Analysis of Activation Energy of Epoxy Resin Insulated Transformer Based on Dynamic Method

Xin Zhang\textsuperscript{1, \*}, Xiaoguang Xi\textsuperscript{1, \*}, Liqing Liu\textsuperscript{1, b}, Yang Wang\textsuperscript{2, c}, Guangzhen Liu\textsuperscript{2, d}, Jialong Li\textsuperscript{1, e} and Xuqiang Wang\textsuperscript{1, f}

\textsuperscript{1}Electric Power Research Institute, State Grid Tianjin Electric Power Corporation, Tianjin, China
\textsuperscript{2}State Grid Tianjin Electric Power Corporation, Tianjin, China
\textsuperscript{3}Chengxi Power Supply Branch, State Grid Tianjin Electric Power Corporation, Tianjin, China
\textsuperscript{4}Information and Communication Company, State Grid Tianjin Electric Power Corporation, Tianjin, China

*Corresponding author e-mail: zhangxin_sgcc@126.com,\textsuperscript{a}xiaoguang.xi@tj.sgcc.com.cn,\textsuperscript{b}254368140@qq.com,\textsuperscript{c}wywdm20@126.com,\textsuperscript{d}guangzhen.liu@tj.sgcc.com.cn,\textsuperscript{e}15822888672@126.com,\textsuperscript{f}13212031871@163.com

Abstract. Epoxy resin insulation transformer is a typical dry-type insulation equipment in power system. The insulation performance diagnosis of such equipment is the current research focus. This paper analyses the basic principles of two typical dynamic methods, FWO method and Kissinger method, and introduces the specific application methods of the two methods in the calculation of the activation energy of epoxy resin insulated transformers, which proves the effectiveness of the method. This article provides theoretical basis and example verification for insulation aging diagnosis of dry-type transformers based on quantitative characterization of activation energy.

1. Introduction
Transformer insulation forms include liquid insulation (such as mineral oil, vegetable oil and other oil-immersed insulation), solid insulation (such as epoxy and other dry insulation) and gas insulation (such as SF\textsubscript{6} gas transformer), of which dry-type transformers are often used as distribution transformers, transformers for substations, user transformers such as factories or buildings. Dry-type transformers are generally insulated with epoxy materials, and are molded after casting and curing. They have the advantages of stable performance, easy operation and maintenance, and high reliability. However, in recent years, the failure rate of dry-type transformers has been high, and more than 63% of them are insulation problems. Dry-type transformer insulation status detection, especially insulation aging diagnosis, has become a key issue in operation and maintenance.

At present, the insulation state detection of dry-type transformers is mainly a macro electrical quantity detection. The main methods include partial discharge detection and dielectric loss measurement. These methods are not very effective for identifying latent insulation defects and sudden insulation faults. In recent years, some scholars have begun to consider the intrinsic characteristics of insulation to study its degradation process. For example, the Arrhenius rate equation can be used to
evaluate the service life of insulating materials, and new progress has been made. T. W. Dakin tests and evaluates insulating materials based on the Arrhenius equation. The chemical reaction rate is used to analyze the aging data and predict the aging degree of the insulating material. Scholars Liu Gang and others used activation energy parameters to evaluate the remaining life of 110kV XLPE insulated cables, and obtained the expected life under different aging conditions. Robert R. Dixon and J. Wise et al. Used the Arrhenius curve to obtain the aging state of materials at different temperatures by extrapolation. The above research revealed that the essential reason for the deterioration of the insulation of the equipment is the change in the properties of the insulating material. [1, 2]

Similarly, dry-type transformers undergo certain chemical reactions at different rates during long-term operation. The insulation degradation of epoxy materials is a pyrolysis kinetic process. And using thermogravimetric analysis (TGA) to solve the chemical reaction rate and activation energy at different temperatures can provide a characterization method to evaluate the dry state of dry-type transformers, as a supplement to the existing macro inspection methods. This paper starts with a dynamic solution of the activation energy of chemical reactions, and performs activation energy analysis on epoxy resin insulated transformers to provide a theoretical basis and practical method for transformer insulation aging diagnosis.

2. Calculation of activation energy based on dynamic method

The dynamic method refers to measuring the change in the conversion rate $\alpha$ of the reaction with time $t$ (or temperature $T$) under the condition of continuous temperature rise. The dynamic method can be divided into a single heating rate method and a multiple heating rate method. Nowadays, researchers have found that the results obtained by the multiple heating rate method are more accurate than those obtained by the single heating rate method.

The basic principle of the multiple heating rate method is as follows:

According to Arrhenius’ definition of the activation energy of a substance, a general kinetic equation for a heterogeneous system under non-constant temperature conditions is given, such as equation (1).

$$
\beta \frac{d\alpha}{dT} = A \exp\left(-\frac{E_a}{RT}\right)f(\alpha)
$$

In the formula, $A$ is a constant coefficient related to the chemical reaction rate being evaluated; $R$ is the universal gas constant; $T$ is the temperature; $\alpha$ is the conversion rate of the chemical reaction; $E_a$ is the activation energy of the chemical reaction; $f(\alpha)$ is a reaction mechanism function, and $\beta=dT/dt$ is a heating rate.

The distinctive feature of the dynamic method is that its temperature changes with time, that is, the temperature $T$ is a function of time $t$, which makes the processing of the equation quite complicated. To solve this problem, some scholars integrate equation (1), and some scholars differentiate equation (1). After long-term development, two major branches based on the dynamic method for solving activation energy have been formed: differential method and integral method. Most of these two methods consider that the function of the chemical reaction rate as a function of temperature $k(T)$ can be described by the Arrhenius formula.

2.1. FWO method

Flynn-Wall-Ozawa (FWO) method is an integration method, which is generally used to solve chemical reaction kinetic parameters without chemical reaction mechanism function.

Integrating equation (1), we get

$$
\int_{\alpha_0}^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^{T} \exp\left(-\frac{E_a}{RT}\right)dT
$$

(2)
Where $T_0$ is the temperature at which the reaction starts. Considering that at the beginning of the reaction, the temperature $T_0$ is low and the reaction rate is small and can be ignored, the above equation can be written as

$$
\int_{0}^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{0}^{\alpha} \exp\left(-\frac{E}{RT}\right) dT
$$

(3)

Make

$$
U = \frac{E_u}{RT}
$$

(4)

By $T = \frac{E}{RU}$, we can get

$$
dT = -\frac{E}{RU^2} dU
$$

(5)

Then the formula (3) can be transformed into

$$
G(\alpha) = \frac{A}{\beta} \int_{0}^{\alpha} \exp\left(-\frac{E}{RT}\right) dT = \frac{AE}{\beta R} \int_{-\infty}^{-e^{-\alpha}} \frac{e^{-\alpha}}{u} du = \frac{AE}{\beta R} P(u)
$$

(6)

Where $E/R$ is constant, so the problem of solving temperature integration becomes a problem of finding a function $P(u) = \int_{-\infty}^{u} \frac{e^{-\alpha}}{u} du$.

Use Doyle approximation here

$$
p_D(u) = 0.00484 e^{-0.0516u}
$$

(7)

$$
\lg p_D(u) = -2.315 - 0.4567 \frac{E}{RT}
$$

(8)

Simultaneous equations (6) and (8) are available

$$
\lg \beta = \lg \left( \frac{AE}{RG(\alpha)} \right) - 2.315 - 0.4567 \frac{E}{RT}
$$

(9)

The activation energy $E$ in equation (9) can be obtained by the following two methods:

(a) Because the values of $\alpha$ at the peak temperature $T_\beta$ of each thermal spectrum under different $\beta$ are approximately equal, the values $\lg \left( \frac{AE}{RG(\alpha)} \right)$ are equal in the range of $0 - \alpha_p$, so $\lg \beta$ and $\frac{1}{T}$ have a linear relationship with a slope of $-0.4567 \frac{E}{RT}$. Then the activation energy $E$ can be obtained from the slope.
(b) Since the same $\alpha$ is selected under different $\beta$, $\lg \left( \frac{AE}{RG(\alpha)} \right)$ is a constant value, $\lg \beta$ and $\frac{1}{T}$ have a linear relationship with a slope of $-0.4567 \frac{E}{RT}$. Then the activation energy $E$ can be obtained from the slope.

2.2. Kissinger method

The Kissinger method proposes a method for calculating the activation energy of a chemical reaction from the peak temperature of a differential thermal weight (DTG) curve, which is a differential method.

Kissinger method is assuming

$$f(\alpha) = (1-\alpha)^n$$

(10)

Then the following equation (11) obtained from Arrhenius formula

$$\frac{d\alpha}{dt} = Ae^{\frac{E}{RT}} (1-\alpha)^n$$

(11)

Differentiate equation (11) on both sides to get

$$\frac{d}{dt} \left[ \frac{d\alpha}{dt} \right] = \left[ A(1-\alpha)^n \cdot \frac{d(e^{\frac{E}{RT}})}{dt} \right] + \left[ \frac{E}{RT} Ae^{\frac{E}{RT}} \frac{d(1-\alpha)^n}{dt} \right] = \frac{d\alpha}{dt} \left[ \frac{F_a}{RT^2} \frac{dT}{dt} - Ae^{\frac{E}{RT}} n(1-\alpha)^{n-1} \right]$$

(12)

Assuming that the reaction rate is maximum at the peak temperature $T_{pi}$ of the DTG curve, then

$$\frac{d}{dt} \left[ \frac{d\alpha}{dt} \right] = 0 \text{ at the temperature } T_{pi}. \text{ So}$$

$$\frac{E_a}{RT^2} \frac{dT}{dt} = Ae^{\frac{E_a}{RT}} n(1-\alpha)^{n-1}$$

(13)

The Kissinger method considers that $n(1-\alpha)^{n-1}$ is not related to $\beta$, and its value is approximately equal to 1. Therefore, we can know from equation (12)

$$\frac{E_a}{RT} = Ae^{\frac{E_a}{RT}}$$

(14)

Take the logarithms on both sides of equation (14) to get equation (15), which is the Kissinger equation:
\[
\ln \left( \frac{\beta}{T_{pi}^2} \right) = \ln \left( \frac{A R}{E_a} \right) - \frac{E_a}{R T_{pi}}
\]

(15)

Using \( \frac{1}{T_{pi}} \) as a variable and plotting \( \ln \left( \frac{\beta}{T_{pi}^2} \right) \), we can get a straight line. Then get \( E_a \) from the slope of the line, and get \( A \) from the intercept.

3. Analysis of activation energy of chemical reaction in dry-type transformer

The following uses the FWO method and the Kissinger method to calculate the chemical reaction activation energy of epoxy resin insulated transformers.

TGA was performed on the epoxy resin samples extracted from the transformer under a nitrogen atmosphere and an air atmosphere. The TG curve and first-order DTG curve of epoxy resin under different atmospheric conditions are shown in Figure 1 and Figure 2. [3]

![Figure 1. TG and DTG curve of epoxy resin in nitrogen.](image1)

![Figure 2. TG and DTG curve of epoxy resin in air.](image2)

It can be seen from the figure that the thermal weightlessness curve of epoxy resin in nitrogen is clearly divided into two weightlessness stages, and the thermal weightlessness curve in air is divided into three weightlessness stages.

The peak temperature of the thermal weight loss curve at different heating rates was obtained from the TG curve and the DTG curve, as shown in Table 1.
Table 1. Peak temperature of TGA curve at different heating rates.

|          | Heating rate | 5°C/min  | 10°C/min | 15°C/min | 20°C/min | 25°C/min |
|----------|--------------|----------|----------|----------|----------|----------|
| Nitrogen | 1st peak     | 211.23°C | 222.22°C | 232.09°C | 237.35°C | 244.98°C |
|          | 2nd peak     | 368.00°C | 381.14°C | 389.48°C | 395.55°C | 397.95°C |
| Air      | 1st peak     | 197.92°C | 209.15°C | 215.76°C | 222.65°C | 226.75°C |
|          | 2nd peak     | 345.46°C | 362.35°C | 372.67°C | 380.04°C | 384.67°C |
|          | 3rd peak     | 511.55°C | 534.58°C | 552.27°C | 560.94°C | 566.00°C |

Figure 3 and Figure 4 show the fitting curve of the chemical reaction activation energy of the transformer based on the FWO method and Kissinger method.

![Figure 3. Fitting curve based on FWO method.](image)

![Figure 4. Fitting curve based on Kissinger method.](image)

According to the activation energy calculation method proposed in the previous section, the chemical reaction activation energy of epoxy resin insulated transformers at different reaction stages (i.e., different peaks) is calculated, as shown in Table 2.
Table 2. Calculation result of chemical reaction activation energy of epoxy resin insulated transformer.

|    | 1st peak    | 2nd peak    | 3rd peak    |
|----|-------------|-------------|-------------|
| Nitrogen | FWO 95.04 kJ/mol | 177.25 kJ/mol |
|       | Kissinger 91.62 kJ/mol | 175.49 kJ/mol |
| Air  | FWO 103.42 kJ/mol | 129.02 kJ/mol | 148.35 kJ/mol |
|       | Kissinger 100.69 kJ/mol | 126.66 kJ/mol | 142.52 kJ/mol |

4. Conclusion
This paper analyzes the principle of obtaining the activation energy of chemical reactions based on dynamic methods, and introduces two typical methods of FWO method and Kissinger method in detail. Combined with the actual epoxy resin insulated transformer, the practical application of these two methods in the determination of activation energy of dry equipment is introduced, and the effectiveness of the dynamic method in the measurement of activation energy is proved. The research in this paper provides the basis for diagnosis and quantitative evaluation of insulation aging of dry-type transformers based on activated energy.

Acknowledgments
This work was financially supported by SGCC Science and Technology Project "Research on Dry Insulation Equipment Defect Detection and Aging Evaluation Technology Based on Quantitative Characterization of Activated Energy" (KJ19-1-29).

References
[1] Buqing Ye, Rui Zhang, Jin Cao, Kai Lei, Dong Liu. The study of co-combustion characteristics of coal and microalgae by single particle combustion and TGA methods [J]. Journal of the Energy Institute, 2019.
[2] Juan Han, Hai-tao Liu, Shun-chang Wang, Cheng-run Wang, Guo-peng Miao. A class I TGA transcription factor from Tripterygium wilfordii Hook.f. modulates the biosynthesis of secondary metabolites in both native and heterologous hosts [J]. Plant Science, 2020, 290.
[3] Proteins - Transcription Factors; Studies from Northwest A&F University Reveal New Findings on Transcription Factors (Genome-wide Characterization and Expression Analysis of Soybean Tga Transcription Factors Identified a Novel Tga Gene Involved In Drought and Salt Tolerance) [J]. Biotech Business Week, 2019.