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Aging Study of Transformer Oil-Impregnated Repulped and Standard Cellulose by Measuring of 2-furfural Content of the Oil

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Abstract

In order to evaluate the reliability of using repulped cellulose in transformers, the aging process was applied on standard and repulped cellulose in a laboratory accelerated model by increasing of temperature to 150 ° C and their behavior was monitored by measuring the amount of 2-furfural released in oil by HPLC (High Performance Liquid Chromatography) in the consecutive aging periods and the results was compared. The results were fitted to estimate the aging behaviors according to the content of 2 - furfural that released in oil. The obtained results showed that behavior of two types of cellulose is almost the same. Therefore, it can be concluded that the moulded insulating parts made of repulped cellulose can be used in the insulation system of power transformers with a good and acceptable reliability.

Keywords: *Power transformers' formed insulating part, Repulped cellulose, Oil impregnated cellulose, Accelerated pyrolysis, 2 – furfural.*

Introduction

Transformers are one of the most important but also expensive components of any power system utility [1].Research experience shows that High rating power transformers can have service lives in excess of 50 years. For

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the user, the concern is to be able to identify the onset of unreliability as the end of life approaches [2]. In India approximately 30% of power transformers are more than 25 years old. So, primary attention should be directed to research into improved diagnostic techniques for determining the condition of insulation in aged power transformers [3]. There are a variety of electrical, chemical and physical conditions monitoring and diagnostic techniques which can be applied. The basic method is a regular analysis of an oil sample to detect the transformer condition [2]. Mostly, Bulk oil equipments are using impregnated paper as the solid insulation between their windings and conducting parts. Insulation grade paper is made by the delignification of wood pulp by the Kraft process. It contains about 90% cellulose, 6-7% lignin and the balance is hemicelluloses. The natural humidity of paper is 4-5% by weight and the insulation is dried after winding to less than 0.5%. [4]. Mineral oil impregnated paper (OIP) is the insulation which is used in transformers and more often this system deteriorates rapidly at accelerated electrical and thermal stresses occurring single and in combination of both [5].

Aging study of power transformers' oil/cellulose insulation system is usually based on two parameters that include the change in the cellulose properties and the analysis of the aging products. Changes in the cellulose properties that mainly deal with the degree of polymerization which generally correlates with the tensile strength has been wide ly used as a basic yardstick. However, it is problematic to measure directly the average DP of insulation paper in a transformer in the operating state, a method has been put forward whereby the insulator's degradation is inferred indirectly from the amounts of degradation products generated during degradation of the paper. The effects of temperature, water, and oxygen are significant factors in the aging of the paper insulation (cellulose) and oil. One of the degradation and deterioration products of oil impregnated cellulosic materials during its pyrolysis, is furfural (Furaldehyd) and its related compounds that is an indicator for aging evaluation of oil/cellulose insulating system (Figure 1). Furanic compounds as the most important products of the pyrolysis of cellulose include the following five major compounds. The chemical structure of these compounds is shown in Figure 2.

1) 5-hydroxy methyl-2-furfural (5HMF)
2) 2-Furfuryl alcohol (2FOL)
3) 2-furfural (2FAL)
4) 2-acetyl-furan (2ACF)
5) 5-methyl-2–furfural (5MEF)

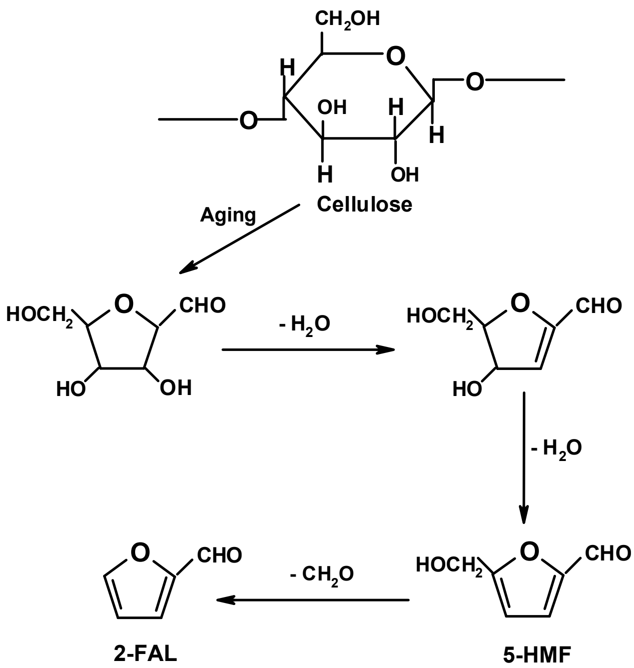

Figure 1. 2-FAL production mechanism of cellulose.

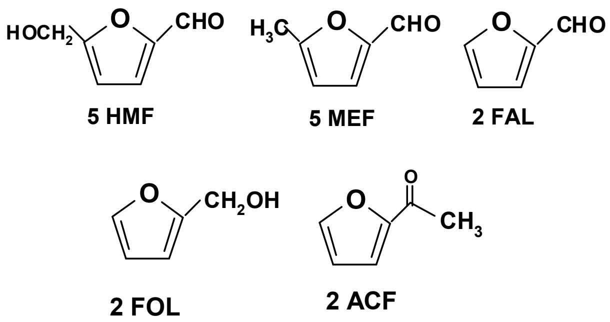

Figure 2. Chemical structure of the furanic compounds.

The present study compares the accelerated pyrolysis behavior of two types of oil impregnated standard and repulped celluloses, based on the aging products. Since 2-furfural has more thermal stability in comparison with other furanic compounds during the aging process [6], so in this research, 2-furfural is selected as the aging product of oil/cellulose insulating system, and its dissolved amount in oil is measured in the consecutive aging periods by HPLC method. The results of this study are very important for the comparison of the aging behavior of two types of cellulose and evaluating the reliability of using repulped cellulose in the manufacturing of power transformers' insulating parts which is made by hand moulding method. To our knowledge, there is so far no report on the extraction and measurement of the 2 - furfural dissolved in oil from oil/cellulose insulation system that its cellulose is repulped.

Experimental

Materials and equipments

Acetonitrile and 2-furfural (HPLC grade) were from Merck and used as received. Standard pressboard samples were prepared from Weidmann production pressboard sheet, type B.4.1 and repulped cellulose samples were prepared from repulping the Waste of the same type of sheet. In order to analysis of the extracted furanic compounds, a HPLC made by Waters Co. equipped with a C18 column and a UV detector has been used. Acetonitrile 30% (v/v) has been used as mobile phase with 1 ml/min flow rate.

Preparation of samples for accelerated pyrolysis

The test specimens of repulped cellulose and standard cellulose, based on the required number of measurements and the corresponding time periods, after drying and impregnation with oil are being placed in special containers and exposed to heat inside the oven. In order to apply the accelerated aging process the temperature of the oven was determined as follows based on the previous researches [7-9]. Oil impregnated cellulose during the life time of transformer is subject to electrical stress and the temperature of maximum 90 º C, and it can stand these conditions up to forty years. The effect of the electrical stresses also affects it in the form of thermal stress during its life time. Since an experimental model for the study of aging behavior needs to use shorter time intervals in practice, higher temperatures can be applied to accelerate the aging process in a laboratory model. Reviewing performed researches in this area, in this research the continuous and constant temperature of 150 ° C is determined for performing the accelerated aging mechanism based on the following calculations. Arrhenius model is an exponential model that based on it an increase of 7 to 10 °C causes a doubling of the rate of pyrolysis. According to the following equation referenced to IEC 60076-7; 2005- in the temperatures of over than 100 ° C, each 6°C increase in temperature causes the rate of pyrolysis of oil impregnated cellulose to double.

$$V = 2^{\frac{\theta - 98}{6}}$$

According to this equation, pyrolysis at 150 ºC increases the rate of aging with a factor of 28.6. If the life time of oil impregnated cellulose at 100 ° C is supposed about 40 years, increasing the pyrolysis temperature to 150 ºC will reduce its life to about 36 days. Thus, assuming two measurements in the first week and one measurement for the next weeks, we will totally have 6 measurement results for each cellulose sample. Before conditioning the test specimens and impregnating the cellulose with oil, the DP value of both repulped and standard cellulose was measured. Generally, each DP measurement result for cellulose is obtained from performing two tests on two separate samples. The oil used in this laboratory modeling is the transformer new mineral oil according to IEC 60296 [10] NYNAS production. Due to the volume of used containers (24 containers of 250 ml) and assuming a weight ratio of about 11.5% according to IEC 60763-2 [11], the weight of cellulose needed for each container was determined 30 g. The standard and repulped cellulose specimens were weighed and grouped. Each group separately were placed inside the special drying vessel to be conditioned according to IEC 60641-2 method [12] as described in the following:

The test specimens inside this container spent the drying process for 24 hours at 105 ºC and less than 1 mbar vacuum pressures in the vacuum oven. After the drying period is completed, the impregnation process of specimens with the preheated oil (90 ° C) is carried out while the pressure of the oven controlled to not exceed 2.5 mbar for at least two hours. Then the specimens as well as the impregnation oil were removed from the vacuum oven and transferred to the 250 ml glass bottles. The bottles containing the impregnated cellulose fulfilled with oil were marked with numbers to be recognizable and were located in a natural circulated oven at 150 ° C to spend the accelerated pyrolysis. The samples were removed from the oven after determined aging periods to measure 2-furfural content released and solved in the oil.

Extracting and Measuring Furanic compounds from oil

The liquid-liquid method was used to extract the furanic compounds from oil. About 20 ml of the aged oil sample was removed from the oven according to the determined time schedule and was weighed with the accuracy of 0.1 mg. It was poured inside a 25 ml volumetric flask and then 5 ml acetonitrile was added. The flask was shaken for 2 minutes to dissolve the furans of the oil in the acetonitrile. Then the samples were left in order to the solvent and the oil layers completely separated. The content of 2-furfural as the indicator of furanic compounds caused by the pyrolysis of cellulose has been measured by HPLC equipped with a C18 column and UV de tector according to IEC 61198[13]. According to the standard for detecting 2-furfural, the wavelength of the UV detector was set in 274 nm. After doing the adjustments and when the chromatograph reached to equilibrium, the extracted samples were injected into the HPLC using a 100 ml syringe. Figure 3 shows the representative chromatograms after 9 minutes.

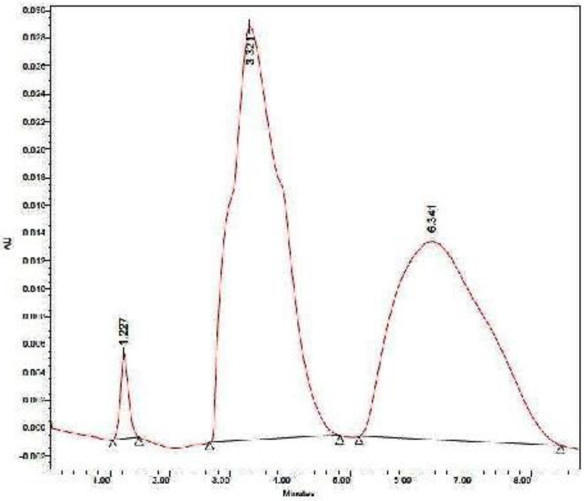

Figure 3. One of the chromatograms resulted from analyzing of furanic compounds extracted from the oil.

Calibration

To realize the peak of 2-furfural in the resulted chromatograms, firstly a pure sample of 2-furfural is needed to inject and detected by the HPLC as the reference material. For this purpose, 862 µl of 2-furfural (HPLC grade) was dissolved in 100 ml distilled water to obtain a solution with a concentration of 10 ppm. The dilute solutions with determined concentrations were obtained from primary solution (10 ppm). Relationship between peak height and different five concentrations of the chromatograms was shown in Table 1.

Table 1. The peak height of the calibration chromatograms versus the concentration of the injected reference 2-furfural.

Concentration (ppm)	0.625	1.25	2.5	5	10
Peak height	24722	74683	140382	310697	631696

According to the retention time of the peaks, which has been about 6 minute in these tests, the peak of 2-furfural will be able to realize in the chromatograms. Figure 4 represents the calibration curve of the reference 2-furfural. By using of this graph, the concentration of 2-furfural can be calculated from the corresponding peak height in a chromatogram obtained from analyzing an unknown sample by HPLC.

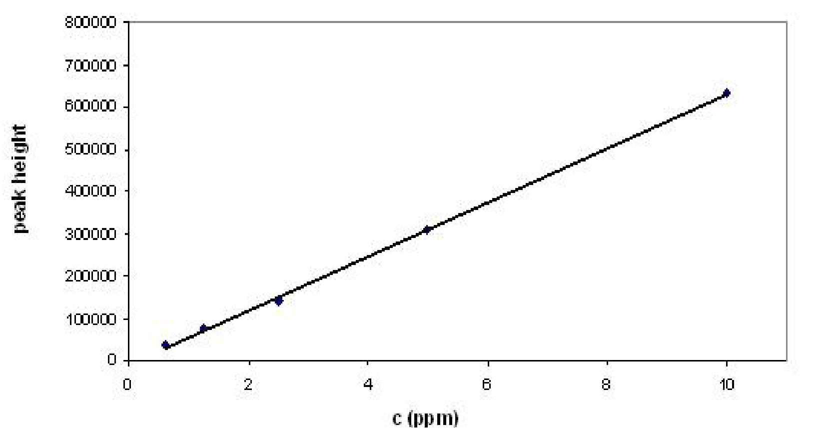

Figure 4. Calibration curve of reference 2-furfural.

Results and discussion

The measured content of 2- furfural released in the oil of the impregnated cellulose samples after successive pyrolysis periods is reported in table 2 for both types of standard and repulped cellulose. In the first week of pyrolysis, the content of 2-furfural has been reached to its maximum value for both types of cellulose. This maximum value is 1273 ppb for the standard cellulose and 866 ppb for repulped cellulose. Table 2 shows that the amount of 2-furfural for both types of cellulose in later periods, gradually decreases during the pyrolysis. The manner of this decrease is the same for both types of cellulose and the graphs converge (Figure 5). The maximum amount of 2-furfural for standard cellulose is 407 ppb more than that for the repulped cellulose. This indicates that in the degree of polymerizations (DP) of more than 1000, degradation of cellulose is more violent for the higher DPs. For more studies in this regard these two references can be useful.

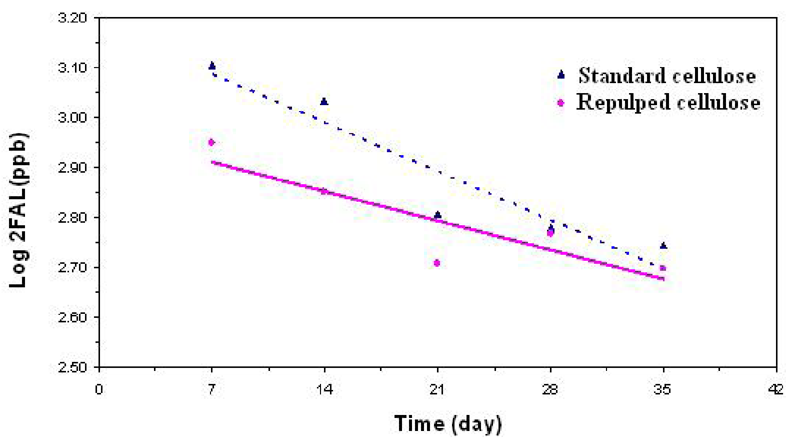

Figure 5. Comparative graphs of 2-furfural versus time for standard and repulped celluloses.

Table 2. 2- furfural results of the oil impregnated cellulose samples after successive pyrolysis periods for both types of standard and repulped celluloses.

Pyrolysis duration(day)	2FAL released in the oil of repulped cellulose (ppb)		2FAL released in the oil of standard cellulose (ppb)	
	each result	Average of two results	each result	Average of two results
3.5	453	411	506	590
	369		673	
7	816	866	1317	1273
	916		1228	
14	616	708	1106	1075
	799		1043	
21	503	510	683	640
	517		596	
28	553	584	669	600
	614		530	
35	530	497	595	555
	463		514	

In the researches performed in the laboratory of SEIMENS in 2002, a determined concentration of 2-Fufural dissolve in oil and maintained in the temperatures of 60 ° C and 90 ° C in air for 18 weeks. Measuring the content of furanic compounds in the successive periods showed that 2-furfural had been converted to the other furanic compounds and mainly to the "5-Hydroxymethyl 2-furfural"[14]. The curve of the 2-furfural decrease is shown in Figure 6 for 60 ° C and in Figure 7 for 90 ° C.

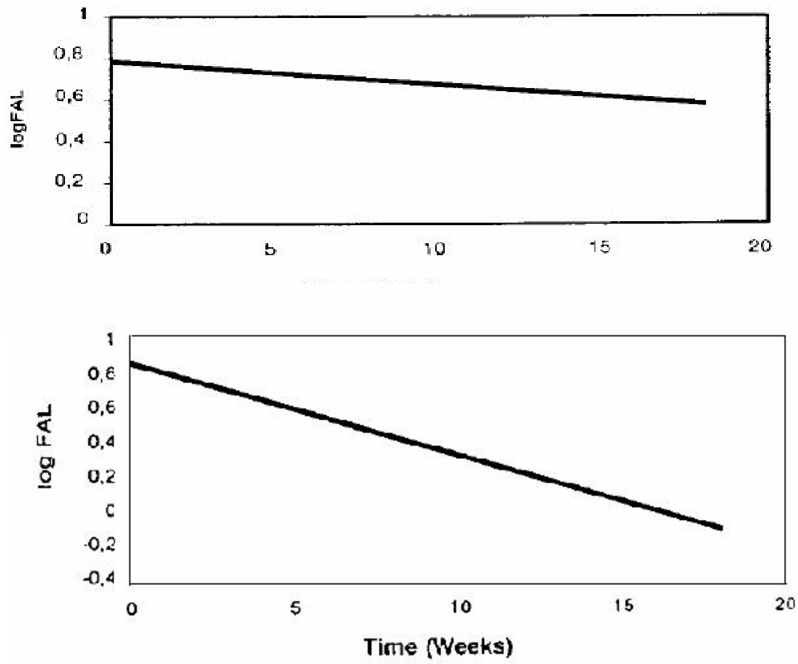

Figure 7. Reduction of 2-furfural content due to thermal decomposition in 90ºC.

The slope of these curves indicates that in higher temperatures the thermal decomposition of 2-furfural is more intense and becomes unstable in the oil. By increasing the temperature to 150 º C in the present study, the rate of thermal degradation of 2 - furfural has been more increased. In some research some equations has been introduced to describe the aging behavior of cellulose in term of degree of polymerization and the 2-furfural content [15-17]. But due to the results of the SEIMENS laboratory's research that represents the thermal decomposition behavior of 2-furfural at 60ºC and 90ºC, indicates this fact that predicting the life time of cellulose based on only the content of furanic compounds without direct measuring the degree of polymerization is not possible and the present study confirms this report. This is certain that the real life time of cellulose can be determined based on direct measurement of the degree of polymerization and calculating the degree of polymerization based on the amount of furanic compounds or 2-furfural released in oil and then predicting the remaining life time of cellulose based on this calculation especially in the condition of unstable temperature will not give correct results. It may seems that measuring the amount of all 2-furfural dependent furanic compounds is a solution in such a situation, but the thermal instability of these compounds and their conversion to aldehydes and acids and especially at the end to unknown compounds makes it complex and impractical to predict the life time of cellulose.

Conclusion

In this research the aging behavior of two types of standard and repulped cellulose was studied based on the content of 2-furfural released in oil at 150 ° C for five weeks. The obtained results showed that the aging behavior of two types of cellulose is the same according to the contents of released 2-fufural in oil during the accelerated pyrolysis. So the moulded insulating parts made of repulped cellulose can be used in the insulation system of power transformers with a good and acceptable reliability.

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