Journal of Chemical and Petroleum Engineering (JChPE)

Print ISSN: 2423-673X Online ISSN: 2423-6721

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

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ARTICLE INFO

Article History:
Received: 30 August 2023
Revised: 21 October 2024
Accepted: 28 October 2024
Published: 01 January 2025

Article type: Research

Keywords:
Chemical Aging Marker,
Condition Monitoring,
Gas Chromatography,
Nondestructive Evaluation,
Power Transformer

ABSTRACT

Insulating paper aging of power transformers, 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, the correlation between novel aging marker methanol and the degree of polymerization (DP) of insulating paper has been studied in this study. Temperature correction factors have been obtained for the markers (2-Fal, water, and methanol), and the under-load transformers' data has improved the correlation formula. Sampling from a real transformer was carried out to optimize the calculated estimation formula. 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 a temperature-corrected concentration of methanol in insulating oil has been provided in this work.

Introduction

Condition monitoring of power transformers can be done in two ways: *i)* measuring the reliability of parts in overhaul *and 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 released 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 critical chemical markers that can estimate the transformer's condition and remaining life [4-6].

On the other hand, destructive methods can measure the insulating paper's age, which is directly correlated with the transformer's age. Standard techniques can measure the degree of polymerization (DP) of insulating documents after sampling the paper from the equipment in overhaul. Therefore, because of the simple nature of oil sampling and the correspondence of the chemical markers to the paper condition, these methods are preferred for direct measuring of DP [7, 8].

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Journal of Chemical and Petroleum Engineering, 2025, 59(1): 53-63.
Publisher: University of Tehran Press *DOI: 10.22059/jchpe.2024.364585.1448*

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 it's creating from both kraft and thermally upgraded (TU) papers (while the furanic compounds are only produced by aging of regular kraft papers) [9-13]. Many efforts have been made to obtain 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 focused on the importance of sampling temperature in the marker's content. The sampling temperature can change the obtained results due to the changes in solid-liquid-gas equilibrium states by different temperatures.

This study reported the correlation formula between methanol concentration and DP and the temperature correcting factor for methanol, 2-FAL, and water during in-lab and in-field experiments. This work focuses on the novel marker methanol to clarify its behavior as a reliable condition-monitoring marker.

Materials and Methods

In general, the materials used in this work are divided into three categories:

- 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). Before conducting tests and also using the reference oil in gas chromatography optimization processes, the quality tests were performed on the purchased oil. The Fuel and Oil Research Laboratory approved the quality of the purchased oil (in NRI).

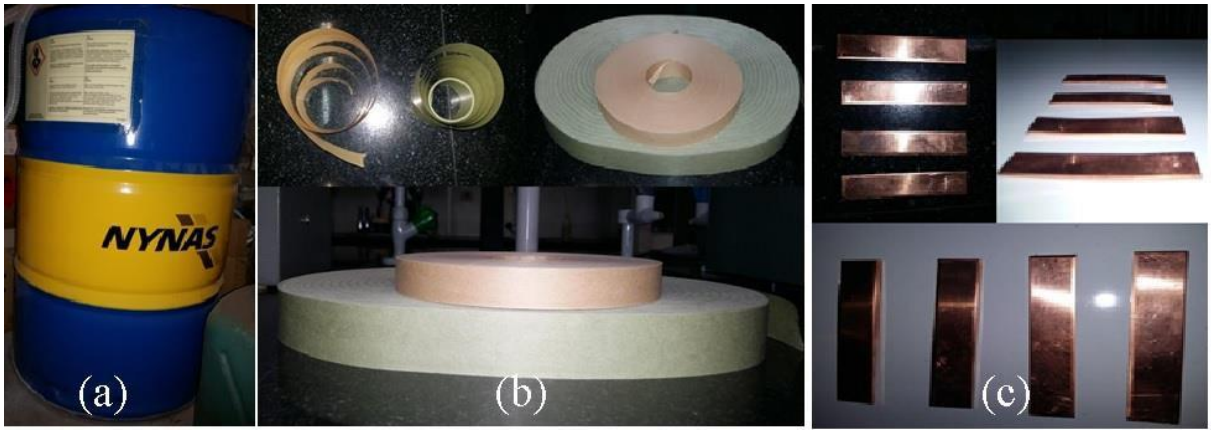

Fig. 1. (a) Insulating oil, (b) insulating paper, and (c) copper blades

Insulation paper (in two types), insulating oil, and copper blades (40×15×2 mm3) 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 assess the status of thermally

upgraded paper. Therefore, the simultaneous examination of these two types of paper is critical 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 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 use 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 the 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.

Equipment and Apparatus

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

Magnetic Hot Plate, Gas Chromatography system, Dynamic headspace, Microliter Syringe, and other standard 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 consists 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).

Establishing Experiment Set-up

The setup is divided into two main sections, as seen in the previous 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.

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 to establish the chromatography analysis. 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 and 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 schedule. The optimized obtained details for the 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 °C
Headspace Conditions
Sample temperature in the oven: 80 °C Loop Temperature: 150 ° C Transmission line temperature: 150 °C 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 to increase the accuracy and improve the correlation coefficient of the calibration curve, the above process was performed in two ranges of ppb and ppm.

Aging Experiments in Oven

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

Thirty-four samples have been provided to cover the transformer age of 0 to 45 years and have been aged in the oven under the mentioned conditions.

Aging Experiments in Oven for Temperature Correction Tests

One of the main issues discussed in this paper is investigating the effect of sampling temperature on the concentration of the insulating paper aging 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 critical role of sampling temperature.

For this purpose, the temperature of 20 °C was taken as the reference temperature, and the correction factor of the markers at other temperatures was calculated. 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 the same time. After about one day, the oven was set to a temperature of 70 degrees 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, 60, 50, 40, and 30 °C temperatures 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 slight 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).

Result and Discussion

Determination of Markers in Aged Samples

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

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:

$$\text{Temperature Correction Factor} = \frac{Concentration\ of\ marker\ at\ 20\ ℃}{Concentration\ of\ marker\ at\ sampling\ temperature}$$

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.

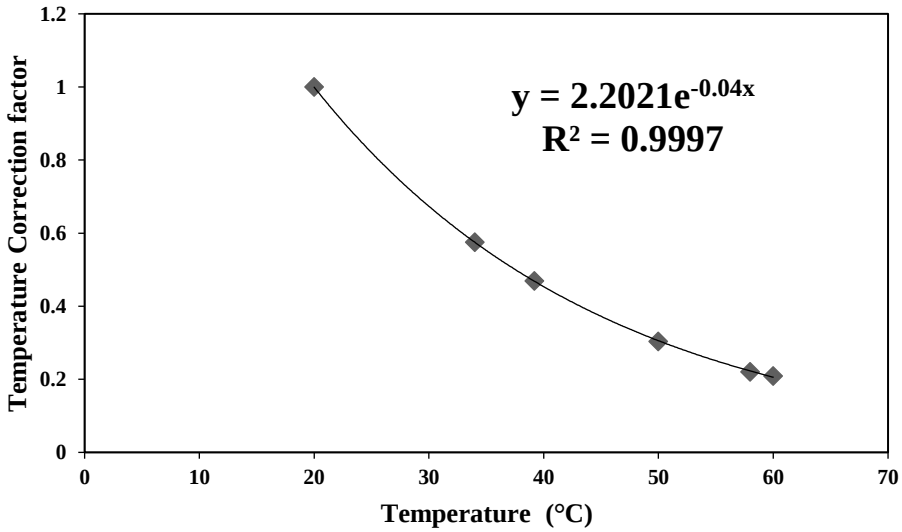

Fig. 2. Temperature Correction for Methanol

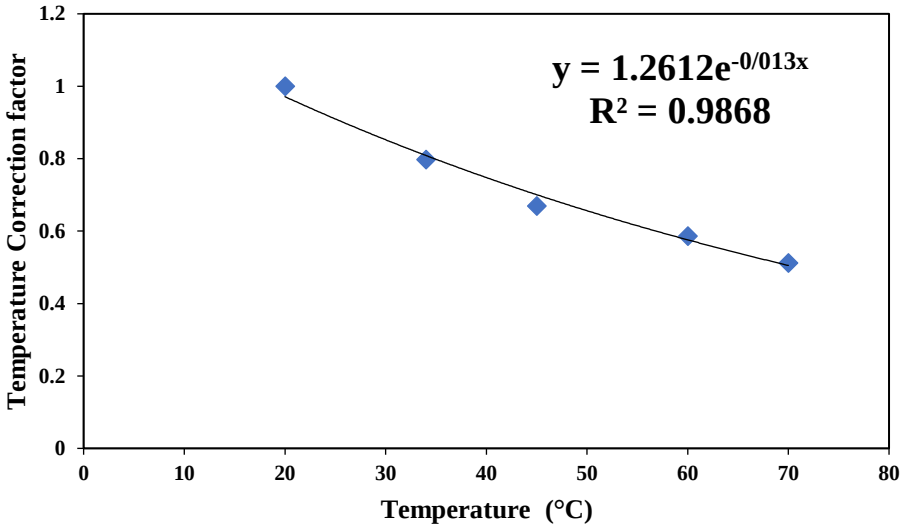

Fig. 3. Temperature Correction for water

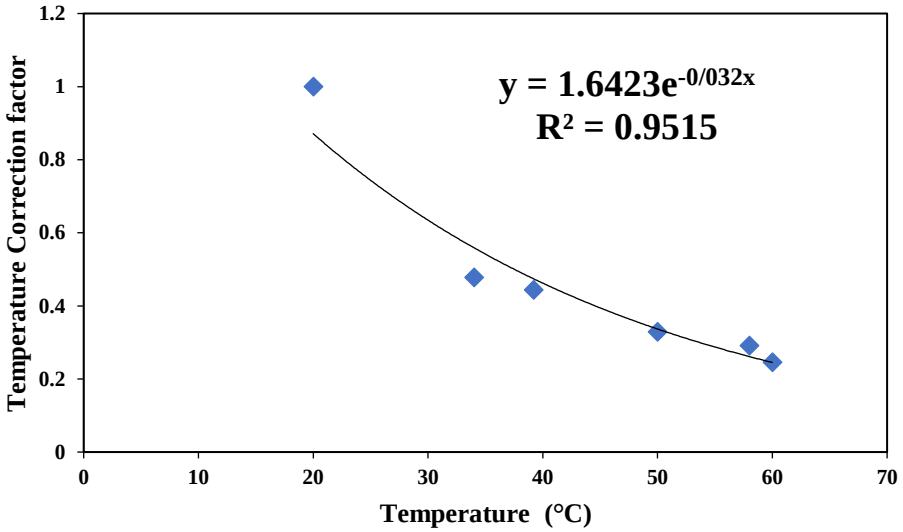

Fig. 4. Temperature Correction for 2-FAL

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

According to the relationships obtained, the measured values and the corrected values of the different aging markers during the accelerated aging tests performed previously 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 the calculated results.

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

Sample	Before temperature correction			Acidity	After temperature correction			Real DP (ASTM D4243)	DP (calculated by obtained Methanol Model)
	Methanol (ppm)	2FL (ppm)	Water (ppm)		Methanol (ppm)	2FAL (ppm)	Water (ppm)		
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, Table 2, is calculated by the obtained correlation between methanol concentration and DP, which is illustrated in Fig. 5.

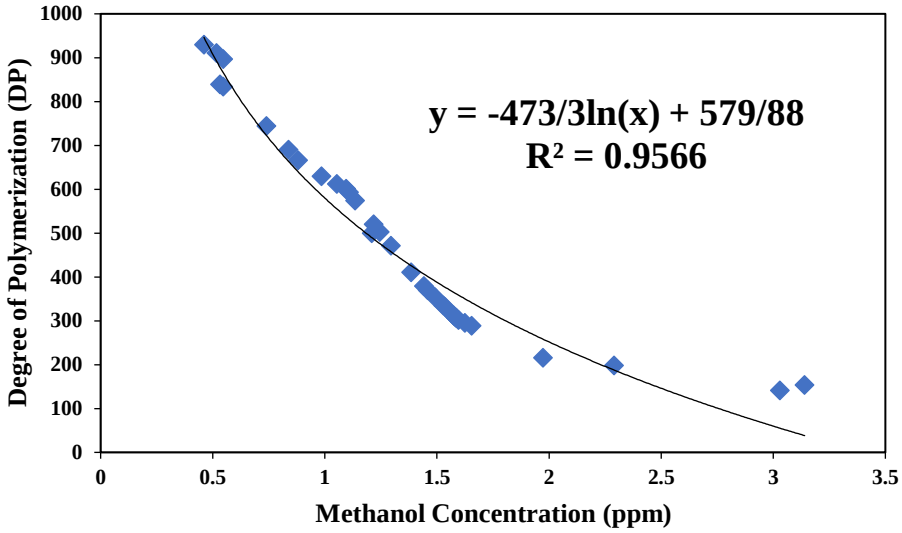

Fig. 5. The correlation of methanol content in insulating oil and DP of insulating paper

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 the methanol marker to estimate the transformer age, regardless of paper type.

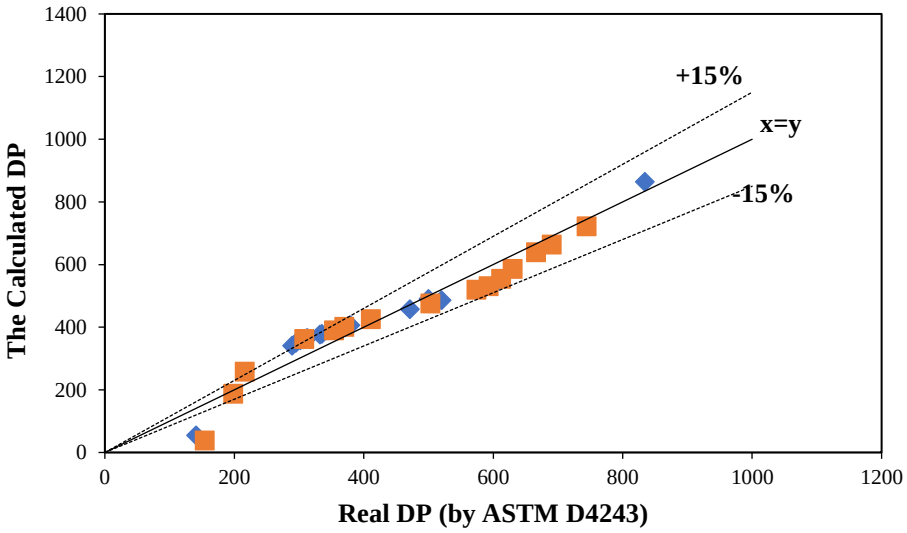

Fig. 6. The difference between calculated DP and real DP (the squares and the diamonds represent thermally upgraded and kraft papers, respectively

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 obtained during the overhauling of the mentioned transformers). The 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 (ASTM D 4243)	DP (before temperature correction)	DP (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

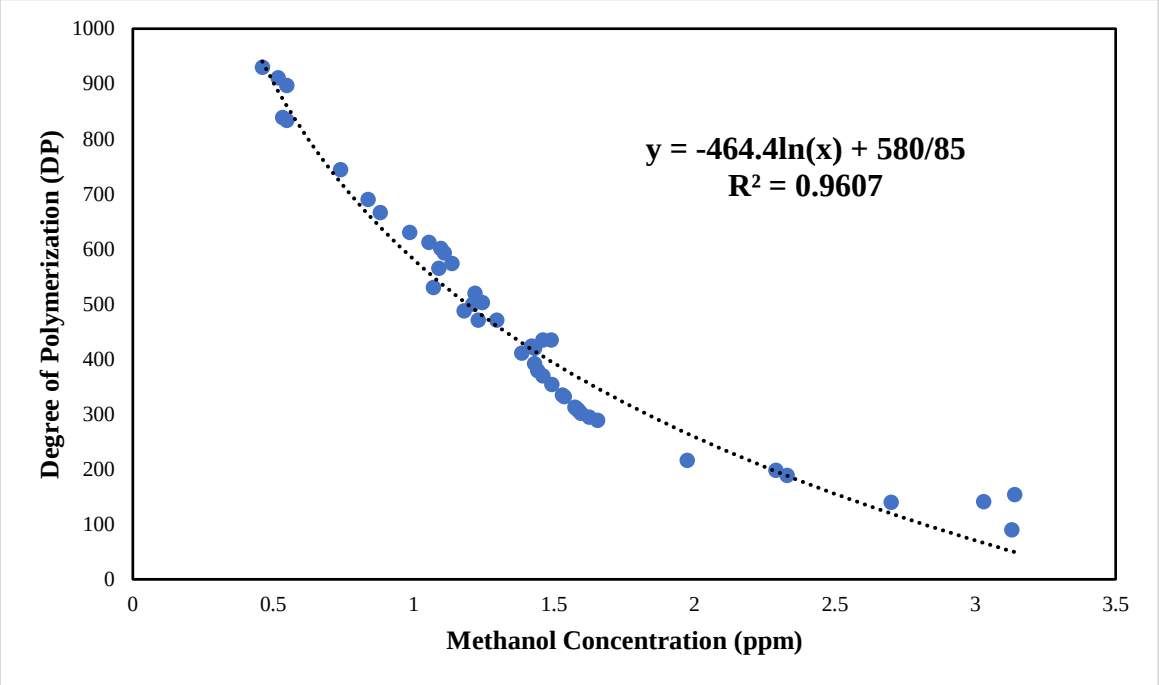

Fig. 7. Optimized model for insulating paper DP calculation using temperature-corrected concentration of methanol in insulating oil

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 markers were analyzed, focusing on the role of oil sampling temperature in accurately estimating 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 were to investigate the role of sampling temperature on the

aforementioned markers. After a 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 marker at different temperatures. The correlation between corrected methanol concentration and DP was also reported.

Sampling from a real transformer was carried out to optimize the calculated estimation formula. 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, 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 is highly accurate 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.

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How to cite: Yousefpour A, Molavi H. Investigation of Oil Temperature Effect on Aging Marker Content of Insulating Paper in Power Transformers, by Gas Chromatography Method. Journal of Chemical and Petroleum Engineering 2025; 59(1): 53-63.