Natural Ester and Synthetic Ester Fluids, Applications and Maintenance

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***Abstract*— 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.

***Keywords*— ester, natural, synthetic, biodegradable, fire, liquid**

I. 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. Fig. 1 illustrates how this shorthand can be expanded into a longer form, showing the carbon and hydrogen elements and their bonds.

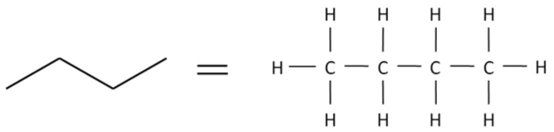

Fig. 1. Chemist's shorthand

Utilising this knowledge of chemical shorthand it is then possible to interpret the chemical structure of mineral oil, as shown in Fig. 2. Mineral oil is essentially a mixture of hydrocarbon structures, being termed 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.

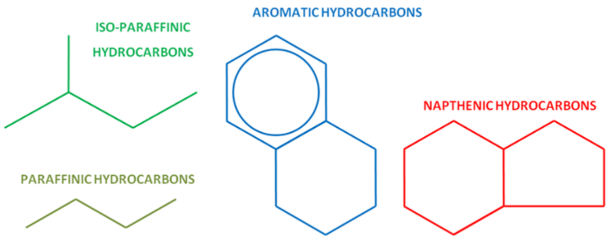

Fig. 2. Typical mineral oil structures

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 Fig. 3.

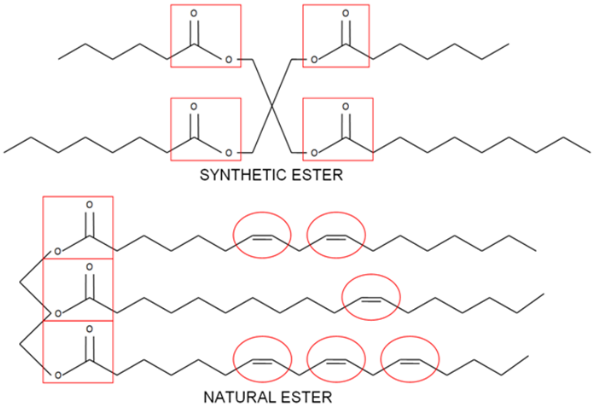

Fig. 3. Typical chemical structure of ester molecules

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.

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.

II. 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 Fig. 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.

The IEEE C57.147 maintenance guide for natural esters[2] 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[3] 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.

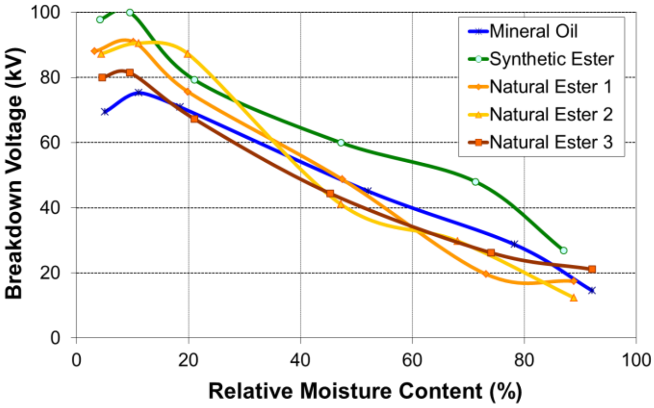

Fig. 4. Breakdown voltage vs relative saturation for a number of fluids[1]

TABLE I. 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

III. 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.

IV. 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.[3] 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 II shows the acid content limits for the different fluids, with the relevant standards.

TABLE II. ACID CONTENT LIMITS FOR IN SERVICE FLUID[3][4]

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

V. 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.

A. Ester 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 III. The ratios of the gasses will be different however and require adjustment to interpretation methods.

TABLE III. 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.

B. Gas Solubility

is the demand for ester transformers at higher voltages that university research into alternative fluids has been conducted in many different research centres around the world. One example of a large scale collaborative project was the 8 year joint research project between National Grid, Alstom Grid, M&I Materials and a number of UK utilities which studied the fundamental behaviour of ester fluids in comparison to mineral oil. The aim of this project was to define what was necessary to use esters at 400kV. This research project incorporated five PhD theses on the subject of ester behaviour under electrical conditions and included both synthetic and natural esters. The outcome of this project was a vast amount of information on the electrical, thermal and ageing behaviour of esters.

Various other institutions have published work on ester fluids, in Europe the other notable independent researchers are Stuttgart University and the Schering Institute at Hannover University. Much of their work mirrored that carried out at the University of Manchester and discovered very similar results. Various other large transformer manufacturers have also carried out their own extensive research work into the use of esters, including Siemens and ABB.

C. Permittivity of Esters

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 IV.

TABLE IV. GAS SOLUBILITY/PARTITION COEFFICIENTS AT 20°C[5]

Gas Symbol	**Mineral Oil**	**Synthetic Ester**	**Natural Ester**
N_2	0.091	0.091	0.074
O_2	0.172	0.152	0.134
H_2	0.0504	0.0479	0.0471
CH_4	0.423	0.378	0.341
C_2H_6	2.88	2.20	2.14
C_2H_4	1.81	1.85	1.67
C_2H_2	1.25	4.26	2.58
CO	0.125	0.130	0.108
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.

D. 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.[6][7] 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 Fig. 5 shows a comparison of the total gas for the three fluid types.

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.

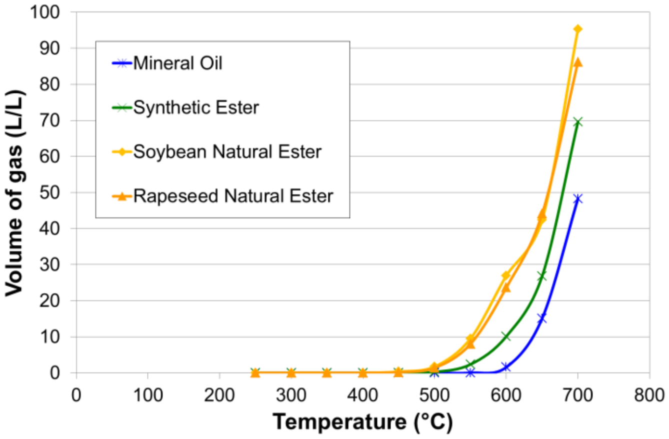

Fig. 5. Gas volume vs. temperature for mineral oil, synthetic ester and natural esters

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 Duval triangles for mineral oil, MIDEL 7131 synthetic ester, BIOTEMP natural ester and FR3 natural ester are shown in Fig. 6 and Fig. 7. [5]

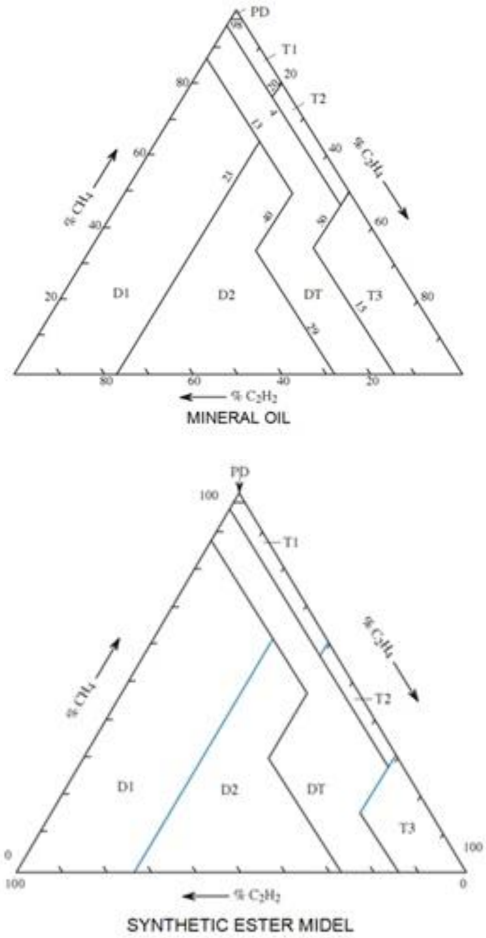

Fig. 6. Duval triangle for mineral oil and MIDEL 7131

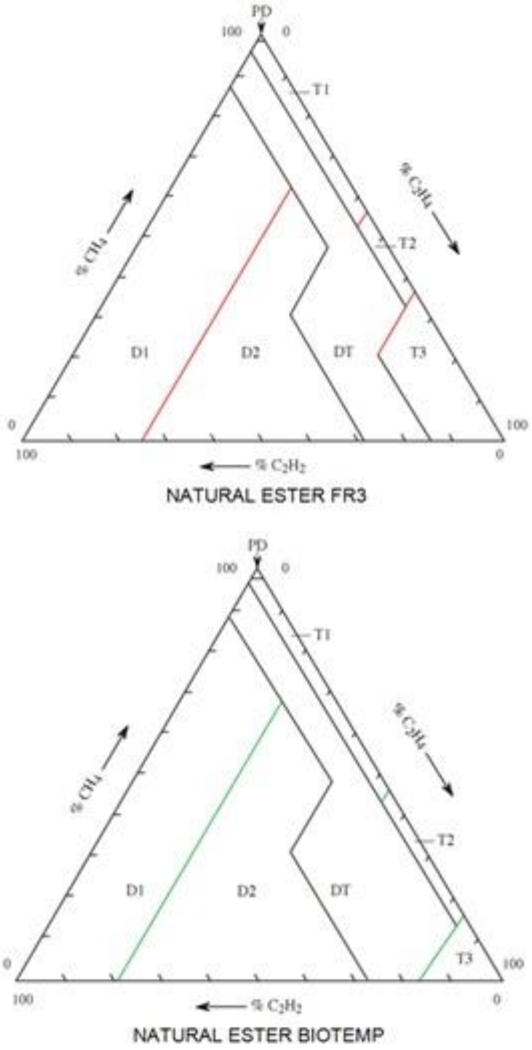

Fig. 7. Duval triangles for natural esters

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.

E. 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 CO_2 is also used to try and interpret whether paper is involved when a thermal of 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 Fig. 8, comparing synthetic ester and mineral oil under arcing conditions where the gas pattern is very similar, apart from the higher level of CO.

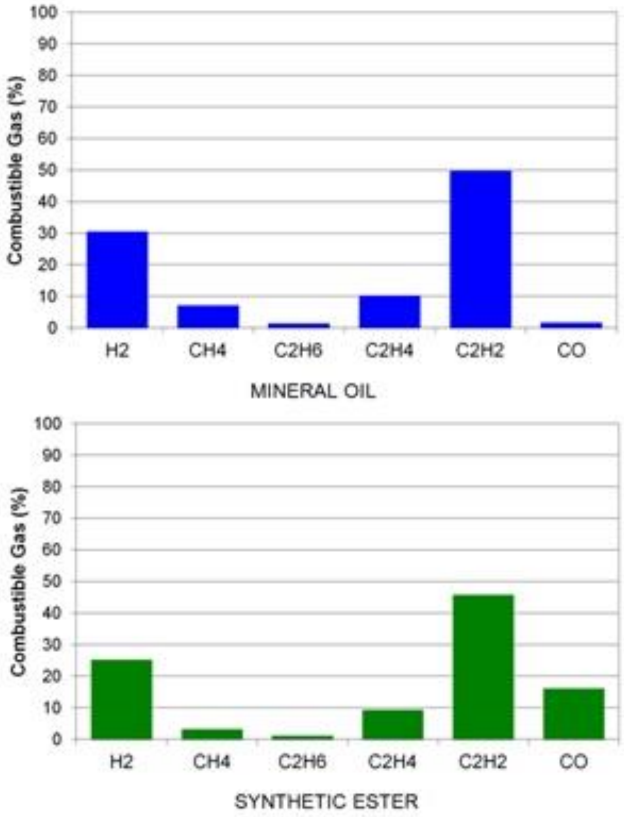

Fig. 8. Comparison of dissolved gas under fluid breakdown conditions

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 CO_2 than mineral oil under the same conditions, as shown in Fig. 9.[8][5] In this case the measured values of dissolved CO and CO_2 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 CO_2 and this is the reverse for mineral oil and synthetic ester. This means that the use of the CO_2/CO ratio may be less valid for natural ester fluids than for mineral oil when determining if a fault involves cellulose.

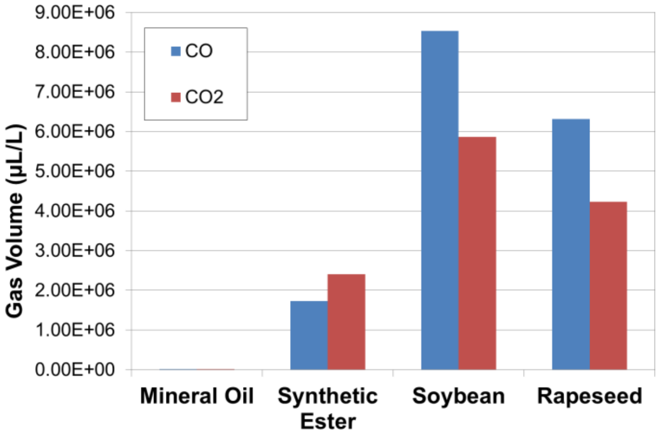

Fig. 9. Comparison of carbon oxide production under thermal stress

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.

F. 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 V 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. [8]

TABLE V. STRAY GASSING RESULTS FOR VARIOUS OILS

	HO Sunflower	**Peanut**	**Soybean**	**Flaxseed**
Poly-unsaturated 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.

VI. 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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