Investigation of Oil Temperature Effect on Aging Marker Content of Insulating Paper in Power Transformers, by Gas Chromatography Method

Abstract

Insulating paper aging of power transformers, which is a reliability factor for this equipment, can be evaluated by non-destructive methods such as measuring chemical markers' content in transformer oil. Since the sampling temperature of oil can affect the accuracy of laboratory measurements, in this study, the correlation between novel aging marker methanol and degree of polymerization (DP) of insulating paper has been studied. Temperature correction factors have been obtained for the markers (2-Fal, water and methanol) and the correlation formula has been improved by under load transformers' data. To optimize the calculated estimation formula, sampling from real transformer has been carried out. Various experiments have been performed on them and their results have been analyzed. The real DP was also measured for the insulating papers, sampled at the overhaul stage. The optimized model for insulating paper DP calculation using temperature corrected concentration of methanol in insulating oil has been provided in this work.

Keywords: Power transformer, Condition monitoring, nondestructive evaluation, Chemical aging marker, Gas Chromatography

1. Introduction

Condition monitoring of power transformers can be done in two ways: *i)* measuring the reliability of parts in overhaul *ii)* evaluating the condition by non-destructive methods while the equipment is under load. Due to the high cost of power transformers, postponing the condition monitoring to overhaul times is not acceptable [1-3]. Chemical markers releasing into the insulating oil, because of paper aging, are reported as proper indicators of transformer operating condition. Furan compounds such as 2-furfuraldehyde (2-FAL), carbon oxides, oil acidity, water content and novel marker methanol are the most important chemical markers that can estimate the transformer's condition and remaining life [4-6].

On the other hand, destructive methods can be utilized to measure the insulating paper's age, which is directly correlated with the transformer's age. Degree of polymerization (DP) of insulating papers can be measured by standard methods after sampling the paper from the equipment in overhaul. Therefore, because of the simple nature of oil sampling and corresponding the chemical markers to the paper condition, these methods are preferred to direct measuring of DP [7,8].

Methanol as a novel marker (introduced by Jalbert et al. [1-3]) has some advantages in comparison with the other markers, such as its temperature stability in oil, its origin (which is only

the insulating paper, while other markers can be produced by insulating oil, and this can make estimating errors) and its producing from both kraft and thermally upgraded (TU) papers (while the furanic compounds are only produced by aging of normal kraft papers) [9-13]. Many efforts have been made on obtaining the exact correlation formula between the DP of transformer paper (which can estimate the transformer's age and operating condition) and methanol (and other markers) concentration in the insulating oil [14-19]. Published studies reported some of these formulas and a few of them focused on the importance of sampling temperature on the marker's content. Considering the sampling temperature can change the obtained results, due to the changes in solid-liquid-gas equilibrium states by different temperatures.

In this study, the correlation formula between methanol concentration and DP and also the temperature correcting factor for methanol, 2-FAL and water have been reported during in-Lab and in-field experiments. The focus of this work is on the novel marker methanol to clarify its behavior as a reliable condition monitoring marker.

2. Experiments

2.1. Materials

In general, the materials used in this paper are divided into three categories according to the tests and analyzes in each part of the study:

- Materials used in gas chromatography optimization experiments
- Materials used in aging tests
- Materials used for the analysis of aged samples

In the optimization stage of chromatography, both insulating oil and methanol are used to make samples. In some cases, insulating oil sampled from under load transformers was used to determine the response of the gas chromatography apparatus under operating conditions.

The new insulating oil used in this paper was NynasNytro Libra, which was purchased as a 220-liter barrel (Fig. 1). Prior to conducting tests and also using the reference oil in gas chromatography optimization processes, the quality tests were performed on the purchased oil. The quality of the purchased oil was approved by the Fuel and Oil Research Laboratory (in NRI).

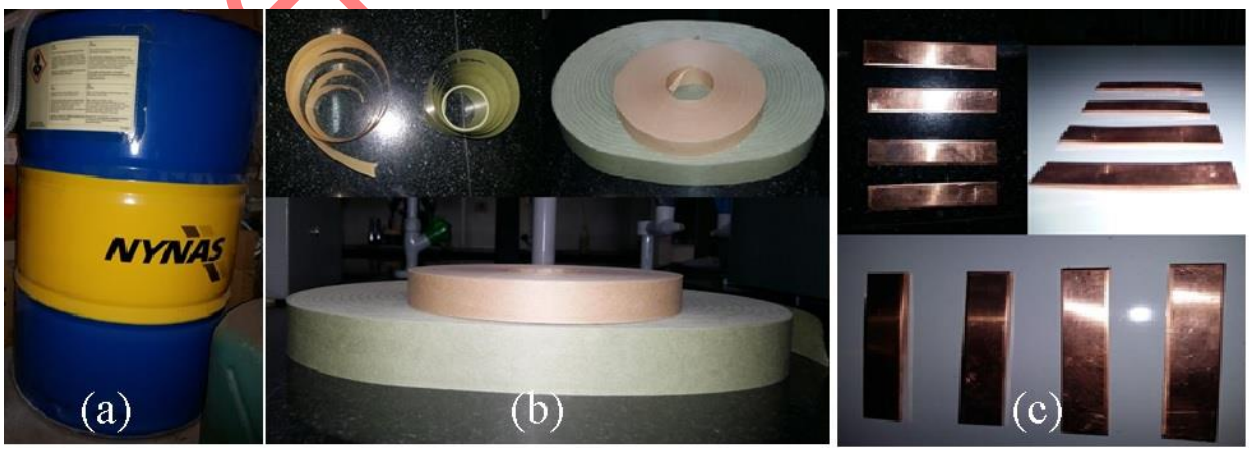

Figure 1 (a) Insulating oil, (b) Insulating paper and (c) Copper blades

Insulation paper (in two types), insulating oil and also copper blades (40×15×2 mm^3) were used in the aging experiments. Two types of insulating paper were used for the aging tests. Insulating papers, including ordinary kraft and thermally upgraded paper, have been purchased from Iran Transfo Company (Fig. 1). As reported before, one of the furan marker's defects in evaluating the status of transformer insulation papers is its inability to evaluate the status of thermally upgraded paper. Therefore, the simultaneous examination of these two types of paper is of great importance in processing tests.

Copper blades have also been used as catalysts in the aging process (Fig. 1). These blades were cut to the required dimensions and used as a core for the insulating paper wrapping during the aging process.

Materials and solvents used in this paper also include acetone, hexane, toluene and hydrochloric acid (for DP measurement, gas chromatography analysis and aging tests).

In the analysis of aged samples as well as samples obtained from under load transformers, hexane (for using in the Soxhlet degreasing process), methanol (to calibrate the gas chromatography apparatus to quantify the amount of methanol in the insulating oil), Cuen (2-ethylene diamine copper solution for direct measurement of degree of polymerization testing according to ASTM D4243 standard), acetone, toluene, hydrochloric acid and nitric acid (for washing the glass viscometer in the degree of polymerization tests) were used.

2.2. Equipment and apparatus

In the first group, related to the optimization of gas chromatography method, the used equipment are as follows:

Magnetic Hot Plate, Gas Chromatography system, Dynamic headspace, Microliter Syringe and other common laboratory facilities (Agilent 6890 N gas chromatography, Agilent 5973 grid mass detector, VF-WAXms chromatography column (60 m × 0.32 mm × 0.5μm) and headspace device Agilent 7697A).

The next group of instruments consist of: aging components (ovens, glass bottles (sealed with resistant caps under thermal stress)) and other analysis systems (Mettler DL70 for acidity analysis, Syknm S2100 device for furan analysis and Mettler DL37 device for water content analysis).

2.3. Establishing experiment set-up

According to the previous parts, setup is also divided into two main sections. The first part consists of a laboratory setup for aging tests, and the second part is an analysis setup using chromatography analysis.

In the case of the aging tests, the desired setup is an oven containing glass containers in which oil, paper and copper were used as the main transformer components.

To establish the chromatography analysis, different methods had to be tested to optimize the applied method to measure methanol using a gas chromatograph equipped with a headspace and a mass detector. The main goal is to achieve the best peak in the right conditions. Suitable conditions can also be defined as the appearance of a peak with a perfect separation from the other peaks as well as an acceptable sub-peak area.

Therefore, some of the effective parameters in methanol peak identification were tested. These parameters include the gas rate, the split ratio and the oven time schedule. The optimized obtained details for chromatography schedule are presented in Table 1.

Table 1 Gas chromatography and headspace operating conditions

Gas Chromatography condition
Helium carrier gas Dividing coefficient 1:5 Injection temperature of 250 ° C injection Oven Condition: Two minutes at 40 ° C, 5 °C per minute to 80 °C (1 minute remaining), 15 °C per minute to 200 °C (7 minutes remaining) and 30 °C per minute of return rate to 40 degrees of Celsius
Headspace Conditions
Sample temperature in the oven: 80 degrees (Celsius) Loop Temperature: 150 ° C Transmission line temperature: 150 degrees (Celsius) Vial equilibration time: 10 minutes Pressuring time: 0.5 minutes Injection time: 1 minute

After achieving the optimum methanol peak, calibration was required to convert the peak areas to methanol concentration. For this purpose, different concentrations of methanol in the oil were prepared in the range of ppb and ppm. After injecting the samples into GC, the quantification of methanol concentration was done by plotting the surface area according to the methanol concentration in the oil. It should be noted that, in order to increase the accuracy and also to improve the correlation coefficient of the calibration curve, the above process was performed in two ranges of ppb and ppm.

2.4. Aging experiments in oven

Accelerated aging is typically performed at elevated temperatures, which results in a shorter time for reaching the insulating paper to its end of life. For this purpose, the temperature of 170 ° C was used to apply at the predetermined aging times in the experiments. The correlation between applied temperature and aging has been investigated in literature [1-3, 20]. It should be noted that, due to the choosing of gas-tight experimental vessels in the aging procedure, methanol marker cannot be leaked and the analysis of concentration has been done at the temperatures close to the room temperature.

34 samples have been provided to cover the transformer age of 0 to 45 years and have been aged in the oven under the mentioned condition.

2.5. Aging experiments in oven for temperature correction tests

One of the main issues discussed in this paper is the investigation of the effect of sampling temperature on the concentration of the insulating paper aging's markers. Since the sampling of insulating oil is carried out from under load transformers and considering the fact of variable

working temperatures which affect the solid-liquid-gas equilibrium and hence the markers' contents, a united method is required to analyze the amount of methanol (and other markers) present in the insulating oil, by considering the important role of sampling temperature.

For this purpose, the temperature of 20 °C has been taken as the reference temperature and the correction factor of the markers at other temperatures have been calculated. The process of testing the effect of temperature on the markers of insulating paper aging began by providing precast glass containers under the same conditions. Five precast glass containers were prepared similar to those used in the accelerated aging experiments. All containers were placed in the oven at 170 °C at a same time. After about one day, the oven was set to temperature of 70 degrees of Celsius, in which the accelerated aging of the oil and paper could be ignored. The glass containers were kept at this temperature for 2 hours to ensure equilibrium between the components at the mentioned temperature. Subsequently, temperatures of 60, 50, 40, and 30 °C were applied to the oven, respectively, for 2 hours. At the interval of each temperature change, one of the containers was brought out from the oven and its oil sample was collected in DGA-specific syringes. It should be noted that, in order to increase the accuracy of the experiments, the above-mentioned steps were performed twice, so that the temperature correction diagrams were drawn in two different aging modes (135 and 170 °C). Therefore, by comparing the temperature correction graphs and their small differences, it can be concluded that these graphs will have the same response for the samples at sampling temperatures, regardless of the processing conditions (aging temperatures).

3. Results and discussion

3.1. Determination of markers in aged samples (for accelerated aging and temperature correction analyses)

After preparation of the samples, furan, moisture and methanol measurements were performed on the samples.

In order to obtain a correction coefficient for each of the markers, the concentration of that marker at 20 ° C should be calculated based on the value of that marker at the measured temperature, which can be summarized as follows:

$$\text{Temperature Correction factor} = \frac{\text{Concentration of marker at 20 °C}}{\text{Concentration of marker at sampling Temperature}}$$

The following figures (Figs. 2-4) show the relationship between concentration and sampling temperature for the three markers of 2-FAL, moisture and methanol, along with their mathematical relationships and R-squared of the correlation.

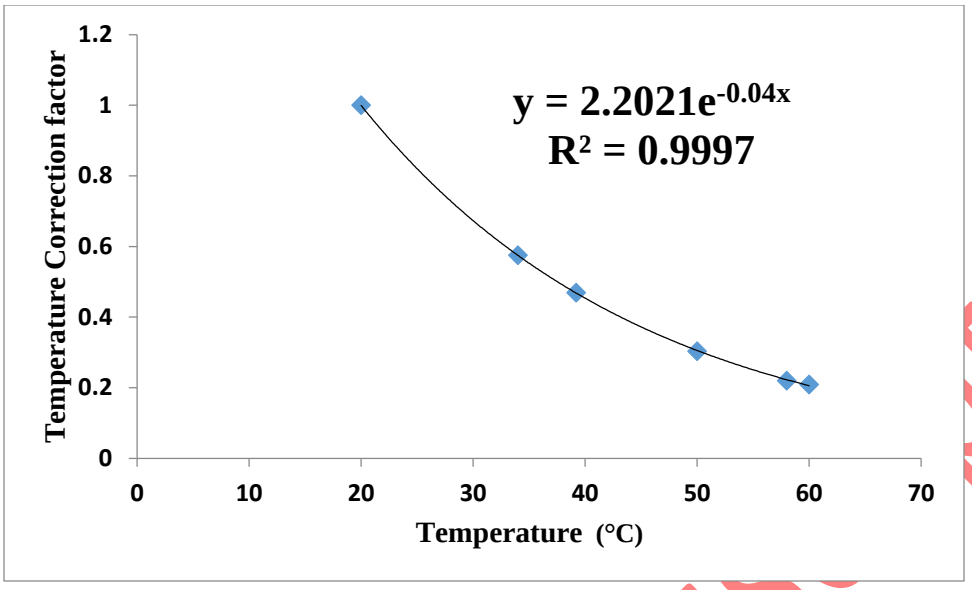

Figure 2 Temperature Correction for Methanol

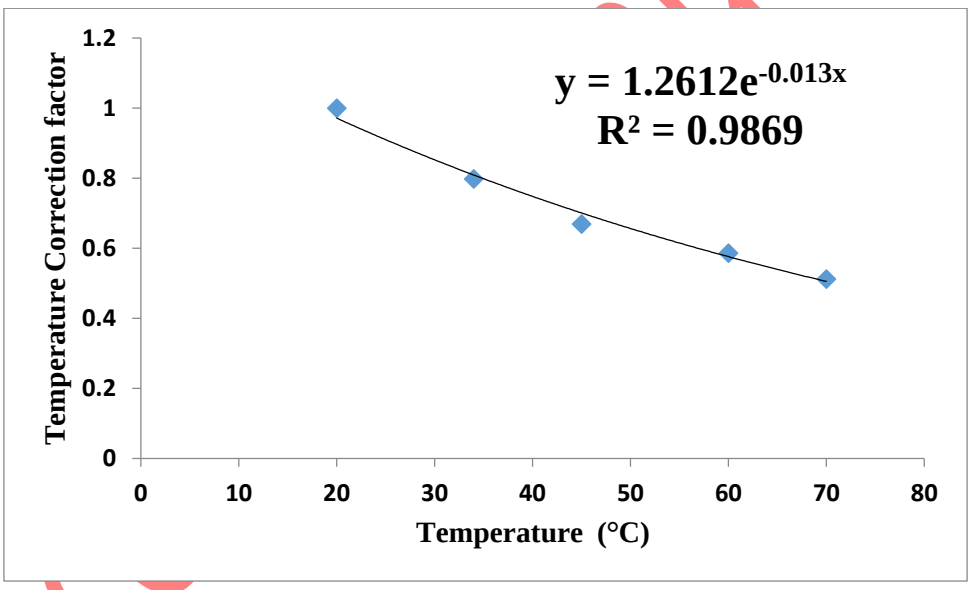

Figure 3 Temperature Correction for water

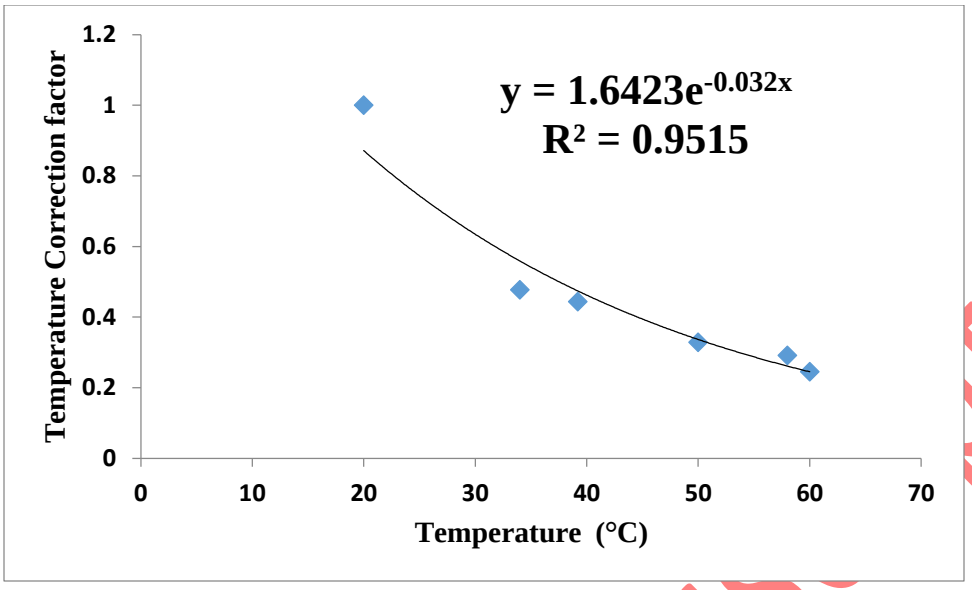

Figure 4 Temperature Correction for 2-FAL

According to Fig. 4, "Temperature correction factor" and the "Temperature" is affected by a data in 20 degrees. Without this data, the correlation seems to be linear.

According to the obtained relationships, the measured values as well as the corrected values of the different aging markers during the accelerated aging tests performed before, are presented in Table 2. It should be noted that the repeatability of the tests has been investigated and a mean error of ±4% has been assigned to all of calculated results.

Table 2 Markers' content and DP before and after temperature correction

Sample name	Methanol (ppm)	2FAL (ppm)	Water (ppm)	Acidity	Methanol (ppm) after temperature correction	2FAL (ppm) after temperature correction	Water (ppm) after temperature correction	Real DP (by ASTM D4243)	DP (calculated by obtained Methanol Model)
1	1.58	0.187	21.5	0.004	1.218	0.132795	19.28865	520	486.5404
2	0.71	N.D	23.2	0.008	0.548	N.D	20.81379	834	864.5605
3	1.87	0.808	22	0.009	1.442	0.573788	19.73722	379	406.6375
4	1.42	0.258	45.8	0.007	1.096	0.183214	41.0893	601	536.4939
5	2.05	1.371	28	0.004	1.586	0.973593	25.1201	307	361.5869
6	1.57	0.925	37.6	0.007	1.296	0.691381	34.44169	471	457.1615
7	2.04	1.842	22.5	0.004	1.578	1.308066	20.18579	311	363.9803
8	1.73	1.393	21.6	0.014	1.53	1.099392	20.22778	335	378.6008
9	1.47	1.528	29.3	0.008	1.21	1.142087	26.83887	500	489.6594
10	1.94	1.889	34.4	0.011	1.596	1.411913	31.51048	302	358.612
11	1.86	0.742	25.7	0.015	1.536	0.5546	23.54126	332	376.7483

12	1.88	2.215	24.3	0.018	1.655	1.748136	22.75625	289	341.431
13	1.84	4.437	30	0.021	1.625	3.501797	28.09414	295	350.0892
14	1.79	1.921	28.2	0.019	1.574	1.516104	26.40849	313	365.1816
15	3.92	4.711	22.5	0.017	3.03	3.345439	20.18579	141	55.19731
16	0.96	N.D	16.1	0.006	0.74	N.D	14.44406	744	722.393
17	1.08	0.126	19.6	0.006	0.838	0.089477	17.58407	690	663.5297
18	1.28	0.114	20.3	0.017	0.986	0.080955	18.21207	630	586.553
19	1.2	N.D	22.6	-	1.054	N.D	21.16425	612	554.988
20	1	N.D	25.8	0.004	0.881	N.D	24.16096	666	639.846
21	1.29	N.D	28.3	0.005	1.136	N.D	26.50214	574	519.5279
22	1.26	N.D	26.7	0.007	1.109	N.D	25.00379	593	530.913
23	1.41	N.D	23.2	0.013	1.245	N.D	21.72614	503	476.1632
24	1.57	N.D	22.1	0.007	1.385	N.D	20.69602	411	425.7261
25	1.7	N.D	23.2	0.023	1.492	N.D	21.72614	354	390.5044
26	1.9	N.D	22.5	0.003	1.46	N.D	20.18579	370	400.766
27	1.92	N.D	22.9	0.009	1.584	N.D	20.97645	308	362.1841
28	3.81	N.D	42.1	0.012	3.14	N.D	38.5637	154	38.31935
29	2.6	N.D	32.5	0.01	2.29	N.D	30.43532	198	187.7264
30	2.56	N.D	22.3	0.005	1.974	N.D	20.00636	216	258.0067
31	0.81	-	73.9	-	0.461	-	59.90599	930	946.3833
32	1.05	-	76.8	-	0.548	-	60.65902	897	864.5605
33	0.84	-	40.1	-	0.517	-	33.36275	911	892.1219
34	1.11	-	74.4	-	0.533	-	57.25526	839	877.6964

It should be noted that, the last column in the above Table is calculated by the obtained correlation between methanol concentration and DP, which is illustrated in Fig. 5.

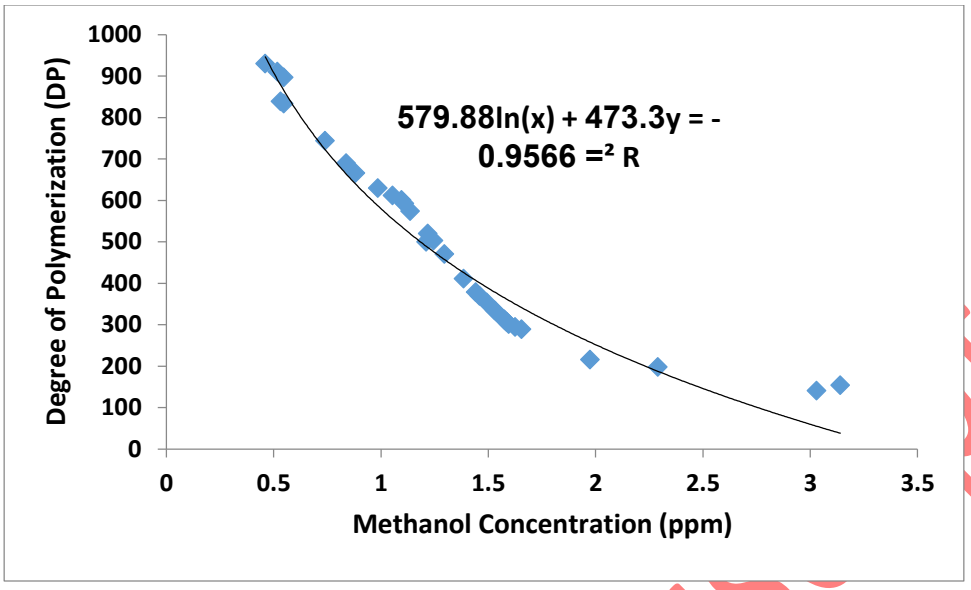

Figure 5 The correlation of methanol content in insulating oil and DP of insulating paper

In Fig. 6, the difference between calculated DP and real DP is presented for both thermally upgraded and kraft papers, which clarifies the ability of methanol marker in estimating the transformer age, regardless of paper type.

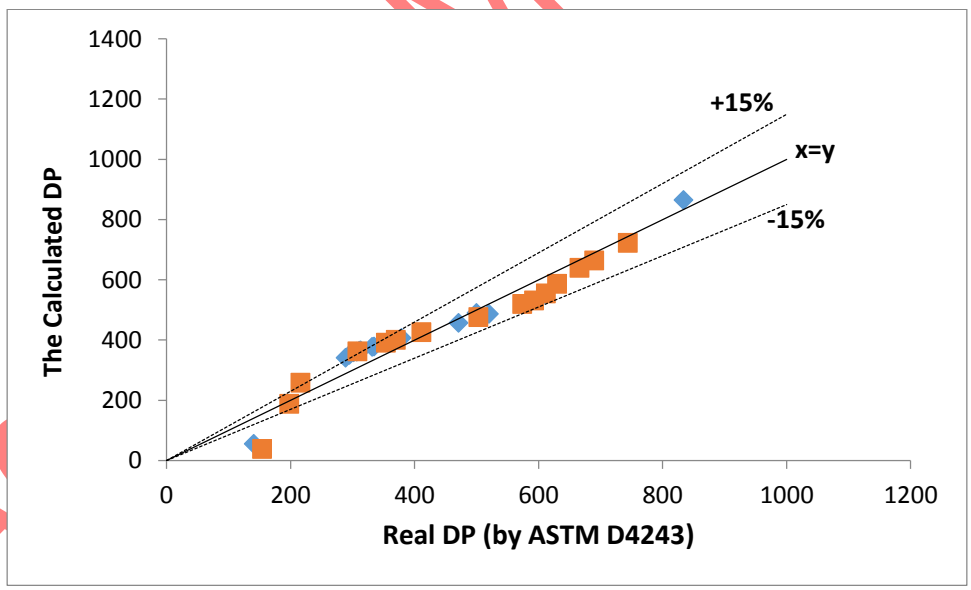

Figure 6 The difference between calculated DP and real DP (the squares and the diamonds represent thermally upgraded and kraft papers, respectively

3.2. Model optimization by obtained results from under load transformers

The values of the markers have been measured for eleven under load transformers (in accordance with Table 3). After temperature correction, the corrected values were analyzed with the real degrees of polymerization (achieved by direct measurement of DP using ASTM D4243 on the

insulating paper samples which obtained during overhauling of the mentioned transformers). The following relationship, presented in Fig. 7, between methanol concentration and DP can be reported as an accurate formula due to the laboratory and field sampling tests.

Table 3 Data from real transformers

Transformer name	Methanol (ppm)	Methanol after temperature correction (ppm)	Real DP (by ASTM D 4243)	Calculated DP by methanol concentration before temperature correction	Calculated DP by methanol concentration after temperature correction
T1	3.24	2.33	189	23	180
T2	2.33	1.43	392	178	410
T3	4.23	2.7	140	-103	152
T4	1.52	1.09	565	382	540
T5	2.09	1.23	471	230	482
T6	2.95	3.13	90	67	40
T7	1.45	1.43	420	403	410
T8	1.11	1.46	435	528	400
T9	1.49	1.42	424	389	415
T10	1.21	1.18	488	490	500
T11	1.61	1.07	530	353	546

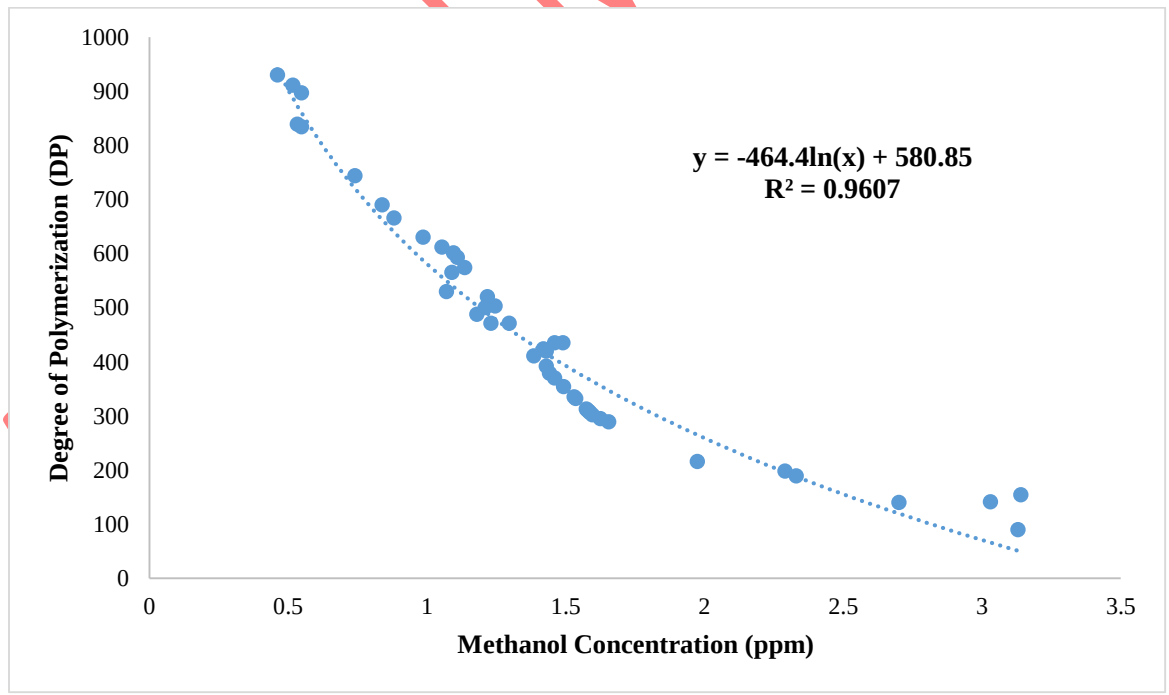

Figure 7 optimized model for insulating paper DP calculation using temperature corrected concentration of methanol in insulating oil

4. Conclusion

In this paper, the aging markers and their ability to estimate the transformer insulation paper condition and remaining life were evaluated from several aspects. Furan, water and methanol were considered as three conventional and novel markers.

The new studies on methanol marker were analyzed focusing on the role of oil sampling temperature in accurately estimation of transformer age. Due to the small number of articles in this field, the importance of the topic for innovative studies was demonstrated. A setup was designed to measure the amount of methanol present in the insulating oil. Accelerated aging was performed on paper-oil-copper samples and the results included the amount of different markers (furan, methanol, water and oil acidity). The degree of polymerization of the insulating paper was also measured by direct method (ASTM D 4243). The most important experiments and calculations performed was to investigate the role of sampling temperature on the aforementioned markers. After precise evaluation of the role of temperature, a marker change diagram was presented after temperature correction and a temperature correction coefficient was proposed for each of the markers at different temperatures. The correlation between corrected methanol concentration and DP was also reported.

To optimize the calculated estimation formula, sampling from real transformer was carried out. Various experiments were performed on them and their results were analyzed. The real DP was also measured for the insulating papers, sampled at the overhaul stage.

At the end of the paper, the results were interpreted and the data was analyzed, and finally, from two perspectives, goals were determined. First, the need for temperature correction on the data obtained in the laboratory with respect to the sampling temperature was proved. Second, the results show that the methanol marker has a high accuracy in assessing the status of the transformer insulation system.

Increasing the operating data to improve the life estimation formula of power transformers will be achieved in further studies.

References

1. Jalbert J, Rodriguez-Celis EM, Arroyo-Fernández OH, Duchesne S, Morin B (2019) Methanol Marker for the Detection of Insulating Paper Degradation in Transformer Insulating Oil. Energies 12 (20):3969
2. Matharage S, Liu Q, Davenport E, Wilson G, Walker D, Wang Z Methanol detection in transformer oils using gas chromatography and ion trap mass spectrometer. In: 2014 IEEE 18th International Conference on Dielectric Liquids (ICDL), 2014. IEEE, pp 1-4
3. Liao R, Lin Y, Guo P, Liu H, Xia H (2015) Thermal aging effects on the moisture equilibrium curves of mineral and mixed oil-paper insulation systems. IEEE Transactions on Dielectrics and electrical insulation 22 (2):842-850
4. Matharage S, Liu Q, Wang Z, Mavrommatis P, Wilson G, Jarman P Ageing assessment of transformer paper insulation through detection of methanol in oil. In: 2015 IEEE 11th International Conference on the Properties and Applications of Dielectric Materials (ICPADM), 2015. IEEE, pp 392-395
5. Jalbert J, Rodriguez-Celis E, Duchesne S, Morin B, Ryadi M, Gilbert R (2015) Kinetics of the production of chain-end groups and methanol from the depolymerization of cellulose during the ageing of paper/oil systems. Part 3: extension of the study under temperature conditions over 120 C. Cellulose 22 (1):829-848
6. Rodriguez-Celis E, Duchesne S, Jalbert J, Ryadi M (2015) Understanding ethanol versus methanol formation from insulating paper in power transformers. Cellulose 22 (5):3225-3236

7. Arroyo OH, Fofana I, Jalbert J, Ryadi M (2015) Relationships between methanol marker and mechanical performance of electrical insulation papers for power transformers under accelerated thermal aging. IEEE Transactions on Dielectrics and Electrical Insulation 22 (6):3625-3632
8. Matharage S, Liu Q, Wang Z (2016) Aging assessment of kraft paper insulation through methanol in oil measurement. IEEE Transactions on Dielectrics and Electrical Insulation 23 (3):1589-1596
9. von Steinkirch Souza EMP, Mildemberger L, Akcelrud L, Andreoli MC, dos Santos K, da Silva GC, da Motta HN, Gulmine JV, Munaro M (2016) Evaluation of the chemical stability of methanol generated during paper degradation in power transformers. IEEE Transactions on Dielectrics and Electrical Insulation 23 (5):3209-3214
10. Matharage S, Liu Q, Wang Z, Krause C, Smith P, Mavrommatis P Methanol and furan detections in a gas to liquid hydrocarbon oil for indicating cellulose insulation ageing. In: 2016 IEEE International Conference on Dielectrics (ICD), 2016. IEEE, pp 601-604
11. Arroyo-Fernández OH, Fofana I, Jalbert J, Rodriguez E, Rodriguez LB, Ryadi M (2017) Assessing changes in thermally upgraded papers with different nitrogen contents under accelerated aging. IEEE Transactions on Dielectrics and Electrical Insulation 24 (3):1829-1839
12. Arroyo OH, Jalbert J, Fofana I, Ryadi M (2017) Temperature dependence of methanol and the tensile strength of insulation paper: kinetics of the changes of mechanical properties during ageing. Cellulose 24 (2):1031-1039
13. Jalbert J, Lessard M-C, Ryadi M (2013) Cellulose chemical markers in transformer oil insulation Part 1: Temperature correction factors. IEEE Transactions on Dielectrics and Electrical Insulation 20 (6):2287-2291
14. Jalbert J, Lessard M-C (2015) Cellulose chemical markers relationship with insulating paper post-mortem investigations. IEEE Transactions on Dielectrics and Electrical Insulation 22 (6):3550-3554
15. TC10 I (2007) IEC 60422 Ed. 3.0 b: 2005, Mineral insulating oils in electrical equipment-Supervision and maintenance guidance, Multiple. Distributed through American National Standards Institute (ANSI)
16. Lessard M-C, Jalbert J, Ryadi M Establishing correction factors for the partitioning of furanic derivatives between oil and paper insulation. In: 2013 Annual Report Conference on Electrical Insulation and Dielectric Phenomena, 2013. IEEE, pp 132-135
17. Jalbert J, Gilbert R, Denos Y, Gervais P (2012) Methanol: a novel approach to power transformer asset management. IEEE Transactions on Power Delivery 27 (2):514-520
18. Ali M (2019) Inspection technique for lubricant condition detection in static mechanisms.
19. Molavi H, Yousefpour A, Mirmostafa A, Sabzi A, Hamedi S, Narimani M, Abdi N (2017) Static headspace GC/MS method for determination of methanol and ethanol contents, as the degradation markers of solid insulation systems of power transformers. Chromatographia 80 (7):1129-1135.
20. CIGRE Working Group. (2018). Ageing of liquid impregnated cellulose for power transformers. In CIGRE: Paris, France (Vol. 1, p. 53).