In a closed experimental set-up, transformer oils are subjected to a predefined heating program followed by dissolved gas analysis



Dissolved gas analysis is a common technique in the supervision and maintenance of transformers. It can give hints on defects and faults in oil-immersed transformers by determining and quantifying the gases arising due to thermal or electrical stress. Different algorithms for the assessment of transformers, which utilize data obtained from dissolved gas analysis, have been published so far. However, only few investigations exist that deal with the influence of the oil's composition on the oil's tendency of releasing gases. This research study presents a comparison of four commercially available transformer oils of different composition regarding that aspect. The results indicate that an oil mainly consisting of paraffinic hydrocarbons shows a different gassing pattern compared to naphthenic oils when it is exposed to thermal stress. Some explanations for this phenomenon are given in the report as well.

## **KEYWORDS**

dissolved gas analysis, thermal stress, transformer oil, fault gases

# Transformer oil fault gases under thermal stress at 160 °C – Part II

## 1. Closed experimental set-up

In this article, we present several key experiments in which four different transformer oils were subjected to a heating program with a well-defined temperature profile, followed by an investigation of the fault gases developed during the heating period. Two experimental set-ups were used: (a) an open system which enabled the exchange of matter and energy with the environment, and (b) a closed system, where only the exchange of energy with the environment was possible, Figure 1. With the open experimental set-up (a), three different transformer oils were tested, while a comprehensive investigation was expanded to four different oils with a closed experimental set-up (b). The results received by experiments with an open experimental set-up were published in the previous edition of Transformers Magazine [1].

The experiments were performed using a temperature calibrator (TP M 225 S-U, SIKA Dr. Siebert und Kühn GmbH & Co. KG, D-34260 Kaufungen, Germany): A volume of 450 ml transformer oil destined for examination was poured in the heating cell of the temperature calibrator and the heating cell was closed with a reinforced plastic screw plug which contained five holes (diameter 15 mm) and a drill hole (diameter 3 mm). During the second experimental sequence with a closed, modified experimental set-up (b), Figure 1, the five holes (diameter 15 mm) and the drill hole (3 mm) were capped with silicone stoppers. In addition, two of those silicone stoppers were pierced by two cannulas in order to connect three syringes (100 ml) via tubing and three-way valves to the gas phase inside the heating cell of the temperature calibrator. The syringes had been sealed by coating their plungers with degassed oil before introducing the

plungers into the barrels of the syringes. Each of these sealed syringes was filled with 60 ml air as a gas reservoir at the beginning of the experiments with a closed experimental set-up (b). Accordingly, the total volume of the gas phase consisted of around 69 ml air in the experimental vessel plus 10 ml air in the tubes and 180 ml in the syringes. The three syringes were not destined for sampling. They served as a reservoir for the expansion and diminution of the system's volume. First, the volumes of the gas and liquid phase expand due to heating, reaching a maximum after five to six hours. Afterwards, a diminution of the gas phase's volume can be observed, which is caused by dissolution of gases in the liquid phase. At the beginning of our experiments with the closed experimental

set-up (b) we used only one syringe. The experiments failed because the pistons ran out of the barrels of the syringes due to the increase of the system's volume. Therefore, two syringes were necessary at least. Moreover, a third syringe was fixed as a reserve, in case one piston of the other two syringes got stuck. In advance, the silicone stoppers had been tested for their gassing behavior by heating them without oil at 160 °C (100 h), not showing any gassing. Therefore, a possible contamination by the silicone stoppers could be excluded. Within this experimental sequence, the test oils were heated from 25 °C at a gradient of 5 °C/min to reach a maximum of 160 °C. This maximum was maintained for 100 h before the oil was cooled down to 25 °C at -2°C/min. The temperature of 160°C is on

A naphthenic mineral oil without inhibitor (NA-UI), two inhibited naphthenic mineral oils (NA-Ia and NA-Ib) and a mainly paraffinic Gasto-Liquid oil with inhibitor (PA-I) were tested



Figure 1. Schematic diagram of the experimental set-up (b) with exchange of energy only

## Significant concentrations of fault gases were detected in the oils after a heating period of 100 hours at 160 °C

the upper limit of a phenomenon, which is called "stray gassing" [2]. Furthermore, the temperature of 160 °C could be maintained with high precision by the temperature calibrator. In addition, 160 °C is a "common" maximum temperature in the windings of a transformer according to the authors' knowledge. During the entire heating period, the oils were not stirred. Test samples from the sampling liquid were taken just before the start and after the termination of the heating program and cooling down. In addition to the samples of the liquid phase, samples from the gas phase were taken just before and after the termination of the heating program. After that, the remaining gas volumes in the syringes were noted. Subsequently, DGAs were performed in triplicate on the liquid and gas samples by means of a calibrated multi-cycle vacuum extractor coupled with a gas chromatograph (TOGA GC version 2, equipped with a vacuum

extractor and automatic sampling system, Energy Support GmbH, D-41468 Neuss, Germany). The new transformer oils examined in this study are commercially available and they were used directly after degassing (p <0.5 mbar; T=50-60 °C; Type AP 60 H Super, Wilhelm Hedrich, Vakuumanlagen GmbH & Co. KG, D-35630 Ehringshausen-Katzenfurt, Germany) and cooling down to the ambient temperature in an air-tight aluminium bottle. A degassing unit enables the reduction of gas content in oil from 10 vol-% to 0.05 vol-% in one cycle by heating and vacuum treatment. In addition, a degassing unit reduces the oil's moisture up to  $2 \mu g/g$  oil (2 ppm). Extra treatments or the addition of supplementary anti-oxidative substances were not performed on the oils. A naphthenic mineral oil without inhibitor (NA-UI: naphthenic uninhibited), two inhibited naphthenic mineral oils (NA-Ia and NA-Ib: naphthenic inhibited) and a mainly paraffinic Gas-to-Liquid (GtL)-oil with inhibitor (PA-I: paraffinic inhibited) were chosen for the experiments. The acronyms NA-UI, NA-Ia, NA-Ib and PA-I do not imply a general representativeness of the oils for all naphthenic and paraffinic oils on the market; they were simply used for a more facile readability. According to the manufacturers, the naphthenic oils are based on mineral oils, whereas the paraffinic oil is synthesized from natural gas and oxygen via syngas (CO and H<sub>2</sub>) in a Fischer-Tropsch reaction, followed by a catalytic hydrocracking process. For that reason, this paraffinic oil is denoted as "Gas-to-Liquid - (GtL)"-oil by its manufacturer. The selected oils are widespread in transformers all over the world and they are regularly purchased by transformer manufacturers from oil suppliers.

## 2. Results

After the astonishing results obtained with an open experimental set-up (a) [1], which showed unexpected, differing fault gas patterns, especially with oil PA-I forming definitely lower concentrations of fault gases, the authors decided to use a more sophisticated experimental set-up, a



Figure 2. Photograph of the experimental set-up (b) with exchange of energy only

	NA-UI	NA-la	NA-lb	PA-I
Aromatic hydrocarbons [%] <sup>1</sup>	5	7	6	1
Paraffinic hydrocarbons [%]	47	47	45	73
Naphthenic Hydrocarbons [%]	48	46	49	26
Inhibitor [%]²		0.31	0.33	0.21
Color <sup>3</sup>	0.5	0.5	0.5	0.5
Breakdown voltage [kV] <sup>3</sup>	72.2	75	77.3	75
Dielectric Dissipation Factor <sup>3</sup>	0.0030	0.0010	0.0010	0.0030
Neutralization value [mg KOH/g] <sup>3</sup>	0.01	0.01	0.01	0.01
Water content [mg/kg] <sup>3</sup>	1	4	2	2
Interfacial tension [mN/m] <sup>3</sup>	45.3	45.3	45.3	45.3
Sediment and sludge [%] <sup>3</sup>	<0.02	< 0.02	< 0.02	< 0.02
Particles <sup>3</sup>	17/16/13	-/12/9	17/16/13	17/16/13
Boiling point [°C]⁴	>280	>232	>280	>280

Table 1. Composition and properties of the transformer oils used for testing the trend of generating fault gases during thermal stress with the closed experimental set-up (b)

<sup>1</sup> acc. to [3]; <sup>2</sup> acc. to [4]; <sup>3</sup> acc. to [5] and references therein; <sup>4</sup> acc. to the manufacturer's technical and safety data sheets

closed set-up, which enables the exchange of energy, but not of matter with the environment, Figure 1. In addition, another inhibited, naphthenic mineral oil (NA-Ib degassed and air saturated) was included in the experiments. The oil NA-Ib was not available to us when we started the experiments with the open experimental set-up (a). Nevertheless, the oil NA-Ib gave the opportunity to study the influence of air saturation on the generation of fault gases with the closed experimental set-up (b) as we were able to acquire that oil later in sufficient quantity to test it in an air saturated and in a degassed condition. NA-Ib and NA-Ia were of different brands, and therefore their chemical composition should differ as well.

Similar to the results obtained with the open experimental set-up (a) [1], significant concentrations of the fault gases  $CO_2$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $CH_4$ , CO,  $C_3H_6$ ,  $C_3H_8$  and  $H_2$  were detected as dissolved gases in the oils after a heating period of 100 h at 160 °C when oils NA-UI, NA-Ia, NA-Ib, NA-Ib<sup>\*</sup> (air saturated) and PA-I were tested with the closed experimental set-up (b). The fault gas  $C_2H_2$  was not detected or was

## In the presence of inhibitor, higher concentrations of carbon oxides (CO and CO<sub>2</sub>) and hydrogen are formed

only detected in traces in all experiments. Once again, the gases detected with the highest concentrations were carbon dioxide (CO<sub>2</sub>) and carbon monoxide (CO) for all five transformer oils. The naphthenic mineral oils (NA-UI, NA-Ia, NA-Ib, NA-Ib<sup>\*</sup> (air saturated)) formed higher amounts of the fault gases methane (CH<sub>4</sub>), ethane (C<sub>2</sub>H<sub>6</sub>) and propane (C<sub>3</sub>H<sub>8</sub>), but fewer amounts of the fault gases ethylene (C<sub>2</sub>H<sub>4</sub>) and propylene (C<sub>3</sub>H<sub>6</sub>) compared to the paraffinic (GtL)-oil PA-I. Interestingly, the uninhibited oil NA-UI showed significantly lower concentrations of carbon oxides (CO and CO<sub>2</sub>) than naphthenic mineral oils containing inhibitor, in contrast to our assumption that an uninhibited oil would be attacked by oxygen to a higher extent and therefore generate more carbon oxides (CO and CO<sub>2</sub>) than an inhibited oil. The trend of forming hydrogen seems to be lower in the case of the uninhibited oil NA-UI, where the lowest concentrations were found in the oil (liquid phase) and in the gas phase. The exact composition of each transformer oil used with the closed experimental set-up (b) is listed in Table 1. The results of all experiments with the set-up (b) are demonstrated in Table 2 to Table 6.

In the closed experimental set-up, the oils NA-UI and NA-Ia show higher levels of degradation after heating than the oils NA-Ib and PA-I

	Concentration in oil		Concentration	Difference <sup>2</sup>	
Gas <sup>1</sup>	[µl gas /l oil]		[µl gas/l g	[µl]	
643	before heating	after 100 h at 160 °C	before heating	after 100 h at 160 °C	
CO <sub>2</sub>	43.0	1757.7	652.3	1341.3	877.4
C <sub>2</sub> H <sub>4</sub>	n.d.	16.2	n.d.	8.5	9.0
C <sub>2</sub> H <sub>2</sub>	n.d.	n.d.	n.d.	n.d.	
C <sub>2</sub> H <sub>6</sub>	n.d.	419.0	n.d.	116.3	213.2
CH₄	0.1	460.3	2.6	735.0	353.9
СО	0.3	969.3	0.9	3866.0	1205.9
C <sub>3</sub> H <sub>6</sub>	n.d.	46.9	n.d.	12.8	23.8
C <sub>3</sub> H <sub>8</sub>	n.d.	329.0	n.d.	28.9	155.0
H <sub>2</sub>	n.d.	57.7	n.d.	531.3	131.5
O <sub>2</sub>	1430.3	2258.3	210513.3	88072.3	-35897.9
N <sub>2</sub>	4624.0	83375.3	729257.7	725637.3	-6555.9
	Liquid p	hase - oil	Gas phase		
Volumes	[n	nl]	[ml]		
	before heating	after 100 h at 160 °C	before heating	after 100 h at 160 °C	
Experimental	453.7	453.7	255.3	198.3	
Calculated <sup>3</sup>			240.0	162.6	

Table 2. DGAs and volumes of oil NA-UI, before and after heating (100 h; 160 °C) with the closed experimental set-up (b)

Table 3. DGAs and volumes of oil NA-Ia, before and after heating (100 h; 160 °C) with the closed experimental set-up (b)

	Concentra [µl gas	a <b>tion in oil</b> s /l oil]	Concentratior	Difference <sup>2</sup>	
Gas'	before heating	after 100 h at 160 °C	before heating	after 100 h at 160 °C	
CO <sub>2</sub>	37.7	3635.3	723.7	2748.7	1956.1
C₂H₄	n.d.	31.7	n.d.	13.7	16.9
C <sub>2</sub> H <sub>2</sub>	n.d.	n.d.	n.d.	n.d.	
C <sub>2</sub> H <sub>6</sub>	n.d.	102.8	n.d.	33.5	52.6
CH₄	0.1	368.0	2.5	565.7	273.9
со	2.3	1430.0	6.2	5006.0	1608.7
C₃H <sub>6</sub>	n.d.	57.7	n.d.	9.5	27.7
C <sub>3</sub> H <sub>8</sub>	n.d.	77.1	n.d.	7.9	36.1
H <sub>2</sub>	n.d.	107.7	n.d.	749.3	193.5
<b>O</b> <sub>2</sub>	1260.0	2110.7	204952.7	83924.7	-36816.7
N <sub>2</sub>	3902.7	82669.0	736312.0	736655.3	-13973.9
	Liquid pl	hase - oil	Gas phase		
Volumes	[ml]		[ml]		
	before heating	after 100 h at 160 °C	before heating	after 100 h at 160 °C	
Experimental	448.1	448.1	260.9	193.9	
Calculated <sup>3</sup>			245.8	160.9	

<sup>1</sup> n.d.: not detected; <sup>2</sup> the volumes of each gas were determined by multiplying the concentration with the volumes in the liquid phase and the gas phase, respectively. In an additional step, the difference between the volumes after and before heating was formed and depicted in the table; <sup>3</sup> the volumes of each gas in the gas phase were calculated by multiplication of the concentration with the volume in the gas phase and then summed up for both cases: before heating and after heating, respectively.

	Concentration in oil		Concentration	Difference <sup>2</sup>	
Gas <sup>1</sup>	[µl gas /l oil]		[µl gas/l gas phase]		[µl]
003	before heating	after 100 h at 160 °C	before heating	after 100 h at 160 °C	
CO <sub>2</sub>	30.7	3136.0	755.3	2021.7	1623.8
C <sub>2</sub> H <sub>4</sub>	n.d.	17.5	n.d.	6.1	9.1
C <sub>2</sub> H <sub>2</sub>	n.d.	n.d.	n.d.	n.d.	
C <sub>2</sub> H <sub>6</sub>	n.d.	65.4	n.d.	15.3	32.6
CH₄	n.d.	178.7	2.3	215.0	124.5
СО	0.5	1230.3	4.0	3274.7	1231.6
C₃H <sub>6</sub>	n.d.	28.7	n.d.	8.5	14.7
C₃H <sub>8</sub>	n.d.	41.9	n.d.	2.3	19.4
H <sub>2</sub>	n.d.	137.0	n.d.	832.7	234.2
<b>O</b> <sub>2</sub>	1151.3	2746.3	214163.3	133945.7	-26814.0
N <sub>2</sub>	3564.0	86818.3	731520.3	732457.3	424.4
	Liquid p	hase - oil	Gas phase		
Volumes	[n	nl]	[ml]		
	before	after 100 h	before	after 100 h at 160 °C	
Experimental	450.9	450.9	258.1	207.1	
Calculated <sup>3</sup>			244.3	180.7	

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Table 5. DGAs and volumes of oil NA-Ib\* (air saturated), before and after heating (100 h; 160 °C) with the closed experimental set-up (b)

	concentration in oil		concentration	Difference <sup>2</sup>	
Gas <sup>1</sup>	[µl gas /l oil]		[µl gas/l gas phase]		[µl]
000	before heating	after 100 h at 160 °C	before heating	after 100 h at 160 °C	
CO <sub>2</sub>	404.3	4195.0	714.0	2426.7	2100.2
C <sub>2</sub> H <sub>4</sub>	n.d.	26.2	n.d.	8.7	13.9
C <sub>2</sub> H <sub>2</sub>	n.d.	n.d.	n.d.	n.d.	
C <sub>2</sub> H <sub>6</sub>	n.d.	87.9	n.d.	21.8	44.8
CH₄	0.7	256.0	3.1	204.0	162.7
СО	11.9	1857.7	4.7	2918.7	1523.0
C <sub>3</sub> H <sub>6</sub>	n.d.	46.2	n.d.	12.4	23.8
C <sub>3</sub> H <sub>8</sub>	n.d.	62.8	n.d.	5.9	29.7
H <sub>2</sub>	n.d.	313.0	n.d.	751.7	319.3
O <sub>2</sub>	20746.3	2541.3	215603.3	166998.3	-24258.8
N2	64921.3	96438.0	736560.7	729814.7	-2856.7
	Liquid p	hase - oil	Gas phase		
Volumes	[n	nl]	[ml]		
	before heating	after 100 h at 160 °C	before heating	after 100 h at 160 °C	
Experimental	450.9	450.9	258.1	237.1	
Calculated <sup>3</sup>			245.9	214.1	

<sup>1</sup> n.d.: not detected; <sup>2</sup> the volumes of each gas were determined by multiplying the concentration with the volumes in the liquid phase and the gas phase, respectively. In an additional step, the difference between the volumes after and before heating was formed and depicted in the table; <sup>3</sup> the volumes of each gas in the gas phase were calculated by multiplication of the concentration with the volume in the gas phase and then summed up for both cases: before heating and after heating, respectively.

Gast	<b>Concentra</b> [μl gas	a <b>tion in oil</b> s /l oil]	<b>Concentratio</b> r [μl gas/l g	Difference² [µl]	
Gas	before heating	after 100 h at 160 °C	before heating	after 100 h at 160 °C	
CO <sub>2</sub>	41.0	3501.0	709.0	3317.3	2074.0
C₂H₄	n.d.	44.2	n.d.	27.8	25.8
C <sub>2</sub> H <sub>2</sub>	n.d.	n.d.	n.d.	n.d.	
C <sub>2</sub> H <sub>6</sub>	n.d.	6.2	n.d.	2.5	3.3
CH₄	0.1	39.7	2.4	92.7	36.7
со	0.3	898.3	6.7	4316.3	1309.9
C₃H₀	n.d.	48.9	n.d.	16.8	25.6
C₃Hଃ	n.d.	6.7	n.d.	n.d.	3.0
H <sub>2</sub>	n.d.	89.6	n.d.	779.7	204.2
<b>O</b> <sub>2</sub>	1310.0	8664.7	214756.0	133296.3	-24104.6
N2	3746.7	63444.3	733354.7	714800.0	-12182.2
	Liquid phase - oil		Gas p		
Volumes	[ml]		[ml]		
	before heating	after 100 h at 160 °C	before heating	after 100 h at 160 °C	
Experimental	450.9	450.9	258.1	210.1	
Calculated <sup>3</sup>			244.9	180.0	

Table 6. DGAs and volumes of oil PA-I, before and after heating (100 h; 160 °C) with the closed experimental set-up (b)

<sup>1</sup> n.d.: not detected; <sup>2</sup> the volumes of each gas were determined by multiplying the concentration with the volumes in the liquid phase and the gas phase, respectively. In an additional step, the difference between the volumes after and before heating was formed and depicted in the table; <sup>3</sup> the volumes of each gas in the gas phase were calculated by multiplication of the concentration with the volume in the gas phase and then summed up for both cases: before heating and after heating, respectively.

## Saturated hydrocarbons as fault gases are mainly generated by naphthenic, i.e. cyclic and aromatic hydrocarbons in case of thermal stress

Some indicators of the decomposition of the oils were determined after heating the oils in experimental set-up (b): all inhibited oils lost between 0.01 % and 0.07 % of the inhibitor, whereas the color increased in only one case – NA-Ia. The

		NA-UI	NA-la	NA-lb	NA-lb*	PA-I
				-	-	
Inhibitor	Start		0.31	0.33	0.33	0.21
<b>[%]</b> <sup>1</sup>	End		0.30	0.30	0.26	0.18
Color <sup>2</sup>	Start	0.5	0.5	0.5	0.5	0.5
Color	End	0.5	2.5	0.5	0.5	0.5
Neutralization value [mg KOH/g]²	Start	0.01	0.01	0.01	0.01	0.01
	End	0.01	0.04	0.01	0.02	0.02
Interfacial tension	Start	45.3	45.3	45.3	45.3	45.3
[mN/m]²	End	38.4	37.7	45.3	45.3	45.3
Sediment and sludge [%]²	Start	<0.02	<0.02	<0.02	<0.02	<0.02
	End	<0.02	<0.02	<0.02	<0.02	<0.02

Table 7. Characteristic figures indicating the oils' degradation before and after the heating period (100 h; 160 °C) with the closed experimental set-up (b)

<sup>1</sup> acc. to [4]; <sup>2</sup> acc. to [5] and references therein; \* air saturated

neutralization number rose moderately for three oils (NA-Ia, NA-Ib\* (air saturated), PA-I), while the interfacial tension fell in two oils (NA-UI and NA-Ia) after heating. A change in the content of sediment and sludge could not be stated for all oils examined. It seems that the parameters, determined after heating the transformer oils in the closed experimental set-up (b), indicate a higher degradation for the oils NA-UI and NA-Ia than for the oils NA-Ib and PA-I, since oils NA-Ib and PA-I showed "better" values in the measurements. Obviously, the persistence of the oils NA-Ib and PA-I is superior to the other oils involved in this experimental section. Characteristic figures demonstrating the degree of the oils' degradation after heating them in the closed experimental set-up (b) are displayed in Table 7.

Figures 3 to 6 illustrate the concentrations of fault gases received in the experiments with the closed experimental set-up (b).

### 3. Discussion

The conclusions which can be derived from the experiments performed with the closed experimental set-up (b) are somehow different from the conclusions reached after the experiments with the open experimental set-up (a) [1]. Lower amounts of CO2 and CO were formed by the naphthenic, uninhibited mineral oil (NA-UI) compared to the other oils. Instead, the oil NA-UI generated definitely more saturated hydrocarbons (CH4, C2H4 and C<sub>3</sub>H<sub>8</sub>) than any of the other oils. In contrast, the oil PA-I tends to produce the unsaturated fault gases (C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub>) in case of thermal stress. Interestingly, the inhibited, naphthenic mineral oil, which was used air saturated (NA-Ib\*), showed the highest concentration of hydrogen in the oil and formed the highest amount of hydrogen in total.

A sensible explanation for the different patterns of fault gases under thermal stress would be the assumption that the formation of fault gases depends directly on the oil's composition. Some indications support this explanation: (1) the oil with the lowest percentage of naphthenic and aromatic hydrocarbons (PA-I) showed the "best" values of the characteristic figures after heating (see bottom of Table 3 in [1] and Table 7); (2) the DGAs after heating showed significantly more oxygen (O<sub>2</sub>) and less carbon oxide (CO and CO<sub>2</sub>) for



Figure 3. Concentrations of  $CO_2$  and CO in oils NA-UI, NA-Ia, NA-Ib, NA-Ib\* (air saturated) and PA-I after heating (100 h; 160 °C) with the closed experimental set-up (b)



Figure 4. Concentrations of CH<sub>4</sub>,  $C_2H_6$  and  $C_3H_8$  in oils NA-UI, NA-Ia, NA-Ib, NA-Ib<sup>\*</sup> (air saturated) and PA-I after heating (100 h; 160 °C) with the closed experimental set-up (b)

oil PA-I than for the other inhibited oils (see top of Table 3 in [1], and Table 2 to Table 6); and (3) significantly less hydrocarbons were formed by oil PA-I during the heating period (see top of Table 3 in [1], and Table 2 to Table 6). Obviously, the oil PA-I consists of molecules which are attacked by oxygen more slowly or to a lesser extent than the molecules from oils NA-Ia, NA-Ib and NA-UI. In other words, the oil PA-I is more stable to oxidative degradation due to the molecular structure of its components. Furthermore, the results for the gases methane (CH<sub>4</sub>), ethane (C<sub>2</sub>H<sub>6</sub>) and propane (C<sub>3</sub>H<sub>8</sub>) (see Fig. 6(b) in [1], and Figure 4) indicate that the oil PA-I generated about ten times less saturated hydrocarbon gases during the heating period than the naphthenic min-

eral oils NA-UI, NA-Ia and NA-Ib. Such a discrepancy can only be explained by unequal chemical reaction pathways owing to different molecular structures of the oils' components. Due to the fact that the oil PA-I with the lowest percentage of naphthenic and aromatic hydrocarbons forms the smallest amount of saturated hydrocarbons in both experimental set-ups, the following deduction can be drawn: saturated hydrocarbons as fault gases are mainly generated by naphthenic, i.e. cyclic and aromatic hydrocarbons in case of thermal stress. Further theoretical investigations to derive appropriate reaction mechanisms concerning the plausibility of this hypothesis will be part of later studies. The concentrations of gases in the oils received after the heating experiments



Figure 5. Concentrations of  $C_2H_4$  and  $C_3H_6$  in oils NA-UI, NA-Ia, NA-Ib, NA-Ib\* (air saturated) and PA-I after heating (100 h; 160 °C) with the closed experimental set-up (b)





with the closed experimental set-up (b) (see Table 2 to Table 6) were evaluated by application of existing interpretation schemes [6, 7, 8, 9, 10, 11, 12, 13]. The results are outlined in Table 8. Interestingly, the interpretation schemes did not result in the same diagnostic indication for each of the five oil samples examined.

### Conclusion

In key experiments, four degassed, commercially available and well-established transformer oils were subjected to thermal stress by heating them at 160 °C for 100 h in an open and a closed experimental set-up using a well-defined temperature profile. The oils' compositions differed relating to the percentages of aromatic, paraffinic and naphthenic hydrocarbons, respectively. Compared to the naphthenic mineral oils, the transformer oil mainly consisting of paraffinic hydrocarbons showed the lowest amounts of saturated hydrocarbons as fault gases, while a tendency towards the formation of gaseous, olefinic hydrocarbons could be recognized. Some results received from the heating experiments by DGA were subjected to six transformers' diagnostic interpretation schemes resulting in partly differing indications. Obviously, there is a dependence between an oil's chemical composition and its gassing behavior with consequence to resultant, diagnostic recommendations, if an oil is exposed to thermal stress. Additionally, Different patterns of fault gases formed under thermal stress depend directly on the oil's chemical composition, thus affecting the diagnostic recommendations

it seems that the gassing behavior is influenced by the oil's air saturation as well. A necessity for the modification of the existing interpretation schemes, e.g. [6, 7, 8, 9, 10, 11, 12, 13], cannot be excluded if the insulation liquids containing mainly paraffinic (GtL)-oils are used. Besides, an adjustment of gas monitoring systems, installed on transformers, towards a lower limit of detection and lower alarm settings appears to be inevitable in case of mainly paraffinic (GtL)-oils as insulation liquids.

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Table 8. Diagnostic recommendations derived by existing interpretation schemes on concentrations of gases in oil samples after heating in the closed experimental set-up (b) and cooling down – see section 1 of this article.

Interpretation Scheme	NA-UI	NA-la	NA-Ib	NA-Ib NA-Ib*	
IEC 60599 [6]	T1: thermal fault T <300 °C	T1: thermal fault T <300 °C	T1: thermal fault T <300 °C	T1: thermal fault T <300 °C	D1: discharges of low energy
Doernenburg ratio [7]	thermal degradation	thermal degradation	thermal degradation	thermal degradation	thermal degradation
Key gas [8]¹	overheated cellulose	overheated cellulose	overheated cellulose	overheated cellulose	overheated cellulose
Duval triangle [9, 10, 11]	T1: thermal fault T <300 °C	T1: thermal fault T <300 °C	T1: thermal fault T <300 °C	T1: thermal fault T <300 °C	T3: thermal fault T >700 °C
Duval pentagon [12]	T1: thermal fault T <300 °C	T1: thermal fault T <300 °C	T1: thermal fault T <300 °C	S: stray gassing of oil T <200 °C	T3: thermal fault T >700 °C
Rogers ratio [13]	thermal fault range 150 – 300 °C	thermal fault range 150 – 300 °C	thermal fault range 150 – 300 °C	no fault	no fault

<sup>1</sup> in case of scheme [8], a definitely correct indication was not possible - instead, the most "suitable" was depicted; \* air saturated

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