1. Introduction

Mineral oil is the most frequently applied liquid in power devices. However, for the last 20 years we have been observing interest increase of alternative liquids, including synthetic esters and natural esters [1, 10]. These liquids, in comparison to mineral oil, have properties which are considered as their advantages. These properties are, first of all, ecological values (biodegradability, non-toxicity), operation safety linked with a high flash point and fire point [1, 2, 4, 13, 14], and also high water solubility [1, 19, 20].

Fire safety is one of the most important problems faced by manufacturers and users of electrical power devices. It refers mainly to devices filled with electroinsulating liquids. However, it is still with substantial wariness. It results from the fact that, opposite to mineral oil, properties of these liquids are not well-known yet. One of the most essential properties involving transformer operation safety are gas properties of the liquid. A few scientific centres in the world are doing research on an analysis of gasses generated in alternative electroinsulating liquids when there are discharges of low energy and also overheating in the insulating system. These researches are targeted at pointing gases which are characteristic for a given type of defect and at determining values of typical concentrations of particular gases. These investigations are necessary to conduct Dissolved Gas Analysis (DGA) for transformers insulated with the new electroinsulating liquids. We should note here that the DGA method is considered as the one of the most important diagnostic method of the power transformers.
2. Physical foundations of gases generation in electroinsulating liquids

Mineral oils are a mixture of naphthenic hydrocarbons (CₙH₂ₙ₋₂, paraffin hydrocarbons (CₙH₂ₙ₊₂), and aromatic hydrocarbons (CₙHₙ). In their structure they have groups of CH, CH₂, and C≡C which can be caused by electrical or thermal faults. In their structure they have groups of CH, CH₂, and CnH2n-2, paraffin hydrocarbons (CnH2n+2), and aromatic hydrocarbons. Due to the chemical composition of oil and esters, we should expect significant differences in the amount of the generated gases. Acetylene is thus formed in significant quantities as partial discharges, the weakest C-H bonds can be broken (338kJ/mole), which is caused by the ionisation effect. Much higher energy is necessary for the scission of single bonds C-C (607 kJ/mole), double bonds C=C (720 kJ/mole) or triple bonds C≡C (960 kJ/mole) [16, 17].

It results from the literature that the characteristic gases which are generated in mineral oil as a result of discharge of high energy are C₂H₂, H₂, CH₄, C₂H₄, where acetylene is considered as the key gas [6, 11, 16, 17].

Generation of acetylene requires the temperature of at least 800°C, and its rapid quenching to lower temperatures, which enables the stability of this gas. Acetylene is thus formed in significant quantities mainly in arcs, where the conductive ionized channel is at several thousand of degrees Celsius, and the interface with the surrounding oil is necessarily below 400°C. This gas can also be generated at the temperature below 800°C, but in much smaller amounts. At the temperature within the range from 500°C to 800°C, we can observe formation of carbon molecules. This effect takes place mainly when the arc occurs or the oil is locally overheated [17].

As it was mentioned before, the main reasons of gas generation, both for mineral oil and esters is breaking carbon-hydrogen and carbon-carbon bonds. Therefore, the gases which are generated as a result of decomposition of these liquids are mainly hydrogen and hydrocarbons. Due to the chemical composition of oil and esters, we should expect significant differences in the amount of the generated gases.

3. Qualitative and quantitative analysis of gases generated in electroinsulating liquids - literature review

According to standard IEC 60599 [17], electric defects which occur in the insulating system can be divided into partial discharges, discharges of low energy and discharges of high energy. Below is a review of literature concentrating on the analysis of gases generated as a result of discharges of low energy in different electroinsulating liquids.

I. U-Khan, Z. Wang, I. Cotton, and S. Northcote presented in [23] results of DGA investigations for electroinsulating liquids exposed to the discharges of low energy. The research was done in the point-to-plate electrodes configuration with the interelectrode gap of 15 mm. In order to provide a sufficiently high concentration of the gases, they led to twenty breakdowns in each of the investigated liquids. After the breakdown, voltage was immediately switched off using an overcurrent relay, whose value was set for 3 A on the primary winding of the test transformer. The duration of discharge was in the range from 20 to 100 ms. Samples for the experiments were taken by means of a valve placed in the bottom of a tight vessel. According to the authors of [23], when we can provide a sufficiently long time between the breakdown and taking the sample, we can expect a uniform distribution of the gases in the whole volume of the liquid. Unfortunately, the authors did not reveal the value of this time. Table 1 presents their research results.

<table>
<thead>
<tr>
<th>GAS</th>
<th>LIQUID</th>
<th>GAS CONCENTRATION, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MINERAL OIL</td>
<td>NATURAL ESTER</td>
</tr>
<tr>
<td></td>
<td>BEFORE</td>
<td>AFTER</td>
</tr>
<tr>
<td>H₂</td>
<td>5</td>
<td>901</td>
</tr>
<tr>
<td>CH₄</td>
<td>154</td>
<td>28</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0</td>
<td>24</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>1</td>
<td>270</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>1</td>
<td>1540</td>
</tr>
<tr>
<td>CO</td>
<td>18</td>
<td>6</td>
</tr>
<tr>
<td>TDGC</td>
<td>26</td>
<td>2886</td>
</tr>
</tbody>
</table>

On the basis of the conducted experiments concerning exposure of electroinsulating liquids to discharges of low energy, the authors of [23] pointed out that acetylene is one of the key gases generated in the case of all the investigated liquids. All the investigated samples were characteristic of a high concentration of this gas. Despite the same exposure of the liquids, they found from 5 to 10 times greater acetylene concentration in mineral oil than for esters. The authors of [23] also found high concentration of hydrogen and ethylene for the liquids exposed to discharges of low energy. They also pointed out less intense generation of combustible gases in esters, in comparison to mineral oil. According to the authors of this work, this can make identification of defects more difficult.

M. Jovalekic, D. Vukovic, and S. Tenbohlen presented in [12] research results of the influence of discharges of low energy on gas generation in different electroinsulating liquids. The investigated liquids underwent 90 lightning impulses (1.2/50 µs) in the point-to-point configuration (interelectrode gap equal to 4 mm) in a tightly closed vessel of the volume of 1618 ml. Next, each of the liquids was stirred so as to obtain a uniform gas distribution in its whole volume. At the next step, a sample was taken and the chromatographic analysis was done. The results are presented in Table 2.

Table 1. Research results obtained by the authors of [23] concerning exposure of different electroinsulating liquids to discharges of low energy
Impulse voltage was equal to 134 kV, which meant energy in capacitors equal to 409.6 J (four-stage generator). However, only from 0.1 to 1% of this energy was used in liquid decomposition process. Most of the energy was converted into heat in the damping resistor of the generator.

On the basis of the obtained results, the authors of [12] found that the key gases generated at this type of defect are hydrogen and acetylene. For esters, they also found the presence of carbon monoxide, as opposite to mineral oil, where this gas was not found.

R. Eberhardt et al in [5] also analysed the influence of discharge of low energy on gas generation in mineral oil, natural ester, and synthetic ester. The investigations were done in a vessel of the volume of 17 litres in the plate-to-U-shape electrode. There was pressboard placed between the electrodes. Alternating voltage was raised in such a way that the discharge appeared after about 20 seconds. Each sample underwent the electric breakdown ten times. The authors found that acetylene is the key gas at this type of defect. Its largest increase was found for natural ester. The increase of acetylene concentration in mineral oil and synthetic ester was similar. They found a considerable difference in gas generation between natural ester and synthetic ester. For natural ester, they proved the presence of acetylene and ethane. They also concluded that there is no increased generation of carbon monoxide and dioxide for both natural and synthetic ester.

C. Perrier, M. Marugan, M. Saravolac, and A. Beroual proved in [15] that when mineral oil and esters are exposed to discharges of low energy then mainly hydrogen and acetylene are generated.

Summing up the presented above literature review, we can conclude that in the research conducted up to now, the authors have concentrated mainly on the analysis of gases generated as a result of short duration discharges of low energy. The authors of this article conducted experiments of exposing the liquids to the discharge in the form of the electric arc of very high energy, reaching 5 kJ. The conditions of these experiments and their results are presented in the subsequent chapter.

4. Investigations of gases generated in electroinsulating liquids by discharge of high energy

4.1. The aim of the study

The aim of the research was to compare gases generated in mineral oil, natural ester (manufactured on the basis of soybean oil), and synthetic ester by discharge of high energy. The comparison was done both in terms of gas composition and their concentration. The purpose of the study was to give an answer to the question: which of the analysed liquids ensure higher operation safety if there is a discharge of high energy in the insulating system.

Resulting from the discharge of high energy, very large quantities of gases were generated in the liquids in the form of bubbles, which migrated to the headspace. The quantity of the generated gases was so large that it caused significant pressure changes in the chamber. Due to a short discharge time (5, 10, or 15 s) and taking the samples immediately after the arc extinction, only a slight amount of the generated gas was able to dissolve in the liquid. That is why the authors analysed the gas mixture taken from the headspace.

4.2. System for gas generating and research procedure

For exposing the investigated liquids to discharge of high energy, the authors used a hermetic chamber which had been used before for investigations of the dielectric response of pressboard samples [7, 8]. The chamber was rebuilt for the needs of this experiment (Fig. 1). The walls of this chamber were made of a glass pipe, whereas the base and the lid were discs made of organic glass. All screw connections were made as gas tight using oil resistant seals of the O-ring type. After assembling the chamber, a tightness test was done using compressed air. No pressure drop was found in the whole system (within forecast pressure ranges which could occur during the experiment), thus the system was considered as gas tight.

The volume of the chamber was 1800 cm³, after including the volume of the electrode (which was 106 cm³) the authors determined the volume of the liquid in the chamber. The height of the liquid column in the chamber was 15.5 cm, thus knowing the dimensions of the chamber, it is possible to calculate the oil volume. The calculated oil volume was equal to 1360 cm³. The volume of the air remaining in the chamber (the volume of headspace) was thus equal to 334 cm³.

The electric arc was generated in the point-to-plate electrodes configuration. The gap between the electrode was 3 mm. The point electrode was connected to a source of high voltage, whereas the plate electrode was grounded. A special point electrode was designed to allow investigating pressure changes in the chamber and taking gas samples from headspace without any contact with atmospheric air.
The electrode was made in the form of a brass pipe (of external diameter 3 mm and internal diameter 2 mm) ending with a copper cone on one side. The pipe, in the part which was above the liquid level had a gas extraction hole of the diameter of 1 mm. The other end of the point electrode was connected by means of dielectric pipes made of PCV with a three-way valve. The valve allowed connecting the system with the pressure meter or a gas tight syringe used for taking gas from headspace.

Voltage was supplied to the chamber by means of the system presented in Figure 2. An autotransformer (AT1) was applied in the voltage regulation system, current and voltage in the autotransformer circuit were measured. The voltage supplied from the autotransformer was raised using a high voltage transformer (TR1) of the ratio of 110000/220. On the HV side, voltage was measured using electrostatic kilovoltmeters, and current by means of a milliammeter. For reducing discharge current, the authors used a non-linear damping resistor R1.

After arc ignition in the chamber (arc ignition took place at 25 kV for mineral oil, 24 kV for synthetic ester, and 25 kV for natural ester), voltage values on upper windings of AT1 and TR1 decreased. Voltage and current of arc for all liquids were similar and they were 2.5 kV and 140 mA, respectively.

The arc current corresponds to the value of the current measured on the low side of the transformer TR1, which was 70 A during arc ignition (the TR1 ratio is 500, thus current transforming took place on the low side of the transformer TR1, which was 70 A during arc and 140 mA, respectively. Therefore, the ignition (the TR1 ratio is 500, thus current transforming took place on the low side of the transformer TR1, which was 70 A during arc and 140 mA, respectively.

All the investigated liquids were exposed to electric arc for 5, 10, and 15 s. The procedure of exposing the liquid to the electric arc was proceeded as follows:

1. Liquid conditioning in the air of atmospheric pressure to obtain relative saturation of the liquid equal to 40%, 4.5 litre of each investigated liquid was prepared.
2. Filling the chamber with the investigated liquid: the volume of the liquid was 1360 cm$^3$.
3. Sealing the chamber by tightening all screw connections.
4. Connecting the pressure meter.
5. Connecting the supply and grounding wires to the suitable electrodes.
6. Setting the three-way valve in a position which allows pressure measurement.
7. Raising voltage until the moment of arc ignition.
8. Keeping the arc for 5 s.
9. Leasing the chamber for 1 minute to let the gas bubbles generated in the liquid migrate to the headspace.
11. Suitable setting the three-way valve and taking 12 ml of the gas for the chromatographic analysis.

Then for each of the liquids the above presented activities were repeated twice (excluding first activity) increasing every time the duration of arc by 5 s.

The authors used a gas chromatograph type 8610C TOGA supplied by SRI Instruments for the analysis of generated gases. The chromatograph is equipped with two detectors: the flame ionisation detector FID and the thermal conductivity detector TCD. By means of the FID we can subsequently detect the following gases: carbon monoxide, methane, carbon dioxide, ethylene, ethane, acetylene, propane, propylene, whereas by means of the TCD we can detect subsequently: hydrogen, oxygen, and nitrogen.

### 4.3. Research results and conclusions

Table 3 and Figures from 3 to 15 present results of a qualitative and quantitative analysis of the gases generated in mineral oil, natural ester, and synthetic ester during discharge of the time of 5, 10, and 15 s.

In order to measure the pressure of headspace a manometer was used. Table 4 and Figure 16 present results of these investigations.

<table>
<thead>
<tr>
<th>GAS LIQUID</th>
<th>MINERAL OIL</th>
<th>NATURAL ESTER</th>
<th>SYNTHETIC ESTER</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 s</td>
<td>10 s</td>
<td>15 s</td>
</tr>
<tr>
<td>H$_2$ %</td>
<td>6.228</td>
<td>8.671</td>
<td>12.82</td>
</tr>
<tr>
<td>O$_2$ %</td>
<td>17.30</td>
<td>16.73</td>
<td>15.06</td>
</tr>
<tr>
<td>N$_2$ %</td>
<td>73.25</td>
<td>70.96</td>
<td>63.41</td>
</tr>
<tr>
<td>CO %</td>
<td>0.0409</td>
<td>0.0204</td>
<td>0.0380</td>
</tr>
<tr>
<td>CH$_4$ %</td>
<td>0.3111</td>
<td>0.4609</td>
<td>0.7092</td>
</tr>
<tr>
<td>CO$_2$ %</td>
<td>0.0694</td>
<td>0.1175</td>
<td>0.0483</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>0.2827</td>
<td>0.3789</td>
<td>0.5804</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>0.0055</td>
<td>0.0086</td>
<td>0.0133</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>2.816</td>
<td>3.763</td>
<td>5.678</td>
</tr>
<tr>
<td>C$<em>4$H$</em>{10}$ area</td>
<td>32.90</td>
<td>48.30</td>
<td>71.40</td>
</tr>
</tbody>
</table>
On the basis of the results presented above, the following conclusions were drawn:

- for all tested liquids a very high concentration of hydrogen and acetylene were measured, while in the case of esters also a high concentration of carbon monoxide was found; for the experimental conditions, the concentrations of these gases exceed 1% (10,000 ppm); these gases can be used to identify a high energy discharge defect,
- the sum of combustible gases (excluding butane for which it was impossible to carry out a quantitative analysis due to the lack of this gas in the gas mixture used for calibration of the chromatograph) is about 38% higher for mineral oil than for both esters (Fig. 15) – this indicates a greater exploitation safety of esters in the case of electric arc ignition,
- during high energy discharge the increase of headspace gas pressure for all investigated liquids was observed (Fig. 16).

A substantial concentration increase of combustible gases in the insulating system generated during electric arc leads to a very high risk of ignition of these gases. Such ignition was observed while investigating synthetic ester at the time of exposing to the discharge equal to 15 seconds. Figure 17 presents the gas concentration in headspace in the situations when gas ignition took place and it did not.

The authors found a significant difference between the composition of the gas mixture in synthetic ester in the case of the experiment with and without combustible gas ignition. In the case with no ignition, the sum of combustible gases was 12.9%, whereas in the case of ignition the concentration of these gases was merely 3.8%. Moreover, in the experiment where gas ignition took place, the authors observed...
much lower oxygen concentration and considerably higher concentration of carbon monoxide in comparison to the experiment where ignition did not occur. Gas ignition resulted in negative pressure in the measurement system at the level of 402 mbar in reference to the atmospheric pressure. In the experiment where gas ignition did not occur, the increase of pressure was found at the level of 154 mbar over the atmospheric pressure.

In all the liquids, at the moment of electric arc ignition, sudden oil degradation was observed, whose result apart from generation of combustible gases was the occurrence of carbon particles. This effect was the most noticeable for mineral oil. Figure 18 presents photographs of mineral oil colour changes during the investigation.

4. Conclusions

The conducted research confirmed that during the discharges of high energy in natural ester and synthetic ester, the same gases are generated as for mineral oil. These gases are: hydrogen, hydrocarbons (first of all with one, two, or three carbon atoms), carbon monoxide and dioxide. This conclusion is very important due to the diagnostics of devices insulated with these liquids. Generation of the same gases allows perform the gas analyses at the same configuration of the chromatograph.

It is important, however, that in the particular electroinsulating liquids, at the same type of defect, gases are generated of completely different concentrations, which is vital in terms of interpretation of research results obtained by means of the DGA method.

It was found a greater value of total combustible gases by about 38% in mineral oil than in both esters. This points out higher operation safety of esters in the case of arc ignition. For all the investigated liquids, the characteristic gases occurring at a very high concentration were hydrogen and acetylene, whereas for esters, the authors also found a high concentration of carbon monoxide. These...
gases can be applied for identifying the defect which is discharge of high energy.

Most of the conclusions resulting from the conducted research are in agreement with the experiment results described in articles [12, 15, 23], by contrast they are not in agreement with the experiment results described in [5]. The authors of this work did not find excessive generation of carbon monoxide for both natural and synthetic esters.

Acknowledgement

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References


Fig. 18. The changes of mineral oil colour during the experiment: 0 s – before arc ignition, in the 3rd, 6th, 9th and 12th second of discharge duration, and in the 16th s – after the arc extinction.

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