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Methanol Equilibrium Curves of Power Transformer Oil–Paper Insulation

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Abstract: To eliminate the problem of the aging of cellulose insulation in the manufacturing stage, a new drying method is being developed based on the use of methanol vapors. Previous studies have shown that the complete removal of methanol from the cellulose insulation after the drying process is very difficult. Therefore, it is necessary to check how the remaining methanol after drying affects the properties of both the cellulose materials and mineral oil. To conduct such studies, it is necessary to know the methanol content in oil that can be expected depending on its initial content in the cellulose materials and the temperature of the insulation system. Therefore, the main goal of this work is to develop methanol equilibrium curves for oil–paper insulation. To achieve the assumed goal, three-stage studies were conducted. A gas chromatograph equipped with a flame ionization detector was used in all stages of these studies. The gas partition coefficient between oil and air was determined for a temperature of 70 °C. The key experimental finding was the development of methanol equilibrium curves for oil–paper insulation. Thanks to this achievement, it is possible to estimate the methanol content in cellulose materials and mineral oil depending on the insulation temperature. Such data are necessary, among others, to plan appropriate studies aimed at assessing the impact of methanol content on the dielectric and physicochemical properties of these materials, important from the point of view of the operation of power transformers.

Keywords: power transformer; oil–paper insulation; drying; methanol; equilibrium; gas chromatography; flame ionization detector

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1. Introduction

A very important issue in the stage of both the production and operation of power transformers is the problem of moisture in their insulation. In the case of high-voltage power transformers, the insulation system is most often composed of cellulose materials impregnated with mineral oil. Insulation with a high level of moisture has poor dielectric properties [1], which results in the deterioration of its mechanical properties and shortening of its service life [2,3]. In such insulation, there is also a greater probability of dangerous phenomena in the transformer, such as partial discharges [4,5] or the bubble effect [6–8]. For this reason, it is very important to maintain a very low level of moisture in the insulation, starting from the device production stage.

In the stage of transformer production, the moisture content of its insulation is determined by atmospheric conditions, such as relative humidity and temperature in the factory hall. These conditions cause the moisture content of the insulation to reach 6–8% [9]. The manufactured transformer should have insulation with a water content not exceeding 1%, and the moisture content of the very well-dried cellulose insulation does not exceed 0.5% [10,11].

To achieve such a low moisture level, various drying techniques are used for cellulose insulation. A common feature of all effective drying techniques is the need to heat the insulation. This is achieved by placing the windings in a large-sized drying oven or by heating the transformer windings with a low-frequency current [12,13]. To intensify the

drying process, the pressure is reduced to below 1 mbar. The use of a high insulation temperature significantly improves the efficiency of the method but also leads to cellulose depolymerization. In the drying stage of cellulose insulation, its degree of polymerization can decrease by up to a dozen or so percent [14,15], reducing its service life by several years.

To eliminate this problem, a new transformer drying method is being developed based on the use of methanol vapors to reduce the level of water content in the cellulose insulation prior to impregnation with oil [15]. This method involves introducing methanol vapors into the transformer tank. The carrier gas for methanol is dry nitrogen. The drying procedure assumes the removal of methanol by blowing dry nitrogen through the insulation after its completion [15]. This is a completely new approach to drying transformer insulation at the stage of its production. Currently, this method is being tested in laboratory conditions in terms of drying efficiency and its safety of use in power transformers.

Unfortunately, this does not ensure the complete elimination of methanol from the cellulose insulation due to the hydrogen bonds that are formed between the hydroxyl groups in the cellulose molecule and the water molecules [15].

During the experimental studies [15], it was established that depending on the drying procedure used, the methanol content can range from 1.4 to 4%. To safely use this drying method, it is necessary to demonstrate the lack of a negative impact of the presence of methanol in the insulation on the operation of the transformer. For this reason, work is being carried out to assess the impact of the methanol content in the cellulose material on its electrical strength and its aging process. It should be remembered that cellulose insulation cooperates with an electrical insulating liquid. The most commonly used liquid is mineral oil. Therefore, it is necessary to check whether the methanol bound to cellulose can migrate to the oil and, if so, to what extent this migration occurs.

Studies of methanol content in mineral oil have been conducted earlier in the aspect of determining the degree of aging of cellulose insulation. The first information on this subject appeared in the publication [16]. The research results presented in this paper showed an unequivocal relationship between the presence of methanol in the transformer insulation system and the disintegration of 1,4-ß-glycosidic bonds occurring in the cellulose molecule. Methanol in the transformer insulation system is formed mainly as a result of paper degradation and, to a small extent, as a result of the aging processes that occur in oil [17]. Other alcohols, carbon oxides, and dioxides [3,18] as well as furan compounds [19–21] are also used as aging markers of cellulosic materials. However, methanol is generated mainly from cellulose, the main component of papers and pressboards. Therefore, according to the authors of [22], methanol can be used to determine the normal aging of paper occurring at working temperatures. The advantages of methanol over other aging markers (CO, CO_2, 2-FAL) are good stability and high concentrations [23].

The great interest in the use of methanol and ethanol as aging markers led to the development of a standard in 2021 [24], which proposed methods for the quantitative assessment of the methanol and ethanol content in electrical insulating liquids. The standardization of methods to measure the content of methanol in electrical insulating liquids and the deepening of knowledge on the correlation of the content of methanol in oil and the degree of cellulose polymerization favor the use of this marker to assess the degree of the aging of power transformers, as exemplified by research results presented, among others, in [25–27]. In recent years, further articles have been published, the authors of which focus on various methods of detecting methanol in the insulation of power transformers [28] as well as improving the assessment of the degree of insulation aging by enriching the analysis of methanol concentration with other aging markers [29,30].

The presence of alcohols is not considered to be a factor influencing the aging of the insulation system or reducing the insulation efficiency of the system [17]. Nevertheless, this information appears in the literature in the context of a very low content of methanol in the insulation system resulting from the natural aging processes of mainly cellulose materials. The influence of high values of methanol content in pressboard materials (up to 4%), which

is crucial in the context of the developed method of their drying using methanol vapors, is unknown.

The main objective of the research is to develop methanol equilibrium curves in the oil–paper insulation system. These curves will allow us to determine what methanol concentration in oil can be expected for a given methanol content in the cellulose material. This will enable us to conduct further studies on the effect of methanol concentration in oil on its dielectric and physicochemical properties.

2. Materials and Methods

To achieve the assumed goal, i.e., to determine the equilibrium curves of methanol in the oil–paper system, the experimental studies were divided into three stages, as illustrated in Figure 1.

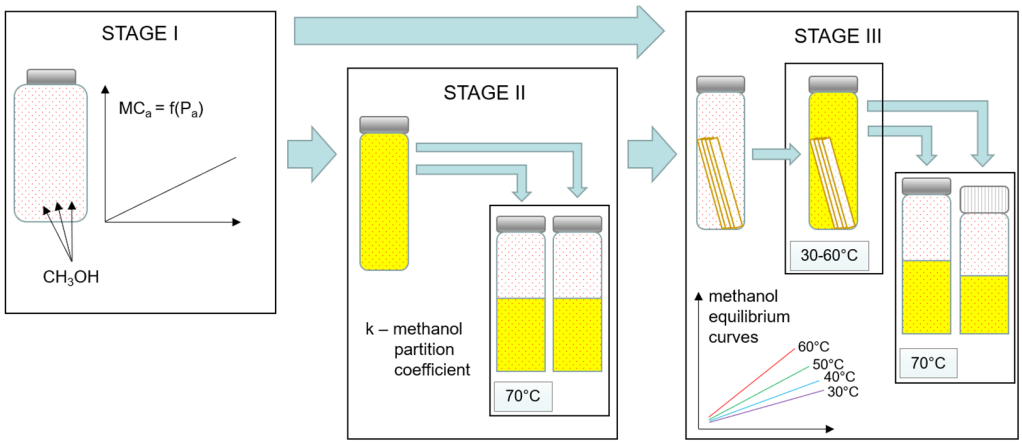


Figure 1. Research stages leading to the determination of equilibrium curves for methanol in the oil–paper system.

The purpose of the first stage of the study was to determine the dependence of the methanol concentration in the air (MC_a) as a function of the peak surface area (P_a) obtained by chromatographic analysis. To achieve the assumed goal, vials were prepared with a known concentration of methanol (CH_3OH) in the air. To calculate the methanol concentration in individual vials, information on the volume of the vial and the mass of added methanol was used. Then, air with methanol dissolved in it was sampled and analyzed using a gas chromatograph. Thus, the peak surface areas corresponding to the methanol concentrations in the individual vials were determined. On the basis of the obtained data, it was possible to determine the dependence (MC_a = f(P_a)).

The purpose of the second stage was to determine the methanol partition coefficient k between oil and air. For this purpose, oil samples with known methanol content were prepared. To determine the concentration of methanol in the oil in individual vials, information on the mass of the oil and the mass of methanol added to the oil was used. Each of the oil samples was divided into two vials. Then, the vials were heated at 70 °C to obtain equilibrium of the methanol content between oil and air. In the next step, air with methanol was sampled from the oil headspace and chromatographic analysis was performed. On the basis of the determined peak area, the methanol concentration in the air was calculated using the relationship developed in the first stage of the study. Based on the calculated methanol content in air and oil, it was possible to calculate the methanol partition coefficient k. To calculate the k factor, the mass of methanol in oil was divided by the mass of methanol in air.

The purpose of the third stage of the study was to develop equilibrium curves of the methanol content in the oil–paper system. Pressboard samples were prepared with four levels of methanol content. To calculate the methanol content in the pressboard samples, information on their mass and the mass of added methanol was used. The samples were

then impregnated with oil and conditioned in laboratory ovens, where the temperature was maintained at 30 °C, 40 °C, 50 °C, and 60 °C, respectively. In the next step, the oil was poured into two vials, leaving an air cushion above its surface. The vials prepared in this way were heated at 70 °C; then, the air was sampled from the oil headspace, and the concentration of methanol was determined based on the chromatographic analysis and the determined relationship (MC_a = f(P_a)). On the basis of this information as well as on the partition coefficient of methanol k and the values of the air and oil volumes, it was possible to calculate the methanol concentration in the oil. Based on the data obtained in this way, the equilibrium curves of methanol in the oil–paper system were determined.

The air methanol concentration analyses were performed using an 8610C TOGA gas chromatograph from SRI Instruments (Torrance, CA, USA). A Hayesep T packed column of 1 m length and a flame ionization detector FID were used to determine methanol. The operating temperature of the chromatographic column was 120 °C. Argon 6.0 was used as the carrier gas. The retention time of methanol was approximately 2 min.

In the studies, analytical grade methanol from Chempur (Piekary Śląskie, Poland) and uninhibited NYTRO Taurus mineral oil from Nynas (Stockholm, Sweden) were used.

3. Results

3.1. Measurement of Methanol Content in Air

Six 0.11 L volume vials filled with air were prepared for the study (Table 1). Methanol was injected into five of them using a microliter or milliliter syringe to obtain different concentrations of methanol in air. To determine the mass of injected methanol, the syringes were weighed before and after the injection of methanol. After 48 h, it was found that methanol had dissolved in air in three vials to which the smallest volumes had been injected. Extending the methanol dissolution time to 7 days did not change the situation. In the two vials with the largest amount of methanol, its presence was still observed. For this reason, these samples were not included in further studies.

Table 1. Data on air samples with methanol prepared for testing, together with the results of the chromatographic analysis.

Vial No	Mass of Methanol —M_{ma}, mg	State of Methanol in the Vial	Air Volume —A_v, L	Methanol Concentration in Air —MC_a, mg/L	Peak Area —P_a, mV×s
1	0	vial without methanol	0.116	0	0
2	1.0	dissolved	0.116	8.621	755
3	4.9	dissolved	0.116	42.241	2997
4	8.3	dissolved	0.116	71.552	5532
5	41.1	undissolved	-	-	-
6	79.2	undissolved	-	-	-

To collect air with dissolved methanol from the vials, 0.006 L of air was introduced into them using a glass syringe. The air injected caused an overpressure in the vial and pushed the syringe plunger, enabling the collection of the sample. The calculation of the concentration of methanol in the air took into account the volume of air added to the vial during the collection of the sample. The collected air was injected into the sample loop in the gas chromatograph.

Table 1 presents data on air samples and the results of the chromatographic analysis in the form of peak surface areas P_a that are related to the different concentrations of methanol.

Figure 2 presents chromatograms showing the results of the air analysis with different concentrations of methanol for samples taken successively from vials 1, 2, 3, and 4. With the increasing concentration of methanol in the air, an increase in peak surface area is observed.

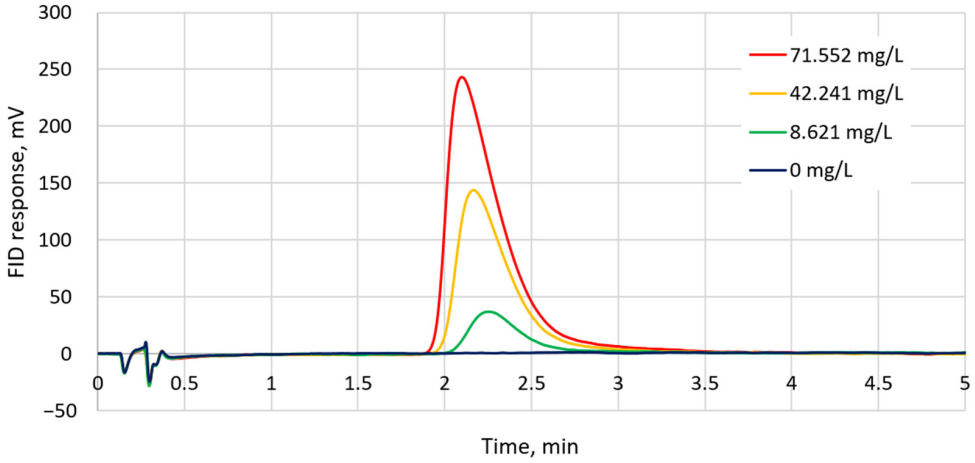


Figure 2. Chromatograms obtained for three different concentrations of methanol in air: 0 mg/L, 8.621 mg/L, 42.241 mg/L, and 71.552 mg/L, respectively.

Based on the results obtained, the dependence of the concentration of methanol in air on the peak area was prepared (Figure 3).

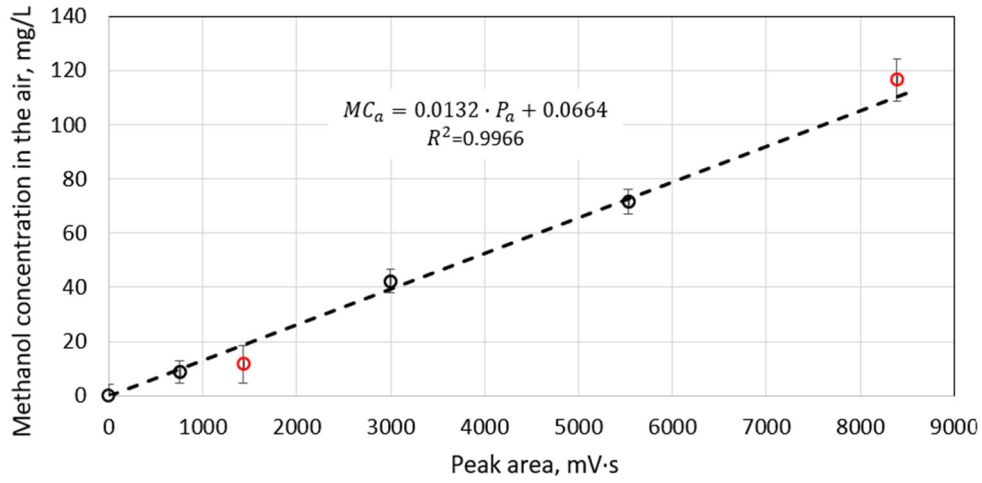


Figure 3. Methanol concentration in the air as a function of its peak area; two additional measurement points obtained in a separate experiment, the purpose of which was to validate the method, are marked in red.

A straight-line relationship between the methanol concentration in the air and peak area was found. The correlation coefficient R^2 was high and was equal to 0.9966. The figure also shows the determined expanded uncertainty of methanol concentrations in air for the prepared samples. Furthermore, two additional measurement points obtained in a separate experiment, the purpose of which was to validate the method, are marked in red in Figure 3. Detailed data on this experiment are presented in Table 2.

Table 2. Data used to validate the method for determining methanol in air.

Vial No	Mass of Methanol—M_{ma}, mg	State of Methanol in the Vial	Air Volume —A_v, L	Methanol Concentration in Air—MC_a, mg/L	Peak Area—P_a, mV×s
1a	0.792	dissolved	0.068	11.647	1431
2a	7.92	dissolved	0.068	116.471	8392

The method of sample preparation and the chromatographic analysis was the same as in the above-described study, with the only difference being that smaller vials of 0.058 L volume were used, and during sampling, an additional 0.010 L of air was injected into the vial. This resulted in a greater uncertainty of the determined methanol concentration in the air. The results of the experiment confirmed the linear nature of the dependence of the methanol concentration in the air as a function of the peak area.

3.2. Determination of Methanol Content in Oil–Methanol Partition Coefficient Between Oil and Air

Six vials, each with a volume of 57.35 mL, were prepared for the study. The vials were filled with oil, and then, methanol was added to obtain the appropriate, previously assumed concentration of methanol in the oil (Table 3). Glass beads were placed in the vials to help mix the oil (Figure 4). The samples prepared in this way were shaken for 168 h to ensure that methanol was dissolved in the oil.

Table 3. Data on oil samples with different methanol content.

Vial No	Mass of Oil —M_o, g	Mass of Methanol—M_{mo}, g	Methanol Concentration in Oil —MC_o, %
1	48.5992	0.1020	0.210
2	48.0497	0.0493	0.103
3	48.2527	0.0112	0.023
4	48.7236	0.0052	0.011
5	48.4122	0.0008	0.002
6	48.4071	0	0



Figure 4. Vials of oil with various methanol content.

The oil from each vial was then divided into two volumes, each of which was poured into a separate vial. In this way, 12 vials filled with oil were prepared (Table 4). An air cushion was left above the oil surface (Figure 5). Each vial was weighed before and after pouring the oil. In this way, the mass of oil (M_o) in each vial was determined. The oil vials were then heated in a heating oven at 70 °C to ensure the equilibrium of methanol between the oil and the headspace. After each vial was heated, an air sample was taken from it and injected into the gas chromatograph sample loop to determine the concentration of methanol in the air above the oil surface.

Table 4. Data on samples prepared for the calculation of the methanol partition coefficient between oil and air.

Vial No	Mass of Oil —M_o, g	Volume of Oil —V_o, mL	Volume of Air —V_a, mL	Peak Area —P_a, mV×s	Mass of Methanol in Air —M_{ma}, mg	Methanol Content in Oil —M_{co}, mg	Methanol Content in Oil @70 °C —M_{co70}, mg	Methanol Partition Coefficient $k \pm u(k)$
1-1	18.6554	21.4430	35.9070	13171	6.2452	39.1540	32.9088	5.27 ± 0.15
1-2	18.7969	21.6056	35.7444	13326	6.2900	39.4509	33.1610	5.27 ± 0.15
2-1	20.0685	23.0672	34.2828	7085	3.2083	20.5907	17.3824	5.42 ± 0.16
2-2	19.0710	21.9207	35.4293	6738	3.1534	19.5672	16.4138	5.21 ± 0.15

Table 4. *Cont.*

Vial No	Mass of Oil —M_o, g	Volume of Oil —V_o, mL	Volume of Air —V_a, mL	Peak Area —P_a, mV×s	Mass of Methanol in Air —M_{ma}, mg	Methanol Content in Oil —M_{co}, mg	Methanol Content in Oil @70 °C —M_{co70}, mg	Methanol Partition Coefficient $k \pm u(k)$
3-1	19.7299	22.6780	34.6720	1641	0.7534	4.5795	3.8261	5.08 ± 0.17
3-2	18.5294	21.2982	36.0518	1529	0.7301	4.3009	3.5708	4.89 ± 0.16
4-1	18.5323	21.3015	36.0485	696	0.3334	1.9778	1.6445	4.93 ± 0.23
4-2	19.6492	22.5853	34.7647	745	0.3440	2.0971	1.7531	5.10 ± 0.23
5-1	20.1849	23.2010	34.1490	112	0.0527	0.3336	0.2808	5.33 ± 1.17
5-2	20.4970	23.5598	33.7902	115	0.0536	0.3387	0.2851	5.32 ± 1.15
6-1	20.0611	23.0587	34.2913	0	0	0	0	-
6-2	20.0760	21.4430	34.2741	0	0	0	0	-



Figure 5. Oil samples with different methanol content prepared for heating in the laboratory oven.

The volume of oil V_o in each vial was calculated by dividing its mass (M_o) by the density of the oil equal to 0.87 g/mL. In turn, the volume of the air headspace (V_a) was calculated by subtracting the volume of oil (V_o) from the volume of the vial equal to 57.35 mL. In the next step, the peak area (P_a) was determined on the basis of the chromatographic analysis performed for the air sample taken from the headspace. Then, using the relationship presented in Figure 3 and the information on the volume of air in the vial (V_a), the mass of methanol in the air (M_{ma}) was calculated using the following formula:

$$M_{ma} = \frac{0.0132 \cdot P_a + 0.0664}{1000} \cdot V_a \quad (1)$$

The initial methanol content in the oil (M_{co}) was calculated based on the methanol concentration (MC_o) in the individual oil samples (Table 3) and the mass of oil (M_o) in each of the vials (Table 4). In turn, the methanol content in oil (M_{co70}) after the heating process was calculated using the following formula:

$$M_{CO70} = M_{CO} - M_{ma} \quad (2)$$

The partition coefficient of methanol k between oil and air was calculated from the following formula:

$$k = \frac{M_{CO70}}{M_{ma}} \quad (3)$$

The arithmetic mean value of the methanol partition coefficient between oil and air, calculated based on the results of 10 measurements presented in Table 4, is 5.18. The estimated standard uncertainty $u(k)$ for the methanol partition coefficient is given in Table 4. As the methanol concentration in air decreases, the uncertainty value increases.

Figure 6 shows the relationship between the percentage of methanol concentration in the oil before heating it as a function of the methanol concentration in the air above the oil surface after heating at a temperature of 70 °C. The presented relationship is linear

and is characterized by a high correlation coefficient R^2. The results obtained show that for the tested range of methanol concentration in the oil (from 0 to 0.21%), it is possible to determine the value of the coefficient *k* that describes the proportional division of methanol between the oil and the air above its surface.

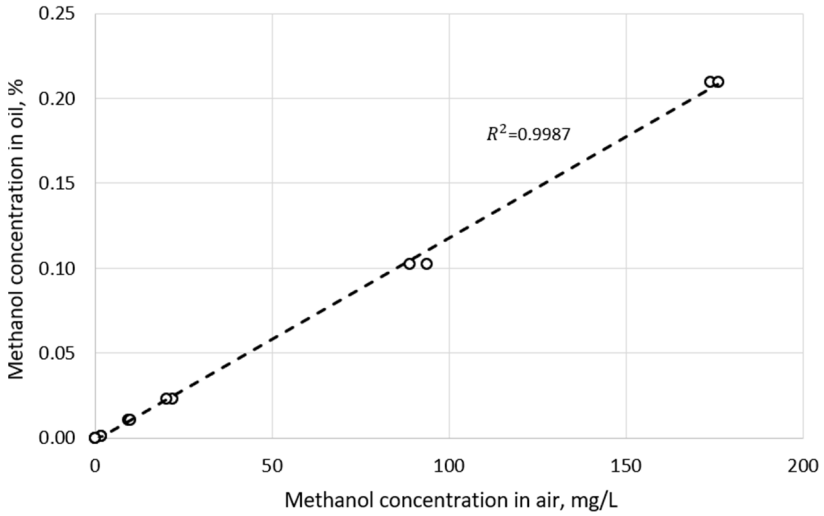


Figure 6. Methanol concentration in oil as a function of methanol concentration in air.

3.3. Methanol Equilibrium Curves of Oil–Paper Insulation

In the first stage of the study, four vials were prepared (Table 5), each containing 16 pressboard samples with dimensions of 70.50 × 14.49 × 1.04 mm (Figure 7).

Table 5. Data used to calculate the methanol content in the prepared pressboard samples.

Vial No	Mass of Dry Pressboard —M_{dp}, g	Mass of Added Methanol— M_{am}, g	Peak Area —P_a, mV×s	Methanol Concentration in Air —MC_a, mg/L	Volume of 16 Pressboard Samples —V_p, cm^3	Volume of Air in Vial—V_a, mL	Mass of Methanol in Air —M_{ma}, mg	Mass of Methanol in Pressboard —M_{mp}, g	Methanol Content in Pressboard —*MCP*, %
1	17.4884	0.0681	226.7	3.0588	17.0606	27.9394	0.0855	0.0680	0.39
2	17.6400	0.2725	866.9	11.5095	17.0606	27.9394	0.3216	0.2722	1.54
3	17.6844	0.4450	1201.9	15.9315	17.0606	27.9394	0.4451	0.4446	2.51
4	17.6587	0.6175	2134.4	28.2405	17.0606	27.9394	0.7890	0.6167	3.49



Figure 7. Pressboard with various methanol content.

The pressboard samples were dried for 24 h in a vacuum chamber at a temperature of 90 ± 5 °C and a pressure of 0.13 mbar, and then, their mass (M_{dp}) was determined.

After drying, an appropriate amount of methanol M_{am} was added to the vials to obtain the assumed content in the pressboard at a level of about 0.5%, 1.5%, 2.5%, and 3.5%. The vials with pressboard and methanol were closed and conditioned at a temperature of 22 °C for 96 h. After this time, the absence of methanol at the bottom of the vials was determined. Then, using gas chromatography, the concentration of methanol in the air in the individual vials was determined. Peak areas (P_a) corresponding to the concentrations of methanol in air (MC_a) were determined, which in turn were calculated based on the relationship presented in Figure 3. Then, on the basis of the dimensions of the pressboard, the volume of 16 samples (V_p) in each vial was calculated. Using the results of these calculations and the information that the volume of the vial was 45 mL, the volume of air (V_a) in each of the vials was calculated. In the next step, on the basis of the information on the concentration of methanol in the air (MC_a) and the volume of air in the vial (V_a), the mass of methanol in the air (M_{ma}) was calculated. In turn, the mass of methanol in the pressboard (M_{mp}) was calculated by subtracting the total mass of methanol (M_{am}) added to the vials and the mass of methanol in the air (M_{ma}). On the basis of the dry pressboard mass (M_{dp}) and the mass of methanol in the pressboard (M_{mp}), the actual concentration of methanol in the prepared pressboard samples *MCP* was determined.

Then, 16 vials were prepared. In the first four vials marked 1-1, 1-2, 1-3, and 1-4 (Table 6), four pressboard samples were placed with a methanol content of 0.39%, 1.54%, 2.51%, and 3.49%, respectively. These vials were filled with oil, closed, and placed in a heating chamber, where the temperature was maintained at 30 °C. The next four sets of samples marked 2-1, 2-2, 2-3, and 2-4 were prepared similarly to those in the previous step and then placed in a chamber, where the temperature was 40 °C. In an analogous manner, vials were prepared and placed in chambers at temperatures of 50 °C and 60 °C.

Table 6. Data on pressboard samples with different methanol content conditioned in oil at different temperatures.

Vial No	Mass of Pressboard—M_p, g	Mass of Oil —M_o, g	Methanol Content in Pressboard —*MCP*, %	Temperature of Sample Conditioning —*T*, °C
1-1	4.4744	31.7928	0.39	30
1-2	4.4503	31.6355	1.54	30
1-3	4.6912	32.1936	2.51	30
1-4	4.6584	31.4254	3.49	30
2-1	4.3724	31.3755	0.39	40
2-2	4.5078	30.8854	1.54	40
2-3	4.3864	31.6534	2.51	40
2-4	4.4789	31.1162	3.49	40
3-1	4.3607	31.9044	0.39	50
3-2	4.5048	31.5168	1.54	50
3-3	4.5140	31.4910	2.51	50
3-4	4.4985	31.4082	3.49	50
4-1	4.3579	31.7437	0.39	60
4-2	4.4550	31.7654	1.54	60
4-3	4.5429	31.4071	2.51	60
4-4	4.6458	30.8232	3.49	60

The conditioning time was assumed to be much longer than that indicated in the literature, necessary to establish the equilibrium state. The research results presented in [31] indicate that the time required to establish the equilibrium state of methanol between oil and paper for temperatures ranging from 40 °C to 80 °C does not exceed 25 h. For three temperature values of 40, 60, and 80 °C, no significant differences were observed in the time of reaching the equilibrium state. On the other hand, the research results presented in [32] indicate a significant effect of temperature on the dynamics of water migration from oil to cellulose material. For a temperature of 20 °C, the time needed to reach the equilibrium of methanol in the oil–paper system was approximately 70 h, while for a temperature of 60 °C, this time was much shorter and amounted to only 7 h. Taking into account these

research results, all prepared vials were conditioned in four heating chambers for a period of 14 days.

To carry out the next stage of the study, another 32 vials were prepared, 16 closed with crimp caps and 16 closed with screw caps. Oil from the vial marked with no. 1-1 (Table 6) was poured into a vial marked with no. 1-1a closed with a crimp cap and vial marked with no. 1-1b closed with a screw cap (Table 7).

Table 7. Data necessary to determine the methanol concentration in oil after the conditioning process.

Vial No	Mass of Oil —M_o, g	Volume of Oil —V_o, mL	Volume of Air —V_a, mL	Peak Area —P_a, mV×s	Methanol Concentration in Air —MC_a, mg/L	Methanol Concentration in Oil —MC_o, mg/L
1-1a	20.4872	23.5485	37.8015	124.2	1.7058	11.57
1-1b	9.2327	10.6123	38.3877	83.4	1.1673	10.27
1-2a	20.0847	23.0859	38.2641	802.4	10.6581	72.87
1-2b	9.2844	10.6717	38.3283	655.7	8.7216	76.50
1-3a	20.0532	23.0497	38.3003	1540.8	20.4050	139.60
1-3b	9.7476	11.2041	37.7959	1211.2	16.0542	137.32
1-4a	20.585	23.6609	37.6891	-	-	-
1-4b	8.6451	9.9369	39.0631	1937.1	25.6361	233.57
2-1a	20.7932	23.9002	37.4498	140	1.9144	12.92
2-1b	8.7405	10.0466	38.9534	90.6	1.2623	11.43
2-2a	20.6619	23.7493	37.6007	920.9	12.2223	82.66
2-2b	8.2842	9.5221	39.4779	689.1	9.1625	85.45
2-3a	20.212	23.2322	38.1178	2118.1	28.0253	191.15
2-3b	9.3332	10.7278	38.2722	1587.5	21.0214	183.89
2-4a	20.6621	23.7495	37.6005	3958.9	52.3239	353.88
2-4b	8.2058	9.4320	39.5680	2867.5	37.9174	355.48
3-1a	20.1167	23.1226	38.2274	138	1.8880	12.90
3-1b	10.0524	11.5545	37.4455	107	1.4788	12.45
3-2a	19.3569	22.2493	39.1007	1171.6	15.5315	107.75
3-2b	10.1646	11.6834	37.3166	902.8	11.9834	100.35
3-3a	20.4174	23.4683	37.8817	2717.3	35.9348	244.15
3-3b	9.0448	10.3963	38.6037	1962.9	25.9767	231.02
3-4a	19.6043	22.5337	38.8163	-	-	-
3-4b	9.8381	11.3082	37.6918	4214.4	55.6965	474.15
4-1a	20.2923	23.3245	38.0255	146.4	1.9989	13.61
4-1b	9.1325	10.4971	38.5029	113.2	1.5606	13.81
4-2a	20.647	23.7322	37.6178	1586.7	21.0108	142.14
4-2b	8.9889	10.3321	38.6679	1211.9	16.0635	143.33
4-3a	20.1555	23.1672	38.1828	4167.8	55.0814	376.10
4-3b	8.7337	10.0387	38.9613	2924.6	38.6711	350.40
4-4a	20.1146	23.1202	38.2298	7807.5	103.1254	704.71
4-4b	8.1444	9.3614	39.6386	5450.7	72.0156	677.97

The same procedure was followed with the remaining vials. Using the mass of the empty vial and the vial with oil, the mass of oil (M_o) in the individual vials was calculated. The volume of oil (V_o) in vials was calculated by dividing the mass of oil by its density (0.87 kg/L), while the volume of air (V_a) given in Table 7 is the sum of air above the oil surface and air injected into the vial (4 mL) to create overpressure in it, which enabled taking a sample and introducing it into the gas chromatograph sample loop.

All vials were placed in a 70 °C heating chamber for at least two hours. After this time, based on the peak area P_a obtained from the chromatographic analysis, the concentration of methanol in the air (MC_a) above the oil surface in each vial was calculated using the formula in Figure 3. In turn, the methanol concentration in the oil (MC_o) was calculated from the following equation:

$$MC_o = MC_a \cdot \left(k + \frac{V_a}{V_o} \right) \quad (4)$$

The analysis of the MC_o results presented in Table 7 shows that the higher the methanol content in the pressboard, the higher the methanol concentration in the oil. The increase in temperature also contributed to the increase in methanol concentration in the oil. No effect of the type of vial closure on the obtained result was observed (a crimp cap and a screw cap), which indicates the tightness of the vessels used.

Table 8 presents the data and calculations necessary to determine the methanol content in the pressboard and to prepare the methanol equilibrium curves in the oil–paper system for different temperatures.

Table 8. Data necessary to determine the methanol content in the pressboard after the conditioning process.

Vial No.	Methanol Concentration in Oil —MC_{oav}, mg/L	Volume of Oil —V_o, L	Mass of Methanol in Oil —M_{mo}, mg	Mass of Methanol in Pressboard —M_{mp}, g	Mass of Methanol in Pressboard —M_{mpeq}, g	Mass of Dry Pressboard— M_{dp}, g	Methanol Content in Pressboard —MCP_{eq}, %
1-1	10.92	0.036543	0.40	0.0174	0.0170	4.4570	0.38
1-2	74.69	0.036362	2.27	0.0675	0.0648	4.3828	1.48
1-3	138.46	0.037004	5.12	0.1149	0.1097	4.5763	2.40
1-4	233.57	0.036121	8.44	0.1571	0.1487	4.5013	3.30
2-1	12.17	0.036063	0.44	0.0170	0.0165	4.3554	0.38
2-2	84.06	0.03550	2.98	0.0684	0.0654	4.4394	1.47
2-3	187.52	0.036383	6.82	0.1074	0.1006	4.2790	2.35
2-4	354.68	0.035765	12.69	0.1510	0.1384	4.3279	3.20
3-1	12.68	0.036671	0.46	0.0169	0.0165	4.3438	0.38
3-2	104.05	0.036226	3.77	0.0683	0.0646	4.4365	1.46
3-3	237.58	0.036196	8.60	0.1105	0.1019	4.4035	2.31
3-4	474.15	0.036101	17.12	0.1517	0.1346	4.3468	3.10
4-1	13.71	0.036487	0.50	0.0169	0.0164	4.3410	0.38
4-2	142.73	0.036511	5.21	0.0676	0.0624	4.3874	1.42
4-3	363.25	0.036100	13.11	0.1112	0.0981	4.4317	2.21
4-4	691.34	0.035428	24.49	0.1567	0.1322	4.4891	2.94

The average value of the methanol concentration in the oil (MC_{oav}) was calculated on the basis of the MC_o concentration values presented in Table 7. The oil volume (V_o) was calculated based on the oil mass (M_o) (Table 6) and the oil density of 0.87 kg/L. The methanol mass in the oil (M_{mo}) was calculated from the oil volume (V_o) and the average methanol concentration in the oil (MC_{oav}). The methanol mass in the pressboard (M_{mp}) before the conditioning process was calculated from the following formula:

$$M_{mp} = \frac{MCP \cdot M_p}{100 + MCP} \quad (5)$$

The methanol content in the pressboard MCP and the mass of the pressboard (M_p) were taken from Table 6. In turn, the mass of methanol in the pressboard after the conditioning process (M_{mpeq}) was calculated from the difference in the mass of methanol in the pressboard before conditioning (M_{mp}) and the mass of methanol that passed from the pressboard to the oil (M_{mo}) during the conditioning of the samples. Then, subtracting the mass of methanol in the oil (M_{mo}) from the mass of the pressboard (M_p) (Table 6), the mass of the dry pressboard without methanol (M_{dp}) was calculated. The percentage content of methanol in the pressboard after the conditioning process ($MCPeq$) was calculated from the following formula:

$$MCP_{eq} = \frac{M_{ppeq}}{M_{dp}} \cdot 100 \quad (6)$$

Based on the data presented in Tables 7 and 8, the equilibrium curves of methanol in the oil–paper system were developed for four temperature values (Figure 8). Furthermore, Figure 8 shows the scatter of results in relation to the lowest (k = 4.89) and highest (k = 5.42) methanol partition coefficient (Table 4).

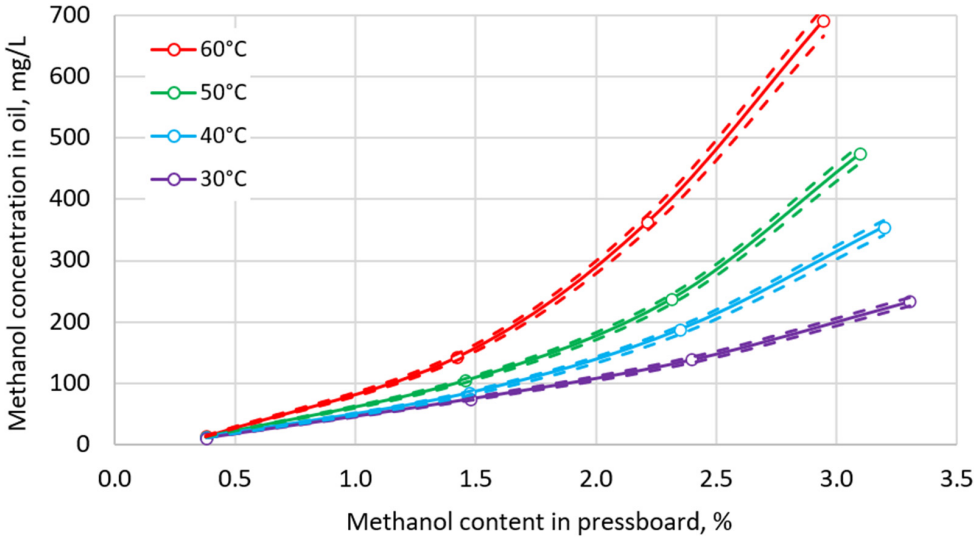


Figure 8. Methanol equilibrium curves of oil–paper insulation–methanol concentration in mineral oil depending on the methanol content in the pressboard for different insulation temperature values equal to 30 °C, 40 °C, 50 °C, and 60 °C; the scatter of results in relation to the lowest (k = 4.89) and highest (k = 5.42) methanol partition coefficient is marked with dashed lines.

4. Discussion

The analysis of the equilibrium curves presented in Figure 8 shows that the increase in the methanol content in the pressboard is accompanied by an increase in the methanol concentration in the mineral oil. It should be noted that most of the methanol in the insulating system is accumulated in the cellulose material. For the experimental conditions, the weight ratio of mineral oil to paper was approximately 7.15, which is a typical value for distribution transformers. For example, at equilibrium, for a methanol content in the pressboard of 2.4% and a temperature of 30 °C, the pressboard contains 95.5% of methanol in total in the insulating system. This indicates a low solubility of methanol in mineral oil in relation to the very high affinity of methanol for cellulose molecules, which are connected with them by hydrogen bonds [15]. These observations are consistent with the results of the studies presented in [33] despite significant differences in the experimental conditions. The authors of [33] have shown that at room temperature, an oil–paper system with mineral oil (20:1 oil-to-paper ratio) could have 90% of the methanol accumulated in the paper.

Based on the research results presented in Figure 8, the dependence of the methanol content in oil was developed as a function of temperature for different values of the methanol content in the pressboard (Figure 9). The presented dependencies are of an exponential nature. With increasing temperature, a significant increase in the methanol content in oil is observed for the same value of the methanol content in the pressboard. Like other polar compounds, methanol migrate from paper into oil with increasing temperature [34–36].

It should be emphasized that the methanol equilibrium curves in the oil–paper insulating system can be influenced by a number of factors, similarly to the moisture equilibrium curves [37,38]. One of these factors is the type of liquid, as demonstrated by the authors of [33]. For example, synthetic ester is characterized by a much greater capacity to bond methanol than mineral oil. Another factor is the degree of liquid aging, most often described by the acid number and corresponding to the polar products of insulation decomposition. This is confirmed by the results of the research presented in [36], in which it was shown that more methanol can migrate from the cellulose insulation to the aged oil than to the new. Moreover, with the progressive aging of cellulose, the ability of this material to store methanol will probably decrease. A similar effect is observed in the case of water [39]. The reason for this is the smaller number of hydroxyl groups capable of attaching polar

molecules, such as water or methanol. The authors of [40] also observed different methanol partitioning depending on the type of standard or thermally upgraded Kraft paper.

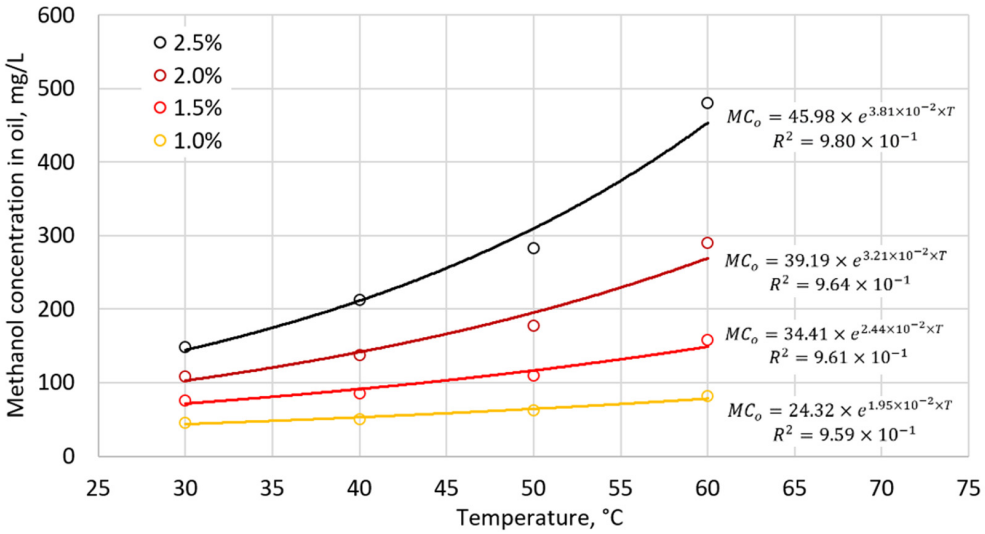


Figure 9. The methanol concentration in oil as a function of insulation temperature for different methanol content in pressboard.

The equilibrium curves of methanol presented in Figure 7 refer to the temperature range of 30 °C to 60 °C. This is the insulation temperature range most often found in power transformers; however, in the situation of transformer operation at a rated load and high ambient temperature, it is likely that the insulation will reach significantly higher temperature values. Therefore, it should be expected that due to the increase in methanol solubility in oil with increasing temperature, its content in liquid insulation may reach significantly higher levels than those indicated in Figure 8. This must be taken into account when studying the effect of the methanol content in oil on its physicochemical and dielectric parameters. To estimate the methanol content in oil at higher temperatures, the equations provided in Figure 9 can be used.

5. Conclusions

The studies carried out confirmed the possibility of the migration of methanol from cellulose insulation to mineral oil. The factor increasing the share of methanol in mineral oil is the increase in temperature. For the adopted experimental conditions, it was found that about 95% of the methanol present in the insulation system is in the cellulose material.

The main objective of the conducted research was to develop methanol equilibrium curves in the oil–paper system. This is an original achievement that allows the analysis of the methanol distribution between mineral oil and cellulose insulation. Thanks to the curves developed, it is possible to estimate the changes in the content of both materials as a result of changes in the insulation temperature. Their application allows us to determine the methanol concentration in oil depending on the methanol content remaining in the cellulose materials after their drying process using methanol vapors. This opens the possibility of checking the effect of methanol concentration in oil and methanol content in pressboard on the properties of these materials, which will be the direction of further research related to the possibility of using methanol vapors to dry the transformer insulation system at the stage of its production.

The gas chromatograph configuration presented in the paper can also be used to assess the methanol content in oil for the purpose of estimating the degree of the aging of cellulose insulation. It is necessary to use the head-space technique, which allows for the separation of methanol between the liquid phase (mineral oil) and the gas phase (air). As part of the

conducted research, the partition coefficient of methanol between mineral oil and air was determined, which for a temperature of 70 °C is equal to 5.18.

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References

1. Arsad, S.R.; Ker, P.J.; Jamaludin, M.Z.; Choong, P.Y.; Lee, H.J.; Thiviyanathan, V.A.; Yang Ghazali, Y.Z. Water Content in Transformer Insulation System: A Review on the Detection and Quantification Methods. *Energies* **2023**, *16*, 1920. [CrossRef]
2. Emsley, A.M.; Heywood, R.J.; Ali, M.; Xiao, X. Degradation of cellulosic insulation in power transformers. Part 4: Effects of aging on the tensile strength of paper. *IEE Proc.-Sci. Meas. Technol.* **2000**, *147*, 285–290. [CrossRef]
3. Fofana, I.; Borsi, H.; Gockenbach, G.; Farzaneh, M. *Ageing of Cellulose in Mineral-Oil Insulated Transformers*; Cigré Technical Brochure 323; International Council on Large Electric Systems (CIGRE): Paris, France, 2007.
4. Jiang, J.P.; Du, B.X.; Cavallini, A. Effect of moisture migration on surface discharge on oil-pressboard of power transformers under cooling. *IEEE Trans. Dielectr. Electr. Insul.* **2020**, *27*, 1743–1751. [CrossRef]
5. Sikorski, W.; Walczak, K.; Przybylek, P. Moisture Migration in an Oil-Paper Insulation System in Relation to Online Partial Discharge Monitoring of Power Transformers. *Energies* **2016**, *9*, 1082. [CrossRef]
6. Gmati, G.; Rao, U.M.; Fofana, I.; Picher, P.; Arroyo-Fernàndez, O.; Rebaine, D. Bubbling Phenomena in Liquid-Filled Transformers: Background and Assessment. *Energies* **2023**, *16*, 3829. [CrossRef]
7. Ariannik, M.; Rezaei-Zare, A.; Kuhnke, M.; Werle, P. A Comparison Between Bubble Formation on Kraft and Thermally Upgraded Papers in Synthetic Ester. *IEEE Trans. Dielectr. Electr. Insul.* **2023**, *30*, 1566–1572. [CrossRef]
8. Yang, C.; Zhao, T.; Liu, Y.; Zhu, W.; Gu, Z. Prediction Model of Bubble Formation in Oil-Paper Insulation Based on the ITBE Envelope. *IEEE Trans. Dielectr. Electr. Insul.* **2022**, *29*, 1735–1744. [CrossRef]
9. Betie, A.; Meghnefi, F.; Fofana, I.; Yeo, Z. Modeling the Insulation Paper Drying Process from Thermogravimetric Analyses. *Energies* **2018**, *11*, 517. [CrossRef]
10. Oommen, T.V.; Prevost, T.A. Cellulose insulation in oil-filled power transformers: Part II maintaining insulation integrity and life. *IEEE Electr. Insul. Mag.* **2006**, *22*, 5–14. [CrossRef]
11. Cybulski, M.; Przybyłek, P. The application of a molecular sieve for drying the insulation system of a power transformer in terms of improving its perational reliability. *Eksploat. i Niezawodn.–Maint. Reliab.* **2022**, *24*, 502–509. [CrossRef]
12. Rindlisbacher, G.; von Ah, M. Cut and Dry: Low Frequency Drying Process in Transformer Production Can Cut Energy Costs in Half. ABB Review 2005. Available online: https://library.e.abb.com/public/22f229958625da3ec125707b004c4466/66-69%203M557_ENG72dpi.pdf (accessed on 8 September 2024).
13. Koestinger, P.; Aronsen, E.; Boss, P.; Rindlisbacher, G. *Practical Experience with the Drying of Power Transformers in the Field, Applying the LFH Technology*; Reference: A2-205_2004; International Council on Large Electric Systems (CIGRE): Paris, France, 2004.
14. Lundgaard, L.E.; Hansen, W.; Linhjell, D.; Painter, T.J. Ageing of Oil-impregnated Paper in Power Transformers. *IEEE Trans. Power Del.* **2004**, *19*, 230–239. [CrossRef]
15. Przybylek, P.; Gielniak, J. The Use of Methanol Vapour for Effective Drying of Cellulose Insulation. *Energies* **2023**, *16*, 4465. [CrossRef]
16. Jalbert, J.; Gilbert, R.; Tétreault, P.; Morin, B.; Lessard-Déziel, D. Identification of a chemical indicator of the rupture of 1,4-β-glycosidic bonds of cellulose in an oil-impregnated insulating paper system. *Cellulose* **2007**, *14*, 295–309. [CrossRef]
17. Lundgaard, L.E.; Lesaint, C.; Martins, M.A.; Bauchemin, C.; Martin, R.; Pagger, E.; Prevost, T.; Jalbert, J.; Lessard, M.C.; Meltzer, L.; et al. *Ageing of Liquid Impregnated Cellulose for Power Transformers*; Cigré Technical Brochure 738; International Council on Large Electric Systems (CIGRE): Paris, France, 2018; Available online: https://www.e-cigre.org/publications/detail/738-ageing-of-liquid-impregnated-cellulose-for-power-transformers.html (accessed on 22 September 2024).
18. Yoshida, H.; Ishioka, Y.; Suzuki, T.; Yanari, T.; Teranishi, T. Degradation of Insulating Materials of Transformers. *IEEE Trans. Dielectr. Electr. Insul.* EI-22, 795–800. [CrossRef]
19. Emsley, A.M. The kinetics and mechanism of degradation of cellulosic insulation in power transformers. *Polym. Degrad. Stab.* **1994**, *44*, 343–349. [CrossRef]
20. Behjat, V.; Emadifar, R.; Pourhossein, M.; Rao, U.M.; Fofana, I.; Najjar, R. Improved Monitoring and Diagnosis of Transformer Solid Insulation Using Pertinent Chemical Indicators. *Energies* **2021**, *14*, 3977. [CrossRef]
21. Ortiz, F.; Fernandez, F.O.; Santisteban, A.; Delgado, F.; Ortiz, A. Estimating the age of power transformers using the concentration of furans in dielectric oil. *Renew. Energy Power Qual. J.* **2016**, *1*, 1011–1015. [CrossRef]
22. Rodriguez-Celis, E.M.; Duchesne, S.; Jalbert, J.; Ryadi, M. Understanding ethanol versus methanol formation from insulating paper in power transformers. *Cellulose* **2015**, *22*, 3225–3236. [CrossRef]

23. Chen, Q.; Sun, W.; Cheng, S.; Huang, G. A review on a novel method for aging evaluation of transformer insulating paper based on methanol. *IET Gener. Transm. Dis.* **2023**, *17*, 1955–1971. [CrossRef]
24. *IEC TR 63025*; Insulating Liquids—Quantitative Determination of Methanol and Ethanol in Insulating Liquids. International Electrotechnical Commission (IEC): Geneva, Switzerland, 2021.
25. Bare, C.E.; Merritt, S.Y. Methanol as an Ageing Marker for In Service Transformers. *IEEE Trans. Ind. Appl.* **2018**, *54*, 6598–6602. [CrossRef]
26. Jalbert, J.; Lessard, M.C. Cellulose chemical markers relationship with insulating paper post-mortem investigations. *IEEE Trans. Dielectr. Electr. Insul.* **2015**, *22*, 3550–3554. [CrossRef]
27. Aciu, A.-M.; Nițu, M.-C.; Nicola, C.-I.; Nicola, M. Determining the Remaining Functional Life of Power Transformers Using Multiple Methods of Diagnosing the Operating Condition Based on SVM Classification Algorithms. *Machines* **2024**, *12*, 37. [CrossRef]
28. Fu, Q.; Peng, L.; Li, L.; Lin, M.; Zhao, Y.; Li, S. Detection of Methanol in Power Transformer Oil Using Spectroscopy. *J. Electr. Eng. Technol.* **2019**, *14*, 861–867. [CrossRef]
29. Wang, J.; Zhou, Y.; Liu, J.; Wang, Z.; Bai, S.; Lu, J. A New Method for the Aging Evaluation of Oil-Paper Insulation Using n-Butanol and Methanol. *CSEE J. Power Energy Syst.* **2024**, *10*, 717–726. [CrossRef]
30. Mihajlovic, D.; Ivancevic, V.; Vasovic, V.; Lukic, J. Cellulose Degradation and Transformer Fault Detection by the Application of Integrated Analyses of Gases and Low Molecular Weight Alcohols Dissolved in Mineral Oil. *Energies* **2022**, *15*, 5669. [CrossRef]
31. Jalbert, J.; Gilbert, R.; Denos, Y.; Gervais, P. Methanol: A Novel Approach to Power Transformer Asset Management. *IEEE Trans. Power Deliv.* **2012**, *27*, 514–520. [CrossRef]
32. Zheng, H.; Shi, K.; Yang, T.; Li, Y.; Zhang, E.; Zhang, C.; Shao, G.; Shi, Z.; Zhang, C. Investigation on the equilibrium distribution of methanol in transformer oil-immersed cellulosic insulation. *Cellulose* **2021**, *28*, 1703–1714. [CrossRef]
33. Matharage, S.Y.; Liu, Q.; Wang, Z.D.; Wilson, G.; Krause, C. Aging assessment of synthetic ester impregnated thermally non-upgraded kraft paper through chemical markers in oil. *IEEE Trans. Dielectr. Electr. Insul.* **2018**, *25*, 507–515. [CrossRef]
34. Jalbert, J.; Lessard, M.; Ryadi, M. Cellulose chemical markers in transformer oil insulation Part 1: Temperature correction factors. *IEEE Trans. Dielectr. Electr. Insul.* **2013**, *20*, 2287–2291. [CrossRef]
35. Liland, K.B.; Linhjell, D.; Lesaint, C.; Ese, M.G.; Lundgaard, L.E.; Mavrommatis, P.; Stjepanovic, N. Comparison between synthetic ester and mineral oil impregnated transformer paper aging markers. In Proceedings of the IEEE International Conference on Dielectric Liquids, Manchester, UK, 25–29 June 2017.
36. Jalbert, J.; Hernandez, L.; Coulibaly, M.L.; Lessard, L.; Lesaint, C.; Lukic, J.; Melzer, L.; Maina, R.; Wang, Z.; Martins, M.A.; et al. *Field Experience with Transformer Solid Insulation Ageing Markers*; Cigré Technical Brochure 779; International Council on Large Electric Systems (CIGRE): Paris, France, 2019; Available online: https://www.e-cigre.org/publications/detail/779-field-experience-with-transformer-solid-insulation-ageing-markers.html (accessed on 22 September 2024).
37. Przybylek, P. Water Saturation Limit of Insulating Liquids and Hygroscopicity of Cellulose in Aspect of Moisture Determination in Oil-paper Insulation. *IEEE Trans. Dielectr. Electr. Insul.* **2016**, *23*, 1886–1893. [CrossRef]
38. Liao, R.; Lin, Y.; Guo, P.; Liu, H.; Xia, H. Thermal aging effects on the moisture equilibrium curves of mineral and mixed oil-paper insulation systems. *IEEE Trans. Dielectr. Electr. Insul.* **2015**, *22*, 842–850. [CrossRef]
39. Przybylek, P. The influence of temperature and aging of cellulose on water distribution in oil-paper insulation. *IEEE Trans. Dielectr. Electr. Insul.* **2013**, *20*, 552–556. [CrossRef]
40. Jalbert, J.; Rodriguez-Celis, E.M.; Arroyo-Fernández, O.H.; Duchesne, S.; Morin, B. Methanol Marker for the Detection of Insulating Paper Degradation in Transformer Insulating Oil. *Energies* **2019**, *12*, 3969. [CrossRef]

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