

A Simple Method to Evaluate the Vapor Pressure of Transformer Oil at Various Temperatures

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Keywords: transformer oil; vapor pressure; thermal balance; experiment data correlation.

Abstract: Transformer oil as an important mineral oil is widely used in power equipments and its fundamental properties can be obviously presented by the vapor pressure which is difficult to be accurately evaluated due to its complex compounds. According to the testing mechanism of thermal balance, a simple method is proposed to evaluate the vapor pressure of transformer oil at various temperatures. The thermal stability and chemical components of the tested oil are characterized and discussed. The experiment data correlation to the vapor pressure of transformer oil is further performed by the typical Clausius-Clapeyron equation. It reveals that the vapor pressure of transformer oil is positively related to temperature environment. Moreover, a deep comparison between the experiment data and the correlated result confirms that the applied evaluating method is a suitable way to evaluate the vapor pressure of transformer oil and other liquid compounds system.

Introduction

The industrial revolution and increased population in the last two centuries have resulted in an increased consumption of fossil fuels [1]. For over 100 years, petroleum-based mineral oils have been used in liquid-filled electrical transformers. Large amounts of mineral oil are used in electrical equipments as insulation and cooling medium [2,3], which are complex mixtures of linear saturated hydrocarbons (paraffins), cyclic saturated hydrocarbons (naphthenes), aromatic hydrocarbons and a small fraction of non-hydrocarbons, with hundreds of individual compounds [4].

Transformer oil is a derivative of petroleum crude which serves both an insulating and heat [5]. In extra high voltage power equipments, the oil-filled power transformers account for more than 90% of all transformers [6]. The transformer oil suffers from continuous deterioration and degradation due to electric and cyclic thermal stresses because of the loading and the climatic conditions which may affect the performances and life of the electrical transformer [7]. To avoid damages and cut-off of power electricity supply it is necessary to evaluate the mineral oil condition [2]. Vapor pressure is a fundamental physicochemical property indispensable for many important studies and applications [8-10]. Knowledge of this parameter is crucially important for a wide variety of materials because it is used as a basis to calculate the acentric factor, surface tension, enthalpy of vaporization, thermal and equilibrium properties [11-13]. For example, a change in fuel vapor pressure may results in significant changes in the fuel atomization, evaporation rates, combustions and emission formation processes in numerical simulations [14].

The accurate determination of vapor pressures, however, is not an easy task, in particular in the low-pressure region and literature data coming from different authors often shows a significant scatter and/or are influenced by systematic errors [8]. Referencing the simple organic composition system, there are several methods for measuring vapor pressure described in the literature. Differential thermal analysis (DTA) instrumentation with the thermocouple-inserted glass capillary configuration is ideally suited for measurement of boiling points at a variety of pressures [15-17]. Based on the similar testing mechanism, a recently developed thermo-gravimetric analysis (TGA) method is partly applied to provide a rapid means of quantifying vapor pressure of selected organic compounds [18]. Although the mentioned DTA method and TGA method can measure the vapor pressure for transformer oil easily, they are terribly limited by their testing pressure which is infeasible in the low temperature environment. Measurements of vapor pressures by transpiration method have been proposed in a substantial broader temperature ranges with a good experimental condition of saturation by variation of flow rates of the carrier gas [19]. Gas chromatography is another approach used to quickly estimate the vapor pressure of volatile organic compounds [9]. Moreover, some researchers have used different vapor pressures correlations to estimate parameters in equations of state [20,21]. Numerous empirical vapor–pressure equations have been published, the best known are those of Wagner, Lee-Kesler and Ambrose-Walton general models, Clausius, Antoine, Frost–Kalkwarf, Cox, Gomez-Thodos, Riedel Lemmon-Goodwin and Sanjari et al [22,23].

The above methods for measuring the vapor pressure of liquid organic composites are generally available for the pure component or those separable mixture systems which the chemical constants can be provided by the present researches. However, it is well known that petroleum-based transformer oils used in transformers have a diverse and large number of compounds which consists of complex blends of more than 3000 hydrocarbons [24]. It is not practical, indeed it may be impossible, to perform a complete component analysis to such systems [25]. To overcome the mentioned testing deficiency and provide the detailed fundamental data for engineering fields, the vapor pressure of transformer oil was measured at various pressures by a constructed apparatus. The thermal stability and chemical structure of the tested transformer oil were characterized considering of the effects of thermal decomposition and aging during the testing process. Furthermore, the experiment data were correlated by the typical Clausius-Clapeyron equation and the vapor pressure measured at low temperature was regressively calculated.

Experimental Section

Experimental Apparatus

According to testing principle of the TGA method and DTA method, the vapor pressure data of transformer oil was measured by the constructed apparatus using a thermal balance [26]. The measuring apparatus which is well sealed during the whole testing process is schematically shown in Figures. 1. It includes a vacuum chamber with temperature controller used to heat the testing oil at a wide temperature region of 25 °C to 200°C, a light inside and a camera setting on the vacuum chamber installing to observe the boiling status of transformer oil, a vacuum pump and a pressure control system introducing to adjust the testing pressure at a large pressure range of 50 Pa to normal atmospheric pressure. With several layers of seal assemblies, the measuring apparatus can accurately control the testing temperature and the vacuum pressure during the whole determination process.

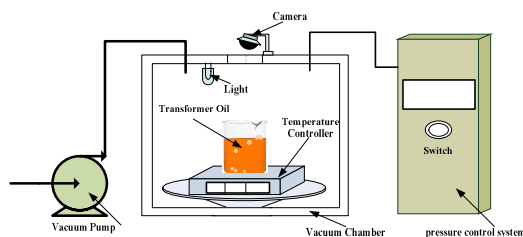


Fig.1 Schematic diagram of the constructed vapor pressure measuring apparatus for transformer oil

Testing Process

The vapor pressure of transformer oil was measured by the mentioned experimental apparatus. After the air impermeability testing, the transformer oil was initially placed inside the vacuum chamber which was continually heated to the testing temperature. When the transformer oil reached the set temperature stably, turned on the vacuum pump and the oil was kept vacuuming until it boiled violently. As the tested transformer oil reached the boiling point, it is assumed that liquid-vapor equilibrium is established inside the sealed chamber [27]. In other word, it was deemed that the related vacuum pressure was the saturated vapor pressure at this testing temperature. Therefore, the temperature, the vacuum pressure and the testing time were recorded. Moreover, 2 ml tested oil was collected as the experiment sample for its chemical characterization. Consideration of the actual degassing temperature and working temperature of power transformer insulation, the testing temperature rang was set from 40°C to 150°C.

Characterization

The thermal stability of the transformer oil was analyzed by TG 209 F3 where the transformer oil was heated from 25°C to 400°C with a stable N₂ atmosphere. The heating rate was set at 10°C/min. The fourier transform infrared spectra (FTIR) of the transformer oil was recorded in the range of 4000–400cm⁻¹ on a Bruker Vertex FT-IR spectrometer. KBr was chosen as the background and the testing sample was prepared by adding the oil to KBr with a soaking operation for one minute.

Results and discussion

Chemical analysis of transformer oil

During the vapor pressure testing process, the transformer oil may be thermal decomposed which will limit the practical application of the proposed vapor pressure measuring method. Therefore, the thermal analysis and the chemical composition analysis are performed and relevant results are exhibited.

The thermal stability of the transformer oil is shown in Fig.2. From this figure, it can be seen that the quality loss of the transformer oil occurs when the temperature is raised to 80 °C under the normal pressure. According to the obtained TG curve in Fig.2, the loss rate of the transformer oil is gradually increased accompanied with temperature rise. When temperature increased to 235 °C, transformer oil is volatilized completely which means that the transformer oil is volatilized. From the DTA curve of transformer oil, there is a gradual heat absorption peak deemed as the volatile heat that can be observed at the range of 80~235 °C without any other decomposition peaks. This indicates that the transformer oil may be a mineral oil whose components can volatilize at similar temperature and the oil did not be decomposed during the thermal analysis process.

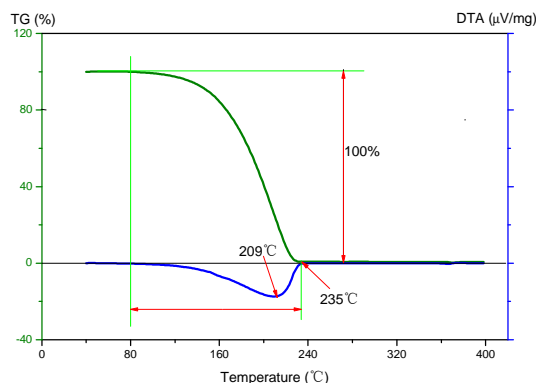


Fig.2 The thermal analysis results of transformer oil in the normal atmosphere

In order to a further research about its volatilization and decomposition, the chemical composition of transformer oil was analyzed by FTIR measurements. The testing samples were prepared when the oil kept the boiling state for 10 min (named t_1) and 2 h (named t_2), respectively. As shown in Fig.3, there are four strong peaks observed at 2932cm^{-1} , 2859cm^{-1} , 1454cm^{-1} and 1372cm^{-1} which are assigned to $-\text{CH}_3$ and $-\text{CH}_2-$ stretching vibrations, implies that the transformer oil is mainly consisted of alkanes compounds. The two weak peaks exhibited at 3650 and 3185 are attributed to the $-\text{OH}$ stretching vibration and other two weak peaks at 2729cm^{-1} and 2623cm^{-1} represents the C-H vibration of aldehydes. The weak peaks at 1609cm^{-1} and 1156cm^{-1} are caused by $\text{C}=\text{O}$ absorption and the saturated acyl groups. The other weak peak at 732cm^{-1} is corresponded to the wagging vibration. The above discussion indicates that the FTIR spectrum of the tested oil is according with the normal transformer oil. From Fig.3, it also can be found that there are obvious reducing tendency when the oil is vacuumed for longer time, which means that the transformer oil volatilized during the vapor pressure measurement. However, although distinct volatilization has been observed, there are no new peaks appeared on the FTIR spectrum, revealing that the transformer oil did not distinctly aged and no redox reactions were happened during the testing process. In other words, it demonstrates that the proposed vapor pressure testing method is available to measure the vapor pressure of transformer oil without any side reactions.

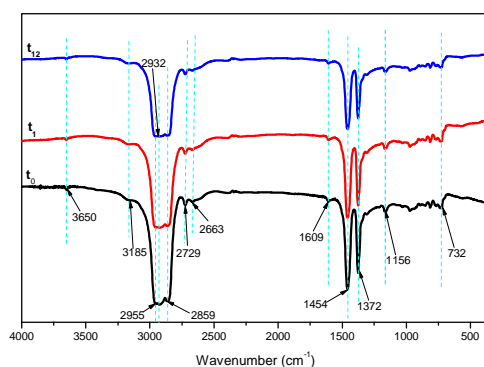


Fig.3 FT-IR spectrums of transformer oil (t_0) and those kept boiling for 10 min (t_1) and 2 h (t_2)

Experiment data of transformer oil

The experimental data of transformer oil is summarized in table 1. It is clearly observed that the vapor pressure increases from 160 Pa to 940 Pa as the temperature is enlarged from 40°C to 150°C which preliminarily indicates that the vapor pressure of transformer oil is positively related to the applied temperature. This result is according with the present approved relationship between

the vapor pressure and the temperature which means that the proposed vapor pressure testing method is available and the experimental data are effective. Based on the testing results, the vapor pressure-temperature relation curve is drawn as shown in Fig.4. Obviously, the vapor pressure of the transformer oil is seriously influenced by the applied temperature. Furthermore, it can be found that the vapor pressure is distinctly increased when the temperature is above 100 °C while it slightly changed when the temperature is below 100 °C. It can be inferred that a non-negligible error is generated when the testing temperature is below 100 °C by using the adoptive vapor pressure measuring method. Therefore, the evaluation of the vapor pressure in a lower temperature is invalid only by the experiment test and a followed data correlation analysis is extremely essential for transformer oil.

Table 1. Experimental Data on Vapor Pressure of transformer oil

Temperature [T/°C]	Vapor Pressure [P/Pa]
40	160
50	185
60	170
70	165
80	215
90	245
100	245
110	325
120	470
130	600
140	770
150	940

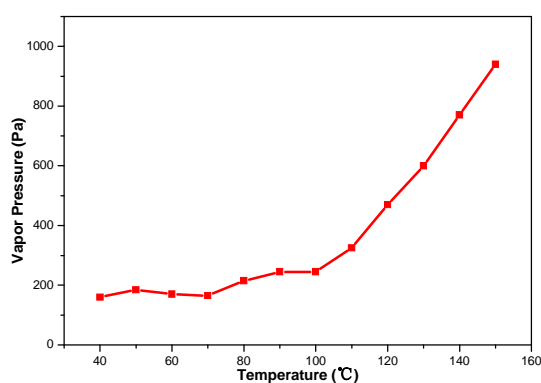


Fig.4 The relation curve of the measured vapor pressure and its related temperature

Experiment data correlation for transformer oil

Based on the above experiment data and discussion, the vapor pressure of transformer oil in a lower temperature environment is high-error which is limited by the measuring apparatus. Therefore, the data correlation is necessary to fit the vapor pressure data by the tested correlating vapor pressure equations. Theoretically, the vapor pressure is regularly related with temperature, as shown in the typical Clausius-Clapeyron equation:

$$\ln P = -\frac{\Delta H_{\text{vap}}}{R} \frac{1}{T} + B \quad (1)$$

where P is the vapor pressure of transformer oil (Pa), T is the testing temperature ($^{\circ}\text{C}$), ΔH_{vap} is the molar vaporization enthalpy ($\text{KJ}\cdot\text{mol}^{-1}$), R is the molar gas constant and B is the integration constant. The experiment data are initially treated and the relationship between $\ln P'$ and $1/T$ is displayed in Fig.5. Compared with the obtained vapor pressure data tested below 100°C , $\ln P'$ and $1/T$ presents a obvious linear relationship when the testing temperature is above 100°C which confirms again that the proposed vapor pressure measuring method is suitable for transformer oil at high temperature environment. When the testing temperature is below 100°C , the vapor pressure measurement is seriously influenced by testing apparatus and circumstances.

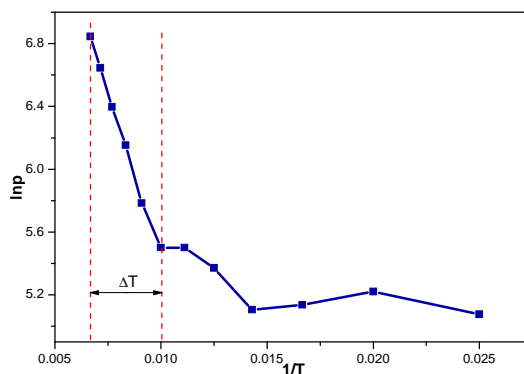


Fig.5 the treated experiment data on vapor pressure for transformer oil that tested from 30°C to 150°C

The correlation results for the measured vapor pressure that tested in the temperature range of ΔT ($100^{\circ}\text{C} \sim 150^{\circ}\text{C}$) is exhibited in Fig.6. It is clear that the mentioned Clausius-Clapeyron equation describes satisfactorily the measured vapor pressures of transformer oil. Moreover, relevant fitting equation is obtained as listed below:

$$\ln P' = -410.95605 \frac{1}{T} + 9.57225 \quad (2)$$

Where the value of $-\frac{\Delta H_{\text{vap}}}{R} = -410.95605$ and the constant B is 9.57225 . Thus the value of

$\Delta H_{\text{vap}} = 3.42 \text{ KJ}\cdot\text{mol}^{-1}$ on transformer oil.

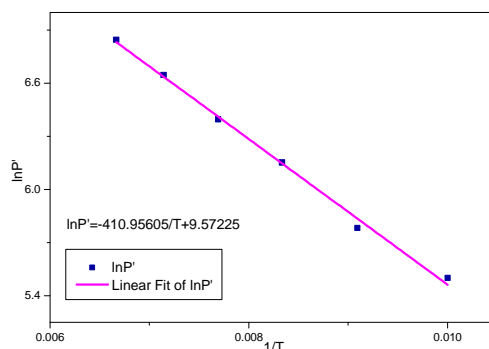


Fig.6 the vapor pressure for transformer oil correlated by Clausius-Clapeyron equation from 100 °C to 150 °C

According the above fitting equation (2), the theoretical vapor pressure of transformer oil is regressively calculated. The relating results are listed in table 2 and the comparison between the experiment data and the correlated vapor pressure of transformer oil is described in Fig.7. It can be observed that the vapor pressure is calculated from 30 °C to 180 °C, corresponding to a pressure religion of 0.0161 Pa to 1464.3 Pa. Obviously, the obtained theoretical vapor pressure of transformer oil fits well with the experiment data when the testing temperature above 100 °C. While compared with the measured vapor pressure in the low temperature region (30 °C~100 °C), the calculated vapor pressure is much lower which is difficult to be tested effectively by experiment measuring method. Thus, the vapor pressure for transformer oil can be easily obtained by the mentioned experiment testing method combined with a reasonable correlation calculation from very low temperature to high temperature.

Table 2. The calculated data (P') and experiment dada (P) on vapor pressure for transformer oil

$T/^{\circ}\text{C}$	P'/Pa	P/Pa
30	0.0161	170
40	0.4958	160
50	3.8695	185
60	15.225	170
70	40.505	165
80	84.377	215
90	149.32	245
100	235.73	245
110	342.50	325
120	467.60	470
130	608.53	600
140	762.69	770
150	927.55	940
160	1100.8	1000
170	1280.3	1300
180	1464.3	1500

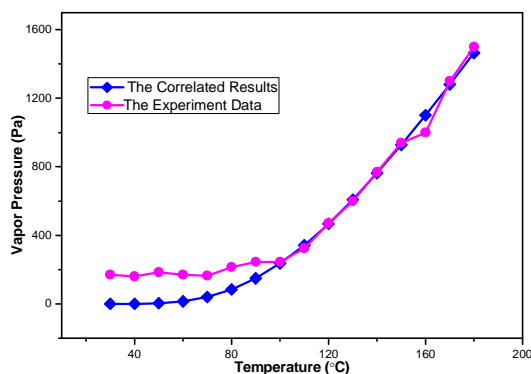


Fig.7 Comparison between the experiment data and the correlated vapor pressure of transformer oil

Conclusions

The vapor pressure of transformer oil is effectively obtained by the proposed experiment measurement combined with followed regressive calculation. It indicates that the vapor pressure of transformer oil is positively related to temperature environment which is in good agreement with the present research result. The TG and FTIR results demonstrate that the transformer oil is a typical mineral oil with complex components and no obvious aging phenomenal is observed. The experiment data is continually correlated by the typical Clausius-Clapeyron equation. Comparison between the measured data and the correlation results reveals that the tested vapor pressure is reliable when the testing temperature is above 100 °C and it shows non-negligible errors when the applied temperature is below 100 °C. Based on the experiment data, the value of the molar vaporization enthalpy $\Delta H_{vap} = 3.42 \text{ KJ} \cdot \text{mol}^{-1}$ is calculated by the correlation equation. The study results further demonstrate that the proposed vapor pressure evaluation method is suitable for transformer oil and other liquid materials with complex components especially in low temperature testing environment. This is a fundamental research which is essential to the further development of the insulation oils and the electronic industries.

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