DGA have been refined over the years to the point where interpretation of faults is possible by using oil samples. With the greater adoption of ester fluids in high power transformers there is a need to understand the similarities and differences with these fluids to effectively maintain them and the transformers that contain them.

Ester fluids have a different interaction with water and produce different acids when aged, so the maintenance limits for water content and acid number need to be revised upwards for these fluids. There are also fundamental differences in the molecular structure of esters which mean that parameters such as volume resistivity are different. This in turn affects measurement methods such as transformer insulation resistance, although it does not affect normal operation. By understanding these differences users can properly analyse the results they obtain.

In terms of dissolved gas analysis the methods applied to mineral oil are still mostly valid for esters. There are some differences in interpretation and work is still to be done to fully understand how to perform DGA with esters. Similar key gasses are expected to occur if there is a fault in an ester transformer and as with mineral oil the presence of elevated levels of gas is cause for further investigation. One area where users need to be mindful however is with the stray gassing of ethane in natural esters, which is something not seen in mineral oils or synthetic esters.

As the use of esters expands it is expected that more data will become available from the field and ester DGA will become further refined.

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