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Review

State-of-Art Review on Chemical Indicators for Monitoring the Aging Status of Oil-Immersed Transformer Paper Insulation

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Abstract: Chemical compounds dissolved in insulating oil, as indicators can excellently monitor the paper aging condition, which has attracted increasing interest in areas of transformer condition monitoring and fault diagnosis. Because of their outstanding features, such as good correlation with the degree of polymerization of cellulose paper and the aid of non-destructive online monitoring, chemical indicators have been effectively used for transformer condition assessment. In this study, a comprehensive, in-depth insight into the indicators of the aging of insulating paper from aging characteristics, physico-chemical characteristics, shortcomings of various compounds, generation pathways and mechanisms, and monitoring technologies are provided. It is expected that these chemical indicators can provide better guidance for the evaluation of paper insulation performance and transformer aging. In addition, the latest research progress, as well as current challenges and future prospects are also outlined. This study provides a theoretical basis and reference for chemical indicators in the fields of microscopic formation mechanism, diffusion equilibrium phenomenon, and insulation aging state assessment.

Keywords: chemical indicators; monitoring; aging status; power transformers; insulation paper

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Citation: Zhang, E.; Liu, J.; Zhang, C.; Zheng, P.; Nakanishi, Y.; Wu, T. State-of-Art Review on Chemical Indicators for Monitoring the Aging Status of Oil-Immersed Transformer Paper Insulation. *Energies* **2023**, *16*, 1396. https://doi.org/10.3390/en16031396

Academic Editor: Pawel Rozga

Received: 18 November 2022
Revised: 5 January 2023
Accepted: 20 January 2023
Published: 30 January 2023

1. Introduction

Oil-impregnated transformers are the core equipment of the power system [1,2], which undertakes various heavy tasks such as voltage boost, voltage drop, and voltage regulation in the power grid. In order to provide an uninterrupted power supply, the aging condition and remaining life of transformers have attracted great attention from scholars. During the long-term operation of the equipment, the performance of oil-paper insulation gradually declines due to the effects of thermal field, electric field, moisture, and other factors. This makes the deterioration of oil-paper insulation one of the main reasons for transformer failure [3,4].

Insulating paper is used as the solid insulating medium in the oil-paper insulation system of a transformer, which typically includes paper or paperboard [5]. Compared with insulating oil, its aging process is irreversible and replacement is difficult. Studies [6,7] have shown that the aging of insulating paper mainly leads to a decrease in the mechanical strength and short-circuit resistance of the transformer. It is worth mentioning that the degradation of electrical insulation properties such as its breakdown voltage is not obvious. When the aging is serious, the insulating paper embrittlement occurs, indicating the end of the transformer's lifespan. Therefore, the aging of the paper insulation is widely acknowledged as the key determinant of oil-immersed transformer service life [8,9].

The main component of insulating paper is cellulose, accounting for more than 90%. It is a linear polymer composed of β-D glucose monomer connected by 1,4 glycosides [10,11]. The monomer units are combined in long straight chains, with an average chain length and degree of polymerization (*DP*) often stated to be 5000 to 10,000 monomer units in the natural state [12]. The insulating paper is subjected to various stresses during the operation of the transformer, which will gradually depolymerize the cellulose polymer, resulting in the reduction of the *DP* and the mechanical properties of the insulating paper [4,10,13]. Tensile strength (TS) is another intrinsic parameter to directly judge the mechanical properties of the insulating paper. It can be used to determine the aging rate of insulating paper at different aging stages [14,15]. However, TS measurement has high requirements for sample pretreatment, measuring environment, and operators, and has disadvantages such as difficulty in collecting paper samples and poor repeatability of test results. Therefore, the average polymerization degree (DP_v) is preferred in characterizing the degree of aging of insulating paper in practical applications [16,17], and the correlation between DP_v and TS has been proved by studies [18]. However, the DP_v distribution of transformer windings at different heights has a certain degree of dispersion [19]. Especially, the measurement of the DP_v can only stay in the offline state. Moreover, it needs to sample the transformer power outage crane cover, which is a destructive measurement method that is difficult to realize in the field [20,21].

At present, the indirect method based on an oil-paper chemical indicator is used to monitor the insulation state of the transformer. Studies [10,19,22–26] show that the degradation process of cellulose will be accompanied by the breakage of cellulose molecular chains, and some chemical indicators with aging information will be generated, such as carbon-oxygen, furfural, alcohol, etc. These chemical indicators will further gradually diffuse into the insulating oil. Importantly, CIGRE [19] pointed out that the chemical indicator in oil is an online detection and non-destructive method to evaluate the aging degree of insulating paper. This benefits from the easy sampling of transformer oil. Furthermore, the relationship between the chemical indicator in oil and DP_v of insulating paper can be established. This can effectively characterize the aging state of oil-paper insulation and monitor the health state of the power transformer.

Although research based on dissolved chemical indicators in oil has been available for more than half a century, and much progress has been achieved [1,3,10,18,20,24], unfortunately, the fascinating properties and the application of these chemical indicators are rarely reviewed. Specifically, this study [1] proposes several on-line and off-line state monitoring technologies for oil-immersed transformers. Reference [3] reviews the root causes of transformer failures and possible remedial measures. In addition, research [10] focused on the thermal deterioration and failure mechanism of oil-immersed transformers and discussed the insulation life prediction model. The literature [18] summarizes various factors leading to the aging of transformer oil-paper insulation. Fault diagnosis techniques for old transformers are illustrated in detail [20]. Reference [24] classifies transformer insulation states based on furfural, methanol, and dissolved gas by using a neural network. Based on the above, most of the emerging review topics revolve around the causes of transformer failures and fault diagnosis techniques. However, there is no comprehensive overview of methods for chemical indicators in oil to transformer oil-paper insulation. Thus, we try to summarize the chemical indicator method relevant research of the past 15 years so as to inspire forthcoming studies. The novelty of this review lies in the detailed analysis and summary of the research and physicochemical properties of chemical indicators in oil. Furthermore, the current research status of analyzing chemical indicators from the atomic level is illustrated. Finally, the field monitoring methods of chemical indicators are summarized.

The paper is organized in the logical order of aging of oil-impregnated transformer paper insulation. In the second section, the foundational principles of transformer paper insulation are introduced, which include factors affecting paper insulation aging, paper insulation aging mechanism, and cellulose degradation kinetics equations. The third section is the classification of the chemical indicators generated by the degradation of insulating paper, and there are currently seven main types of chemical indicators. Moreover, their generation pathways, basic characteristics, and research status are described. The fourth section first introduces the production mechanism of these indicators from a microscopic perspective and focuses on the monitoring technology of chemical indicators. Ultimately, we will conclude with a critical analysis of the current opportunities and challenges in this area, as well as a perspective on the future development of dissolved chemical indicators in insulating oil. This is expected to provide a potential reference for the application of the chemical indicator method to the transformer insulation state assessment and life prediction.

2. Foundational Principles of Transformer Paper Insulation Aging

2.1. Influence Factors of Aging for Transformer Oil-Impregnated Insulating Paper System

In a review of transformer experience in the UK prior to privatization, the CEGB found that 50% of 650 MVA power transformers would reach their expected life (25 years) by the year 2000, and 30% of 275 and 400 MVA transformers will have attained 90% of life (40 years) [10,27]. In addition, when CEGB counted 15 faults of the 275–400 kV transformers, up to one third of the accidents could be directly attributed to paper insulation faults. Often, power transformer health is connected to the quality of its insulation system. Therefore, it is necessary to adopt appropriate monitoring and diagnosis techniques to judge the aging fault of insulating paper, so as to improve the reliability of the equipment. Furthermore, protecting the normal operation of the transformer and strengthening the reasonable maintenance of the insulation system can ensure that the transformer has a relatively long service life [28,29]. Figure 1 summarizes the main factors that cause transformer failures and typical insulation types.

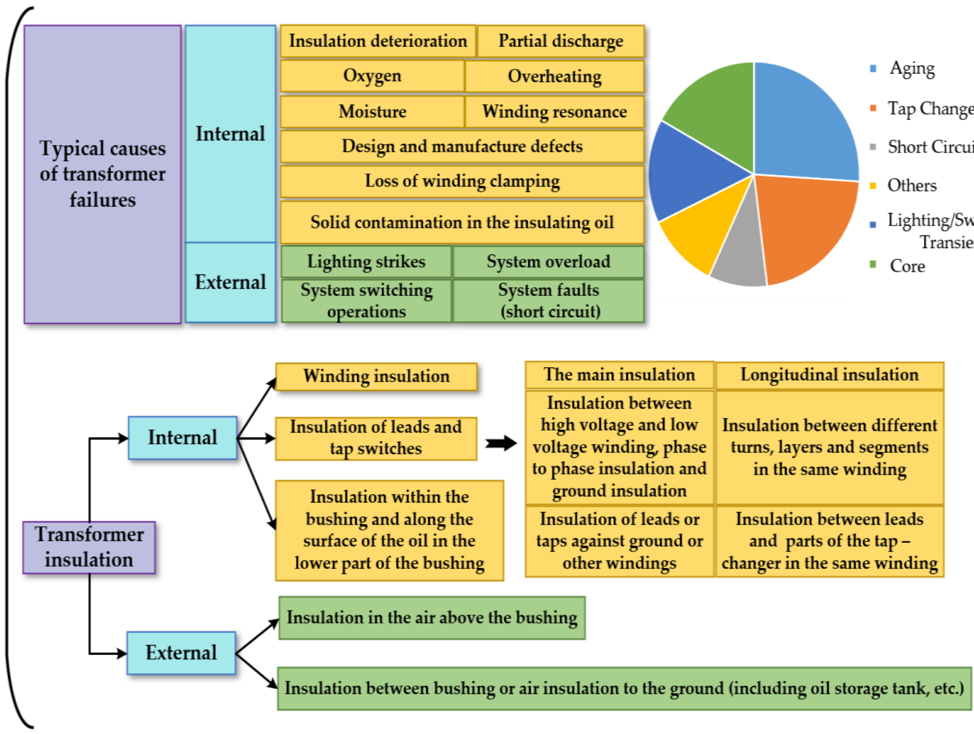


Figure 1. Main factors of transformer failure and typical insulation types.

The insulating paper will gradually be affected by various factors during long-term operation, which can lead to the shortening of the cellulose chain and reduce the overall physical properties of the insulating paper [4,7,30]. As shown in Figure 2, according to the classification of aging factors, the factors affecting the aging of transformer oil-paper insulation can be divided into three categories: thermal aging, electrical aging, and mechanical aging [4,10,18,31]. The early signals and indicators produced are summarized and classified.

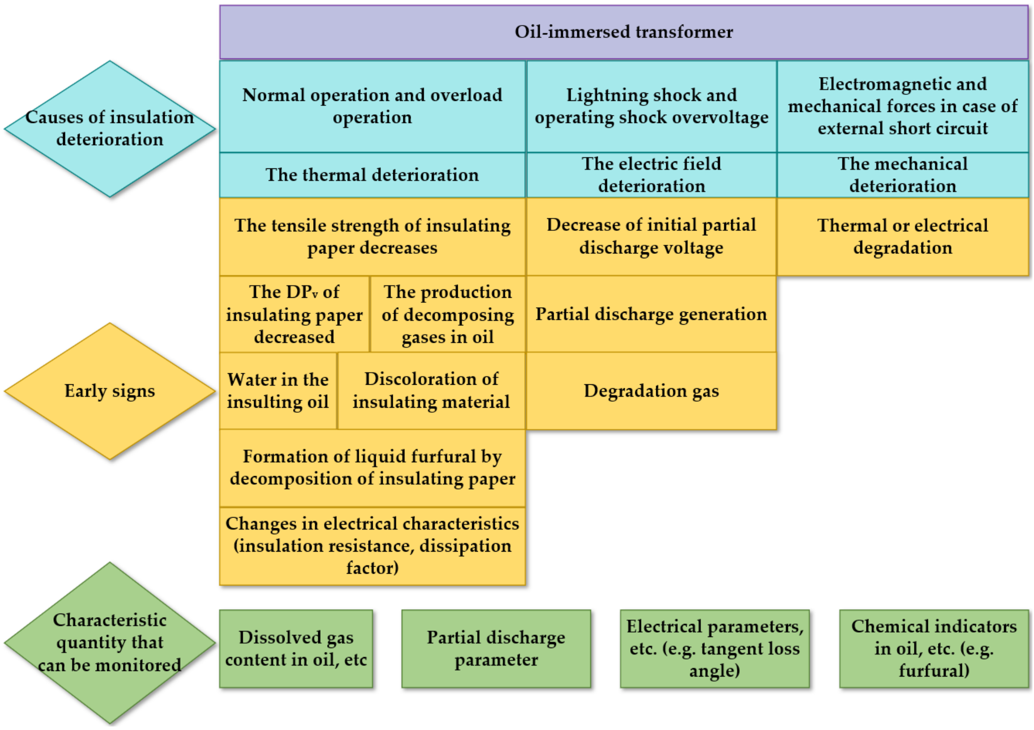


Figure 2. Oil-paper insulation aging factors and their early signal and monitoring indicators.

2.2. Aging Mechanism of Transformer Paper Insulation

The cellulose chains in the cellulose crystalline region are closely arranged, the structure is regular and the intermolecular stress is strong, so it is difficult to degrade. On the contrary, aging degradation occurs first in the amorphous region because the cellulose chains are loosely connected and disordered. The chemical bonds between cellulose chains and within molecules will gradually break during the aging process, accompanied by the generation of chemical indicators. The cellulose degradation process is an extremely complicated internal reaction, which is the result of the synergy and antagonism of multiple factors. Furthermore, researchers have assumed three independent degradation processes: oxidation, hydrolysis, and pyrolysis, each of which functions within a specific temperature range [32–35]. As shown in Figure 3, the positions of the broken bonds and the intermediate by-products of the three degradation processes are classified.

(i) Pyrolysis [36–38] is the main degradation process above 130 °C. The direct degradation of cellulose caused by pyrolysis is generally more obvious above 200 °C. Below 200 °C, pyrolysis mainly accelerates other forms of degradation, similar to the normal aging of cellulose, but faster than normal aging. From the microscopic mechanism, the thermal stability of cellulose C-O bonds is much weaker than the C-H bonds of insulating oil. Under the effect of temperature, C-O bonds can be broken, the degree of polymerization of cellulose will be reduced, and the mechanical strength will be continuously reduced. Because insulating paper has a low thermal conductivity, heat easily accumulates in the paper. With the accumulation of heat, local chemical bonds are cleavaged, and products such as aldehydes, carboxyl groups, and carbon dioxide are produced. Macroscopically, the rate of pyrolysis is determined by the interaction of oxygen, water, acid concentration, and temperature.

(ii) Hydrolysis [17,26,34,39] is the main degradation process in the range of 70 °C –130 °C. Cellulose is hygroscopic in nature, and not only water molecules can accumulate in the cellulose chains, but the pyrolysis of cellulose can also produce water. The hydrolysis reaction between water and cellulose is the main form of aging of insulating paper. The hydrolysis reaction causes the 1,4-β-glycosidic bond between glucose groups to be broken to produce short-chain molecules, which are further hydrolyzed to form low-molecular carboxylic acids and water. Lundgaard et al. believed that each break of the cellulose glycoside bond absorbed one water molecule and then released three water molecules, so a total of two water molecules are generated each time the bond was broken. In addition, chain fission can indicate the rate of hydrolytic degradation.

(iii) Oxidation [17,39,40] is mainly dominant at temperatures below 75 °C. Cellulose is relatively sensitive to oxidation, and its hydroxyl groups are easily oxidized to carbonyl and carboxyl groups, resulting in secondary chain cleavage reactions. However, free oxygen atoms were not formed inside the transformer during the aging process of transformer oil and cellulose paper. Some scholars have proposed that transition metal ions such as Cu^{+}/Cu^{2+} and Fe^{2+}/Fe^{3+} in transformers catalyze the reaction of oxygen and water to generate hydrogen peroxide and that the oxidation process can be catalyzed by hydroxyl radicals (·OH) produced by the decomposition of hydrogen peroxide.

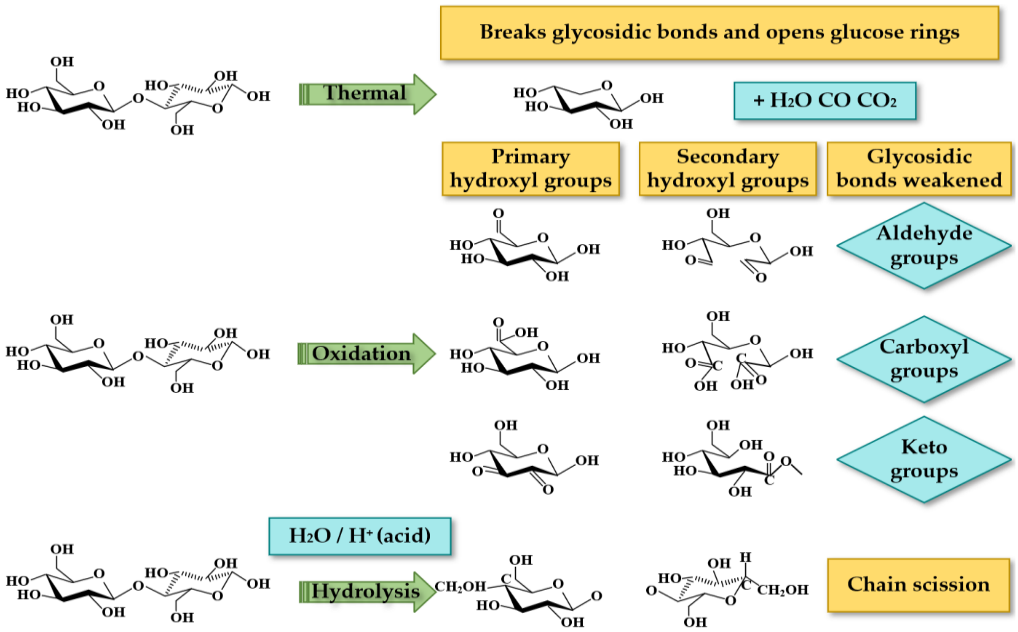


Figure 3. Classification of cellulose degradation types and their degradation processes.

2.3. On the Kinetics of Degradation of Cellulose

The study of aging dynamics based on paper insulation has been widely used in the residual life monitoring of transformers. Researchers have carried out a lot of exploration on the aging kinetic model of oil-paper insulation [10,15,17,41–44]. Currently, the commonly used aging kinetic model of oil-paper insulation includes a first-order kinetic model, second-order kinetic model, and accumulative loss kinetic model of the degree of polymerization of insulating paper. Ekenstam [42] proposed a first-order kinetic model for the aging of insulating paper in 1963, based on the first-order random break hypothesis, which stated that the probability of glycosidic bond breaks was the same everywhere on each cellulose chain. This equation is according to a uniform system and is appropriate for uniform insulating paper:

$$\frac{1}{DP_t} - \frac{1}{DP_0} = kt \tag{1}$$

where DP_0 is the initial degree of polymerization, DP_t is the degree of polymerization at time t after aging, and k is the reaction rate.

The life of the transformer predicted by the first-order kinetic model depends largely on the initial state of insulation and the DP_v of termination life. When the aging of insulating paper is carried out to the middle and late stages and the DP_v of insulating paper is about 200, it is not applicable to use a first-order kinetic equation to fit the data of this period. However, the critical value for DP_v equal to 200 is particularly important for monitoring the paper insulation life [45]. Therefore, in 1997 Emsley and Heywood made further improvements to the first-order kinetic model [46]. It is pointed out that the aging rate of the insulating paper is not a constant k, but a monotonically decreasing function k_t on the aging time t, and a second-order kinetic model is established by derivation.

Calvini suggested the leveling-off degree of polymerization (LODP) of cellulose degradation based on Emsley and introduced it into the Emsley Equation [47]. Through the study of first-order kinetics, Calvini proposed a new model of cellulose degradation based on the structure of cellulose consisting of crystalline and amorphous regions in 2008 [44].

Because thermal aging is the most common cause of transformer oil-paper insulation deterioration, the rate of thermal aging is determined by the chemical reaction rate. The Arrhenius Equation is followed when the insulating paper is gradually aged in a constant temperature, humidity, and oxygen concentration environment [48]. Equation (2) is obtained by combining the Arrhenius Equation with the aging kinetics equation [10].

$$\frac{1}{DP_t} - \frac{1}{DP_0} = A \cdot e^{\frac{E_a}{R \cdot T(t)} \cdot \Delta t} \quad (2)$$

where E_a is the activation energy of the aging reaction in J/mol, A is the pre-exponential factor, which mainly depends on the chemical environment, R is the gas constant equal to 8.314 J/mol/K, and T is the hot spot temperature at the top of the winding. In order to consider the separate effects of hydrolysis, oxidation, and pyrolysis, Equation (2) can be decomposed into a combination of three parts [33].

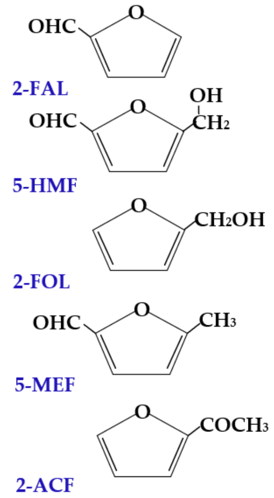
3. Chemical Indicators for Monitoring the Aging Condition

3.1. Furan Compounds Analysis

3.1.1. Research on Furan Compounds

At present, the thermal decomposition of paper insulation materials is mainly characterized by furan compounds generated during the oxidation and hydrolysis of cellulose in engineering or power enterprises [10,22,49]. In the early 1980s, furan was first identified to be associated with paper aging by the Central Electricity Generating Board (CEGB) in the UK [27]. Furan compounds mainly include furfural ($C_5H_4O_2$, 2-FAL), 5-hydroxymethyl-2-furaldehyde ($C_6H_6O_3$, 5-HMF), 2-furfurol ($C_5H_6O_2$, 2-FOL), furoic acid ($C_5H_4O_3$), 2-acetylfuran ($C_6H_6O_2$, 2-ACF), and 5-methyl-2-furaldehyde ($C_6H_6O_2$, 5-MEF), as shown in Figure 4a [50,51]. Figure 4(b1) indicates some of the causes of different furanic compounds based on in-service experience [50]. The furan content of insulating paper containing both cellulose and hemicellulose is much higher than that of pure cellulose [35]. In reference [52], the origin of furan compounds has been experimentally studied under the aging condition of 130 °C. The results of the experiment are clear given the yield of furanic compounds from different components in the paper as shown in Figure 4(b2). The determination of furan compounds in transformer insulating oil is well-known as a valuable method for diagnosing the aging state of paper insulation. Urquiza et al. [53] calculated the number of furan compounds in transformer oil. The 90th, 95th, and 98th percentile of 5-HMF, 2-FAL, 2-ACF, and 5-MEF were calculated for the database of 18,280 records in Figure 4(c1). Figure 4(c2) shows percentile values of furanic compounds for the database of 18,280 records.

a



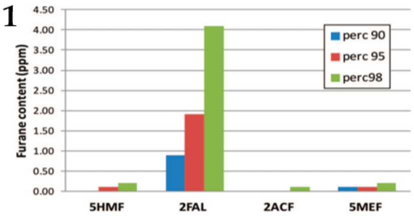
b 1

	Weight (g)	2-FAL (ppm)	5-HMF (ppm)	2-FOL (ppm)	5-MEF (ppm)	2-ACF (ppm)
Cellulose	0.5	176	15.5	14	12	5
Pentosan	0.5	600	ND	ND	4	2
Lignin	0.5	1.1	0.4	1.1	0.2	1
Laevoglucosan	0.3	28	12	14	0.8	0.2

2

Furan compounds	Observed cause	Content in insulating oil	stability
5-HMF	Oxidation	Low	Poor
2-FAL	Normal aging or overheating aging	High	Relatively good
2-ACF	Rare, causes not fully defined	Low	Good
5-MEF	High temperatures	Low	Good
2-FOL	High moisture	Low	Poor

c 1



2

Percentile	Furanic content (ppm)			
	5-HMF	2-FAL	2-ACF	5-MEF
90th	0.1	0.9	0	0.1
95th	0.1	1.9	0	0.1
98th	0.2	4.1	0.1	0.2

Figure 4. The structure characteristics of furan compounds from cellulose degradation and the measured results in transformer oil are summarized.

(i) Furfural, also known as furan formaldehyde, is the main component of furan compounds. As can be seen from the preceding studies, furfural has the highest concentration of all furan compounds, and it is also the most commonly used parameter for determining the aging degree of insulating paper [23,24,27,49,54–56]. The following fault conditions can be effectively judged by the determination of furfural content in oil. (1) Further judge whether the existing faults in the known transformer involve paper insulation. (2) Determine whether there is a phenomenon of low-temperature overheating that causes local aging of the coil. (3) Assess the insulation aging degree of equipment that has been in operation for a long time.

In addition, when the relevant insulation parameters cannot meet the standard requirements, the oil replacement measures of filtering oil, oil replenishment, or even using new oil to completely replace old oil are often adopted [56,57]. After the oil change, the furfural indicator dissolved in insulating oil is also cleaned up. In order to determine the paper insulation status more accurately, scholars have begun to focus on correcting the effect of oil change and other factors on the content of furfural. Sans et al. [58] showed that for a transformer in service for a short time after the oil change, the furfural loss rate was as high as about 85%, and found that it took about half a year for furfural to reach the equilibrium distribution state in oil-paper. Lelekakis et al. [34] investigated a decommissioned transformer that had been in use for 47 years, compared the amount of furfural in the oil before and after the oil change, and proposed a method for eliminating furfural after the oil change. Lin et al. [59] performed laboratory-accelerated thermal aging experiments. By comparing the changes in furfural content in oil before and after the oil change, the law of the correction function was studied and the Arrhenius Equation was used to extend the field operating temperature.

(ii) 5-hydroxymethyl-2-furaldehyde. It was found that the stability of furans was 2-ACF ≈ 5-HMF > 2-FAL > 5-MEF > 2-FOL when the temperature was between 100 °C and 160 °C [23,35,60,61]. Meanwhile, during the analysis of furan compounds produced by paper insulation decomposition, these compounds could generate and transform each other [60]. As shown in Figure 5, there are three typical pathways for furfural production. It can be seen that all three pathways first generate 5-HMF and then remove one molecule of methylol and finally converted it to furfural [50,62]. Moreover, 5-HMF is the most important product in the early stage of cellulose decomposition [63]. In addition, 5-HMF is relatively lively and is easily oxidized and reduced due to its structural characteristics [64].

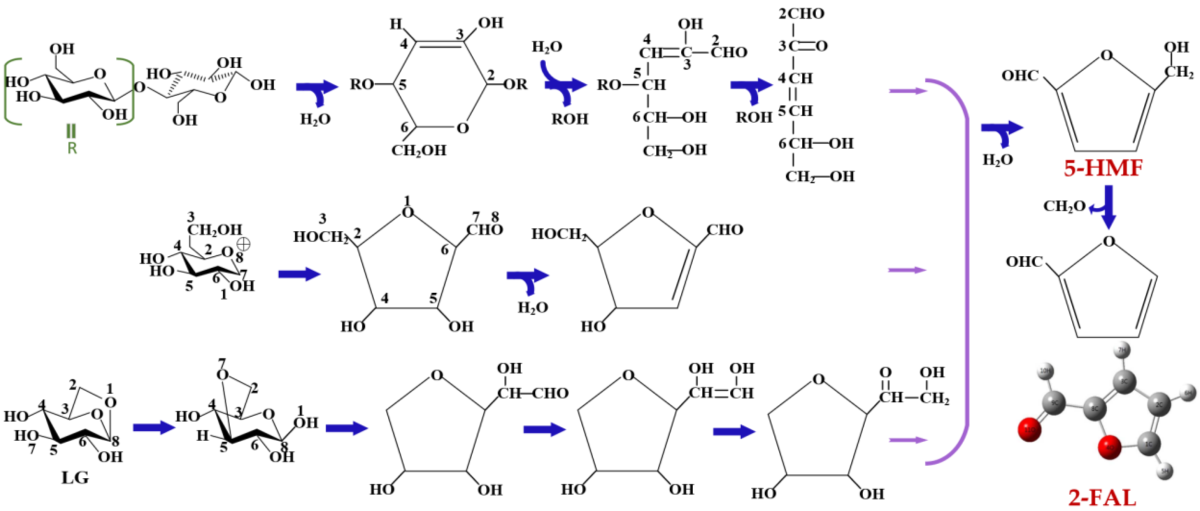


Figure 5. Three pathways of 5-hydroxymethyl furfural and furfural.

3.1.2. Characteristics of Furan Compounds

(i) Furfural is a pentacyclic compound with a chemical formula of C_4H_3OCHO, a density of 1.162 g/cm^3~1.168 g/cm^3. It is liquid and not volatile at normal temperatures, which is the characteristic product of fiber paper, and it has good stability and an accumulation effect in oil [35,65]. Since its inception, scholars in many countries have conducted a lot of research on furfural markers, and the main work is to establish the relationship between furfural in oil and the degree of polymerization of insulating paper. The following is the relationship between furfural and the degree of polymerization obtained from experiments conducted by researchers [49,53,66–68]. That is, Depablo model, Pahlavanpour model, Vuarchex model, ChenDong model, Scholniket model, Burton model and Heisler model. The Pahlavanpour model evolved from the Depablo model, both of which are theoretically derived from the analysis of the relationship between cellulose paper and furfural. Both the ChenDong model and the Scholniket model are obtained from experiments. Figure 6 shows five typical models and their fitted curves.

The originator of an equation	Form of equation	
Heisler and Banzer	DP=325×(19/13-$\log_{10}$(2-FAL))	100≤DP≤900
Chendong	$\log_{10}$(2-FAL)=1.51-0.0035 DP	150≤DP≤1000
DePablo	DP=1850/(2-FAL+2.3)	150≤DP≤600
Burton	$\log_{10}$(2-FAL)=2.5-0.005 DP	
Paul Vuarchex	$\log_{10}$(2-FAL)=2.6-0.0049 DP	

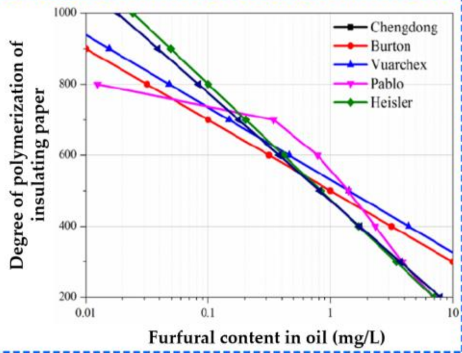


Figure 6. Relationships between furfural content in oil and *DP* of insulating paper.

It can be found that each curve has a good coincidence in the middle stage of insulation paper degradation, but there is a large difference in the early and late stages of aging.

The reason for this difference may be the experimental conditions of scholars in various countries, such as the difference in the type of insulating paper and the proportion of oil-paper [69,70]. To calculate the *DP* of insulating paper, the Chendong and Depablo methods are currently widely used in the power industry.

The stability of furfural in oil directly determines reliability in monitoring the aging state of insulating paper. However, different researchers have different opinions on the effect of temperature on the stability of furfural. Kan et al. [71] demonstrated that temperature had no effect on the furfural content of oil. Emsley et al. [23] carried out degradation stability tests under different temperature gradients (high temperature) and found that the furfural concentration only changed significantly when the temperature was above 160 °C. Jalbert and Pahlavanpour et al. studied the effect of temperature on the distribution of furfural in oil-paper systems, and the results showed that the higher the temperature the greater the proportion of furfural in oil [72,73]. Unsworth and Mitchell et al. also conducted stability tests under low-temperature gradients (20 °C, 80 °C, 110 °C), and found that furfural content began to decrease at 110 °C and was related to diffusion time [60]. Allan, Lewand, and Li et al. tracked and measured the furfural content of the insulating oil. The experimental results revealed that the addition of oxygen reduced the furfural content [54,74,75]. Griffin et al. added copper and silicon steel sheets to the oil-paper insulation system. Despite the fact that the single factor of copper was not studied, the experimental results revealed that copper had an effect on the stability of furfural [76]. Liao et al. conducted an accelerated thermal aging experiment with three factors taken into consideration. The experimental results showed that the effects of high temperature, copper, and oxygen on the stability of furfural appear to be a synergistic effect [77].

(ii) 5-hydroxymethyl-2-furaldehyde. As an important production of cellulose decomposition, 5-HMF has had little research with respect to the aging of insulating paper, but it starts to be produced in an earlier stage of aging. These advantages give it a broad research prospect. The experimental results revealed that the concentration of 5-HMF increased with aging time, with a more stable trend than furfural in the early aging period ($DP_v > 600$) or at a lower aging temperature [78,79]. By combining the experimental data with the Arrhenius equation, Hill et al. [80] found that the formation rate of 5-HMF increased faster than that of furfural as the temperature increased. Moreover, Zhuang et al. [81] found that the content of 5-HMF was the highest, reaching 40.67%, at the ultra-low acid condition of 0.05% sulfuric acid, 40 × 105 Pa, and 215 °C. Burton et al. [82] proposed that the difference between the activation energies of furfural and 5-HMF can be used as a basis for monitoring the hot spot within the transformer winding, but this method has limitations.

3.2. Carbon-Oxygen Gases Analysis

3.2.1. Research on Carbon-Oxygen Gases

Dissolved gas analysis in oil (DGA) is one of the earliest methods to indirectly monitor the aging state of transformer paper insulation [4,5,10,83]. Detecting the types, concentrations, and evolution trend of dissolved gas in transformer oil, is an important monitoring indicator of transformer operation status and health condition [84–86]. Carbon-oxygen gases (carbon monoxide and carbon dioxide) are key gases dissolved in transformer oil, which are mainly produced by the thermal decomposition of cellulose paper [10,20,24,84,86–88].

However, the use of carbon-oxygen gas in oil to monitor paper insulation degradation has obvious drawbacks, as stated by the Institute of Electrical and Electronics Engineers Std. C57.104 (IEEE) [89]: 'Many techniques for gas detection and measurement have been developed. However, it must be acknowledged that analyzing these gases and interpreting their significance is currently not a science, but rather an art subject to variation.' This art is also sophistic. Carbon-oxygen gases are not only produced by the aging of insulating paper, but also by the long-term oxidation of insulating oil [90]. Furthermore, carbon oxides would disappear or escape in the case of oil degassing or regeneration, or even open-breathing equipment. Not only that, the operating environment of the transformer (load fluctuations, etc.) can also cause large fluctuations in CO and CO_2 content within a year. Therefore, the paper insulation aging state cannot be identified only according to CO and CO_2. The analysis usually requires the combination of furfural and other characteristic products.

3.2.2. Characteristics of Carbon-Oxygen Gases

As listed in Table 1, except for carbon monoxide and carbon dioxide, all other dissolved gases are formed by the decomposition of insulating oil, which cannot characterize the aging degree and mechanical properties of paper insulation materials. Hohlein et al. summarized the parameters that affect the concentration of carbon monoxide and carbon dioxide produced in dissolved oil [88]. References [17,60,91] also reported that oxygen in oil promoted the formation of carbon monoxide and carbon dioxide in oil-paper insulating materials, and that water had a significant effect on the production of these gases.

Table 1. Transformer fault classification for monitoring of dissolved in oil.

Characteristic Faults			
Thermal		Electrical	
Oil	**Paper**	**Partial Discharge**	**Arcing**
150–300 °C H_2, CH_4, C_2H_4, C_2H_6	CO, CO_2	H_2, CH_4	H_2, C_2H_2
300–700 °C H_2, CH_4, C_2H_4, C_2H_6			
>700 °C H_2, C_2H_2, C_2H_4			

By changing the oil temperature, Kan and Miyamoto et al. [71] found that the concentration of CO and CO_2 was dependent on temperature changes, which was closely related to the absorption and release of carbon-oxygen gases by the insulating paper. This explains why the carbon-oxygen gases increase in summer and decrease in winter as the CO and CO_2 at lower temperatures are more easily absorbed into the insulation paper than at higher temperatures.

3.3. Low Molecular Alcohols Analysis

3.3.1. Research on Low Molecular Alcohol Compounds

In recent years, some scholars [25,92,93] at home and abroad have proposed low molecular alcohol compounds dissolved in oil as indicators to characterize the aging state of insulating paper. Jalbert [94] and Schaut [93] used gas chromatography-mass spectrometry (GC-MS) to find that methanol and ethanol were more stable than other aging products at different temperatures in all the markers (nearly 30 kinds of products) studied. Moreover, their formation is generated by the degradation of paper, which has special significance for studying the aging state of paper insulation.

Jalbert research group has carried out kinetic studies on the relationship between molecular chain breakage and methanol generation during cellulose cleavage in (1) kraft paper (60–130 °C) [45], (2) thermal upgraded insulating paper (60–130 °C) [90], and (3) high temperature (130–210 °C) [95]. Through an accelerated thermal aging experiment at 170 °C, it is revealed that a linear relationship exists between the tensile strength of insulating paper and methanol concentration in oil [96]. The improved Calvini kinetic equation was used to simulate the dynamic phenomenon of the change of mechanical properties in the aging process of cellulose [97]. The concentration of the furfural indicator is relatively low due to the widespread use of thermally upgraded paper [98]. However, there is no chemical bond interaction between alcohol markers and stabilizers [94,99], so methanol and ethanol can be used as indicators of cellulose degradation to track different stages of aging regardless of the type of insulation material or the content of nitrogen additives. In addition, studies have shown that methanol may be a better early marker than furfural [94,100,101]. Because it appears from the first stage of cellulose degradation (DP_v > 900), the entire cracking stage of insulating paper is accompanied by the formation of methanol.

Methanol was routinely used in 2012 to monitor the insulation status of power transformers in Hydro-Québec and Électricité substations, located in Quebec and France, respectively [92]. Surprisingly, methanol has a higher adsorption capacity on insulating paper compared to carbon-oxygen gases, and it tends to rebalance after an oil change. After analysis of laboratory aging results and comparison with actual transformer oil samples, it was found that the content of methanol is often higher than ethanol [102]. However, the ethanol concentration detected in some actual transformer oil is higher than the methanol concentration and has certain specificity for judging the condition of insulating materials [99]. Bruzzoniti et al. [103] detected ethanol as well as methanol when testing transformer oil samples in service. When the temperature exceeds 250 °C, levoglucosan, the main by-product of cellulose, is further decomposed into a large amount of ethanol, resulting in ethanol content higher than methanol [94,99,104]. Rodriguez-Celis et al. [104] sampled a retired transformer with insulating paper (there were carbonized areas due to local overheating). It was found that the DP_v at the sampling site could not reflect the state of the winding hot spot, whereas the generation of ethanol may be related to the hotspot and thermal faults of transformer paper insulation. Therefore, there is potential to use ethanol to monitor and distinguish between normal and abnormal aging of the cellulosic insulation.

3.3.2. Characteristics of Low Molecular Alcohol Compounds

The literature [94,105,106] summarized the basic physical and chemical properties of methanol and ethanol, as well as the degradation of basic compounds constituting cellulose paper into alcohol chemical compounds. The degradation of paper into low molecular alcohol compounds is well-known in the paper industry. However, by 2007, the relationship between methanol with ethanol and the aging of insulating paper was confirmed by laboratory thermal aging experiments (Figure 7d,e,g), macroscopic experimental analysis of the generation path (Figure 7g), stability experiment (Figure 7f), oil-paper distribution experiment and a series of studies and measurements on insulating oil samples of in-service transformers (Figure 7a–c) [94,102]. The linear relationship (regardless of insulating paper type) between methanol and the number of 1,4-β-glycosidic bonds in cellulose molecules was obtained for the first time.

It is worth noting that Wang and her research group pointed out [25] that the methanol content in oil in the early stage of paper insulation aging is higher than furfural. However, during the late aging period (DP_v < 250), methanol may undergo esterification reactions with acids dissolved in the oil, resulting in a reduction in its content. Moreover, it was found that the insulating oil may also produce ethanol during the aging process, which weakens the application value of methanol and ethanol in monitoring the aging of paper insulation [105]. The concept of using methanol to dry insulating paper emerges at the right time with the comprehensive development of insulating paper drying technology [107]. Whether this will lead to the adsorption of methanol molecules on insulating paper in advance remains to be further studied. In a word, there is no doubt about the disadvantages of the new indicators, and the deficiencies still need to be proved and corrected by a large amount of data in the future.

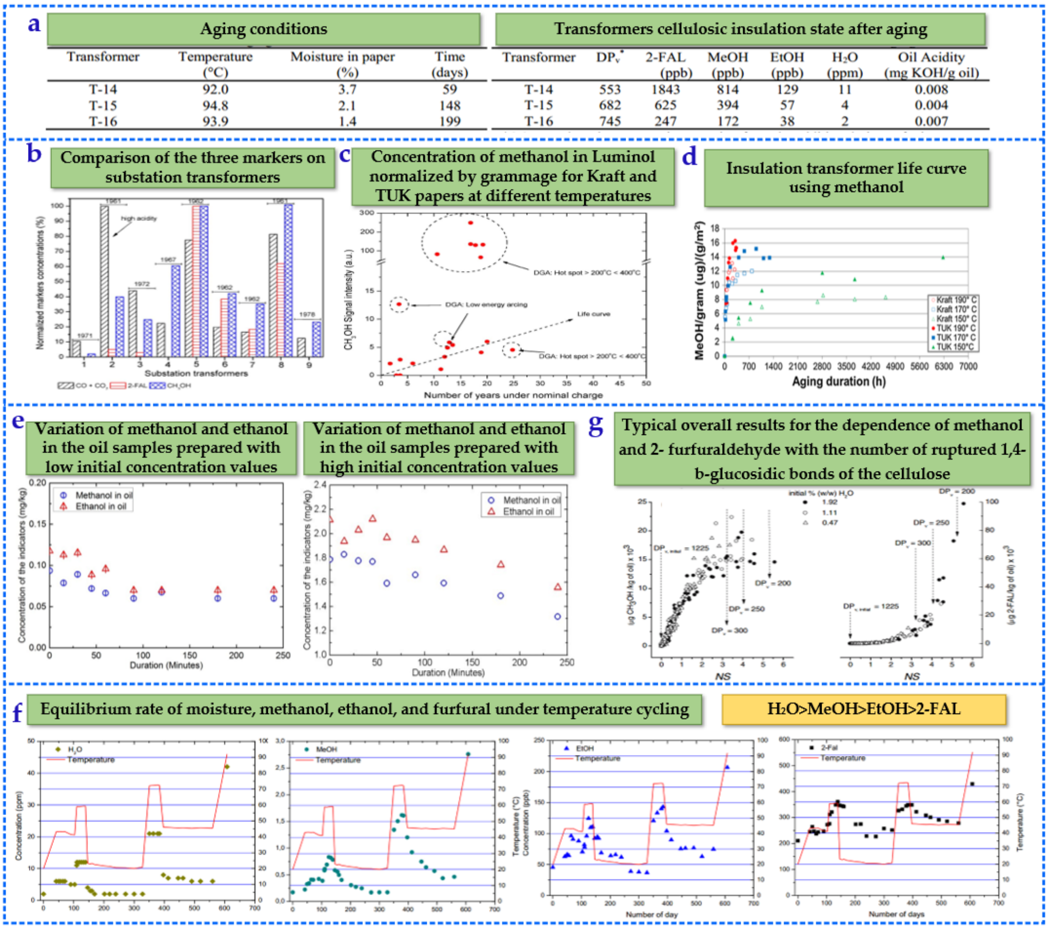


Figure 7. Summary of the basis for methanol and ethanol as chemical indicators of cellulose degradation. (**a**) experimental conditions for the detection of methanol and ethanol, (**b**) comparison of $CO+CO_2$, furfural and methanol content in field transformers, (**c**) the relationship between the normalized concentration of methanol and the temperature for different types of insulating paper, (**d**) variation of methanol concentration with time under multivariate laboratory conditions, (**e**) relationship between methanol and ethanol and aging time, (**f**) comparison of the stability of moisture, methanol, ethanol and furfural, (**g**) association of methanol with cellulosic 1,4-β glycosidic bonds.

3.4. Acid Compounds Analysis

3.4.1. Research on Organic Acids

Mander et al. [108] showed the degradation process of paper insulation materials during thermal aging in Figure 8. The process is that cellulose is degraded to glucose, then to furan compounds to furoic acids and finally small chain carboxylic acids are formed. The acid in oil comes from the degradation of oil and paper insulation, and the change of acid in oil can more comprehensively reflect the aging status of the transformer oil-immersed paper insulation system [109]. In addition, the mass fraction of the acid products accumulated in the insulating paper is a dozen or even hundreds of times that of the acid products in the insulating oil. In the field, the acid compounds generated by the aging of the oil-paper insulation increase with the operating time. Furthermore, the production of carboxylic acid has been shown to decrease the degree of polymerization [10,17,109].

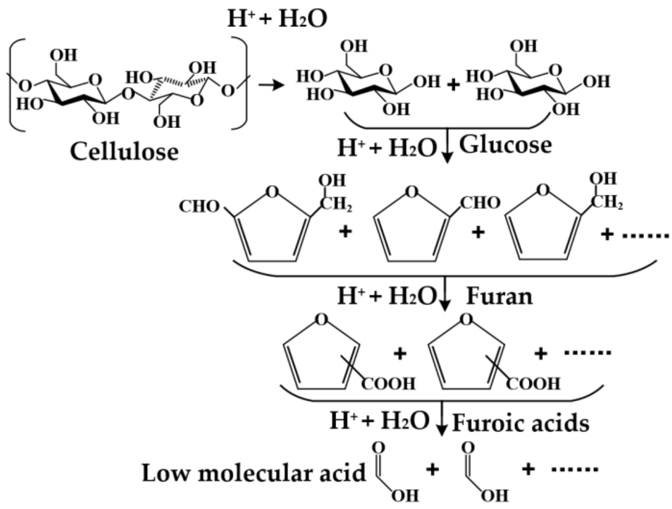


Figure 8. Pathway of cellulose to generate small molecule carboxylic acid.

Figure 9 shows the chemical reaction is the principle of cellulose acid hydrolysis reaction proposed by Xiang et al. [110], which was verified by Lundgaard et al. [17]. According to the reaction mechanism, it can be found that the degradation rate of the insulating paper depends on the moisture content and the number of free H^+ in the acid molecule. Acid compounds combine their protons with water (transport into water molecules) to form hydronium ions, which is the basic mechanism of acid hydrolysis. Hydronium ions "play hard to get" by transferring the only protons into the cellulose, and the remaining water molecules can hydrolyze with the cellulose [111]. As demonstrated by Lelekakis et al. [112], the aging rate of transformer insulation paper mainly depends on the moisture content of the paper and has no direct relationship with the acid value content of insulation oil. In other words, the acid is recovered in the aging reaction but is consumed by water molecules.

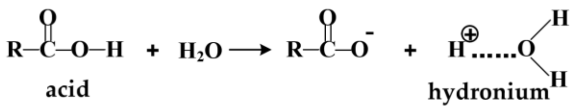


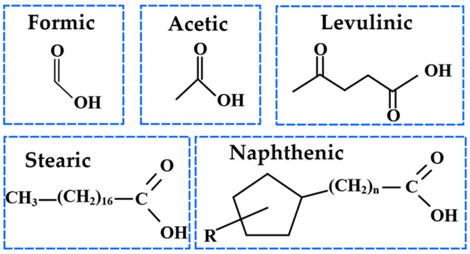
Figure 9. The principle of cellulose acid hydrolysis reaction.

3.4.2. Characteristics of Organic Acids

Lundgaard pointed out [17,109] that five organic acids were mainly produced in the aging of oil-paper insulation, which are formic acid, acetic acid, levulinic acid, naphthenic acid, and stearic acid. The first three acids are low molecular acids (LMA) which are easily soluble in water and are called water-soluble acids, while the latter two acids are high molecular acids (HMA) which are insoluble in water and are called water-insoluble acids.

Figure 10a,b illustrates the chemical structures and basic characteristics of the five organic acids, respectively. Ivanov et al. [113] showed that low molecular acids were mainly concentrated in insulating paper and high molecular acids were mainly concentrated in insulating oil. Study [114] explored the correlation between the blank oil sample and five acids and the DP_v of insulating paper. The acidity of water-soluble acid was found to be stronger than that of water-insoluble acid, causing greater harm to the mechanical properties of paper insulation materials. Furthermore, Kouassi et al. [115] investigated the effects of three different concentrations of low molecular acids on the degradation of insulation systems based on a thermal aging experiment. The results show that compared with acetic acid and levulinic acid, paper absorbs formic acid more easily, which makes the aging rate of insulating paper more significant.

a



b

Acid Type	M_r(g/mol)	pKa	T_{boil}(°C)
Formic	46	3.8	101
Acetic	60	4.8	118
Levulinic	116	4.6	243
Stearic	240	5.5	-
Naphtenic	285	10.5	232

Figure 10. Structures and characteristics of five typical organic acids.

(i) Dissolution characteristics: the low molecular acid can fully dissolve in the insulating paper, and simultaneously destroy the amorphous and crystalline areas of the insulation paper, which greatly accelerates the degradation rate of the insulating paper. The high molecular weight acid is not aggressive and does not affect the insulation paper too much. (ii) Diffusion characteristics: it has been pointed out in the literature [116] that low molecule acids have a fast diffusion rate and are easily absorbed by the insulating paper, and high molecular acids, represented by stearic acid, have a slow diffusion rate and are easily absorbed by transformer oil. Low-molecule acids can influence water distribution between oil and paper, whereas high-molecule acids have little to no effect. (iii) Polarity level: the adsorption capacity of acid compounds and insulating paper is analyzed from another aspect. Free hydroxyl groups in cellulose paper have a strong affinity for polar compounds. Both low molecular and high molecular acids are composed of a strong polar carboxyl group and a non-polar alkyl group. It can be seen that the larger the molecular weight, the smaller the proportion of the carboxyl group, and the weaker the molecular polarity [109,117].

3.5. Ketone Compounds Analysis

3.5.1. Characteristics and Research on Acetone

Acetone is C_3H_6O, with a melting point of −95 °C and a boiling point of 56 °C. It is a colorless liquid with a special smell and can dissolve acetate and nitrocellulose. The experimental study has obtained the correlation between the residual average degree of polymerization, the amount of (CO_2 + CO), furfural, and acetone content of the insulating paper at 60% residual tensile strength as is shown in Figure 11.

In the early days, acetone indicator use to monitor the insulation performance of cellulose paper was rarely studied. Finally, Awata et al. [118] carried out the determination of acetone concentration in insulation oil in 1997. Okabe et al. [119] collected 98 insulation oil samples from field transformers. According to the results of the oil sample composition, the concentration of acetone was about 100 ppb or even more than 1000 ppb in many samples aged for 10 years or more. In addition, the detection concentration of acetone is higher than ethanol, and the acetone content in equipment below 275 kV has a tendency to increase with aging time. Moreover, it was found that the concentration of acetone in the insulating oil has a good correlation with DP_v and the experimental value was in good agreement with the actual measured value. However, when Jalbert et al. [94] compared the stability of several indicators, they discovered that acetone became rapidly unstable after 450 h at 110 °C, and inferred that the production of acetone mainly depended on the oxidation deterioration of insulating oil by comparing with the blank oil sample. This is contrary to the study of Okabe et al. The formation mechanism of acetone indicator remains to be studied in the future.

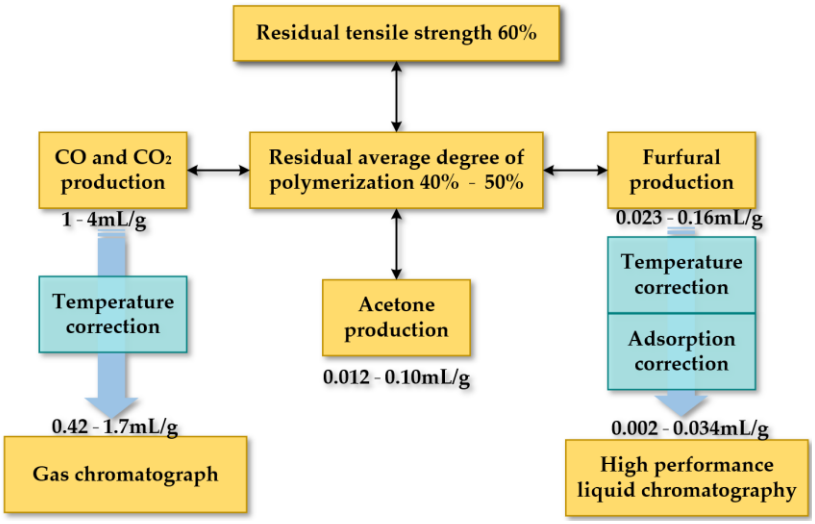


Figure 11. Relationship between acetone and aging indicators of transformer insulation.

3.5.2. Research on Methyl Ethyl Ketone

Okabe et al. [119] also found a ketone when analyzing chemical products in transformer insulating oils, which can also better characterize the aging state of insulation. The results show that the concentration of methyl ethyl ketone is the highest in all chemical compounds regardless of the operation time of the transformer. It is concluded that methyl ethyl ketone is an effective indicator for evaluating insulation aging based on a comparison and theoretical analysis of component concentrations (the higher the detectable concentration, the more obvious the volume resistivity and dielectric loss tangent characteristics).

3.6. Sugar Analysis

3.6.1. Classification and Interrelationship of Sugars

Sugars are carbohydrates composed of three elements: carbon, hydrogen, and oxygen. In the study of Kbyemela [120] and Goto et al. [121], it was found that the hydrolysis and thermal degradation products of cellulose and hemicellulose included monosaccharides dominated by pentose and hexose, such as mannose and rhamnose, fucose, xylose, arabinose and galactose, and oligosaccharides (such as cellobiose, levoglucosan, glucose, and fructose, etc.). These sugars are not necessarily the final products. Studies have found that some sugars can be converted to other sugars under certain conditions. For example, Jumppanen et al. [122] carried out related studies on the further catalytic isomerization of arabinose to ribose, and galactose can be further deoxygenated to fucose. In addition, glucose, fructose, and mannose can be converted to each other.

3.6.2. Characteristics and Research on Sugars

Scheirs et al. [123] demonstrated the presence of sugar in transformer oil samples in 1998. It is proved that sugar is produced before furfural as the first step decomposition product of cellulose and is not easily absorbed by the insulating paper, and the detection results are more sensitive and accurate. By studying the change of sugar concentration with the aging of insulating paper, it is undoubtedly of important practical significance to make a rapid diagnosis of the transformer insulation state at the early stage. Lessard et al. [124] found that cellobiose and levoglucosan not only adsorbed on insulating paper but were also more stable compared to furfural. There is a relationship between the logarithm of the two sugar concentrations and the degree of polymerization, which also provides a new idea for judging the aging of transformer paper insulation. Lessard et al. [125] revealed that mannose and rhamnose produced by the decomposition of transformer insulation paper were dissolved in transformer oil in a subsequent study. Moreover, the logarithm of the two sugar concentration was linearly related to the degree of polymerization of insulating paper, as shown in Table 2.

Table 2. Detection of sugars in oil.

Sugars	Retention Time (min)	DP_v Appearance	Maximum Concentration Level Attained (ppb)
Levoglucosan	2.2	1300	1000
Cellobiose	12.4	1300	10,000
Mannose	5.4	1300	13,500
Rhamnose	4.2	728	3000

To be sure, the actual transformer oil samples also contain ribose and fucose. However, it is regretful to find that the concentration of the two sugars in the oil sample is higher or lower than that in the blank oil sample, and the concentration is not related to the aging state of the transformer, so it is not the product of the insulating paper. On the other hand, the total sugar concentration gradually increases with aging time. When the temperature is higher, the faster the total sugar content increases. Moreover, the total sugar concentration below 90 °C is significantly correlated with the aging time. The conclusion shows that the degree of polymerization of the insulating paper and the logarithm of the total sugar concentration have a good linear relationship, and the total sugar concentration increases linearly with the decrease of the DP_v [124–126].

3.7. Others

At present, some scholars have verified that aldehydes, such as acetaldehyde, are produced during the aging of insulating paper [30], and evaluated the effects of aldehydes on the properties of insulating oil. However, the relationship between acetaldehyde/ormaldehyde and the degree of polymerization of paper insulation materials has not been discussed in detail. On the other hand, the reference [127] used infrared spectroscopy to monitor the change of functional groups in the aging process of insulating oil. According to the appearance of characteristic peaks in a certain range during the reaction, the aldehyde group absorption peak at 1720 cm^{-1}, the characteristic absorption peak of C-H stretching vibration at 2720 cm^{-1}, and the change of hydrocarbon group absorption peak at 3400~3600 cm^{-1}, it is determined that aldehyde compounds are generated during the aging of the transformer oil.

The moisture content of solid and liquid insulation is well known to play a significant role in transformer life [128]. Hohlein et al. [129] studied the influence of moisture on the polymerization degree of insulating paper and found that the moisture content had a significant influence on the degradation of cellulose paper and the formation of furan compounds under the normal operation of the transformer. According to research [10], an increase of 0.5% in the moisture concentration of transformer oil-paper insulation can result in halving the mechanical strength of the insulation paper and doubling the rate of thermal aging. Equation (3) can be derived from empirical data. Fofana [130] and Fabre et al. [19] pointed out that the aging rate of cellulose paper was positively correlated with moisture content. The paper insulation moisture content in the whole operation process can be from less than 0.5% at the beginning to 4–8% under the limit (at the late stage of aging). Several scholars predicted that at the end of the transformer life (temperature is 80 °C), the moisture content in the insulating paper is about 5% and that in the insulating oil is about 0.1% [19,131,132].

$$[\mathrm{H_2O}] = \frac{0.5 \log(DP_0/DP_t)}{\log 2} \tag{3}$$

Other chemical indicators can be generated when the moisture in the insulating paper increases, the acidic components generated by the aging of transformer oil, or the oxygen reacts with the carbon atoms in the fiber molecules due to contact with the air [17,30], such as aldehydes, amines, etc. At this time, the cellulose hydrolysis speed is accelerated, which further leads to the decrease of DP_v, and the fiber becomes shorter, weakening the fiber strength, and thus affecting the mechanical strength of insulation materials. Therefore, the applicability of using other indicators to characterize transformer insulation is a subject worth exploring.

4. Monitoring the Aging Condition of Paper Insulation

4.1. Study on Production Mechanism of Indicators from the Microscopic Perspective

Because of the benefits of clear microscopic modeling and precise calculation, molecular simulation is a computer-aided technology developed in the 1950s and 1960s that has been widely used in many fields such as physics, chemical engineering, material science, and life science. If molecular simulation technology is used, the degradation products of paper insulation and oil insulation are distinguished by analyzing the aging ways and methods of polymer compounds under different stresses. This can play an effective theoretical support role in monitoring the state of high-voltage insulation.

The first cellulose map was obtained in 1913 when molecular simulation was gradually introduced into the study of the aging mechanism of transformer oil-paper insulation [133]. Meyer et al. proposed an epoch-making model of cellulose molecular structure of insulating paper in 1928 [134]. Cellulose is the basic component of insulating paper. From the perspective of molecular microstructure, the aging of cellulose is related to the horizontal break of hydrogen bonds between molecules and within molecules, and the longitudinal break of molecular chain caused by the rupture of 1,4-β-glycosidic bonds. In short, the mechanical life of insulating paper is determined by the average length of the cellulose chains.

The main research method of the aging micro-mechanism of transformer insulating paper is to simulate the temperature rise of the molecular models of the crystalline and amorphous regions in cellulose [135,136]. The simulation technique can observe the chemical reaction paths and the products of each temperature section that cannot be obtained in the macroscopic experiment, which provides strong support and guidance for the results of thermal aging experiments. A large number of scholars compared the crystalline and amorphous regions and analyzed the intensity of molecular chain motion and the changes in the number of hydrogen bonds in the two regions at different temperatures. It was found that the cellulose molecules had stronger interaction forces in the crystalline region, the rehearsing density was well organized and the thermal stability was strong. Moreover, the molecular arrangement in the amorphous region is disordered and the interaction between molecules is small. The physical and chemical properties are susceptible to temperature and other environmental factors, which prompts the aging of insulating paper to begin with the amorphous region. The reaction molecular dynamic force field (ReaxFF) proposed by Van-Duin et al. [137] provided an effective tool for the study of hydrocarbon cracking. The reaction force field defines the interaction between atoms as a function of the bond level. It not only has the advantage of fast simulation speed but also can simulate the formation and breaking of chemical bonds during chemical reactions. This lays the groundwork for simulating chemical indicators during cellulose degradation. The current ReaxFF can handle systems with a million atoms and a time scale of 100 ns.

Reaction molecular dynamics simulation provides an effective way to study the degradation of oil-paper insulation from the atomic level and also provides a new idea for the diagnosis of transformer aging and faults. Figure 12 summarizes the thermal degradation products and reaction pathways of cellulose, hemicellulose, and lignin, which are the main compounds of insulating paper, by simulating the aging process of the transformer oil-paper insulation system [138]. In addition, the molecular dynamics simulation and quantum mechanics model combined with nuclear magnetic resonance (NMR) were used to determine the specific positions and degradation products of the major components of cellulose xylose [139,140] and glucose [141,142] after protonation.

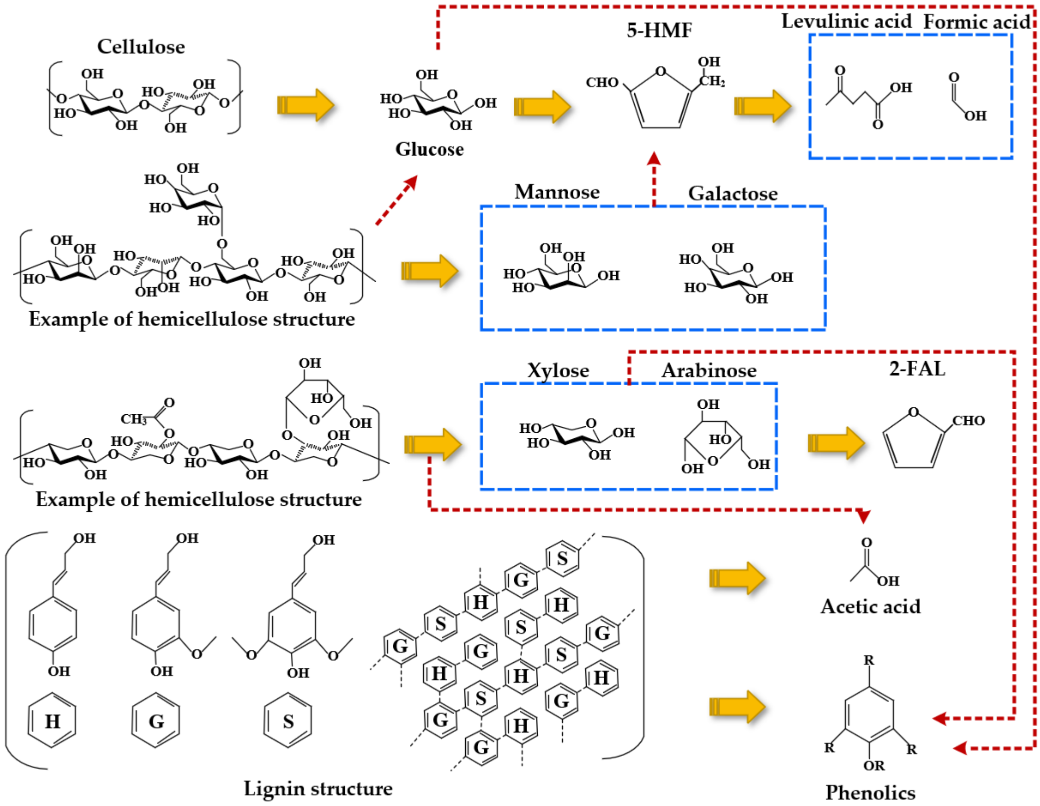


Figure 12. Main composition of insulating paper: cellulose, hemicellulose, and lignin degradation by-products.

At present, scholars have studied the effects of moisture, temperature, and oxygen content on the microscopic mechanism of oil-paper insulation. For example, Lundgaard [109] and Tian [143] et al. analyzed the microscopic mechanism of synergy between acid compounds and water molecules and the law of the diffusion behavior of organic acids based on molecular simulation. Davydov et al. [144] studied several factors affecting laboratory accelerated thermal aging. The study found that there was an exponential relationship between insulation life and temperature, but the proportion of moisture in the oil-paper was constantly changing.

In addition, Hohlein et al. [129] studied the effect of oxygen content and showed that the aging rate under aerobic conditions was three times that of anaerobic conditions. Liao et al. [145] simulated the diffusion motion mechanism of the compound model of dissolved gas in oil from the microscopic level. It is proved that water molecules can eventually diffuse into cellulose and form hydrogen bonds with glycosidic bonds, destroying the originally stable hydrogen bonding network of cellulose. Tanaka et al. [146] compared the arrangement of cellulose molecules with and without water. Under high temperatures, Li et al. [147] simulated the pyrolysis process and product changes of insulating oil and cellulose paper. After dehydration, cleavage, and polycondensation, the cellobiose repeat unit was completely decomposed into small molecular products, such as formic acid, CO_2, and H_2O. Zhang et al. [148] performed a pyrolysis simulation of cellobiose on the basis of the reaction force field and the Monte Carlo method and analyzed the generation pathway of the methanol indicator at the atomic level. Furthermore, it is consistent with the previous research results, indicating that methanol is suitable for the indication of early insulation aging, and later becomes unstable or even disappears.

4.2. Monitoring Technology of Chemical Indicators

4.2.1. Monitoring of Furan Compounds

In labs, almost all the furfural-relevant test data could be acquired under carefully controlled experiment conditions. (i) The most commonly used method for determining furfural is high-performance liquid chromatography (HPLC). Furfural and furan compounds are eluted from the column with acetonitrile-water mixed solvent after the sample is enriched by Solid Phase Extraction Cartridge (SPE), and the measurement results are accurate and reliable [60,80,82,149]. (ii) According to the characteristics of the larger solubility of furfural in water, furfural in insulating oil can also be purified and enriched by water as an extractant, with aniline acetate as the chromogenic agent. The red product of furfural and chromotropic agent in oil can have obvious characteristic absorption peaks at a specific wavelength, and then the content of furfural will be quantitatively determined by a spectrophotometer [150,151]. Of the above two test methods, although HPLC has high accuracy, it requires complicated and time-consuming pretreatment, and a lot of manpower and material resources to maintain. Spectrophotometry has strong anti-interference ability and a simple operation, but the accuracy is not very satisfactory.

In recent years, Abu-Siada [152] and Lei et al. [153] proposed an extraction-free furfural detection method based on ultraviolet-visible spectroscopy (UV-Vis). The absorption peak of furfural was separated from the spectrum of the components in the oil, and the influence of other oil compounds on furfural was reduced. The results show that the method has a good linear relationship between furfural concentration and characteristic absorbance. Chen et al. [154] also investigated the application of Confocal laser Raman spectroscopy (CLRS) in furfural concentration detection, identifying that the CLRS method was simpler and faster than HPLC, with a detection limit of 0.1 mg/L. The currently reported 5-HMF determination method is similar to the furfural detection method, and the common methods include gas chromatography and spectrophotometry [155,156].

Many countries have formulated relevant evaluation standards, which stipulate the threshold of furfural concentration in transformer oil. China power industry standards stipulate that for transformers that have been operating for 20 years, attention should be paid to furfural concentration greater than 1 mg/L. According to DL/T 596 "Preventive Test Regulations for Power Equipment", when the furfural concentration in operating transformer oil is greater than 4 mg/L, it indicates that the aging condition of paper insulation has been relatively serious [157]. Xue et al. [158] tested the data of 77 step-up transformers with rated voltages ranging from 100 to 500 kV in the China State Grid, obtaining statistical data for transformers with varying operating years and furfural concentrations after regression analysis.

4.2.2. Monitoring of Carbon-Oxygen Gases

Carbon monoxide and carbon dioxide are good paper detection indicators. Studies have shown that the content of CO and CO_2 is directly related to the degree of polymerization of insulating paper. Furthermore, the ratio of the contents of the two gases is an important feature for monitoring the degradation degree of cellulose [83,85,86,123,159]. Norazhar et al. [24] made a detailed summary of the dissolved gas detection technology and analyzed the advantages and disadvantages of each method. At present, the detection methods for dissolved gas in oil are widely accepted as gas chromatography (GC), hydrogen on-line monitoring, and photo-acoustic spectroscopy (PSA).

According to Duval et al., if the CO_2/CO ratio is lower than six and accompanied by a significant increase in ethylene, the paper degradation rate can be inferred to be higher [10]. Further research [160] revealed that the value of CO2/CO in oil for transformers in normal operation is typically greater than seven. When the value of CO_2/CO is less than six, it may indicate that the existence of fault leads to rapid aging of the insulating paper. When the value of CO_2/CO is less than two, it may indicate that there is a serious paper insulation fault in the transformer. The relevant guidelines of China provide the relationship between the total amount of carbon monoxide and carbon dioxide generated and the ratio of CO_2/CO to the state of insulating materials [161]: (i) for open transformers, the carbon monoxide content generally does not exceed 300 mg/L. (ii) The carbon monoxide content in diaphragm transformer oil is usually higher than that in open transformers. When CO_2/CO is greater than 0.5, the transformer may be abnormal. (iii) For nitrogen-type transformers, when it exceeds 0.2, the transformer may be abnormal. Mcshane et al. [162] found that when the content of CO + CO_2 was about 1 mL/g, the average residue rate of polymerization degree was 50%. When the content of CO + CO_2 was about 3 mL/g, the average residual rate of polymerization degree was about 30%.

4.2.3. Monitoring of Low Molecular Alcohols

Over time and the test of reality, methanol and ethanol have been identified as oil-soluble by-products generated by the aging of oil-immersed insulation materials in power transformers [25], and their existence provides reliable information for the diagnosis of transformer insulation. A simple, rapid, direct, and accurate detection method is essential, mainly including high-performance liquid chromatography (HPLC), gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS), spectrophotometry, solid-phase micro-extraction (SPME) and headspace sampling-gas chromatography-mass spectrometry (HS-GC-MS). Although the spectrophotometric method is easy to operate and can obtain results quickly, the reproducibility is relatively poor and the accuracy is relatively low [163]. High-performance liquid chromatography (HPLC) and gas chromatography (GC) require time-consuming preparatory work, which reduces detection efficiency [163]. In addition, some scholars use the hydrogen flame ionization detector (FID), which has a high sensitivity to organic compounds, simple structure, and fast response. By comparing mass spectrometry detectors with hydrogen flame ion detectors, it was found that the mass spectrometry detectors were better and have a wider detection range [103]. Finally, a large number of outstanding scholars confirmed that the headspace sample equipped with a gas chromatography-mass spectrometer (HS-GC-MS) was the best detection method [94,102,103,164,165].

Table 3 displays the results of recent studies on the detection and quantitation limits of ethanol and methanol in insulating oil using various methods [166]. By including an internal standard in the sample, the influence of sampling error on quantitative results can be greatly reduced. The principle is to quantify the compound by the area ratio of the target component with the internal standard peak. Studies [102,166] found that deuterium ethanol (ethanol d-6) and 2-propanol can be used as an internal standard of methanol and ethanol. The two compounds are completely separated from the target product and are not produced by the aging of the insulating paper. It is also widely used in practice analysis because of its good stability. Matharage et al. [167] also applied HS-GC-MS to compare the accuracy of the internal and external standard methods for methanol measurement results, respectively. With the increasing innovation of technology, Fu et al. [168] recently proposed a new method for the determination of methanol based on an ultraviolet-visible spectrometer, which is based on the extraction of methanol from oil samples and oxidation with potassium permanganate. Finally, spectrometry can be used to determine methanol after the reaction of chromic acid with the oxidized product formaldehyde to form the purple compound.

Table 3. Detection limits and quantification limits of ethanol/methanol under different methods.

Research Scholars	Method	EtOH/MeOH MDL (ng g^{-1})	EtOH/MeOH ML (ng g^{-1})
J. Jalbert [102]	GC-MS	3.6/4	13/14
M. Bruzzoniti [103]	GC-MS	3.1/1.3	9.3/3.9
M. Bruzzoniti [103]	GC-FID	26.8/12.1	79.6/36
H. Molavi [166]	GC-MS	155/144	495/458
Z. Wang [167]	GC-MS	21.1/19.5	67.1/62.0

4.2.4. Monitoring of Acid Compounds

There is no standard method for detecting hydrophilic low molecular acids in insulating paper at the moment. Literature [114] proposed direct titration with KOH isopropanol solution, but no specific test method flow was given. The method for determining the acid value in oil is relatively mature, with chemical titration being the most common method. The core idea is expressed by the mass (in mg) of KOH required to neutralize the acidic compounds contained in 1 g of oil [109], also known as the neutralization number, with units of 10^{-3}. However, such as Lundgaard [109] and Lelekakis [112] et al. studied the effect of acid on the transformer insulation life and pointed out that the neutralization number cannot represent the strength and corrosiveness of the acids, nor can it distinguish the type of acids [115]. In addition, Ingebrigsten et al. [169] found through experiments that only 15% of the neutralization value of acid concentration in insulating oil is hydrophilic low molecular acid generated by the degradation of insulating paper.

4.2.5. Monitoring of Ketone Compounds

Wang et al. [170] used gas chromatography to determine propanol in insulating oil, which was simple, fast, and reliable because acetone has a low boiling point and is easy to gasify and separate. Following a series of tests, the minimum detection limit of this method was 0.036 mg/L, and the relative standard deviation was 4.2%, which fully met the requirements for determining acetone in transformer oil samples. After a one year inspection of the field transformer, it was verified that the measured acetone volume ranged from 0 to 1.44 mg/L. In recent years, Gu et al. [171] proposed a method of conical laser raman spectroscopy (CLRS) to detect the acetone concentration in transformer insulating oil. The characteristic peaks of acetone were analyzed by comparing acetone plus insulating oil samples, insulating oil samples, and acetone samples. Considering the degree of migration, superposition, and vibration mode, the Raman spectral peak at the high intensity of 780 cm^{-1} was used as the characteristic spectral peak to determine the quality and quantity of acetone. CLRS has a wider detection limit range than traditional methods and is a non-destructive detection method, providing a new technique for on-site analysis of acetone concentration in oil.

4.2.6. Monitoring of Sugar Compounds

An ion chromatograph equipped with a pulse amperometric detector is a better method for detecting sugar in oil [125]. It can solve well the shortcomings of low sensitivity and poor selectivity, and the early pretreatment is simple. Hu et al. [172] proposed an ultraviolet spectroscopy method for determining mixed sugar concentration. By establishing a calibration model of the wavelength spectrum and the content of the corresponding composition, the concentration of sugar in the unknown sample can be predicted by inputting the ultraviolet spectral information into the model. In addition, the method does not require the use of other chemical reagents and has high-level safety and reliability.

5. Perspectives

The status of different organs in the body is assessed by extracting blood and comparing the contents of each component with the health warning threshold, just like in a person's routine medical examination. The same is true for insulating oil, which is periodically sampled and evaluated for the remaining life of the transformer and various failure types utilizing chemical indicators dissolved in the oil. Currently, using the chemical indicators in the oil to analyze the transformer's operational status and send out accident warnings is an irreplaceable and effective detection approach. It is also a trustworthy safety measure for the power grid's online monitoring. In this paper, we express our views on the future research direction of this field for the reference and discussion of researchers. In addition, Figure 13 presents the logic of this work summarizing the existing research and prospect of chemical indicators in oil.

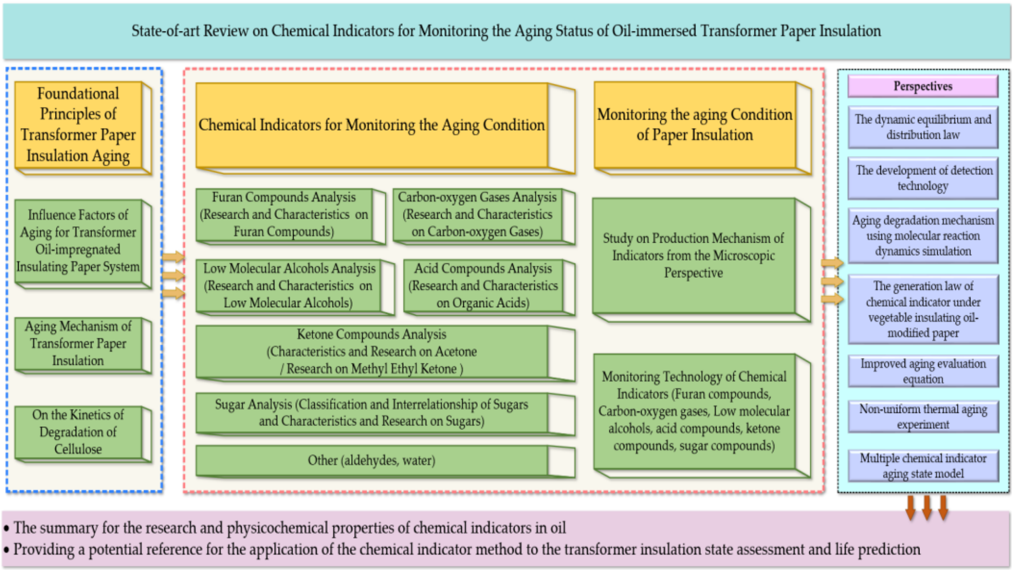


Figure 13. The logic of the existing research and perspectives of chemical indicators in oil.

(i) The dynamic equilibrium and distribution law of chemical indicators in oil-paper are also changed as a result of the complex operating conditions and diverse influencing factors. Therefore, the equilibrium/diffusion mechanism of chemical indicators is the key to aging evaluation and the main focus to determine the accuracy of field detection [36,59,99,105,115]. After a change to the oil, the oil filter, and the oil supplement, it is crucial to modify the chemical indicator's concentration. In addition, it is well known that the concentration of the chemical indicator in oil that can be detected is related to its distribution ratio between oil and paper, as well as to the chemical indicator's solubility in oil and the insulating paper's adsorption capacity for the chemical indicator. So, it is essential to establish the kinetic equilibrium model of the chemical indicator to the oil-paper system in the following three aspects: (1) The adsorption and diffusion mechanism of the chemical indicators in the insulating paper; (2) the diffusion principle of chemical indicators between the oil-paper interface; (3) The solubility and diffusion ability of chemical indicators in insulating oil.

(ii) With the help of the basic theory of interdisciplinary mature platforms (such as classical mechanics, relativity, quantum mechanics and electromagnetism, molecular chemistry, surface science, and so on), the mechanism of cellulose degradation is further explored and the relationship between various chemical indicators and transformer operating faults can be revealed [137,138]. In addition, the development of detection technology for chemical indicators should also be taken into account [154,165,167,168], in order to design the phase analysis platform which is simple to operate and easy to carry for the field transformer to measure chemical indicators in oil.

(iii) Existing studies to analyze the aging degradation mechanism of insulating paper cellulosic mostly depend on molecular reaction dynamics simulation software [136,145,148]. However, current molecular reaction simulation studies are only carried out under the influence of a single environmental factor. In the future, we can further integrate multiple factors for analysis, such as superposition temperature, electric field, and environmental factors. Secondly, the molecular reaction dynamics model is analyzed from the micro level, and the interaction between molecules in the insulating paper cannot be comprehensively simulated. The research direction can be extended to the mesoscopic scale. The process of insulating paper to generate chemical indicators can be simulated from the micro, mesoscopic and macro multi-scale levels.

(iv) A common trend for the present is the development of new, environmentally friendly insulating oil and modified insulating paper. The chemical indicator of aging degradation of the improved oil-paper insulation system is different from that of the traditional oil-paper insulation system. (1) It is found by comparing the fault gas of traditional mineral oil and synthetic ester that the propane content in the synthetic ester is significant and can be used as the key gas for thermal faults, whereas the role of propane in mineral oil as an indicator is minimal [55]. (2) Under the same aging conditions, the gas yield and acid content of vegetable oil are higher than that of mineral oil, but the furfural content of vegetable oil is lower than that of mineral oil [31]. (3) The chemical indicators of modified paper and traditional paper are also different. The concentration of furfural degraded by the modified insulating paper is much lower than that of the traditional insulating paper under the same aging state [98]. However, there is no difference in the content of low-molecular alcohols produced during the aging process regardless of the type of insulating paper. Therefore, it is necessary to study the chemical indicators generated during the deterioration process of the improved insulating oil and paper as well as the analysis of the formation path and the equilibrium diffusion mechanism of chemical indicators.

(v) Considering the influence of multiple factors (temperature, water, aging degree, etc.) on cellulose degradation, the kinetic Equation, the Arrhenius Equation and the existing aging evaluation equation based on chemical indicators can be further modified [45–47]. In addition, the chemical indicator between oil and paper in turn accelerates the deterioration process of insulating paper and needs further research. At present, due to the differences in experimental models and environments adopted by many researchers, there are no universally acknowledged results in this field.

(vi) The transformer winding hotspot temperature is generally 80–140 °C, which is much higher than the normal oil temperature. Therefore, the aging state of the paper insulation in the hotspot area is serious, which is the 'weak area' of the whole transformer paper insulation, and its operation risk is the greatest. However, the traditional electrical detection method has the disadvantage of power failure of the hanging hood. So, it is interesting to explore the relationship between chemical indicators in oil and the winding hotspot's aging state. The existing research also found that the formation of the ethanol indicator is closely related to the winding hotspot area [99]. The authors also observe that the methanol concentration rises gradually along the axial height of the winding (from the top to the bottom) through non-uniform thermal aging experiments [173].

(vii) There are many kinds of chemical indicators dissolved in oil, so it is possible to determine the weight coefficient of each chemical indicator to represent the aging degree of insulating paper through the weighting method. On the basis of the above, a model for the coupling of multiple chemical indicators to characterize the aging state of insulating paper can be established [8]. The establishment of a multiple chemical indicator model can greatly improve the transformer insulation status's evaluation method. This is a crucial direction for our future development.

6. Conclusions

This paper outlines chemical indicators for monitoring the aging condition of oil-impregnated transformer paper insulation, including its generation path, research status, basic characteristics, and defects, as well as the development of monitoring methods. The factors affecting paper insulation failure and the evolution of insulating paper degradation kinetic equations are discussed based on the aging distribution of transformer insulation. It is emphasized that the aging condition of paper insulation is critical in determining transformer service life, and the mechanical properties of insulating paper serve as the foundation for monitoring the aging degree. This paper primarily introduces and analyzes the research progress on the central issues such as the electrical and physico-chemical properties, aging properties, and monitoring techniques of chemical indicators dissolved in oil. Moreover, it summarizes the research on the formation path of the chemical indicators produced by cellulose degradation based on the reaction molecular dynamics microscopic mechanism.

The transformer oil is easy to sample and can be carried out in a way that the equipment power is not cut off. Thus, the aging status of the transformer paper insulation can be effectively monitored by using the relationship between the chemical indicator dissolved in the oil and the DP_v of the insulating paper. However, the interpretation of chemical indicators for determining the condition of paper insulation in power transformers remains a field with many challenges. The following are the key concerns about the perspectives of the chemical indicator method.

First of all, the winding has a temperature gradient at different heights due to the winding structure layout and insulating oil convection heat dissipation. So, the insulating paper under different positions of heat is not the same, resulting in a non-uniform aging state of the insulating paper along the height of the winding. However, the existing research on the chemical indicators method mainly focuses on assessing the insulation state of transformers with uniform aging. The condition of the insulating paper at local hotspots cannot be accurately expressed. In addition, the chemical indicators of dissolved oil under uniform aging and non-uniform aging processes are also different. Therefore, correcting the aging kinetic model obtained under the uniform aging state is also an important research direction.

Secondly, many factors have a significant impact on the concentration of the chemical indicator dissolved in insulating oil. If affected by non-aging factors (temperature, water, oxygen, etc.), the concentration of the chemical indicator will change with its equilibrium distribution ratio between oil and paper. When the influence of non-aging factors on the chemical indicators in the oil is eliminated, the accuracy of monitoring the aging degree of insulating paper can be significantly improved. Based on the above, scholars have studied the distribution of chemical indicators under various non-aging factors and obtained many new findings and conclusions. However, comparing the equilibrium distribution ratio and migration law of each chemical indicator between oil and paper under different factors needs to be further clarified.

Mineral oil has been the main liquid insulation material used in transformers for decades, but it contradicts the concept of being green. Natural ester, also known as vegetable insulating oil, has excellent properties such as environmental protection, high-temperature resistance, good compatibility, etc. Currently, there are more than 600,000 transformers with vegetable insulating oil around the world [174]. The highest operating voltage level in the in-service transformer exceeds 400 kV (420 kV vegetable insulating oil transformer was successfully tested and put into operation at the German power grid operator TransnetBW's Bruchsal Kandelweg substation near Karlsruhe). Moreover, with the widespread popularization of modified insulating paper and vegetable insulating oil, the insulation conditions of the oil-paper system have become more complicated. Fortunately, the improved oil-paper system not only meets environmental requirements but also slows the aging rate of the insulating paper, which can improve the transformer's service life and overload tolerance. However, the types and content of chemical indicators produced by the improved oil-paper insulation also change accordingly. Furthermore, the current standard of monitoring the operation state of the transformer utilizing chemical indicators cannot meet practical needs. As a result, it is essential to investigate the judgment criteria of chemical indicators in oil under various faults.

To sum up, we believe that chemical indicators can achieve more exciting practical applications through in-depth research into chemical indicator mechanisms, advancements in detection technology, design of laboratory non-uniform thermal aging experiments, and improvement of the aging kinetics equation and insulation life evaluation model.

Author Contributions: Conceptualization, C.Z. and E.Z.; investigation, E.Z.; resources, C.Z.; data curation, E.Z. and P.Z.; writing—original draft preparation, E.Z.; writing—review and editing, J.L. and Y.N.; visualization, J.L. and P.Z.; supervision, T.W.; project administration, Y.N.; funding acquisition, C.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China under Grant 52277139 and 51907034, by the China Scholarship Council (CSC) under File No. 202106660008.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: We would like to thank H.B. Zheng of the School of Electrical Engineering, Guangxi University for his many helpful comments and suggestions on earlier drafts.

Conflicts of Interest: The authors declare no conflict of interest.

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