A New Method for the Aging Evaluation of Oil-Paper Insulation by *n*-Butanol and Methanol

Jianyi Wang, *Member*, *CSEE,* Yuanxiang Zhou, *Fellow*, *IET*, Jun Liu, Zhaowei Wang, Song Bai, Jiayu Lu, *Fellow*, *CSEE*

***Abstract*—To improve the accuracy and efficiency of aging life prediction and assessment of transformer oil-paper insulation, and to make up for the deficiencies of traditional characterizers such as 2-furfural, carbon monoxide, and carbon dioxide, a method for the simultaneous determination of methanol, ethanol, *n*-propanol, and *n*-butanol in oil with a single injection was established by headspace-gas chromatography-mass spectrometry. The measured results show that the determination limits of the four alcohol characterizers can be controlled to 10 μg/kg level. Based on this method, the change patterns of the above four alcohols with thermal aging time and degree of polymerization were obtained through thermal aging experimental research. Ethanol, *n*-propanol, and *n*-butanol in oil indicate nearly linear correlations with thermal aging time and degree of polymerization, similar to that of methanol. By analyzing 52 sets of measured data of 500 kV EHV transformers in operation, *n*-butanol was found to have excellent performance, and a new method to evaluate the aging state of oil-paper insulation employing *n*-butanol and methanol was proposed along with the aging attention value model. The measured data of 500 kV EHV transformers in operation indicate that the combination of *n*-butanol and methanol as the preferred characterizers can effectively compensate for the shortcoming of traditional characterizers in the early stage of aging, and the feasibility of the method was verified. Two possible pathways for the generation of *n*-butanol by cellulose cleavage during the aging of oil-paper were proposed from the chemical structure of cellulose.**

***Index Terms*—aging characterization, determination method, methanol, *n*-butanol, oil-paper insulation, 500 kV transformers**

Manuscript received December XX, 2021; revised December XX, 2021; accepted December XX, 2021. Date of online publication December XX, 2021; date of current version December XX, 2021. This work was supported by Innovation Foundation of China Electric Power Research Institute (GY83-18-006).

Jianyi Wang (corresponding author, e-mail: wangjyi@epri.sgcc.com.cn;) is with the Department of High Voltage, China Electric Power Research Institute Co. Ltd, Beijing 100192, China and Electrical Engineering Department, Tsinghua University, Beijing 100084, China

Y.X. Zhou is with the Electrical Engineering Department, Tsinghua University, Beijing 100084, China and wind Solar Storage Division of State Key Lab of Power System and Generation Equipment, School of Electrical Engineering, Xinjiang University, Urumqi 830047, China

J. Liu is with the wind Solar Storage Division of State Key Lab of Power System and Generation Equipment, School of Electrical Engineering, Xinjiang University, Urumqi 830047, China

Z.W. Wang is with the State Grid Wuwei Electric Power Supply Company, Wuwei 733000, China

S. Bai and J.Y. Lu are with the Department of High Voltage, China Electric Power Research Institute Co. Ltd, Beijing 100192, China

I. Introduction

OIL-PAPER insulation is the main insulation form of power transformers, and its aging process will have adverse effects on the mechanical and electrical properties of transformers, thus endangering the safe and stable operation of transformers[1].

The aging of paper insulation is an irreversible process, making the aging degree of paper insulation a crucial factor determining the insulation life of transformers[2]. Because insulating paper can't be directly accessed and detected during the operation, some characterization objects have been developed to evaluate the aging degree of the insulating paper in the equipment. CO_2/CO ratio measured by the analysis of dissolved gas in oil and 2-FAL (2-furfural) are relatively mature methods used worldwide[3]. However, there are still some limitations in practical application[1].

In recent years, the rapid progress of chemical analysis methods has laid a foundation for detecting trace markers. By utilizing gas chromatography-mass spectrometry (GC-MS) technology, the determination limit can be controlled to 10 μg/kg level, and the types of characterization substances that can be considered are significantly increased. Therefore, scholars at home and abroad actively seek other markers and enhance their determination methods.

Jalbert et al. separated and identified more than 30 aging products of insulating paper under laboratory conditions and found methanol in the products[4-6]. This discovery provides a new idea for studying the aging evaluation characteristics of insulating paper. Since then, methanol has gradually become the focus of research in the aging of paper insulation. Studies have revealed that methanol will appear in oil when insulation paper in the transformer begins to age, while 2-FAL can only be detected when the insulation paper ages significantly. As a result, methanol can be used to indicate the degree of paper aging even at the early stage of aging, and it is reckoned as a more effective method to predict the end of transformer life [3,7].

The research on methanol mainly focuses on the following four respects. Firstly, the determination methods have been developed. At present, there are several methods established to detect methanol concentration in insulating oils: GC-MS[2,8-11], Gas chromatography -flame ionization detector (GC-FID), and Raman spectroscopy [13-16]. MC Bruzzomniti compared headspace(HS)-GC-FID with HS-GC-MS, and found that the determination limits of methanol in the two methods were 12 μg/kg (HS-GC-FID) and 1.3 μg/kg (HS-GC-MS), respectively[17].

The second respect is to study the correlation between methanol and polymerization degree in laboratories and explore the correction methods of different influencing factors. It is found that methanol in transformer oil has an excellent linear correlation with the degree of polymerization of insulating paper[18,19]. In contrast, 2-FAL has an exponential correlation with the degree of polymerization[19]. Studies have confirmed that methanol is detected earlier than 2-FAL[4,20], and in the early stage of aging, methanol production rate is always higher than 2-FAL[21]. Relevant experiments also revealed that methanol appears from the first stage of cellulose depolymerization (DP>900)[22], and the methanol content from 10μg/kg to 100 μg/kg has a significant correlation with the aging of insulating paper[9,23]. On the other hand, the influence of temperature[24-26], moisture[27-28], oil-paper ratio[26], transformer oil type[26,29-32], insulating paper type[6,20] (such as ordinary insulating paper and heat modified insulating paper) and other factors and correction methods for methanol are also being studied at this stage.

The third respect is to study the generation mechanism of methanol. Gilbert et al.[5,6,33-35] discovered that after the opening of 1,4-β glycosidic bond in the cellulose chain, methanol was generated in proportion, suggesting that the generation of methanol was directly associated with the cellulose cracking the insulating paper. Jiang Danyu et al.[10] obtained through laboratory simulation that methanol mainly comes from the intermediate products of oxidative cellulose decomposition. The further reaction of the intermediate products of oxidative decomposition to generate methanol requires the synergistic effect of water. Kuiyu Zhou et al.[11,36-37] analyzed methanol generation's mechanism and influencing factors based on molecular simulation technology.

The fourth respect is application research. However, there have been limited applications in actual transformer equipment as of today [19,38-40], and they are mainly limited to lower voltage levels, but the feasibility of methanol as a characterization of oil-paper insulation has been preliminarily confirmed.

Along with methanol, some studies have shown that cellulose may produce ethanol after high-temperature degradation[41-42]. Jalbert, Jocelyn, et al. found that the change rule of ethanol was not as significant as that of methanol[43]. Hanbo Zheng[44] preliminarily confirmed that ethanol can be used as a new characteristic quantity for aging evaluation of insulating paper through theoretical analysis and experimental research, and studied the reaction and generation pathway of ethanol (C_2H_5OH): If the free hydroxyl group on C2 (C2′) of cellobiose is cracked first, and the C1-O5 (or C1′-O5′) bond is broken with C2-C3, (C2′-C3′) bond, the newly generated hydroxyl group on C1-C2 and C1 will form ethanol. However, further theoretical analysis and experimental research are needed on the characterization correlation between ethanol concentration and insulation aging degree (such as DP) of paper and the possibility and stability of other low molecular alcohols as insulation paper aging characteristics.

Based on applying existing research and referring to the idea of combined analysis of multiple gasses in DGA technology, this paper expands the types of new characterization substances. In this paper, a method for simultaneous determination of methanol, ethanol, *n*-propanol, and *n*-butanol in oil by single injection was established. More consistent and effective characterization substances were chosen to match the existing typical characterization substances. The new method described in this paper is aimed to improve the determination accuracy, anti-interference ability, and application feasibility. There is a practical need to accurately evaluate the aging state of the 500 kV UHV voltage transformers. Based on the measured results of 500 kV transformers in operation, starting with new alcohol indicators such as methanol, the changing trend, attention value, and application of alcohol indicators are studied, which can provide a more effective supplement for aging characterization of insulating paper.

II. Establishment of the Determination Method of Alcohols and Aldehydes Based on HS-GC-MS

In this paper, HS-GC-MS was used to determine the 4 alcohols (methanol, ethanol, *n*-propanol, and *n*-butanol) in oil. Agilent7697 headspace sampler,7890B gas chromatograph, 5977B mass chromatograph, DB-Wax UI 30 m× 0.25 mm× 0.5 m chromatographic column are used.

The key steps are the configuration of standard samples, the exploration of headspace conditions (temperature, time), the selection of chromatographic columns, the quantitative method, and the effect validation of the determination method in the process of establishing the actual determination method.

A. Preparation of standard solution

Weigh 0.15 g (accurate to 0.001g) of 4 alcohols, and use standard addition method to dissolve in 150 g new transformer oil to make mother liquor which contains 4 alcohols content of 1.0 g/kg each. The mother liquor was diluted with blank oil to prepare a standard oil sample with a concentration of 10 mg/kg. Then a series of mixed standard solutions of the 4 alcohols were diluted step by step, the contents of which were 800 μg/kg, 400 μg/kg, 200 μg/kg, 100 μg/kg, and 50 μg/kg, respectively.

B. Headspace condition, temperature rising procedure, and qualitative and quantitative ions

In this paper, the headspace condition is determined as the equilibrium temperature: 80 ℃ . Balance time: 30 min. The heating program of chromatographic column box is set as follows: furnace temperature is 40℃ and kept for 3 min, then heating to 100 DEG C at 10 DEG C/min, and then, the temperature is raised to 110℃ at 20℃/min, and the temperature is kept for 3 min, at the final stage, the temperature is raised to 230℃ at 40℃/min, and the temperature is kept for 12 min.

Quantification was performed by selecting the mass-to-charge ratio with the response value. Qualitative and quantitative ions representing methanol, ethanol, *n*-propanol, and *n*-butanol were obtained, respectively, as shown in Table I.

TABLE I
Quantitative And Qualitative Ion Settings Of Several Common Alcohols By Mass Spectrometry

	Methanol	Ethanol	*n*-Propanol	*n*-Butanol

Qualitative ion	31	31	31	31
Quantitative ion	29,32	45,46	59	41,56

C. *Selection of chromatographic column*

Since the tested alcohols are all polar substances, polyethylene glycol columns are preferred, which are polar columns. Further, various polyethylene glycol columns were compared, and the separation capacity and peak output ability were used as the judging criteria.

The experimental results show that the DB-Wax UI 30 m× 0.25 mm× 0.5 μm chromatographic column has the most robust separation ability and peak output ability for the target alcohol, as shown in Fig. 2. The final DB-Wax UI chromatographic column was selected for subsequent testing.

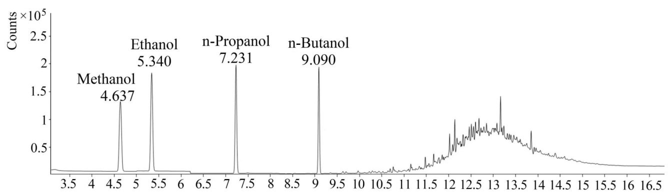


Fig. 1. Separation peak of methanol, ethanol, *n*-propanol, and *n*-butanol using DB-wax UI chromatographic column

D. *Establish standard curve by standard addition method and standard curve method*

Due to the low determination limit of the method and the several substances to be tested, it is challenging to select and make blank samples. In the configuration of the standard solution to establish the standard curve, the original content in the sample is tested by the standard addition method. Each content is corrected using the original content. The sample is tested using the standard curve in Fig. 3, which effectively solves the problem that the original alcohol content in the prepared solution may affect the accuracy of the standard curve.

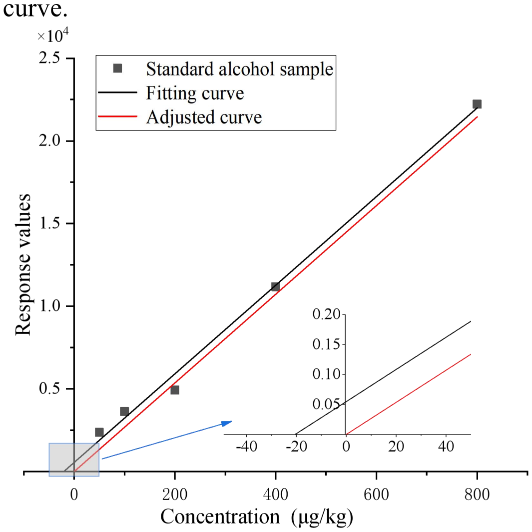


Fig. 2. Schematic diagram of the standard curve establishment process

E. *Effect validation of the method*

The fitted correlation coefficients of the calibrated standard curves for the 4 alcohols are shown in Table II. And all of the calibrated standard curves have good linearity. The determination limits can be controlled to 10 μg/kg level, and the repeatability can be controlled to less than 6% when the concentration is at 50 μg/kg.

TABLE II
LINEAR FITTING CORRELATION COEFFICIENTS OF STANDARD CURVES OF FOUR ALCOHOLS

Correlation coefficient	Methanol	Ethanol	*n*-Propano l	*n*-Butanol
R^2	0.998	0.997	0.998	0.998

III. EXPERIMENTAL STUDY

A. *Test conditions*

The transformer oil used for the experiments was Karamay transformer oil (K oil) and CNOOC transformer oil (H oil), and the insulating paper was Weidmann 22HCC INSULDUR insulating paper with a thickness of 0.088 mm.

The flow of the thermal aging test is shown in Fig.3.

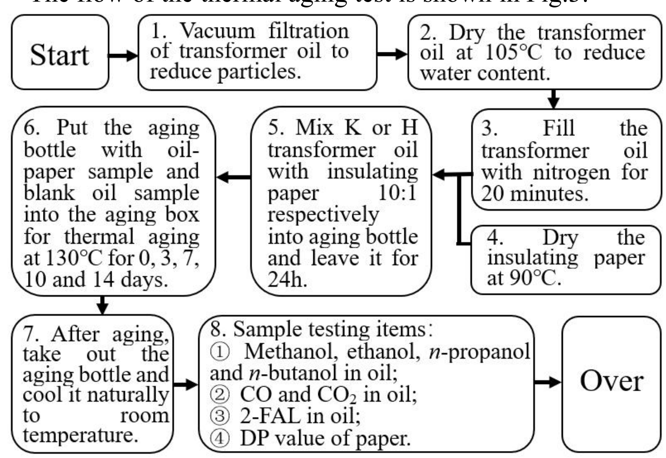


Fig. 3. The flow chart of the thermal aging test

B. *Changes in alcohol content after different aging time tests*

The changes in alcohol content after various aging time tests are shown in Fig. 4. And the comparison of alcohol content in oil between oil-paper samples and blank oil samples after aging for 14 days is shown in Fig. 5.

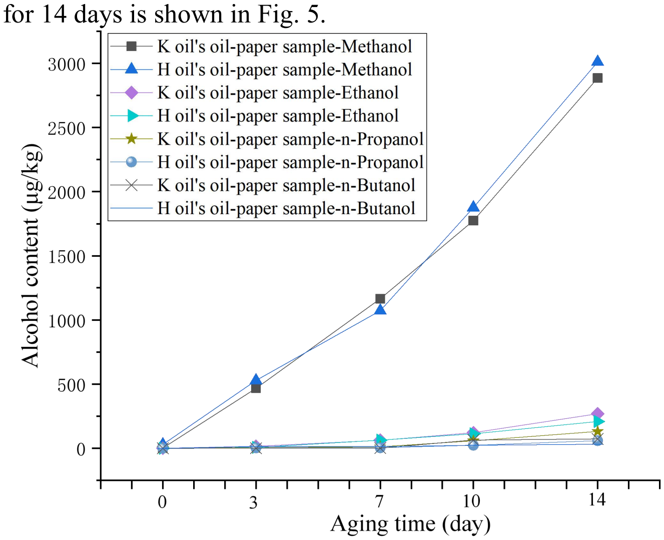


Fig. 4. The trend of alcohol content in oil after aging of oil paper at different aging times

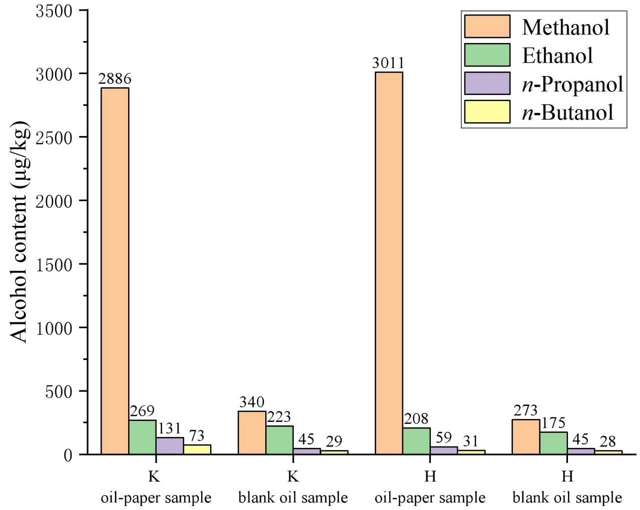


Fig. 5. Alcohol content in oil paper samples and blank oil samples after 14 days of aging

From Fig. 4 & 5 as above, it can be seen that during the thermal aging process at 130°C, the change of methanol with aging time was the most obvious compared to other alcohols. And the change in oil-paper sample was significantly greater than that in blank oil. While the change of ethanol with aging time was the second-largest, and the change is more significant than that of *n*-propanol and *n*-butanol. The content of ethanol, *n*-propanol, and *n*-butanol also increased with aging time, and the changes in the oil-paper samples were slightly greater than those in the blank oil samples. The lower ethanol production than methanol production under the test conditions is consistent with previous studies' phenomenon[45-48]. Similar phenomena and patterns occur with different 2 oils, not the characteristics of one particular oil. These two oils are processed by different manufacturers using different processes and both have practical applications.

C. Changes in the content of traditional characterizations after different aging time tests

All the oil samples were tested by the standard SH/T 0812-2010 (IEC 61198-1993, MOD) to detect 2-FAL content, and none of them had yielded a detectable value. The relevant studies[8] suggest that 2-FAL in oil only appear in the middle and late aging stages, which can explain this phenomenon.

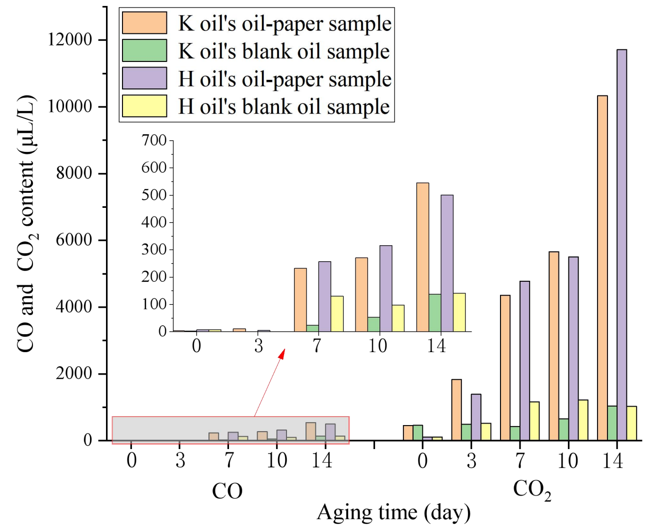


Fig. 6. CO, CO_2 content in oil paper samples and blank oil samples at different aging times

Fig. 6 shows that the CO and CO_2 in the blank oil sample and the oil-paper sample both increase with the increase of aging time, and the CO and CO_2 content in the oil-paper sample are much higher than that in the blank oil sample, which indicates that the aging of the insulation paper mainly generates the CO and CO_2 in the aging process. This phenomenon is consistent with the related research phenomena. Similar phenomena and patterns occur with different 2 oils.

D. Correlation analysis of alcohol content in oil and polymerization degree of insulating paper

The polymerization degree of the insulating paper was tested. And the correspondence between the alcohol content and the degree of polymerization of the insulating paper after different aging times is shown in Fig.7. The following analysis was performed using the more widely used K oil since similar phenomena and patterns occur with the 2 oils.

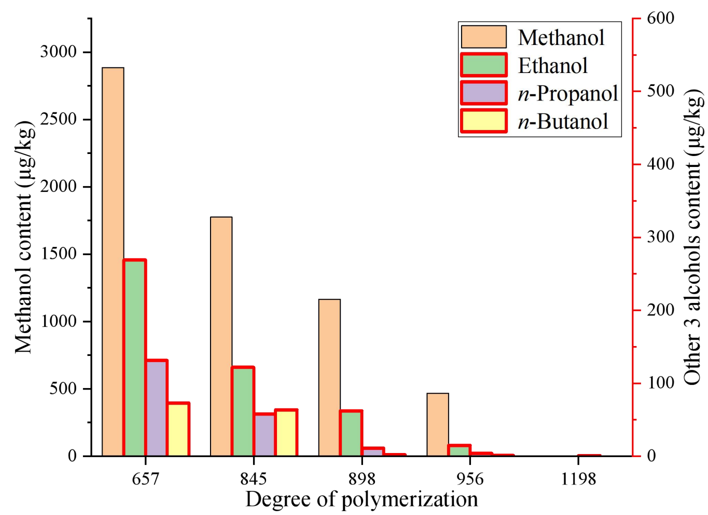


Fig. 7. Relationship between alcohol content and polymerization degree of insulating paper after aging

By fitting methanol, it was found that the polymerization degree of insulation paper showed a linear correlation with the content of methanol and had a high fitting coefficient, which was consistent with related literature[18,19].

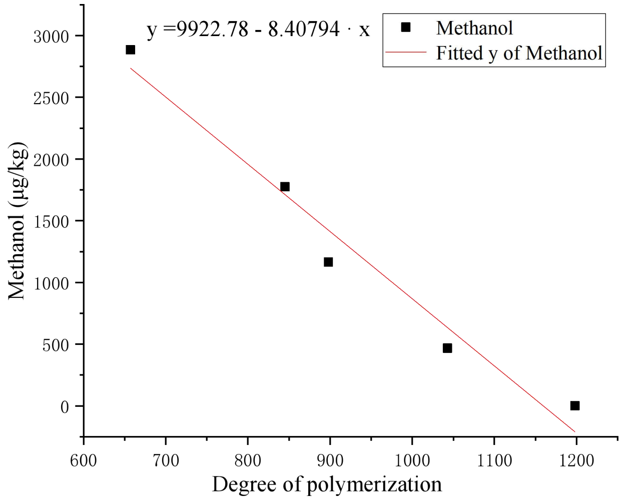


Fig. 8. Relationship between the methanol in oil and the degree of polymerization of insulating paper

Linear fits were also calculated for 3 other alcohols, with the coefficient of determination and correlation coefficients, as shown in Table III.

TABLE III
COEFFICIENTS OF DETERMINATION AFTER LINEAR FITTING OF DIFFERENT ALCOHOLS TO THE DEGREE OF POLYMERIZATION

Substance Category	Coefficient of Determination	Correlation Coefficient
Methanol	0.968	-0.984
Ethanol	0.872	-0.934
n-Propanol	0.780	-0.883
n-Butanol	0.683	-0.826

The analysis of Table III shows that the other three alcohols also have high coefficient of determination, indicating that all other three alcohols are approximately linearly correlated with the polymerization degree. The slightly lower coefficient of determination may be due to the lower content of ethanol, *n*-propanol, and *n*-butanol, which are 1-2 orders of magnitude different from methanol and more susceptible to other factors.

IV. ENGINEERING APPLICATION STUDY OF ALCOHOLIC CHARACTERIZERS

A. Sampling equipment situation

Transformer oil samples were taken from 26 transformers with different operating years, situated in five 500 kV substations. All the transformers are sealed, running on Karamay transformer oil (inhibited mineral oil), and operating with a load factor of no more than 55%. No significant oil changes had occurred to the transformers as of the sampling. The operating years of the transformers are shown in Table IV.

TABLE IV
OPERATING LIFE OF TRANSFORMERS FROM DIFFERENT SUBSTATIONS

Substation number	Number of equipment	Year of commissioning at the time of sampling in 2020	Year of commissioning at the time of sampling in 2021
1	6	1	2
2	6	4	5
3	2	7	8
4	6	12	13
5	3	13	14
	3	14	15

B. Substation oil sample alcohol content

The four alcohols in Table IV were averaged separately for all transformers of the same operating year, e.g., the value corresponding to 13 years in the figure is the average value of the 9 transformers operating for 13 years at the time of sampling, and the value corresponding to 4 years in the figure is the average value of the other 6 transformers operating for 4 years at the time of sampling. The variation of the average value of the different alcohol contents with the number of years of operation is shown in Fig. 8.

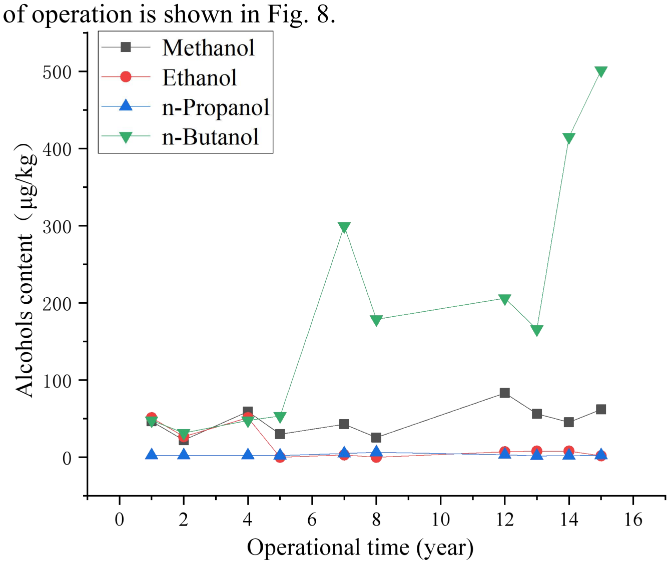


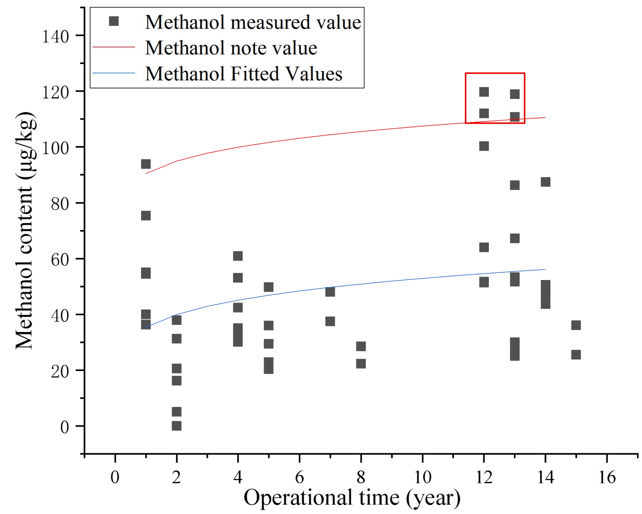
Fig. 9. Substation oil sample alcohols versus operating time

As seen in Fig. 9, the methanol content increases with aging time, consistent with other relevant studies. Meanwhile, a more interesting phenomenon is observed, the *n*-butanol content in the oil increases with aging time. Still, it has a more prominent increase after five years of operation, showing a trend approximate to power function between the content of *n*-butanol and increasing operating time, with the content exceeding that of methanol. The phenomenon of n-butanol has not been reported.

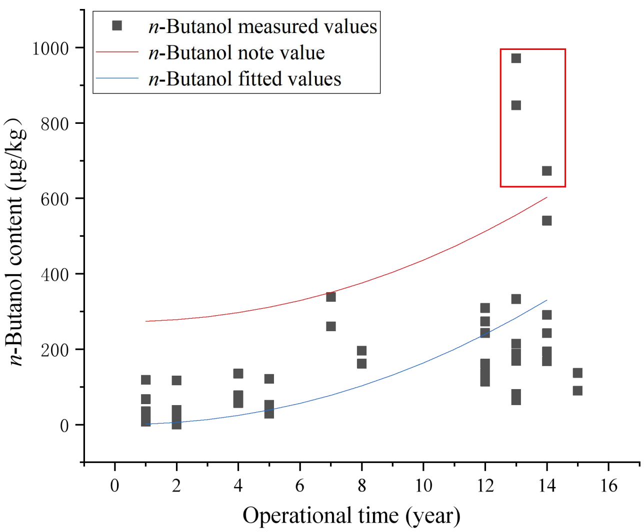
C. Attention value formula for calculating n-Butanol and methanol

To explore the method of utilizing *n*-butanol and methanol in characterizing the aging state of oil-paper insulation in 500 kV transformers, this paper combines field data to fit the correlation between *n*-butanol, methanol, and the operating years. And the values of *n*-butanol and methanol content that should be noticed under different operating lives were proposed, i.e., the formula of the attention value.

The *n*-butanol and methanol contents were fitted to the operating years. By applying the Box-plot method, a common method for identifying outliers in statistics, to the difference between the true and fitted values, the normal upper boundary was calculated as attention values. The fitted and attention value curves for n-butanol and methanol were obtained as shown in Fig. 10. The corresponding attention value equations for n-butanol and methanol were obtained as Eq. (2) and Eq. (3).



(a) Methanol attention value fitting curve



(b) n-Butanol attention value fitting curve

Fig. 10. Alcohol attention value fitting curve

n-Butanol and methanol attention value formula:

$$y_{n-\text{butanol}} = 8.09x^{1.38} + 192.40 \quad (1)$$

$$y_{\text{methanol}} = 1.34x^{2.09} + 272.75 \quad (2)$$

where $y_{n-\text{Butanol}}$ is the n-butanol note value, μg/kg, y_{methanol} is the methanol note value, μg/kg, and x is the operational time, year.

When the n-butanol or methanol content runs up to higher than the attention value of the corresponding year, like the data in the box of the upper right corner, attention should be paid to investigate the aging state of the oil-paper insulation.

D. Outcomes achieved in utilizing attention values of n-Butanol and methanol

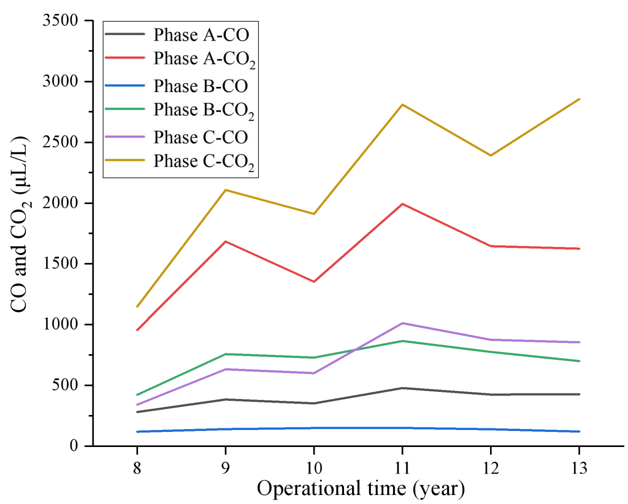
Although the DP value of insulating paper is a direct indicator of aging, the test object is the insulation paper, so it is difficult to take samples, requiring power outages, oil draining, and even lifting the cover to get the paper samples, which cannot be tested directly under normal circumstances. In this paper, the sampling equipment are normal operation, with no sampling test opportunities, so the DP value of insulating paper data can not be obtained.

In the relevant standards, 2-furaldehyde and CO, CO_2 are important paper aging characterizers that can be detected in oil. Using the standard SH/T 0812-2010 (IEC 611981993, MOD), the determination limit of 2-FAL in this laboratory is 0.01 mg/kg. All the field oil samples were tested by this method to detect 2-FAL content, and none of them had yielded detectable value.

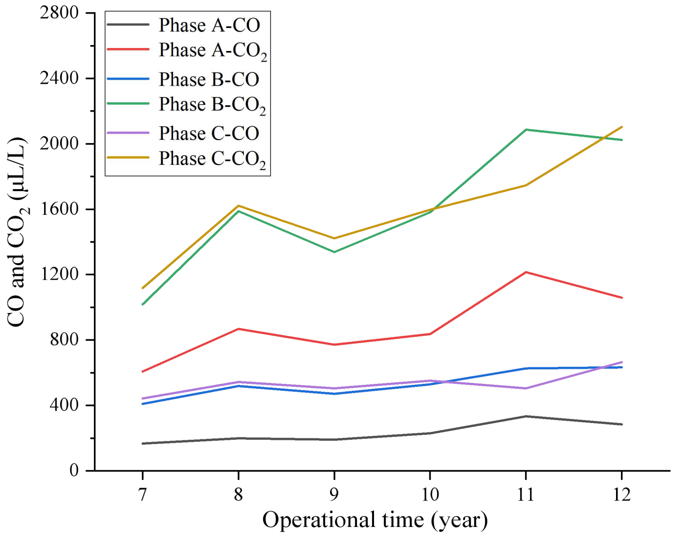
However, by utilizing the formula for the attention values of n-butanol and methanol in chapter Ⅳ C, it was confirmed that the attention values were exceeded for n-butanol in Case I (Phase A and C of transformer 2# in substation 5), and for methanol in Case II (Phases B and C of transformer 2# in substation 4).

Since 2-FAL was not detected in any of the measured field oil samples, the above cases were analyzed in combination with CO and CO_2 changes. It should be noted that, by analyzing DGA field test data, no discharge defect or overheating defect characteristics were seen inside the selected equipment. It can be assumed that the CO and CO_2 changes are mainly affected by the aging of paper insulation.

The CO and CO_2 detection data are historical data collected, and there are usually fluctuations. Therefore, the trend of change is paid more attention to. In order to better reflect the growing trend of the year and eliminate the differences caused by seasonal differences, the CO and CO_2 detection data in the same year are calculated as annual averaging. The CO and CO_2 annual averaging data of cases I and II in calendar years are shown in Fig. 11.



(a) Case I



(b) Case II

Fig. 11. Change of the CO、CO_2 concentrations in two cases over the years

The contents of CO and CO_2 in phases A and C in Case I were higher than those in phase B over the years, proving that more paper aging did occur in phases A and C than in phase B.

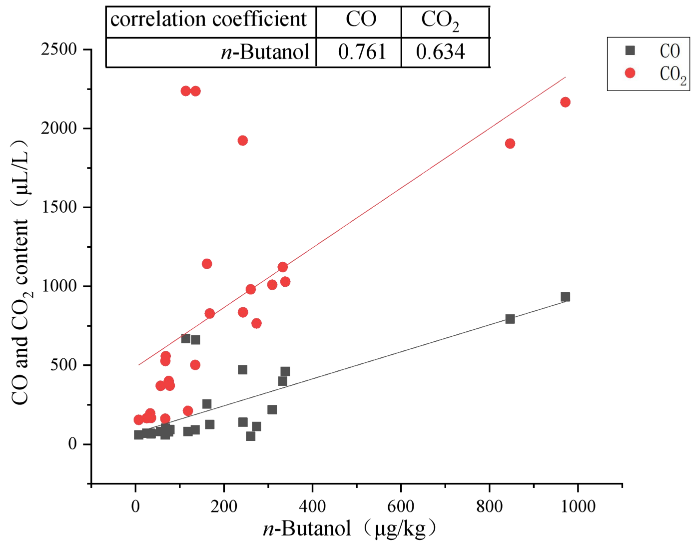
Similarly, the contents of CO and CO_2 in the phases B and C in Case II were significantly larger than those in the A-phase in all the years.

The above two cases prove that paper insulation aging can be effectively identified by *n*-butanol and methanol in oil. Under the circumstances such as 2-furfural is undetectable, CO and CO_2 fluctuate widely due to testing, etc., alcohol can be used as an effective supplement to traditional aging characterizers with excellent sensitivity.

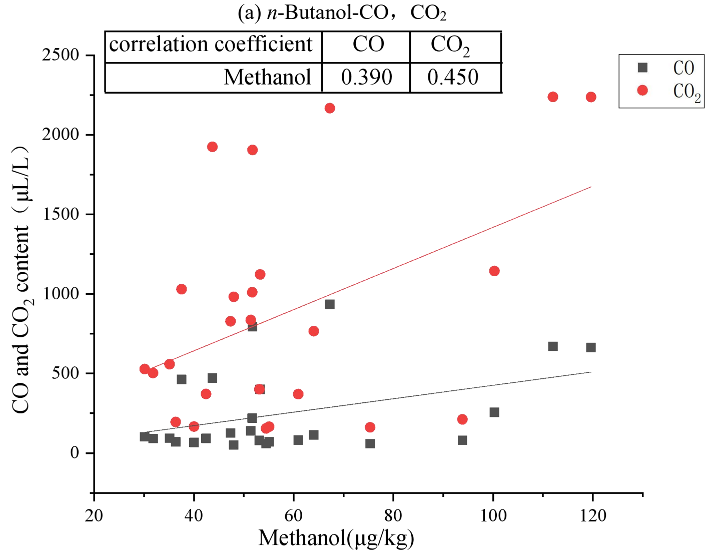
V. Results and Analysis

A. Correlation analysis of n-butanol and methanol content with CO and CO2

The data of *n*-butanol and methanol content and CO and CO_2 content of all the 26 500 kV equipment sampled in the field were analyzed and shown in Fig.12 below. It can be seen that lower *n*-butanol and methanol content are in line with lower CO and CO_2 content in the oil, which is mainly concentrated in the lower-left area of the graph. The correlation between *n*-butanol and CO and CO_2 is better.



(a) *n*-Butanol-CO，CO_2



(b) Methanol- CO, CO_2

Fig. 12. Relationship between the magnitude of n-butanol or methanol content and CO, CO_2

From Fig. 12, the corresponding fits show positive correlations between *n*-butanol and methanol and CO and CO_2, further reflecting that *n*-butanol and methanol can play an excellent complementary role as aging characterizers.

B. Comparative analysis of field application data and experimental data

The results in the field oil samples showed that the most promising new characterizers were n-butanol and methanol. The thermal aging testing results concluded that methanol was the most promising new characterizer. The comparison between the field oil samples and the laboratory oil samples suggested a certain degree of difference in the characterization of *n*-butanol, which may be ascribed to the difference between the field conditions subject to the complicated actual operation and the thermal aging test conditions in the laboratory. The effects of these differences need to be further studied.

In addition to that, methanol has higher volatility[49]. The boiling point of methanol is 64.8℃ (at 1 atm), and that of *n*-butanol is 117℃ (at 1 atm). When the temperature exceeds the boiling point of methanol, it may decrease methanol content in the oil. This is probably related to gaseous methanol at high temperatures[50]. The normal operating temperature of transformers is near or potentially above the boiling point of methanol, but well below the boiling point of *n*-butanol, which may be one of the reasons for the higher *n*-butanol tested in the oil. Though the thermal aging test aging temperature was 130℃, the alcohol contents were tested after the oil samples were back to room temperature. During the aging process and before sampling, the aging containers were kept well sealed, so even if the methanol was vaporized during the aging process, it was liquefied before testing.

In literature[24], the ethanol content was higher than methanol in the field measured results, which differed from the laboratory results. The literature intended to ascribe the higher methanol content to the accelerated aging experiment in a small area, while the higher ethanol content resulted from moderate aging in a large area.

C. Exploration of possible production pathways of n-butanol and methanol

It was found that the initial break positions of the cellobiose of cellulose in the initial cleavage-stage are mainly concentrated at the O atom of the glycosidic bond, C1-O5 (or C1′-O5′), C5-O5 (or C5′-O5′), and partly at C1-C2 (or C1′-C2′) and C2-C3 (or C2′-C3′). Besides, the hydroxyl and hydrogen atoms on the cellobiose also show limited breakage during the cleavage process[44,51-52].

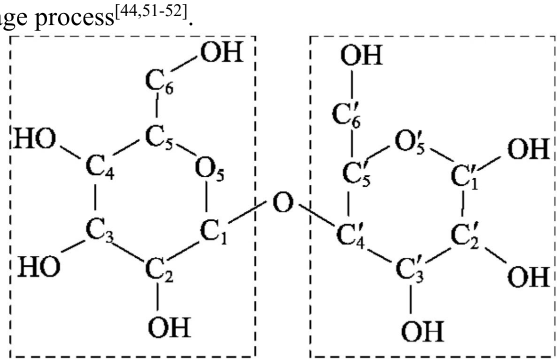


Fig. 13. Molecular model of fibrous disaccharide

There are three possible pathways for the generation of methanol[11]. The first is that the C5-C6 (or C5′-C6′) bond of the cellobiose (as shown in Fig. 13) breaks and C6 (or O6′) binds free H to form methanol. The second is that as the glycosidic bond C4′-O breaks, C1-O5 (or C1′-O5′) and C1-C2 (or C1′-C2′) then break and C1-O (or C1′-O) binds to H to form methanol. The third is that as the glycosidic bond C1-O breaks, C5-O5 and C1-C2 then break, and C1-O5 binds to H to form methanol.

Ethanol (C_2H_5OH) and ethylene glycol may be generated in the following pathway[44]. If the free hydroxyl group on C2 (C2′) of the cellobiose (shown in Fig. 13) cleaves first and the C1-O5 (or C1′-O5′) bond breaks with the C2-C3, (C2′-C3′) bond, then C1-C2 and the newly formed hydroxyl group on C1 will form ethanol. If the C1-O5 (or C1′ -O5′) bond breaks, then the C1-O (C1′-O) bond will form C1-OH (C1′-OH), and when the C2-C3 (C2′-C3′) is also cleaved at C2-C2 (C1′-C2′), then C1-C2 (C1′-C2′) and the hydroxyl groups attached to them may form ethylene glycol.

By this speculation, the pathway of *n*-butanol production may be that in the case of simultaneous breakage of C5-C6 (or C5′-C6′) and C1-C2 (or C1′-C2′) (this process has the potential to produce two methanol molecules). The remaining part of the cleavage produces the C2-C3-C4-C5 structure. When there are free hydroxyl groups on C2 or C5 that are not cleaved and the carbonyl groups on the other three carbon atoms are cleaved, then C2-C3-C4-C5 and their attached hydroxyl groups form *n*-butanol. Similarly, the production of n-butanol may also occur when ethanol and ethylene glycol are produced while cleaving the remaining portion to produce the C3-C4-C5-C6 structure. When one of the free hydroxyl groups on C3 or C6 (C3′ or C6′) is not cleaved, and the free hydroxyl groups on the other carbon atoms are cleaved firstly, then C3-C4-C5-C6 and their attached hydroxyl groups will form *n*-butanol. The specific mechanism of *n*-butanol generation needs to be further investigated in depth.

VI. CONCLUSIONS

1)A single injection simultaneous determination method based on HS-GC-MS for methanol, ethanol, *n*-propanol and *n*-butanol in transformer oil at 10 μg/kg level was established for the first time. It significantly improves the determination efficiency and the feasibility of extension.

2)The law that the content of four alcohols in oil changes with the increase of thermal aging time was obtained through experimental research, and the content of all four alcohols is negatively correlated with the degree of polymerization.

3)Through the data analysis of 52 units of 500 kV transformers in operation, *n*-butanol was found to have excellent performance, which is a discovery. And unlike the thermal aging test data, its content exceeded that of methanol. A new method is proposed to evaluate the aging state of oil-paper insulation by n-butanol and methanol, and the feasibility of the method is verified by field data.

4) Two possible pathways for the generation of *n*-butanol by cellulose cleavage during aging of oil-paper were proposed from the chemical structure of cellulose. The mechanism of *n*-butanol production remains to be further investigated.

REFERENCES

[1] Wang Jianyi, Liu Xueli, Sun Jiantao, Wang Ke, Wang Zhaowei, Bai Song, Liu Jun, Lu Jiayu. Research progress and prospect of new aging characterizers for oil-paper insulation. *Chinese Journal of Electrical Engineering*,41(21):7517-7529,2021.

[2] Matharage S, Liu Q, Davenport E, et al. “Methanol detection in transformer oils using gas chromatography and ion trap mass spectrometer,” in *IEEE International Conference on Dielectric Liquids.* IEEE, 2014.

[3] Schaut A, Eeckhoudt S. Identification of early-stage paper degradation by methanol. 2012.

[4] Gilbert R, Jalbert J, Pierre Tétreault, et al. Kinetics of the production of chain-end groups and methanol from the depolymerization of cellulose during the ageing of paper/oil systems. Part 1: Standard wood kraft insulation. *Cellulose*, vol. 16(2), pp. 327-338, 2009.

[5] R. Gilbert, J. Jalbert, S. Duchesne, P. Tétreault, B. Morin and Y. Denos "Kinetics of the production of chain-end groups and methanol from the depolymerization of cellulose during the aging of paper/oil systems. Part 2: Thermally upgraded insulating paper", *Cellulose*, Vol. 17, pp. 253-269, 2010.
[6] Jalbert J, Rodriguez-Celis E, Duchesne S, et al. 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℃. *Cellulose*, 22(1):829-848,2015.
[7] Schaut, S. Autru, S. Eeckhoudt, "Applicability of methanol as a new marker for paper degradation in power transformers", *IEEE Trans Dielectric Electric Insul*, Vol. 18, pages 533-540, 2011.
[8] Yang Yuling, Yang Xueying, Guo Xinliang, et al. Determination of Methanol in insulation oil by Headspace-Gas Chromatography Mass Spectrometry Method. *Yunnan Electric Power*,45(06): 109-112, 2017.
[9] Tan Qiaotian. Detection and Research of Decomposition Product Aging of Solid Insulation in Transformer Oil. *Wu Han:Huazhong University of Science and Technology*, 2016.
[10] Jiang Dangyu, Gao Bo, Wu Guangning, et al. Approach of methanol deriving from aging of transformer oil-immersed insulation paper.*Guangdong Electric Power*, 30(07):110-114, 2017.
[11] Zhou Kuiyu. Study on Aging Evaluation of Transformer Insulation Paper Based on Methanol in Oil. *Chongqing: Chongqing University*, 2019.
[12] YANG Xueying, LI Zonghong, Song Yufeng, et al.Research on the detection method of aging characteristic products of transformer insulation paper. *Guangdong ChemicalIndustry*,48(12):69-70,2021.
[13] Zhang S, Chen W, Wan F, et al. A SERS Substrate For Detecting Methanol In Transformer Oil.*IEEE 20th International Conference on Dielectric Liquids (ICDL)*, 2019.
[14] Li Guangmao, Qiao Shengya, Zhu Chen, Xiong Jun, Mo Wenxiong, Wang Yong. Quantitative analysis of dissolved methanol in transformer oil by Raman spectroscopy. *High Voltage Technology*, 201,47(06):2007-2014.
[15] WANG, Cong, ZHANG, et al. Study on Quantitative Analysis Method of Methanol Raman Spectra in Oil By Extraction Technology (*CNCLS* 20). 0.
[16] Fu Q, Peng L, Li L, et al. Detection of Methanol in Power Transformer Oil Using Spectroscopy. *Journal of Electrical Engineering and Technology*, 2019.
[17] Bruzzoniti M C, Maina R, De Carlo R M, et al. GC Methods for the Determination of Methanol and Ethanol in Insulating Mineral Oils as Markers of Cellulose Degradation in Power Transformers. *Chromatographia*, 77(15-16): 1081-1089, 2014.
[18] SCHAUT A, AUTRU S, EECKHOUDT S. Applicability of methanol as new marker for paper degradation in power transformers[J]． IEEE Transactions on Dielectrics and Electrical Insulation，2011，18(2)：533-540．
[19] Tran-Duy C, Murin V, Bertrand Y, et al. Chemical indicators and ageing diagnosis of MV/LV distribution transformers[C]// International Conference & Exhibition on Electricity Distribution. IET, 2013.
[20] Gu Z, Chen W, Xiang Y, et al. Detection of methanol dissolved in transformer oil by laser Raman spectroscopy *IEEE International Conference on High Voltage Engineering & Application.* IEEE, 2016.
[21] Bertrand Y, Tran-Duy C, Murin V, et al. MV/LV distribution transformers: Research on paper ageing markers. 2012.
[22] D Laurichesse, Y Bertrand, C Tran-Duy, V Murin. Ageing diagnosis of MV/LV distribution transformers via chemical indicators in oil. *Electrical Insulation Conference*. IEEE: 464-468, 2013.
[23] ARROYO O H, FOFANA I, JALBERT J, et al. 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, 2015.
[24] Jalbert, Jocelyn, Lessard, et al. Cellulose chemical markers in transformer oil insulation Part 1: Temperature correction factors. *IEEE Transactions on Dielectrics & Electrical Insulation*, 2013.
[25] Zheng H, Shi K, Zhang Y, et al. 2020, Effect of Temperature on Methanol Equilibrium in Oil-paper Insulation System of Power Transformers,*IEEE International Conference on High Voltage Engineering and Application (ICHVE)*.
[26] Zheng H, Shi K, Yang T, et al. Investigation on the equilibrium distribution of methanol in transformer oil-immersed cellulosic insulation. *Cellulose*, 28(15–16):1-12, 2021.
[27] QI Liming, Jia Xinmin, ZHANG Zhenmin, et al. Study on aging State Evaluation of Solid insulation of transformer based on The Amount of Methanol produced by unit Mass insulation paper aging. *Automation Applications*, 2019(11):3.
[28] SHI K K. Study on equilibrium distribution characteristics of methanol in oil-paper insulation of power transformer. Guangxi University.2021
[29] Matharage S Y, Liu Q, Wang Z D. Aging assessment of kraft paper insulation through methanol in oil measurement. *IEEE Transactions on Dielectrics and Electrical Insulation*, 2016, 23.
[30] Matharage S, Liu Q, Wang Z, et al. 2016, Methanol and furan detections in a gas to liquid hydrocarbon oil for indicating cellulose insulation ageing. *IEEE International Conference on Dielectrics*.
[31] Matharage S Y, Liu Q, Wang Z D, et al. Aging assessment of synthetic ester impregnated thermally non-upgraded kraft paper through chemical markers in oil. *IEEE Transactions on Dielectrics and Electrical Insulation*, 25(2):507-515, 2018.
[32] Liland K B, Linhjell D, Lesaint C, et al. Comparison between synthetic ester and mineral oil impregnated transformer paper aging markers, 2017 IEEE 19th International Conference on Dielectric Liquids (ICDL). IEEE, 2017.
[33] Jalbert J, Lessard M C. Cellulose chemical markers relationship with insulating paper post-mortem investigations. *IEEE Transactions on Dielectrics & Electrical Insulation*, 22(6):3550-3554, 2016.
[34] J J albert, Rajotte C, Lessard M C, et al. Methanol in oil interpretation model based on transformer post-mortem paper analysis. *IEEE Transactions on Dielectrics and Electrical Insulation,* 25(2):568-573, 2018.
[35] Darian L A, Obraztsov R M, Maksimchenko A V, et al. The Research of Methanol Generation in Aging Paper Insulation[J]. Procedia Engineering, 202:13-19,2017.
[36] Fan X, Zhao H, Sun T, et al. Investigation on Diffusion Mechanisms of Methanol in Paper/Oil Insulation Based on Molecular Dynamics Simulation. *IEEE Access*, 9:13368-13377, 2021.
[37] Yoshimitsu, UEMURA, Keishi, et al. Overall Transesterification Rate of Oil in Methanol-Oil Two-Phase System: A Simultaneous Diffusion-Reaction Model. *Journal of the Japan Institute of Energy*, 98(5):106-109, 2019.
[38] Chen C, Li S . An improved method of detection and concentration of methanol in oil-paper insulation. *IEEE Transactions on Dielectrics and Electrical Insulation*, 27(5):1724-1727, 2020.
[39] Jalbert J, Gilbert R, Denos Y, et al. Methanol: A Novel Approach to Power Transformer Asset Management. *IEEE Transactions on Power Delivery*, 27(2):514-520, 2012.
[40] He Tao. Research on the detection and prediction model of thermal aging products of transformer oil paper insulation. *Huazhong University of Science and Technology*, 2019.
[41] E. Rodriguez-Celis, J. Jalbert, S. Duchesne, B. Noirhomme, and M-C. Lessard, "Chemical markers use for diagnosis and life estimation of power transformers, a preliminary study of their origins", *CIGRE Canada Conference*, CIGRÉ-083, 2012.
[42] E. M. Rodriguez-Celis, S. Duchesne, J. Jalbert, et al. "Understanding ethanol versus methanol formation from insulating paper in power transformers", *Cellulose*, (DOI 10.1007/s10570-015-0693-0), 2015.
[43] Jalbert J, Duchesne S, Rodriguez-Celis E, et al. Robust and sensitive analysis of methanol and ethanol from cellulose degradation in mineral oils. *Journal of Chromatography A*, 1256(Complete):240-245, 2012.
[44] E. Z. Zhang, H. B. Zheng, Y.Y. Zhang, et al. Lifespan Model of the Relationships between Ethanol Indicator and Degree of Polymerization of Transformer Paper Insulation. *IEEE Trans. Dielectr. Electr. Insul*., 2021.
[45] Matharage S, Liu Q, Wang Z D, et al. Ageing assessment of transformer paper insulation through detection of methanol in oil. *Properties & Applications of Dielectric Materials. IEEE*, 2015.
[46] Matharage S Y, Liu Q , Wang Z D , et al. Generation of methanol and ethanol from inhibited mineral oil. *Insucon-international Electrical Insulation Conference*. 1-4. 2017.
[47] E. Rodriguez-Celis, J. Jalbert, S. Duchesne, B. Noirhomme, M. C. Lessard, and M. Ryadi, "Chemical markers use for the diagnosis and life estimation of power transformers: a preliminary study of their origins," *2012 CIGRE Canada Conference, Montreal*, Quebec, 2012.

[48] M. Ryadi, A. Tanguy, J. Jalbert, and C. Rajotte, "Alcohol based ageing chemical markers for the diagnosis of transformer cellulosic insulation," *CIGRE A2 and D1 Joint Colloquium, Kyoto, Japan*, 2011.

[49] Akcelrud, Leni, Munaro, et al. Evaluation of the Chemical Stability of Methanol Generated during Paper Degradation in Power Transformers. *IEEE transactions on dielectrics and electrical insulation: A publication of the IEEE Dielectrics and Electrical Insulation Society*, 2016.

[50] Zheng H., Shi K., Zhang Y., et al. Effect of Temperature on Methanol Equilibrium in Oil-paper Insulation System of Power Transformers.*2020 IEEE International Conference on High Voltage Engineering and Application (ICHVE). IEEE*, 2020.

[51] YAN Jiangyan, WANG Xuelei, LI Qingmin et al．Molecular dynamics simulation on the pyrolysis of insulating paper． *Proceedings of the CSEE2015*, 35(22)：5941-5949, 2015.

[52] Zhang, E., Zheng, H., Zhang, C, et al.. Aging state assessment of transformer cellulosic paper insulation using multivariate chemical indicators. Cellulose, 28(4), 2445-2460, 2021.

Jianyi Wang received a Master degree from Tsinghua University, Beijing, China, in 2008. She is currently pursuing a Ph.D. degree at Tsinghua University. She is a Senior Engineer at China Electric Power Research Institute. She is a member of the China National Standardization Committee on Insulation Materials, China. Her research interests include transformer oil performance evaluation, transformer fault diagnosis and monitoring evaluation, analysis of dissolved gas in transformer oil, etc.