

**STUDY OF LOW MOLECULAR WEIGHT CHEMICALS AS
PAPER AGEING INDICATORS IN TRANSFORMER LIQUID
AND PAPER INSULATION SYSTEM**

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LIST OF ABBREVIATIONS

AC	Alternating Current
2-FAL	2-Furfuraldehyde
5-HMF	Hydroxymethylfurfural
ASTM	American Society for Testing and Materials
CI	Chemical Ionisation
CO ₂	Carbon Dioxide
DBPC	Butylhydroxytoluene
DET	Dynamic Equivalence Point
DGA	Dissolved Gas Analysis
DNO	Distribution Network Operator
DP	Degree of Polymerisation
DPB	Dibutyl Phthalate
EI	Electron Ionisation
EP	Equivalence Point
EU	European Union
EV	Electric Vehicle
FA	Furan Analysis
FID	Flame Ionization Detector
GCMS	Gas Chromatography Mass Spectrometry
HCl	Hydrochloric Acid
HI	Health Index
HMA	High Molecular Weight Acids
HPLC	High Performance Liquid Chromatography
HSGCMS	Headspace Ghromatography Mass Spectrometry
IEC	International Electrotechnical Commission
IPA	IsoPropanol
KHP	Potassium Hydrogen Phthalate
KOH	Potassium Hydroxide
LMA	Low Molecular Weight Acid/Acids
MS	Mass Spectrometer

N ₂	Nitrogen Dioxide
p.a.	Pure
pH	Potential of Hydrogen
SF ₆	Sulfur Hexafluoride
TAN	Total Acid Number
TCD	Thermal Conductivity Detector
TS	Tensile Strength
TU	Thermally Upgraded
UK	United Kingdom

LIST OF SYMBOLS

C	Concentration
C_0	Equilibrium Concentration
$C_{\text{Total 2-FAL, paper}}$	Total 2-FAL Concentration from Paper
$C_{\text{Total Methanol, paper}}$	Total Methanol Concentration from Paper
DP	Degree of Polymerisation
DP_0	DP of paper at time zero
η	Chain Scission Number
$2\text{-FAL}_{\text{oil}}$	2-FAL Concentration in Oil
$2\text{-FAL}_{\text{paper}}$	2-FAL Concentration in Paper
k	Rate of Reaction
m	Mass of the test portion used.
M	Molarity of alcoholic KOH solution, usually 0.1.
$\text{Methanol}_{\text{oil}}$	Methanol Concentration in Oil
m_{oil}	Mass of Oil
m_{paper}	Mass of Paper
$\text{Methanol}_{\text{oil}}$	Methanol Concentration in Oil
$\text{Methanol}_{\text{total oil}}$	Total Methanol Concentration in Oil
M_r	Molecular Weight
$P_{2\text{-FAL}}$	Partitioning Coefficient of 2-FAL
P_{Methanol}	Methanol Partitioning Coefficient
pK_a	Dissociation Constant
I	Current
Q	Charge
R	Resistance
t	Time
t_0	Mean Efflux Time of Solvent
t_s	Mean Efflux Time of Solution
$[\eta]$	Intrinsic Viscosity
ν_s	Specific Viscosity

V_1	Volume of alcoholic KOH solution used to titrate the test portion.
V_0	Averaged volume of alcoholic KOH solution used for blank titration.
56.1	Molecular weight of KOH. A constant.

LIST OF EQUATIONS

(2.1)	58
(2.2)	58
(2.3)	58
(2.4)	65
(2.5)	65
(2.6)	65
(2.7)	66
(3.1)	88
(3.2)	92
(3.3)	99
(3.4)	99
(4.1)	118
(4.2)	122
(4.3)	122
(5.1)	130
(5.2)	132
(5.3)	132
(5.4)	133
(5.5)	134
(5.6)	134
(5.7)	135
(5.8)	138
(5.9)	138
(5.10)	139
(6.1)	159
(6.2)	159
(7.1)	176

ABSTRACT

For over a century, liquid and solid insulations have been widely used in high voltage power transformers. Degradation of paper insulation and the loss of its insulation integrity are one of the major causes for transformer failure. This has stimulated research into the ageing of paper insulation and led to the development of ageing indicators. An ageing indicator is a detectable parameter whose value is directly linked to the state of transformer paper insulation.

This thesis is devoted to an experimental investigation of the behaviour of low molecular weight chemicals in the thermally accelerated ageing process of Kraft paper. A particular focus is directed towards acidity as a paper ageing indicator. Although acidity is a well-known indicator for assessing the ageing condition of the transformer liquid, only more recent studies found that acidity is mainly made up of short and long chain carboxylic acids. The short chain acids, otherwise known as low molecular weight acids (LMA), play a significant role in the paper ageing.

In this thesis, a perfectly sealed oil-paper ageing system was designed and developed. The proposed test and measurement strategy uses oil samples of 10 ml and paper samples of 0.5 g. The perfectly sealed samples completely eliminate mass exchange between the samples and their environment, allowing the realization of strict ageing conditions. Additionally, specific array formations are used to enable a uniform thermal ageing environment for a large number of samples to be aged concurrently.

A high extraction efficiency of LMA from transformer liquid, containing a mixture of LMA and HMA (high molecular weight acids), has been achieved by the development and use of a water based acid extraction system that uses Erlenmeyer flasks equipped with internal mixers. An LMA detection efficiency of >80% for synthetic ester fluid and >90% for mineral was achieved for LMA concentrations as low as 0.017 mg KOH/g of liquid. The change of LMA concentration during the ageing process of Kraft paper at an elevated temperature of 130 °C in two types of transformer liquids with different initial conditions were systematically measured in parallel to the measurement of moisture, 2-FAL and methanol concentrations. This enabled the study of the ageing process from different angles based on experimental results.

Results from samples with different ageing durations show that LMA are produced from the ageing of Kraft paper. The LMA concentration in mineral oil and synthetic ester is different because of the polar nature of the latter, but the liquid LMA concentration is strongly coupled to the change in degree of polymerization (DP) of the paper, providing pivotal evidence for the development of LMA concentration in liquid as a transformer paper ageing indicator.

The effect of the presence of excessive LMA in transformer liquids was also studied. It was shown that an initial LMA-rich ageing environment (with formic acid of 0.4 mg KOH/g added to the liquid) greatly accelerates the ageing of Kraft paper, by a factor of 5 for mineral oil and 2 for synthetic ester. The lower ageing acceleration factor of LMA in synthetic ester manifests its ability to mitigate the catalytic effect of LMA in paper ageing.

DECLARATION

I declare that no portion of the work referred to in the thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

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CHAPTER I

1 INTRODUCTION

1.1 Transformers in Electricity Networks

Transformers form a crucial element in the delivery of alternating current (AC) electric power as they are responsible for voltage step-up and step-down. They are normally installed in substations and are one of the most expensive pieces of equipment in a substation, requiring maximum attention and protection. Supply of electricity may be immediately interrupted when a transformer fails. The electricity network in the United Kingdom (UK) was interconnected and operated as a single synchronous system in 1938 with around 120 power stations and 6,400 km of lines (cables) operating at a maximum voltage of 132 kV at the time of interconnection [1]. It was upgraded with the addition of 275 kV lines at the beginning of the 1950s and further elevated in 1965 to 400 kV to meet the increasing power demand as a result of the industrial growth boom over the period from the 1950s to 1980s [1].

The modern UK power delivery system consists of two parts, the transmission grid (or the super-grid) and the distribution networks. About two-thirds of the transformers serving the transmission grid have a service life of more than 40 years, as detailed in Figure 1.1 [2]. The number of transformers in the transmission grid is relatively small but their capacities can be huge. A typical transformer that steps down the voltage from 400 kV to 132 kV is able to transfer a power of 240 MVA. It has dimensions of 8 metres long by 5 metres wide by 5 metres high and weighs almost 300 tonnes including 100,000 litres of oil. On the other hand, the number of transformers in the distribution networks is much larger, adding to 684,000 units in 2007, but the average capacity is much smaller, at 234 kVA, as shown in Figure 1.2 [3]. By 2008, most distribution transformers had a service time of 40 years. Figure 1.2 also provides a picture of the population of distribution transformers and their average rating across 25 European Union (EU) countries.

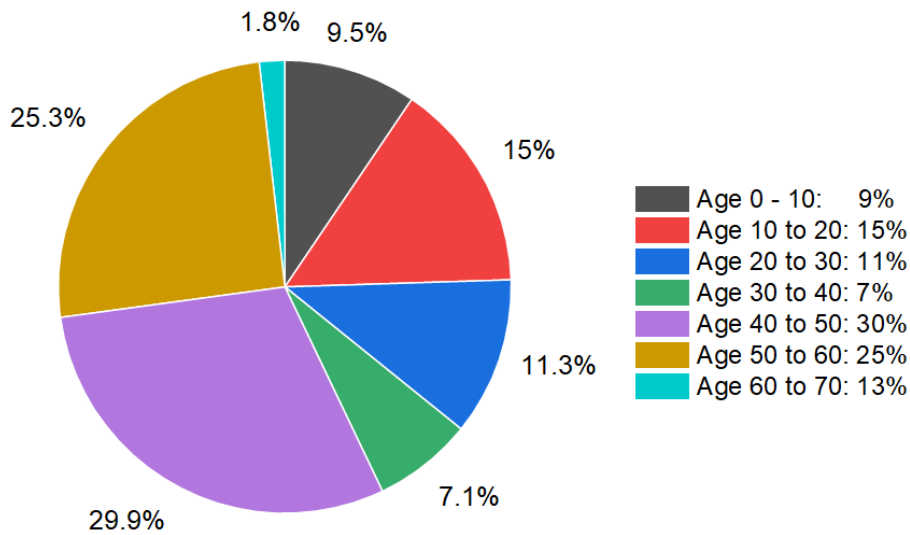


Figure 1.1 Age distribution of in-service transformers in UK National Grid at transmission level [2].

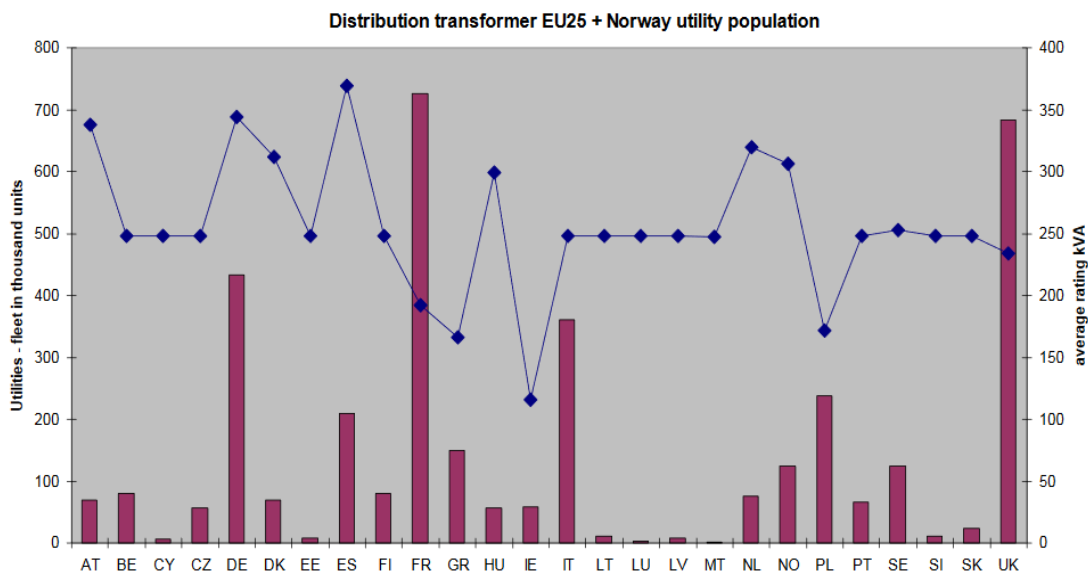


Figure 1.2 Population of in-service distribution transformers in 25 EU countries and the average capacity rating. Bars are for population and filled diamonds for average capacity rating [3].

The best transformer can achieve an energy efficiency (output/input power ratio considering Ohmic heating, I^2R , as power loss) of 99.5% while the majority have an efficiency of 98% [3]. In the UK, electricity from a generation plant passes through at least five transformers before it reaches the consumer with an overall efficiency of about 92% [3]. Adding the loss in the cables or lines, about 8.5% of all generated electricity is wasted in the transmission grid and distribution systems [3].

There are two types of transformers currently in use. The first one is the traditional oil insulated transformer and the second is the dry transformer. A schematic diagram of the different types of transformers are shown in Figure 1.3 and Figure 1.4.

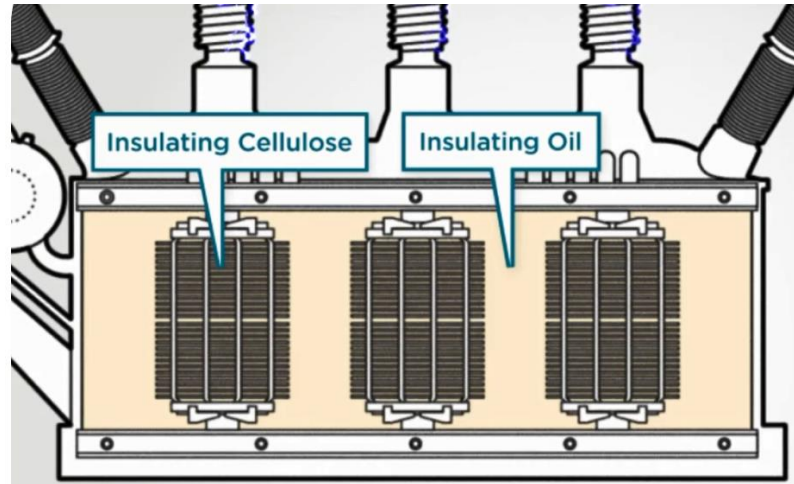


Figure 1.3 Schematic diagram of the main components in a liquid insulated transformer [4].

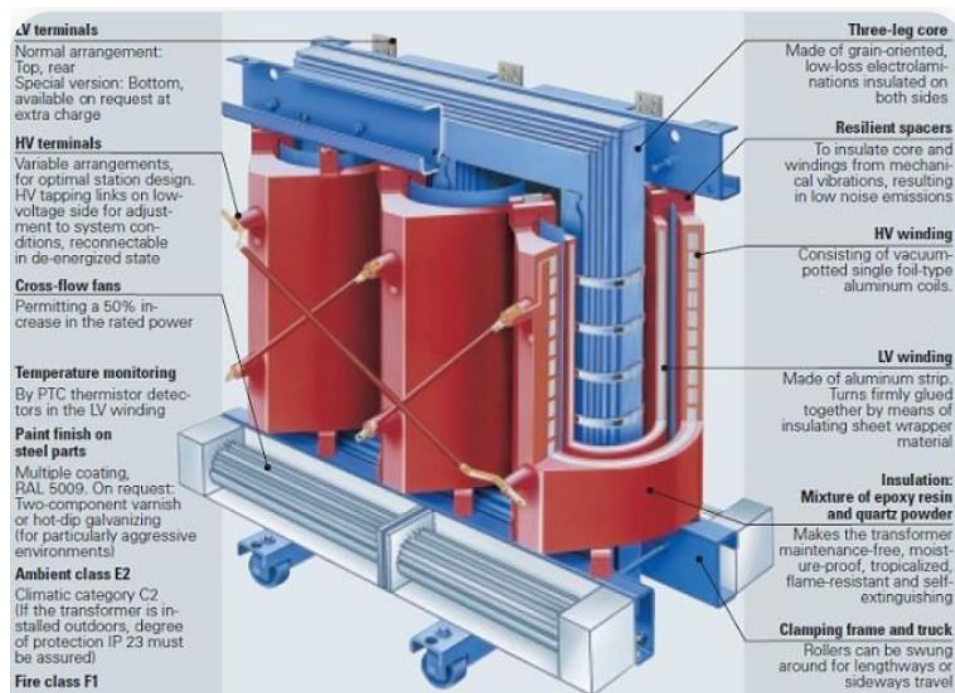


Figure 1.4 Schematic diagram of a dry insulated transformer [5].

Air is the cheapest insulating medium used for gas filled transformers. It is safer in comparison with oil, does not explode and is easy to handle. Gas filled transformers are also lighter and have better noise characteristics (since gas transmits less vibration than

oil). Despite the recent research to explore the use of SF₆+N₂ mixture to improve the voltage ratings of gas filled transformers, the overall performance is still inferior to that of oil filled transformers which dominate high voltage applications. The major problem with oil filled transformers is that oil burns when exposed to flame or heated to its ignition point in the presence of oxygen. The large amount of oil used also means more service effort when the transformer insulation liquid needs to be purified following service contamination.

1.2 Service Life of Transformers and Influencing Factors

The aged transformer assets of the UK electricity grids can be attributed to two reasons. Firstly, many of the transformers are under-loaded and they have parallel units to work in the substations to share the load. Secondly, the transformers are properly maintained and they are still in good operational conditions despite their ages.

Despite the operational faults related to mechanical systems, such as the tap changers, the most vulnerable permanent design feature is the solid insulation used in the transformer, especially the paper insulation. Liquid insulation is important, but it is possible to be reconditioned or replaced when necessary.

It is well known that solid insulation materials age with time, leading to deterioration of their mechanical and dielectric strength. When a transformer is in long term operation, the current passing through the windings will generate Ohmic heating leading to temperature rise of the materials in the transformer tank. The transformer core will also dissipate electric power through eddy current. Transformer temperature rise is defined as the average temperature rise of the windings above the ambient temperature (40 °C as the allowed maximum) when the transformer is loaded at its nameplate rating. For liquid filled transformers, the allowed maximum temperature rise of the windings is 55 °C (when Kraft paper is used) or 65 °C (when thermally upgraded paper is used).

Excessive heating in transformers accelerates the ageing of the solid insulation materials, such as Kraft paper. This can happen when an in-service transformer is overloaded. It has been predicted that the total UK electric power demand will need an

increase of 200 % to 300 % by 2035 due to the uptake of electric vehicles and heat pumps in order to meet the net zero emission of CO₂ by 2050 [6]. Current UK's electric power demand is 40 GW. By 2035, the additional need for Electric Vehicle (EV) and heating is 134 GW, which is roughly 235 % in increase [7]. When the number of new transformer installations cannot meet the projected increase in power demand, the increased load on the transformers will mean they are susceptible to more Ohmic losses and higher temperature rises. In addition, the electricity network in the UK is also in a period of change to become a more responsive and smarter grid. A comparison of the traditional network and the smart grid network is shown in Figure 1.5 [8, 9]. A change in the grid topology brings uncertainty and perhaps more electrical stress to the existing ageing equipment. Thus, maintaining the safe operation of the aged transformers is paramount in asset management. This can only be achieved by adequate condition monitoring and performance prediction to properly schedule the service or replacement of aged transformers.

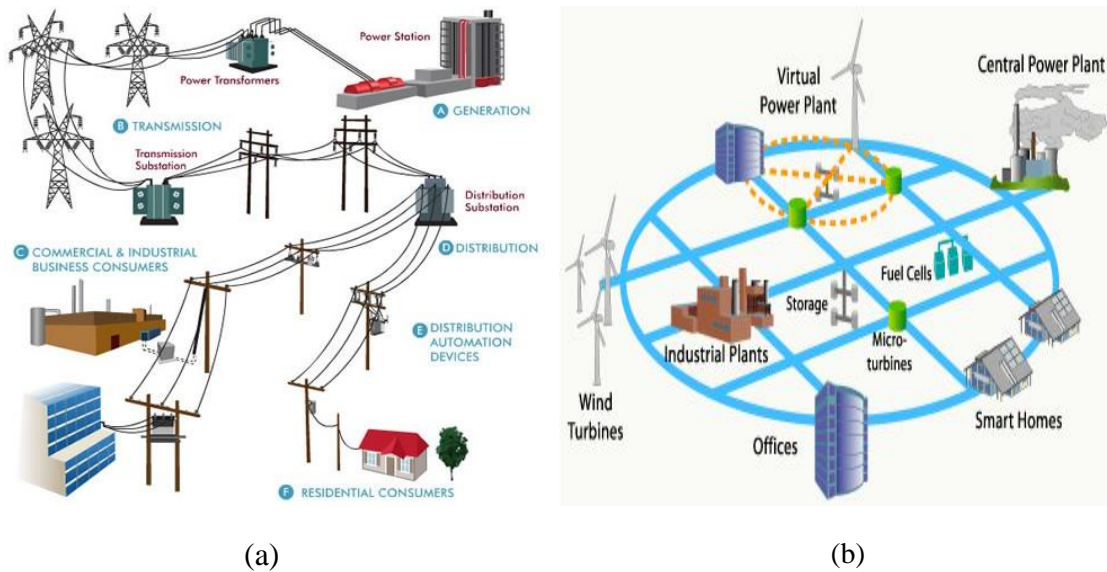


Figure 1.5 Comparison of (a) traditional [8] and (b) smart power network [9]

As the first step, the risk of failure must be estimated for the transformers in service. This requires reliable information on their conditions, especially the dielectric strength of the insulation materials. For most of the transformers, knowledge on the conditions of the insulation paper is crucial because it is permanent and cannot be replaced. In

order to avoid the need of taking transformers out of operation to examine their insulation state, indirect measurement or monitoring techniques are preferred.

Scientific research is needed to support the development of more advanced technology that allows reliable monitoring of the state of the transformers, in-specific their paper insulation. This is still not available and thus forms the aim of the work in this thesis.

1.3 Liquid and Paper Insulation in Transformers

Power transformer insulation consists of liquid, paper and pressboard. For transformers installed in the UK, the most commonly used liquid is mineral oil and for paper it is Kraft paper. During the manufacturing process of the transformers, Kraft paper will be wound round the copper winding conductors to provide dielectric insulation and mechanical stability. Likewise, the pressboard will provide mechanical stability to supporting structures, winding tubes, spacer blocks and formed items for end closing [10]. Once a transformer is built it is basically a tank with internal components. The transformer is first dried to reduce the moisture content of the paper insulation and then submerged with dried mineral oil, afterwards it will be further dried. The final water content of the paper and pressboard should be less than 0.5 % [5, 11].

It is well known that the condition of the transformer paper insulation determines the operating lifetime of a transformer. Therefore, condition monitoring techniques for the paper insulation are incredibly vital in providing information for managing the lifetime of transformers and preventing their failure. The paper wrapped around the windings is to provide sufficient turn-to-earth and turn-to-turn insulation. Newly manufactured insulation paper has high mechanical strength, as indicated by its degree of polymerisation or tensile strength, and also high dielectric strength. The thermal stresses imposed on the paper activate chemical reactions that lead to the degradation of the paper insulation, such as oxidation, pyrolysis and hydrolysis [12, 13], and the production of acids and alcohols. Thermal stresses are the main focus in this thesis. There are experimental suggestions [14, 15] that the acids subsequently accelerate the ageing of the paper and decrease its DP and dielectric strength. Therefore, the concentrations of the acids inside and surrounding the insulating paper form an

important aspect of the ageing environment and have the potential to act as an ageing parameter. It is thus necessary to obtain quantitative information on the presence of the acids to define the boundary conditions for the dynamic ageing process of transformer paper insulation. Because the insulation paper is wrapped on the windings and it is prohibitive to use any intrusive measures to sample the paper for detection of its mechanical and insulation state. It is thus necessary and possible to seek information from the liquid that surrounds the paper insulation.

Mineral oil is traditionally used in transformers for electrical insulation and heat dissipation through mass convection and thermal conduction. In recent years, alternative transformer liquids have been developed which show advantages, such as improved fire safety and better biodegradability [16-18]. Transformers using synthetic esters [19] have been in trial operation. The quality of the transformer liquid is often assessed by its dielectric strength and thermal performance. The heat produced by the windings and iron core due to eddy current has to be taken away by the liquid through thermal conduction due to temperature gradient and natural or forced convection. The dielectric strength of the liquid is influenced by a number of factors, such as the presence of dissolved gas bubbles, liquid globules, solid particles which are formed due to electrical and thermal stresses, and other impurities. At the same time, some of the acids that are produced during the ageing of transformer insulation paper diffuse into the transformer liquid. Over long terms and due to circulation of transfer liquid, the acids will spread out into the whole volume of the oil. This creates a situation where useful information on transformer paper insulation can be indirectly obtained by sampling the transformer liquid without disturbing the insulation of the transformer as a whole.

Nevertheless, the most commonly found options of insulation materials for transformers used in the UK are still mineral oils and Kraft paper. This is due to the massive economic savings due to their mature manufacturing technology as well as the abundance and ease of procuring their raw materials. In fact, a large quantity of existing transformers installed in the past half-century used these materials due to their excellent and synergic insulation properties. The risk of failure must be known for these transformers and this requires more information on their conditions. Indirect measurement techniques are needed for in-service transformers.

1.4 Research Questions

Different chemical reactions have different activation energies. Hydrolysis has an activation energy of 100 kJ/mol and oxidation has an activation energy of 64 kJ/mol [20]. Hydrolysis reactions in paper insulation take place when moisture and hydronium ions accumulate in the amorphous and crystalline regions in the paper insulation. Moisture can come from the atmosphere or from the ageing processes. Hydronium ions come from the dissociation of acids. One water molecule is consumed in the cleavage of the glycosidic bond and a sequence of acid-catalysed dehydration reactions that follow will generate three water molecules. This means there is a net total of two water molecules being generated. The ageing by-products generated from hydrolysis of paper are: water, furans, carbon monoxide, carbon dioxide, alcohols and low molecular acids (LMA). The ageing by-products generated from oxidation of paper are: furans, carbon monoxide, carbon dioxide and water. Pyrolysis is the thermal decomposition of the cellulose chains at high temperatures. They normally start at above 130 °C and generate moisture, carbon monoxide and carbon dioxide.

Due to the ease of access for transformer oils, there have been numerous test parameters for oils in in-service transformers. These include colour and appearance, breakdown voltage, moisture, acidity, etc. For paper insulation there is no direct measurement for in-service transformers. There are currently only two techniques that can give an indication of the condition of in-service insulation paper. They are furan analysis (FA) and dissolved gas analysis (DGA). 2-FAL is considered the most abundant and stable of the furan compounds. Correlation between the concentration of 2-FAL and DP was observed in the test results, but its concentration was also attributed to hemicellulose [21]. Therefore, the reliability of using furan analysis to derive the aging state of the paper insulation needs to be further investigated. DGA only provides indication of the involvement of solid insulation in transformer incipient faults, and it does not provide quantitative information on the paper insulation state.

There is an increasing drive to measure more ageing by-products in transformer liquid that relate to the degradation of paper insulation. Methanol/ethanol analysis is a method under development via analysing transformer oil [22]. It was identified as an potential

ageing marker when analysis was performed using Headspace Gas Chromatography Mass Spectrometry (HSGCMS) [23] because it is produced directly from cellulose rather than the ageing by-products of cellulose.

Existing research has shown that acids, mainly carboxylic acids, are formed during the ageing process of transformer liquid and paper insulation and they accelerate the rate of degradation [24]. It was further suggested that the LMA in the acids may be responsible for accelerating the ageing of paper insulation [25] but experimental evidence was inconclusive. Later, this was investigated and found to be true [12, 14, 24].

HSGCMS experiments, which identified methanol, also identified LMA [23]. The LMA were found to include acetic, formic, and propanoic acid. It is thus fundamentally important to study the potential of using LMA as a parameter to quantify the ageing state of the paper insulation in transformers or the ageing environment (conditions) with the aim to provide the missing information for the detection of transformer paper insulation state.

To facilitate this ultimate objective, it is desirable to create an ageing process in the laboratory environment so the tensile strength (TS) or DP and Total Acid Number (TAN) can be obtained directly during the ageing process with either of the first two as the ageing state parameter. Work that has been done so far [12, 14, 24, 26] on the potential of LMA led to the following findings:

- the acidity of the transformer liquids has a trend of increase when paper ages, which means there is partitioning between the two mediums;
- water is more essential than oxygen for ageing because dry acids have limited catalytic capability;
- water and acids together have a multiplication effect on the acid catalysed ageing of paper insulation;
- LMA are potentially the most influencing acidic components in terms of accelerated paper ageing because most of the LMA are absorbed by Kraft paper due to its hydrophilic nature.

The acidity in transformer liquids is currently measured using either IEC 62021 [27] or ASTM D664-07 [28] via the method of potentiometric titration. The measurement neutralises the acid using potassium hydroxide (KOH) solution until an endpoint pH of 11.5 is reached. This method measures the total acidity of any acidic groups in a sample, which means it could be any acids defined via the Brønsted-Lowry acid-base theory [29]. A potentially novel method to monitor the transformer insulation conditions based on information provided by the LMA will need to ultimately address the following important issues:

- Measurement method with reasonable accuracy of the concentration of LMA in transformer liquids, especially at low concentration.
- Quantitative correlation, through experimental results, between transformer insulation ageing state and concentration variation of LMA and other chemicals in the liquid under well-controlled conditions.
- An insight into the chemical route for the influence of LMA to enable the establishment of a model that can be used to derive the state parameters of transformer paper insulation from transformer operational conditions and system parameters that can be measured on in-service transformers, such as transformer liquid temperature, pH, moisture, concentration of LMA, methanol and 2-FAL.

1.5 Project Aims and Objectives

The main aim of the project is to investigate the potential of LMA and methanol as insulation paper ageing indicators in transformers. In order to accomplish this, the following objectives are established:

- **To develop an ageing test system where ageing conditions can be satisfactorily controlled and develop techniques to improve the measurement accuracy of LMA concentration in oil.**

The usefulness of the experimental results depends on the accuracy of the measurement as well as the control of the ageing conditions. For paper ageing, the isolation of the samples from the environment during the ageing process is a key issue that has not been fully addressed. The volatility of LMA and their separation from high molecular weight acids also leads to uncertainties. An

improvement in accuracy of ageing environment control and LMA concentration measurement will allow reliable baseline data to be obtained.

– **Understanding the thermally accelerated ageing of liquid-paper insulation with a focus on LMA and methanol in well controlled environment**

Thermally accelerated ageing of such an insulation system is extremely complex due to the nature of the chemical reactions taking place and the large variety of molecules initially involved and formed throughout the process. In particular it is important to gain knowledge on the behaviour of LMA and methanol throughout the ageing process with initial conditions that are comparable to those of newly commissioned oil filled transformers.

– **Understanding the influence of LMA in thermally accelerated ageing of Kraft paper**

An effective way to gain insight into the influence of LMA in the ageing process of transformer paper insulation is to change the LMA concentration in the ageing process and study the difference that is activated in the rate of ageing of the paper. A typical choice is to add a specified amount of LMA at the beginning of the ageing process and study the ageing process by measuring relevant parameters such as the Degree of Polymerisation (DP), moisture level, LMA concentration in oil and paper, and concentration variation of other chemical species such as 2-FAL and methanol.

– **To investigate the ageing behaviour of Kraft paper in synthetic ester fluid with a focus on LMA and methanol**

Synthetic ester is a polar material. Thermally accelerated ageing of Kraft paper in synthetic ester may behave differently from that in mineral oil. With increased use of ester fluid in power transformers in the future, it is necessary to gain knowledge on how Kraft paper ages in ester fluid, especially if LMA could be used as a paper ageing indicator.

1.6 Major Achievements

LMA are a sub-group of the acid class which are believed to act as a catalyst to cellulose paper degradation in transformers [24]. This project considers Kraft cellulose paper and LMA with different types of transformer liquid (inhibited mineral oil and synthetic

ester). These different systems represent what is known to occur in the large population of installed transformers and ones that will be installed in large numbers in the future. Experiments have been designed to investigate, identify and quantify the LMA found via thermal ageing of paper insulation. The results obtained are expected to make a valuable contribution to the knowledge pool concerning the degradation of insulation paper, and also to make novel contributions towards more accurate measurement of LMA in transformer liquid and paper.

The major achievements of this PhD projects include:

- The development and verification of a completely gas tight ageing system (Chapter 3) that has been successfully used to study the ageing of Kraft paper in one mineral oil (Chapter 5, Gemini X) and one synthetic ester liquid (Chapter 7, MIDEL 7131). It completely isolates the ageing samples from the environment to stop any mass exchange through leakage and ingress, enabling trusted ageing conditions to be set. The size of the samples is significantly reduced, down to 10 ml for oil and 0.5 g for paper. Such a system allows better observation and assessment of low molecular weight chemicals that are usually more volatile. It also allows long-term partitioning to be carried out on aged samples, so these chemicals can reach equilibrium partitioning between the liquid and solid insulations.
- The proposal and successful use of an improved method of liquid LMA concentration measurement based on water extraction and the use of Erlenmeyer flasks (EF) (Chapter 4). Its extraction efficiency, with and without the presence of high molecular weight acids (HMA) in the oil, has been proven to be better than 80% for MIDEL 7131 and better than 90% for Gemini X in cases with a concentration as low as 0.017 mg KOH/g of LMA.
- It is the first time, to the author's knowledge, that the concentration of LMA in paper and in liquid has been systematically measured as well as those of moisture, 2-FAL and methanol during the ageing process where the DP of the paper decreases from 1000 to around 200. This provides multiple sets of baseline data that can be used to assess the ageing process from multiple angles, especially the evolution of LMA concentration during the ageing process and

the effect of an added LMA (formic acid) on the ageing of Kraft paper in mineral oil and synthetic ester.

- When the ageing starts with filtered dried oil and dried paper (with a moisture level less than 0.5%), Kraft paper ages at the same rate in Gemini X (as a mineral oil) and in MIDEL 7131 (as a synthetic ester), representing an ideal ageing system. The addition of formic acid with an initial concentration of 0.4 mg KOH/g in oil greatly accelerates the ageing of the paper in Gemini X, by a factor of 5.3. For MIDEL 7131, the acceleration factor is 2.3, demonstrating the ability of MIDEL 7131 in mitigating the effect of LMA on paper ageing.
- The variation of the concentrations of 2-FAL and methanol has also shown clear correlation with the change in paper DP under conditions similar to those of new transformers, confirming the findings in previous works that these two chemical species are produced by paper ageing and can be considered as paper ageing indicators.
- Clear evidence has been shown in the present work that, with initially dry conditions for paper and oil, the total LMA generations as a result of paper ageing in the two transformer fluids (Gemini X as a typical mineral oil and MIDEL 7131 as a synthetic ester fluid) follow the same trend line over the DP range of 850 – 300. This DP range is critical to the monitoring of transformer insulation deterioration. The LMA concentrations in paper and in the two types of transformer liquids are also strongly correlated to the paper DP during the ageing process. Thus the present work enables a firm step forward to be made in establishing LMA concentration as an indicator of transformer paper ageing in different transformer liquids.

1.7 Outline of Thesis

This thesis starts with an introduction to the background, aims and objectives, and major achievements of the project in Chapter 1, to help the reader build up a general picture of the work. This is followed by a literature review in Chapter 2 to introduce the important concepts, existing knowledge and understanding in relation to transformer liquid and paper insulation ageing. The literature review will also help establish

reference data that can be used for comparison with results from the present work in late chapters.

Chapter 3 is devoted to the experimental and measurement strategy and techniques. It provides vital information on the selection of experimental conditions and technical details to ensure confidence in the results.

The work to develop and verify an improved LMA separation method for the measurement of acidity in transformer liquids is reported in Chapter 4. The focus is on the improvement of the lower measurement limit of LMA through the use of a gas tight water based LMA separation configuration.

The measurement results from thermal ageing of Kraft paper at 130 °C in an inhibited mineral oil (Gemini X) in perfectly sealed glass ampoules are reported in Chapter 5. Results are presented in the order of moisture level, DP, chain scission, 2-FAL and methanol concentrations, LMA concentration, and correlation of different ageing parameters. The first set of baseline data is obtained in this chapter.

The influence of initially added formic acid as a typical LMA on Kraft paper ageing in Gemini X at 130 °C is studied in Chapter 6. The emphasis is on the change of ageing rate of Kraft paper and how the concentrations of different chemicals such as 2-FAL, methanol and LMA change with the ageing time and how well they correlate to the paper DP.

The work in Chapter 7 focuses on the ageing of Kraft paper in a synthetic ester fluid (MIDEL 7131) for use in transformers. The ageing processes of Kraft paper in MIDEL 7131 with and without initially added formic acid are studied under conditions identical to those in Chapter 5. The suitability of using LMA as a paper ageing indicator is scrutinised by analysing the measurement data obtained under well controlled conditions and a comparative study with results obtained in Chapter 5 and Chapter 6.

An overall summary of the major outcomes from the present research is given first in Chapter 8. The limitations of the work are also discussed from different angles, which

is followed by the proposal of several possible improvements that can be made through further research.

CHAPTER 2

2 LITERATURE REVIEW

2.1 Introduction

This chapter is devoted to the introduction of basic concepts and a literature review of the existing work relating to transformer liquid and paper ageing. The focus is on the role of 2-FAL, methanol and low molecular weight acids (LMA) and their potential as markers for the dynamic ageing process of transformer insulation paper. To understand how ageing markers work; it is crucial to understand how the insulation system is designed; what materials are used to build it; and how it degrades. This knowledge will be helpful to understanding how the chemicals are generated during the ageing process and why some are assumed to be very potent to the degradation of the cellulose insulation. Secondly, a review on existing work relating to ageing indicators and those that are under development, such as 2-FAL, will be conducted.

2.2 Common Insulation Design in Liquid Filled Transformers

Liquid filled transformers rely on paper and pressboard to provide insulation around winding conductors and between the windings, as shown in Figure 2.1. Mechanical support to the conductors is provided by pressboard or other strong insulating materials that last at least 40 years. The spacers are a typical example. The liquid that fills the transformer tank has two distinct roles in the operation: to take away heat from the current carrying conductors and transformer cores (eddy current creates heat) and to provide enhanced insulation in voids and gaps. The lifetime of a liquid filled transformer is limited by the degradation of the solid insulation, especially the paper. Influenced by the design and operational conditions, heating inside a transformer due to electrical power dissipation is never uniform. The so-called hot spots exist in specific locations inside a transformer tank where electrical heating is largely balanced by thermal conduction. For example, in transformers using Kraft paper for insulation, the maximum allowed temperature is 98 °C, while that using thermally upgraded paper is 110 °C. The life time of the transformer depends on how fast the paper insulation degrades at the operation temperature. This has been the question to answer in the past

70 years and is also the topic that this thesis is related to since there is still no clear answer on this so far.

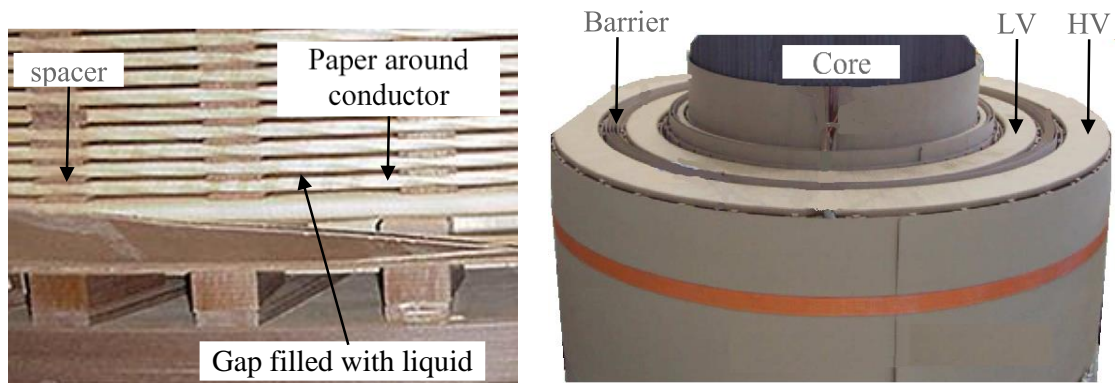


Figure 2.1 Common insulation design of a liquid filled transformer. The coil conductors are wrapped with insulation paper. Spacers are used to separate the winding coils. All gaps are filled with insulation liquid [3, 30].

The main type of liquid used in transformers is mineral oil although there has been an increasing presence of ester fluids in more recent decades. The latter can be synthetic or natural-originated. To make the transformers safer and environmentally compatible, the industry has embarked on a quest for clearer understanding of the fundamental differences between esters and mineral oil and how to adapt the designs to allow the use of esters at ever higher voltages.

2.2.1 Hydrocarbon Oils

Mineral oils are extracted from crude oils through industrial fractional distillation. They are mainly composed of hydrocarbon functional groups with small traces of oxygen, nitrogen and sulphur containing compounds [31]. The chain lengths of mineral oils typically range from C_{15} to C_{40} [32] and can be separated into four groups: naphthenes, paraffins, olefinics and aromatics [33]. The general structures of these chemicals are shown in Figure 2.2. Due to the higher content of paraffins and naphthenes in mineral oils they are often categorised as either paraffinic or naphthenic. If the percentage of naphthenic content is greater than approximately 50% it is considered to be naphthenic [31]. If the naphthenic content is less than 50% it will be paraffinic. The

main process that mineral oil degrades by in a transformer is via oxidation, which will be discussed in more detail later in this chapter.

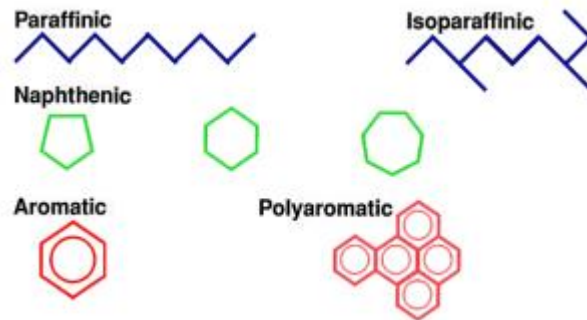


Figure 2.2 Different types of hydrocarbon structures in mineral oil [31]

Additives, which contain oxidation inhibitors, are normally added to the oil to slow down the chemical degradation reactions until they are all used up. Once this occurs the oil would be prone to an increased rate of chemical degradation. In fact, mineral oils can contain two types of inhibitors. They are natural and synthetic oxidation inhibitors. Natural inhibitors are usually peroxide destroying compounds, whereas synthetic inhibitors are dominantly hindered phenols (DBPC and DPB) [34].

2.2.2 Ester Liquids

Esters have been used as dielectric fluids for transformers. They are biodegradable and have advantages over traditional mineral oils with less adverse environmental impact, better fire safety, and potential life extension. Synthetic esters were first used for transformer insulation in the mid-1970s whereas natural esters were introduced in the 1990s [35]. With typical flash point values exceeding 250 °C, they provide a high level of fire safety compared with the flash point of 145 °C for mineral oil.

Natural esters are mainly made of triglyceride whose fatty acid chains can contain up to 22 carbon atoms. They can be in saturated or unsaturated form [36], which influences their properties, including viscosity and oxidation stability. Their viscosity and oxidation stability increase with the number of saturated bonds [36, 37]. Esters are polar and able to draw out and absorb water molecules from paper, thus help reducing the

moisture level in the paper and slow down the paper degradation. As a result, the paper insulation system can last longer than that in a mineral oil filled transformer.

Synthetic esters can be made by reacting alcohols and acids. Typical alcohols include neopentylglycol, trimethylol-propane, pentaerythritol and dipentaerythritol [38]. The viscosity and oxidation stability of the synthetic esters can be controlled by varying the functional groups in the carboxylic acids.

Esters bear many similarities with mineral oils in their behaviour. For example, esters also degrade by oxidation. Esters also degrade by hydrolysis. With sufficient level of moisture in esters, reactions will take place to produce alcohol and carboxylic acids. Again, the acids can catalyse ageing reactions to the liquid and paper. Esters tend to hold a high level of moisture in comparison with mineral oil due to their polarity [39]. Figure 2.3 shows the esterification and hydrolysis process of a triglyceride [37]. The reversible reaction represents that under the right conditions the reaction can shift in a certain direction. Both forward and reversible reactions are taking place at the same time and an equilibrium is eventually achieved. The main direction of the reaction is dependent on conditions such as the concentration of the reactants, the concentration of the products, temperature, pressure, etc. For transformer applications the main reaction is the forward reaction.

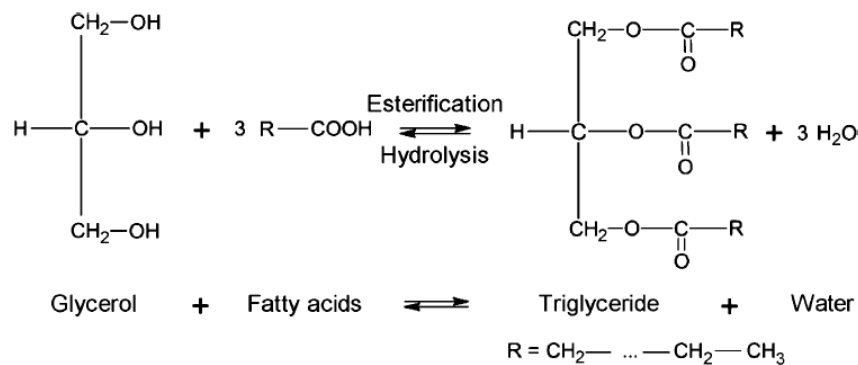


Figure 2.3 Reversible reaction for synthesis of esters [37].

2.2.3 Kraft Paper

There are different types of transformer insulation paper. The most commonly used paper for insulation is non-thermally upgraded Kraft paper due to its great oil impregnation characteristics, abundance, low cost, and excellent electrical and mechanical properties [2, 40]. It is made from softwood to take advantage of its longer fibre chains [41]. Table 2.1 is a summary of the different types of paper insulation used in transformers.

The micro and macro fibres in paper join together by intermolecular hydrogen bonding. This type of bonding is due to strong electrostatic attraction forces between highly electronegative molecules. These forces occur when an H atom is bound to nitrogen, oxygen or fluorine and are the strongest type of intermolecular forces to form strong and stable structures.

Table 2.1 Special purpose solid insulation used in transformers [42]

Paper Type	Characteristics
Cotton paper	Longer fibres than cellulose paper, weaker intermolecular bonds, weaker electrical and mechanical properties than Kraft paper. Can be mixed with Kraft paper to make paper insulation with good electrical and mechanical properties and with excellent oil absorption capability.
Thermally Upgraded (TU) paper	Used for special applications; higher thermal stability; can withstand higher thermal stress compared with ordinary Kraft paper.
Creped Paper	Provides extra extensibility for awkward layouts.
Highly Extensible Paper	Improved burst, stretch and cross properties to refrain from tearing; can withstand rough conditions and are useful for high stress operational areas.
Diamond Dotted Paper	Provides high mechanical strength.

Paper contains cellulose, hemicellulose and lignin (Figure 2.5) [43]. Glucose molecules can have two configurations as either α and β glucose units. α glucose units form helical glycosidic bonds whereas β glucose units form straight long chains. Most of the glucose units in cellulose form β glucose units, which lead to straight long chain fibres in the form of cellulose bundles. Figure 2.4 shows 1-4- β -glycosidic bonds in cellulose [44]. Most of the mechanical strength of the paper is due to these fibrils and fibres, while the hemicellulose and residual lignin are amorphous, gummy substances that make the cellulose bundles stick together [44].

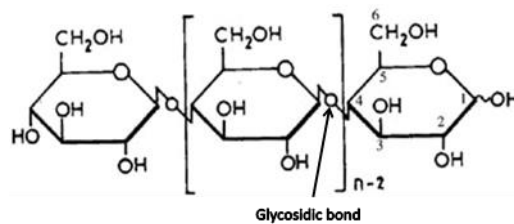


Figure 2.4 1-4- β -glycosidic bonds in cellulose [44].

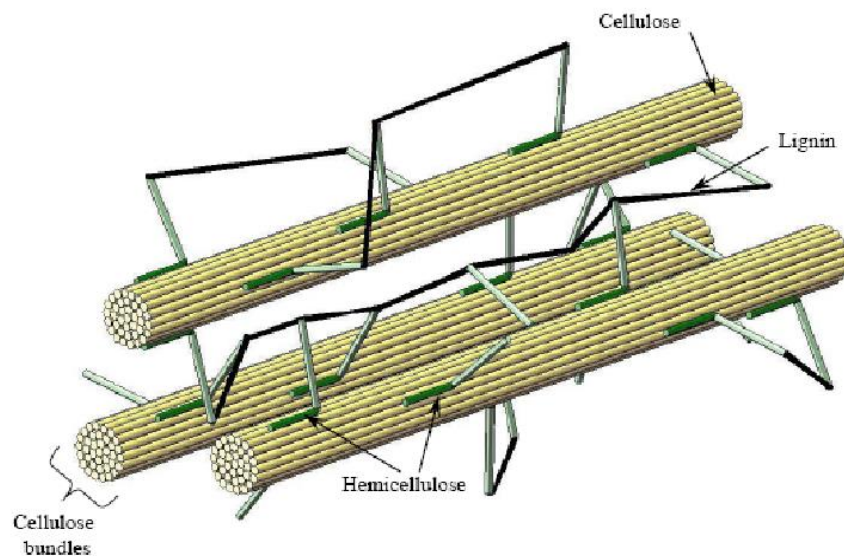


Figure 2.5 Diagram showing the location and connection of cellulose, hemicellulose and lignin in Kraft paper [43].

2.3 Introduction to Important Concepts and Processes Relating to Ageing of Transformer Insulation

2.3.1 Ageing and Ageing Markers

The ageing of transformer insulation is unavoidable once a transformer starts its operation. The main causes of ageing are due to electrical stresses and thermal stresses which promote unwanted reactions with species present in the transformer. The main chemical reactions are hydrolysis, oxidation and pyrolysis. Some of these chemical reactions are more dominant for the different types of insulation. This is mainly due to the different type of chemical bonding in the species.

Transformer papers are impregnated in liquid. When a new transformer starts its service, the moisture level is low, typically <0.5% in paper and 5-6 ppm in liquid. While paper ageing is a more complex process, the main ageing mechanism in mineral oil is oxidation [34, 42]. The energy supplied for the activation energies of these chemical reactions come from thermal stresses when the transformer is loaded. Activation energies for oxidation to take place can vary depending on the type of oil, and is around 70 kJ / mol [45].

Figure 2.6 shows the oxidation process and by-products that are formed. First, hydrocarbons will react with oxygen containing compounds with the energy being supplied from heat to produce free radicals and peroxides. The peroxides can then further react with free radicals to produce aldehydes, ketones, and alcohols. Alternatively the radicals can also react with oxygen containing compounds to produce more free radicals [33]. The aldehydes and ketones will eventually react as well to form acids and release carbon dioxide.

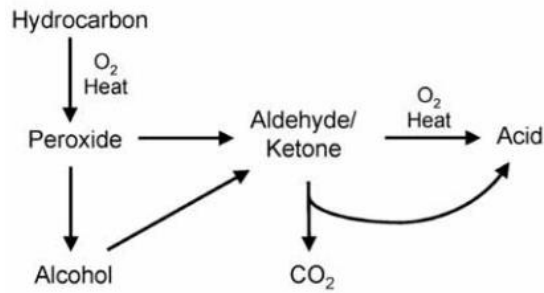


Figure 2.6 Oxidation reactions forming by-products in transformer oils [46].

Liquid samples can be conveniently taken from an in-service transformer for test. There are a large number of parameters that can be measured and used as indicators of the health state of the insulation liquid, as can be seen in Figure 2.7. The three groups of parameters serve for different purposes. Since direct sampling from transformer paper insulation is not possible, certain information obtained from the insulation liquid has to be established as the indicators of the health state of the insulation paper. Two techniques can give an indication of the condition of in-service insulation paper. They are furan analysis (FA) and dissolved gas analysis (DGA). Although the information is from the liquid, the chemical species either in aqueous form or gas are unique to the ageing process of paper [47]. An ageing marker is a piece of information that is related to the ageing process of a medium (paper or liquid) in a unique way. Firstly, it must be a direct result of or a product that is produced by the ageing process. Secondly, there is a reliable and repeatable correlation between this piece of information and the mechanical strength of the paper such as the degree of polymerization (DP) or tensile strength (TS) that cannot be directly measured for in-service transformers.

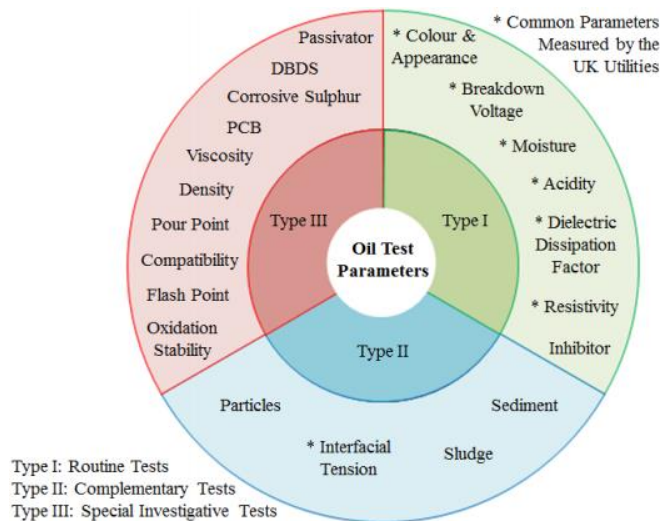


Figure 2.7 Transformer oil test parameters [2, 48, 49].

There is an increasing drive to measure ageing by-products in transformer liquid that relate to the degradation of paper insulation, due to the easy accessibility of oil samples. Much laboratory based research has been carried out to identify ageing by-products present in transformer liquid, such as furans, carbon oxide gases, alcohols, acids, etc., that directly relate to paper degradation [50]. More details will be given in sections 2.5 – 2.7.

2.3.2 Tensile Strength and Degree of Polymerisation

Tensile strength (TS) is a property that directly relates to the mechanical strength of paper. There are two types of TS measurements, wide-span and zero-span. Wide-span aims to measure the strength of the inter-fibre bonding, which is related to bursting, folding and tearing [51]. The standard measurement procedures are found in BS EN 4415 [52]. A load is applied to a sample of the paper and slowly increased until the sample breaks. The maximum load is recorded and divided by the paper length to obtain the TS. The size of the paper sample has to be sufficient to make the measurement result representative. For papers with different thicknesses, the concept of tensile index is used to represent the quality of the paper. The tensile index of paper is its TS divided by the grammage of the paper (g/m^2). When the tensile strength of paper reaches approximately 20% of its original value, the paper insulation has reached its end of life criteria [12].

Similarly, Zero-span aims to measure the strength of the paper related to rolling. Figure 2.8 shows the wide-span (paper strength relating to bursting, folding and tearing) and

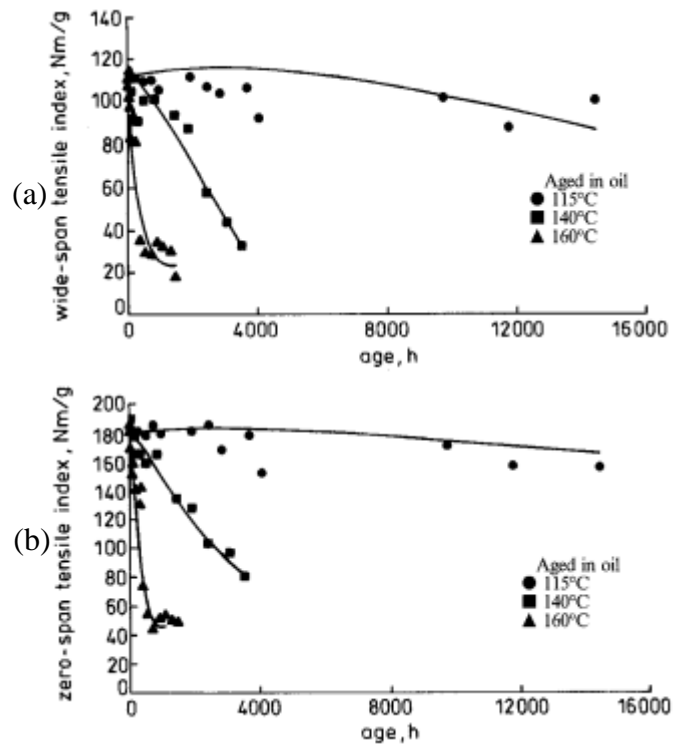


Figure 2.8 Tensile strength measurement results with ageing time, (a) wide-span and (b) zero-span methods [51].

zero-span (paper strength relating to rolling) TS measurement results of thermally aged paper in oil at 115 °C, 140 °C and 160 °C [51]. It is clear that at 115 °C the TS of paper is not affected significantly. There is only a minor decrease. At 140 °C and 160 °C, the rate of degradation of the TS has increased dramatically, showing the severe adverse effect of excessive temperature on paper ageing speed.

The degree of polymerisation (DP) is a measure of the number of anhydro- β -glucose monomers, in a cellulose molecular chain, as shown in Figure 2.9. The size of the molecular chains may be different for each of the cellulose molecules so the mean value is selected as an analytical parameter. The particular method commonly used in transformer sector to measure new and aged cellulosic insulating materials is known as the “average viscometric degree of polymerisation” (DP_v or DP in this thesis for convenience).

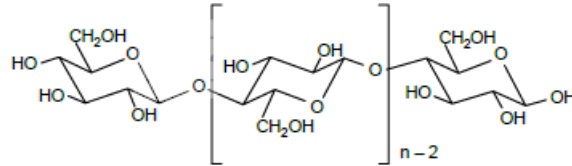


Figure 2.9 Chemical structure of glucose monomers in cellulose [53]

The method used to measure the DP was according to the standard ASTM D4243-99 [54], which follows the IEC standard 60450: 2004 [55] closely. The measurement of DP is given in Section 3.6.3. Kraft paper in new transformers starts off with an initial DP of around 1000, which will degrade to 200 when the transformer approaches its end of life [12]. The strong correlation of DP and TS, as shown in the experimental results in Figure 2.10, means that the reciprocal of DP is linearly proportional to TS.

Therefore, both parameters are adequate at representing the condition of transformer insulation paper. However, they still cannot be directly measured for in-service transformers and therefore there is a real need to research and identify paper ageing parameters.

The DP of new paper can be different depending on the preparation process. Before installed on transformer windings, the new paper has a DP of about 1200.

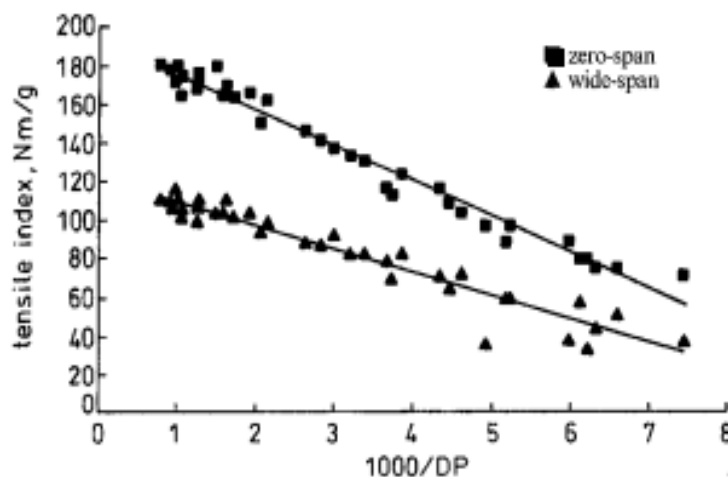


Figure 2.10 Correlation of TS with DP measured for thermally aged transformer insulation papers [51].

After going through the factory drying process, the DP of the paper in a transformer drops to typically 900 - 1000 with a water content around 0.5% in practice. It is commonly accepted that when the DP has fallen to about 200, the TS of the paper drops to 20% of its original value, and the inter-fibre forces diminishes [51].

2.3.3 Basic Ageing Mechanisms and Chemicals Produced in Transformers

Several early significant experimental studies have established that temperature, moisture, and oxygen are major factors influencing the aging of cellulose in transformers [56-61]. The temperature of the oil and paper is not a constant and affected by changes in operational conditions and environments, including loading and atmosphere temperature. Field data on transformer ageing is limited and for most of the times the measurements were not carried out as rigorously as in the laboratory environment. A simple example given in a field study in 2012 of a failed transformer with an age of 47 years old [62, 63] shows that the DP values are different at different locations in the transformer, ranging from 230 to 700. The lowest measured DP was 231, in the LV winding at the top of phase B which is between phase A and phase C. The DP at the location of failure is 380. The average water content in the paper is 2.5%. This high water content is partly because the transformer is free breathing.

2.3.3.1 Hydrolysis and its By-Products

Paper is hygroscopic and absorbs moisture easily. Initial moisture level significantly affects the degradation speed of DP. Hydrolysis of paper is an irreversible process of chemical breakdown due to its reaction with water. It involves the scission of glycosidic bonds in the cellulose polymer chains [64, 65]. For this reason, insulation paper used in transformers is dried before impregnated in oil or other transformer liquid to a moisture level typically less than 0.5%. However, water is still present in in-service transformer paper due to either ingress from the environment or chemical reactions in the ageing process producing water as by-product. Over the life of a transformer, the moisture level can increase to as much as 5% [66]. In laboratory tests, a moisture level of below 0.7% is regarded as a dry condition and a level of above 2.4% is regarded as a wet condition [14].

Hydrolysis can be catalysed by H⁺ ions from dissociated carboxylic acids and the aging rate is proportional to the amount of H⁺ ions. When the insulating oil degrades, acids build up in the transformer and act as catalysts for the hydrolytic reactions. It is rare that temperatures for pyrolysis will be reached during the normal operation of transformers. Therefore hydrolysis is considered the most dominant process due to the multiplicative effects of accelerated degradation by water and acids [12, 14]. Hydrolysis takes place when moisture and hydronium ions accumulate in the amorphous and crystalline regions of the paper [50]. Moisture can come from the atmosphere or from the ageing processes [50]. Hydronium ions come from the dissociation of acids [12]. It is believed that one water molecule is consumed in the cleavage of the glycosidic bond and a following sequence of acid-catalysed dehydration reactions will generate three water molecules [12]. This means there is a net total of two water molecules being generated. Therefore in theory the moisture level should increase with the ageing of the transformer paper. The ageing by-products generated from hydrolysis of paper are: water, furans, carbon monoxide, carbon dioxide, alcohols and low molecular weight acids (LMA) [12, 67].

Furan is an organic compound that contains a five-membered aromatic (stable) ring with four carbon atoms and one oxygen atom. The ring is called heterocyclic because it contains at least two different elements (carbon and oxygen). Any chemical compounds with such rings are referred to as furans. Furan is flammable and highly volatile because its boiling point is close to room temperature. Different types of furanic compounds have been found in transformer ageing tests, including the following species whose chemical structures are shown in Figure 2.11 [68]:

- 2-furaldehyde (2-FAL)
- 5-hydroxymethyl-2-furaldehyde (5-HMF)
- 2-furfuryl alcohol (2-FOL)
- 5-methyl-2-furfural (5-MEF)
- 2-acetylfuran (2-ACF)
- 2-furoic acid

2-furaldehyde (2-FAL) is considered the most important out of these because it is more stable and the most abundant. As a result, it is well regarded for paper insulation condition monitoring. This will be discussed in more detail in Section 2.5.

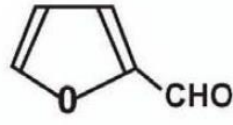
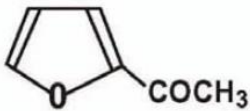
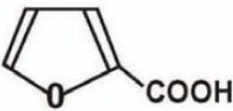
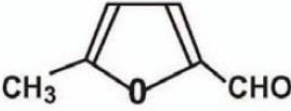
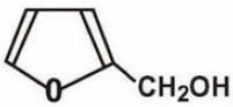
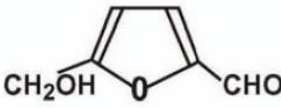
	
2-FURFURAL (2-FAL) 2-FURALDEHYDE 2-FURFURALDEHYDE	2-ACETYLFURAN (2-ACF) 2-FURYL METHYL KETONE
	
2-FUROIC ACID	5-METHYL-2-FURFURAL (5-MEF) 5-METHYL-2-FURALDEHYDE
	
2-FURFURYLALCOHOL (2-FOL) FURFURYLALCOHOL 2-FURFUROL	5-HYDROXYMETHYL-2-FURFURAL (5-HMF) 5-HYDROXYMETHYL-2-FURALDEHYDE

Figure 2.11 Chemical structure of furanic derivatives found in transformer ageing. The number in front of the functional group indicates the position in the ring that start with the oxygen atom as 1 [69].

The alcohols include methanol and ethanol (Figure 2.12) with a boiling temperature of 64.6 °C and 78.24 °C, respectively [70]. Due to their low molecular mass, they are volatile. Methanol is considered to be a paper ageing indicator and it is currently being developed into an IEC standard as a condition monitoring technique for paper insulation. Methanol will be reviewed in more detail in Section 2.6.

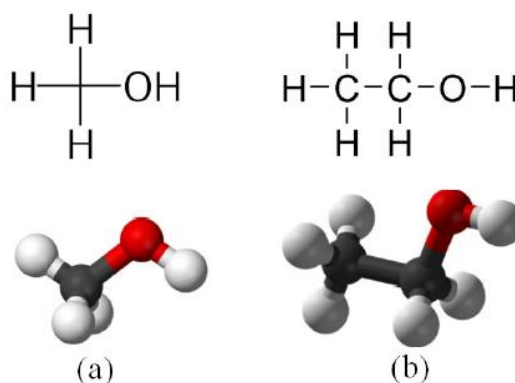


Figure 2.12 Chemical structure of methanol and ethanol that are produced in the ageing process of transformer insulation [70].

Figure 2.13 is a schematic diagram of the very basic hydrolysis process for paper [35]. The carbon skeleton of the glucose units is converted into a derivative of furan. Cellulose first produces 5-hydroxymethyl-2-furaldehyde. However, it is not stable and decomposes further into levulinic acid and formic acid. Since insulation ageing (both oil and paper) produces moisture (water molecules), it can be used as a parameter to reflect on the progress of hydrolysis. Paper is hydrophilic and hence majority of the moisture in an oil-paper insulation would be in paper.

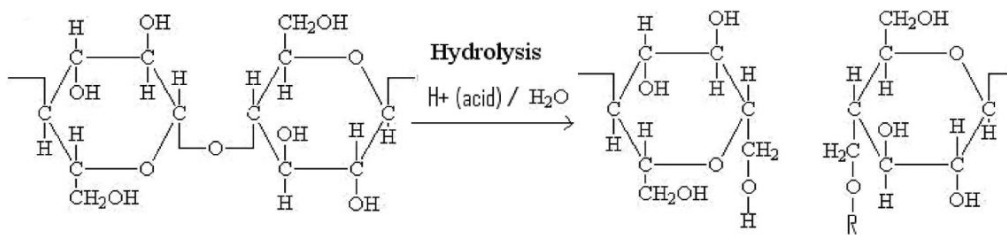


Figure 2.13 Hydrolysis of cellulose by acid or water [35]

2.3.3.2 Oxidation and its By-Products

Oxidation reactions occur at low temperatures during transformer operation. They can be considered the initiator of degradation reactions in paper insulation. The reactions involve dissolved oxygen in transformer oil attacking alcohol groups on the cellulose chains [62]. This reaction can be catalysed by hydroxyl radicals, which are formed from the dissociation of peroxide ions [12]. The ageing by-products generated from oxidation of paper are: furans, carbon monoxide, carbon dioxide and water. Oxidation of the oil produces both low molecular weight acids and larger acids (high molecular weight). It is found that a significant fraction, or even most, of the low molecular weight acids found are paper degradation products [71].

2.3.3.3 Pyrolysis and the Associated By-Products

Pyrolysis refers to the thermal decomposition of the cellulose chains at high temperatures. There is no clear threshold temperature value for this. For example in [50], it is stated that below 140 °C the effect due to pyrolysis is negligible, but in [26] it is reckoned that pyrolysis can take place above 100 °C while Burton et al cited a value of 110 °C in his work [47]. In fact, pyrolysis experiments of cellulose were mostly performed at much higher temperatures, well above 200 °C, for other applications such

as fire performance and combustion behaviour of cellulose as industrial materials [72]. Pyrolysis of cellulose generates moisture, carbon monoxide and carbon dioxide as ageing by-products [62]. In the present work, a temperature of 130 °C has been used in all ageing tests. Pyrolysis should not have a certain effect on the results reported in this thesis because the reactions will be dominantly hydrolysis for the generation of by-products.

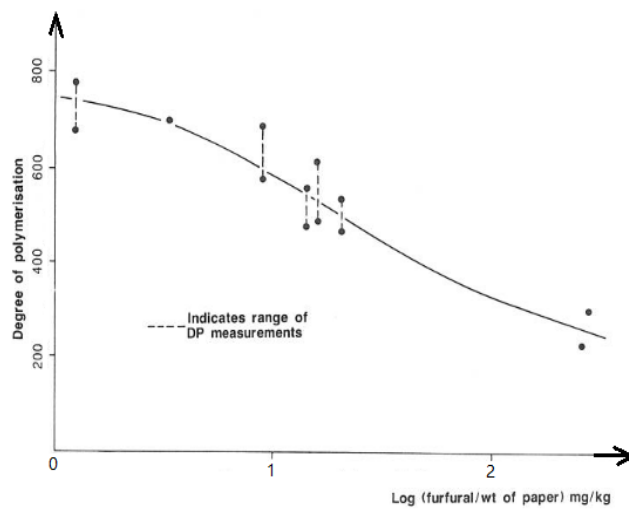
2.4 Existing Research on Transformer Ageing – Variation of Mechanical Strength Over Time

After going through the factory drying process, the paper in a transformer will have a DP of about 1000 and a water content around 0.5%. The DP will slowly decrease with the ageing of the insulation system and eventually reach a value around 200 to complete its life cycle. It must however be noted that the temperature inside the transformer tank is not uniformly distributed and hot spots exist where the local temperature can reach 120 °C or above in heavily loaded or short circuit situations. So failure of a transformer can be due to locally decayed paper insulation. Another point is that not all failures of transformers are caused by the low DP of the paper insulation. This has been shown to be the case in field tests [35]. An extensive literature survey was conducted in 1994 by Emsley and Stevens [21, 73] who concluded that a so-called “thermally activated” kinetic process can describe most of the results from paper aging. The activation energy describes how the aging rate depends upon temperature. Due to the large amount of work relating to the measurement of DP, only results of interest to this PhD project will be reviewed in the following sections where it is meaningful to report DP results together with the measurement of other parameters.

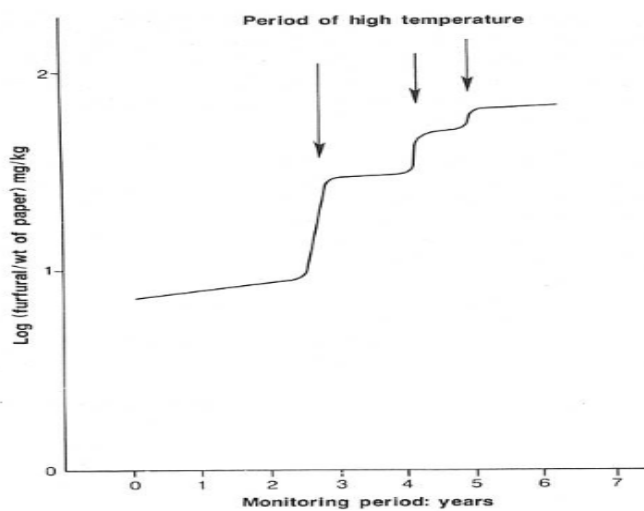
2.5 Existing Research on Transformer Ageing – Generation of Furanic Compounds and their Variation during Ageing

Furanic compounds as introduced in Section 2.3.3.1 were found in thermal decomposition experiments on cellulose as early as in the late 1950s [74, 75] but their formation mechanisms have remained unclear due to the difficulties in determining their chemical pathways. Transformer paper insulation ageing test was first conducted

in 1960 by Fabre and Pichon [57] and furan measurement as the basis for in-service transformer monitoring was first proposed in 1984 by Burton et al [47] and further studied by numerous researchers [61, 76, 77]. Burton et al [76] reported their test results on the generation of furfurals due to paper decomposition in transformer oil using a small scale model transformer where the hot spot temperature is simulated. The measurement was conducted with liquid chromatography in the temperature range from 140 °C to 170 °C. Typical results are shown in Figure 2.14 for reference [76].



(a)



(a)

Figure 2.14 Re-organised results of [76]. (a) DP variation against 2-FAL for operational transformers in UK National Grid. (b) 2-FAL against monitoring period for a 22/400 kV, 600 MVA generator transformer exposed to high operating temperatures.

Hill et al. [77] placed a section of newly wound conductor by Kraft paper with a length of 20 cm in a glass ampoule for ageing at 129 °C. Their measurements included 2-furfuraldehyde (2-FAL), 5-hydroxymethyl-2-furfuraldehyde (HMF), 5-methyl-2-furfuraldehyde (5-MEF), acetyl-furan (2-ACF), furfuryl alcohol (2-FOL), and furoic acid. The measurement for total furanic products and 2-FAL is plotted in Figure 2.15. It can be seen that 2-FAL is the dominant product among all furan derivatives and it is in fact used to obtain information on the ageing state of the transformer insulation paper.

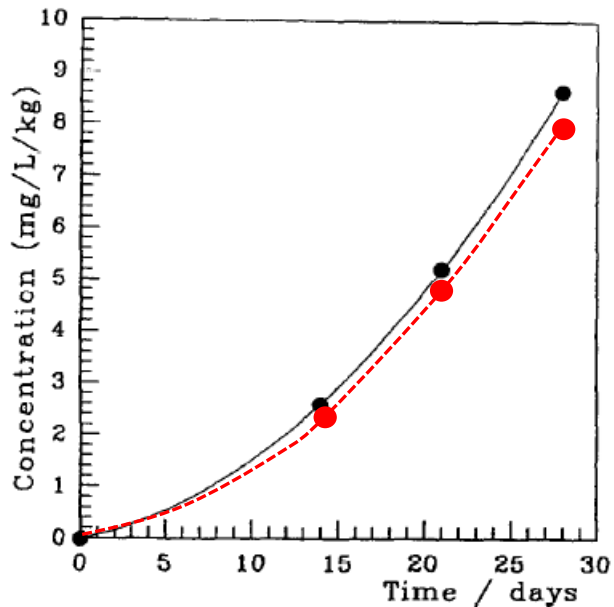


Figure 2.15 Results from [77] on total furan concentration (solid curve) and 2-FAL (dashed curve) at 129 °C. The oil used is Shell Diala B.

Despite this, clear evidence to relate the formation of furanic compounds to the degradation of different constituents in Kraft paper (cellulose, lignin, and hemicellulose) in the transformer environment (oil and cellulose in a temperature range below 130 °C) was only reported by Scheirs et al [78] more recently in 1998.

Several correlation functions between the DP of paper and concentration of 2-FAL in oil have been proposed based on laboratory ageing of Kraft paper [76, 79, 80], which are, respectively,

$$\text{Burton: } \log(2\text{-FAL}) = 2.5 - 0.005 \cdot \text{DP} \quad (2.1)$$

$$\text{Chendong: } \log(2\text{-FAL}) = 1.51 - 0.0035 \cdot \text{DP} \quad (2.2)$$

$$\text{De Pablo: } \text{DP} = 7100 / (8.88 + 2\text{-FAL}) \quad (2.3)$$

where 2-FAL is the concentration of 2-FAL in oil with the unit of mg/L. It is worth mentioning that the initial DP of the paper was assumed as 800 in De Pablo's study, which was lower than the expected value in real transformers which is approximately 1000. The differences between these three expressions are shown in Figure 2.16.

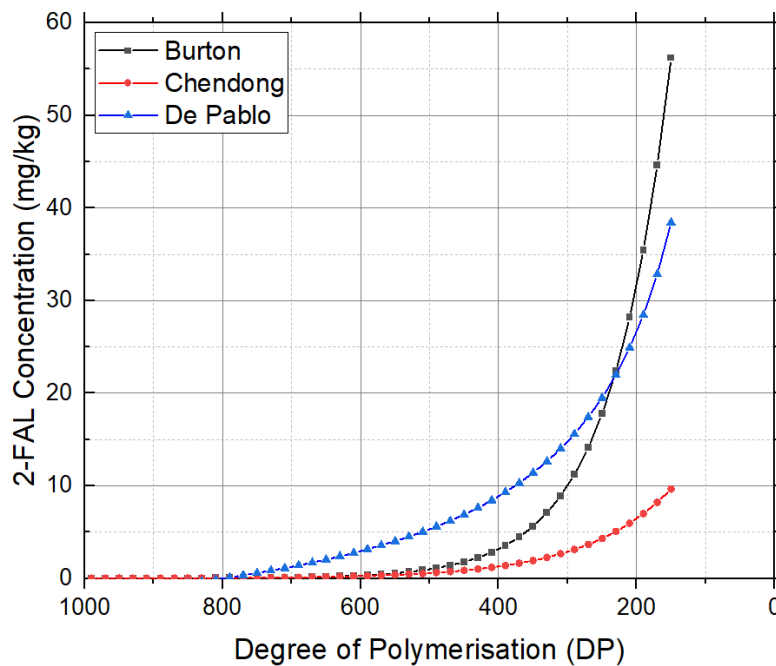


Figure 2.16 Predicted 2-FAL concentration as a function of DP by different researchers, Burton [REF], Chendong [REF] and De Pablo [REF]

In reality the situation is much more complex. The 2-FAL concentration measurement on 49 in-service UK National Grid transmission transformers (400/132 kV, 275/132 kV, 120-240 MVA, 17-57 years old) over the period of 2006 -2011 was reported in [81]. This study shows that there was large scattering in the data over the range of 0.1 – 4.3 mg/L for transformers at the same age, demonstrating the complexity of reality when 2-FAL is to be used as an ageing marker. Oil filled transformers typically have an oil to paper mass ratio of 20:1. 2-FAL concentration in the order of 0.5 mg/L is considered significant. And a value of 1 mg/L gives cause for concern. A correlation between the estimated DP using a thermal model and the 2-FAL concentration produced and dissolved in oil has been attempted. It is clear that the fitted curve based on De Pablo's function [80] can only give a rough indication of the averaged DP but cannot be used as a practical means for transformer condition monitoring. It also means that due to the

variable operating conditions and different design characteristics of the field transformers, it is not sensible to directly apply lab-derived correlations to field transformers.

One point that is worth to note is that for normally functioning transformers, the concentration of 2-FAL is below 5 mg/L with the highest value of 4.3 mg/L among 49 operating transformers around 2009. A value of 1.6 mg/L from continuously monitoring over 2 years on a large transformer around 1981 was also given [47], which is nearly 30 years ago. On contrast, in a failed 22/400 kV generator transformer due to an inter-turn fault on the LV winding of phase B overheating the paper insulation, the concentration of 2-FAL increased from 0.7 to 1.7 mg/L over a period of 16 weeks [47].

In conclusion, 2-FAL alone cannot be used as a marker for transformer insulation life time prediction because of the large scattering in field transformer measurement results of its concentration against the estimated DP of paper. Its concentration can also be affected by services and maintenance of transformers and it may also change with time over the service interval.

2.6 Existing Study on Transformer Ageing – Methanol and their Concentration Variation during Ageing

Methanol analysis is relatively recent in an attempt to prove its effectiveness as a transformer ageing marker. Although methanol was discovered relatively early in the 1960s its development was overshadowed by furanic compounds which were much more popular [33]. When low temperature overheating exists, electrical properties do not change significantly in short time but mechanical strength do change significantly. It was identified as an potential ageing marker when research was conducted in [23] via Headspace Gas Chromatography Mass Spectrometry (HSGCMS). Methanol was identified along with many other chemicals such as formic acid, propionic acid, acetone, ethanol, 1-butanol, etc. Experimental test results from [23] show that methanol is produced directly from cellulose rather than the ageing by-products of cellulose.

Similar to other chemicals detectable in transformer oil, use of methanol as a transformer ageing marker requires a number of criteria to be met, such as being stable in the transformer operational environment, known partitioning in oil and paper, and understood interactions with other chemicals [3]. Results of stability and partitioning experiments of methanol in oil-paper are shown in Figure 2.17 and Figure 2.18, respectively.

It can be seen that methanol stay stable up to 130 °C in oil and paper and the partitioned concentration settles down within 20 hours up to 80 °C and 400 hours at 130 °C. This settling time is acceptable in view of the fact that the service interval of transformers is in the order of 10000 hours. The methanol content in Figure 2.17 is seen to decrease, which is a result of it being absorbed by the paper insulation.

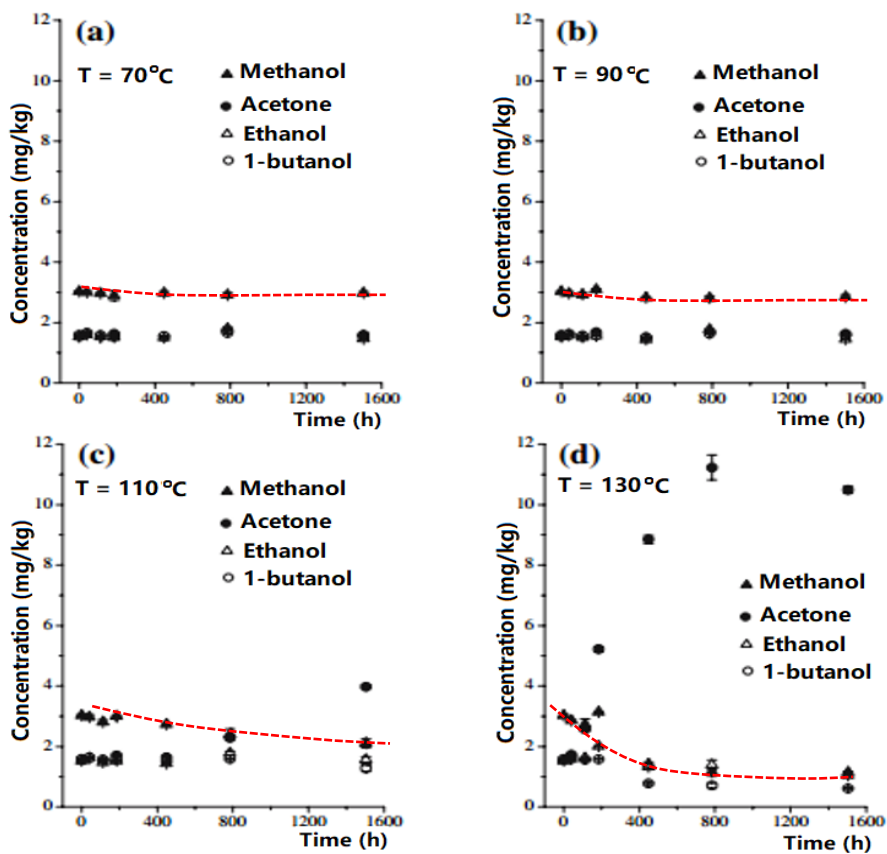


Figure 2.17 Stability measurements of methanol showing concentration vs time at different temperatures [23] in oil.

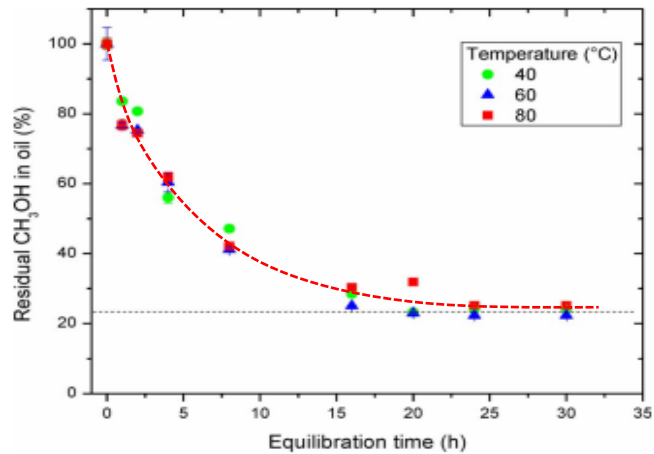


Figure 2.18 Partitioning experiments of methanol at different temperatures [82] in oil and paper system. The time to reach equilibrium is about 20 hours.

Methanol concentration in laboratory thermal ageing experiments was measured in [23] and [83] with different initial moisture level. Typical results are shown in Figure 2.19 and Figure 2.20. In Figure 2.19 it can be seen that there is a linear correlation of methanol and bond scissions up to a DP of 400 where the results become more scattered. It should also be noticed that the influence of moisture is insignificant on the methanol concentration. These results suggest that methanol could be used as an early paper ageing indicator. Figure 2.20 shows that methanol concentration has a linear relationship with DP, but due to the large scattering in the data, it is difficult to apply the relationship to predict the DP of the paper. More research is still needed.

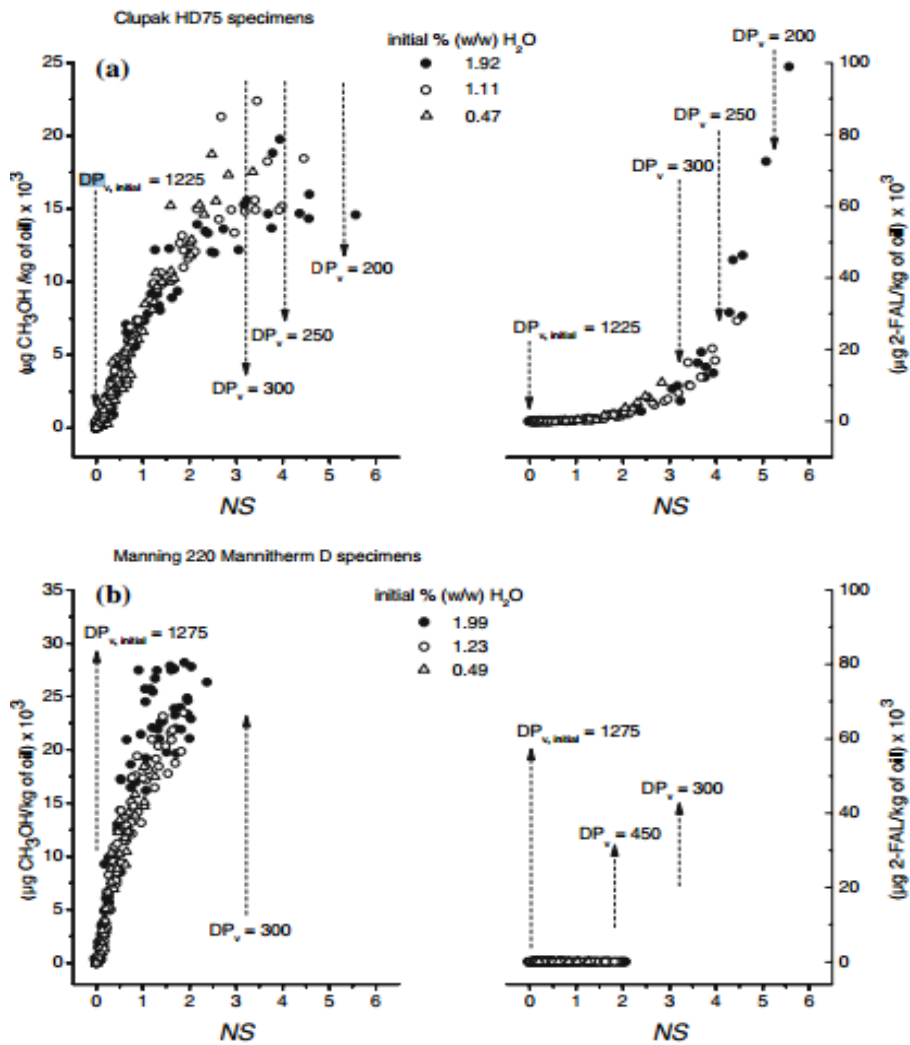


Figure 2.19 Correlation of cellulose bond ruptures with DP and 2-FAL in (a) Kraft paper, (b) Thermally upgraded paper [23].

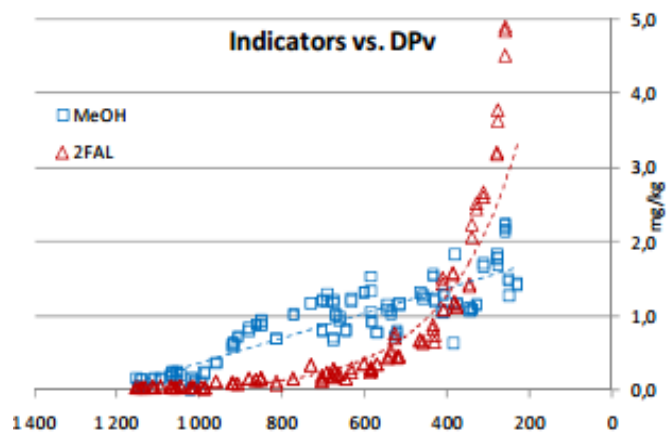


Figure 2.20 Correlation of concentrations of methanol and 2-FAL with DP for thermally aged paper insulation [83].

2.7 Existing Work on Transformer Ageing – Role of Water and Acids and their Concentration Variation during Ageing

2.7.1 Basics of Acids and Bases and their Theories

The theory of acid or acidity is a well-developed concept in chemistry and many other fields (e.g. chemical engineering, soil science, etc.) with hundreds of years of history dating back to the 18th century [84]. However, in the field of power transformers its relation to insulation materials has not been well understood, in particular the presence and activeness of acids involved in the weakening of the electrical and mechanical properties of the liquid-solid insulation system. To better understand the problem that acids contribute to ageing of insulation a good understanding is needed of the acid theories proposed; what is appropriate to the study and what makes acids harmful to the system.

Since the times of the ancient Greeks the concepts of “acids” and “bases” have been constantly evolving. Many scientists (Laurent Lavoisier, 1743-1796; Humphry Davy, 1778-1829; Justus von Liebig, 1803-1873; Svante August Arrhenius, 1859-1927; Gilbert Lewis, 1875-1946) have contributed to the incredible development of the theory, which has given greater understanding to further advance a science that is key to so many different fields [84]. In addition to this, was the development of the instruments that have allowed the possibility of measuring acidity accurately and precisely by the ingenious entrepreneurship of: Hermann Walther Nernst, S.P.L. Sørensen, Duncan McInnes, Malcolm Dole and Arnold O. Beckman. Both of these causes have allowed the study of how acids affect the “degradation environment” of transformer insulation today.

In modern times, there are two important acid-base theories. The first theory was initiated by Svante Arrhenius, a Swedish chemist, in 1884 [85]. He proposed one of the first favourable definitions for acids and bases known as the “Arrhenius acids and bases”. It stated that:

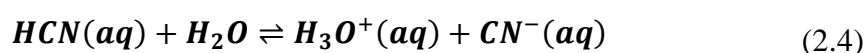
“An acid is a compound that contains hydrogen and reacts with water to form hydrogen ions. A base is a compound that produces hydroxide ions in water” [86].

This definition was found to be weak by chemists because it only addressed water as a solvent. In the case of non-aqueous solvents, the definition was no longer appropriate. In 1923, the definition was further developed by two separate chemists, Thomas Lowry and Johannes Brønsted, working independently in two different countries, England and Denmark, respectively [86]. They proposed a more in-depth definition suggesting that *the key process for a compound to function as an acid was the transfer of a hydrogen ion (proton) from one substance to another* [86]. This formed the Brønsted-Lowry theory, which defines [86]:

- acids as a proton donor,
- and bases as a proton acceptor.

In this thesis, for the ease of understanding, the term “proton” will mean an H^+ ion. As the acid donates a proton, the species that is left is called the conjugate base. Likewise the base that accepts the proton will be known as the conjugate acid. A good example of this occurrence is the reaction of hydrogen cyanide (HCN) with water (H_2O), as seen in (2.4). The HCN loses a proton to water to form an CN^- and H_3O^+ ion. The CN^- ion is known as the conjugate base of HCN because it accepts a proton to form HCN again.

The H_3O^+ ion is known as the conjugate acid.



The second theory is known as the “Lewis acid and base theory”. In 1923, Gilbert N. Lewis refined the acid-base theory to include dissolution events in non-aqueous solvents. It devised that [87, 88]:

- an acid is an electron pair acceptor,
- and a base is an electron pair donor.

This definition means a much wider range of substances were accepted as acids and bases, such as complex ions. When a Lewis acid accepts a pair of electrons from a Lewis base a coordinate covalent bond is formed [87, 88]. This is a bond in which both electrons come from one atom [86]. Under this definition a proton can be considered to be a Lewis acid because it can accept an electron pair. As a result, a Brønsted acid can

be considered a supplier of a particular type of Lewis acid (the proton). Similarly, a Brønsted base can be considered a particular type of Lewis base because it can donate an electron pair to form a covalent bond. Therefore, it can be understood that all Brønsted acids are Lewis acids but not all Lewis acids are necessarily Brønsted acids. This is because Lewis acids do not necessarily need to contain a hydrogen atom.

There are also a special group of acids and bases. These substances can react with both acids and bases. This behaviour is known as amphoterism. A common example of a molecule which exhibits this behaviour is water, which is generated during the ageing of transformer insulation. An example of this is shown in (2.5) and (2.6), where it can be seen water reacts with ammonia (NH₃) as an acid and with hydrochloric acid (HCl) as a base.



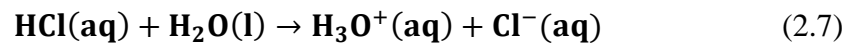
The medium that the water molecule is in affects how it behaves. A water molecule does not act as an acid molecule in an acid medium and does not act as a base in a basic medium. Therefore the medium of such acids is crucial to determining how their properties change.

The theory most appropriate to describe the acids and bases in transformers is the Brønsted-Lowry theory. This is because based on the study of literature it is well understood that the degradation of the paper insulation is closely linked with the production of organic acids and water. The theory defines both and therefore is sufficient without unnecessary complication [89].

There are many different types of acids in the transformer liquid-insulation system. It is however difficult to distinguish which acid groups exist and which do not. It is thus crucial to distinguish the type of acids that are present. Acids are divided into strong and weak acids. A strong acid will fully dissociate into a negative ion and a hydronium ion (H⁺) in a solvent; whereas a weak acid will only partially dissociate. Hydrochloric acid is a strong acid. For every molecule added to water there will be a chloride ion and

a hydronium ion. Therefore, it has fully dissociated. Acetic acid is a weak acid. For every 250 acetic acid molecules one acetate ion will be formed along with one hydronium ion.

The process in which a proton has migrated from one compound to another is known as a “proton transfer reaction”. This means hydrochloric acid can be said to be fully deprotonated in solution. The stoichiometric equation of this is shown in (2.7):



It should be noted that acid reactions are reversible, however, because strong acids become nearly fully deprotonated at any one time in solution it is often considered to be a one directional reaction.

Strong acids will be difficult to find in transformers. They are mostly removed during the processing stage of the paper insulation and any small amount will have reacted instantly based on its strong ability to dissociate in water. This means that nearly all acids studied in transformers are weak acids.

The acidity of the transformer liquid for in-service transformers are measured according to IEC 62021-1 (mineral oil) and IEC 62021-3 (non-mineral oil), which are commonly done via automatic potentiometric titration methods (more details are given in Chapter 3). The results are expressed as the total acid number (TAN), mg KOH/g, which is a measure of the amount of potassium hydroxide (KOH) used to neutralise the acids per gram of the sample. Typical acidity levels in in-service transmission transformers in the UK can be seen in Figure 2.21. The figure shows that a majority of transformers in most of their service lives will be within the “fair condition” of IEC 60422 [19].

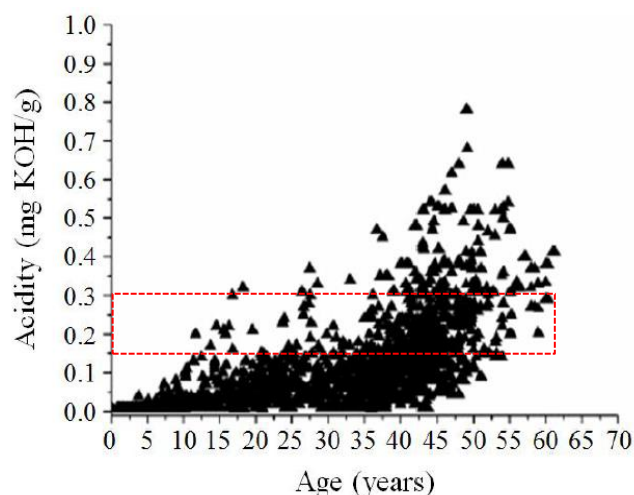


Figure 2.21 Plot of acidity (mg KOH/g) against age of in-service transformers (years) [90, 91]. The upper side of the rectangle indicates the low limit for poor performance transformer and the lower side indicates the fair performance transformer [90, 91].

2.7.2 Existing Study on Acids in Transformers – Total Acidity Measurement

Early research (up to 2000) on transformer insulation ageing focused on the measurement and profiling of the tensile strength (TS) and Degree of Polymerisation (DP) of transformer insulation paper and the generation of furfurals under different conditions (temperature, headspace medium such as vacuum or oxygen or air) and with different paper materials. The overall aim was to gain more understanding in the kinetics of the ageing process and to identify an ageing marker for transformer paper insulation. The progress was well summarised in the reviews by Emsley and Stevens [21, 73]. The reaction energy for Kraft paper ageing was found to be around 111 kJ/mol on average from a large collection of measurements. Furfurals were the focus in the measurement of the ageing by-products because of their close association with the ageing process of the paper. Acids drew little attention except the work by Painter [92, 93] and Ivanov [67] which was conducted in the 1970s. Painter explained from basic theory and proved by experiments the catalytic effect of acids in the hydrolysis of cellulose through the interaction of H^+ with the O linkage bonds between the glucose units in cellulose. The acids used in the experiment were aqueous sulphuric, phosphoric, hydrochloric and hydrobromic acids. The tests were performed in the temperature range from 30 °C to 100 °C depending on the strength of the acids. Although the work was not carried out directly for the investigation of transformer insulation ageing, it did

provide the very first evidences that acids are able to accelerate the hydrolysis of cellulose. Ivanov [25] further directed the influence of acids towards that of the low molecular weight acids (LMA). Emsley and colleagues [94-97] published a series of 4 papers in 2000 on the degradation of cellulose insulation in power transformers but acids were largely neglected in their discussions.

In the last two decades, there has been significant development in the research of the influences of acidity on transformer liquid and paper insulation [12, 14, 23, 24, 91]. There are many sources of acidic chemicals that could lead to acidity, especially in natural esters as a transformer insulation liquid [38]. Poor understanding of the chemical mechanisms transpiring during the slow ageing process in transformers is a clear limitation to the understanding of the role of acidity. Conjectures as to why acids are generated and how they decompose the insulation have been antagonizing engineers and scientists working in transformer research for a long time [12].

Lundgaard and colleagues reported their work on ageing behaviour of Kraft paper [12] in 2004 where the total acidity of the aged oil was measured. The insulation paper used was Kraft paper (strip size of 121x12 mm) of 19 layers per mm and weighed 75.8 mg per strip. The oil was a dried and degassed naphthenic, inhibited oil (NYTRO 10X). 1300 strips of paper (100 g) were placed in a bottle of 2.32 L that were sealed with lead screw caps. 1.8 kg of oil (~ 2 L) was used to impregnate the paper strips, giving an oil to paper mass ratio of 18:1. Each bottle had an expansion volume above the oil of about 250 cm³ filled with nitrogen. One feature that needs to be specifically noted is that whenever an oil sample (60 ml) was taken from the bottle, an equal volume of dried oil was injected into the bottle and the headspace was flushed with nitrogen to remove the air. This implies that the remaining liquid and paper left in the bottle were disturbed during the ageing process by the addition of new oil and the flush of headspace with nitrogen. Despite this, their work has shown that the total acidity of the oil slowly increases at 130 °C for dry paper, from nearly 0 to 0.03 mg KOH/g in 365 days despite the regular injection of new dried oil. What is interesting is the role of moisture added to the paper. With 1% initial moisture in the paper (moisture added before the paper was impregnated by dried oil), the acidity of the oil rise from nearly 0 to 0.04 mg KOH/g within only 83 days. With an added moisture level of 3%, the acidity of the oil rise to 0.23 mg KOH/g in 83 days. Unfortunately, no firm conclusion can be drawn on the

correlation between the acidity of oil and chain scissions with the absence of measurement uncertainty in acidity and DP. An additional difficulty in interpreting the results is that the types of acids present in the oil were not identified (LMA or HMA).

Acids found in the transformer liquid and solid insulation system are mainly carboxylic acids. It was further suggested in [14] that these acids can be separated into LMA and HMA. Experiments in [23], which identified methanol, also identified LMA in the ageing products. The LMA that were identified were acetic, formic, and propanoic acids. LMA are often determined by their low molar mass (M_r) in comparison to the longer chain HMA [12, 91]. From the work reported in [12, 14], three LMA and two HMAs were identified, and selected to represent the acid groups formed during the ageing process of cellulose paper. The properties of these acids are shown in Table 2.2. The logarithmic acid constant is a measure of how well an acid dissociates to form hydronium ions. A higher pKa value will generally have poor dissociation. Due to their high pKa values, the LMA have all been considered as weak acids.

The role of LMA in paper ageing was further studied in [24]. The acids were first added to the oil to obtain a particular acidity before the paper samples were impregnated. Formic acid as a typical LMA has strong affinity with paper. This is evidenced by the overwhelming drop of formic acidity in the oil from 0.38 mg KOH/g (prepared at room temperature) to 0.02 mg KOH/g at 130 °C when paper was impregnated in oil.

Table 2.2 LMA and HMA properties [2]

Acid Class	Acid Name	Main Origin	Molar Weight, M_r (g/mol)	Log. Acid Constant (pKa)	Water Affinity
LMA	Formic	Paper Ageing	46	3.8	Hydrophilic
	Acetic		60	4.8	
	Propanoic		74	4.9	
	Levulinic		116	4.6	
HMA	Naphthenic	Oil Ageing	240	5.5	Hydrophobic
	Stearic		285	4.9	

This shows that the majority of LMA are held in paper instead of oil. For stearic acid, there was only a very small drop in the acidity when paper was impregnated in oil, from 0.37 mg KOH/g to 0.34 mg KOH/g at 130 °C. The uncertainties in end-point determinations are estimated to be 5 - 20%. With this level of measurement uncertainty, the change of 0.03 mg KOH/g implies that stearic acid is hardly absorbed by paper. It must also be noted that in the work [24], only 80% of the added acidity can be detected using the titration method for oil and water extraction plus titration method for paper. This has to be taken into account if data are to be compared in a quantitative manner.

Results from [24] showed clearly the catalytic effect of formic acid in transformer paper ageing (Kraft paper), as reproduced in Figure 2.22 which will be referenced in Chapter 5. Five samples were taken from each bottle containing 100 g of paper and 2 L of oil at different times. It can be seen that there is a clear transition of the rate of change of DP when LMA were added, especially the formic acid. This sudden change was smoothed when the molecular weight of the added acids increases. The second pattern was that the added moisture in the paper significantly shortened the time for the DP to decay to 200, from 65 days to 20 days based on the trend lines for formic acid. With the same amount of moisture of 2.4%, the addition of formic acid reduces the time to half the DP from 9 days to 2 days.

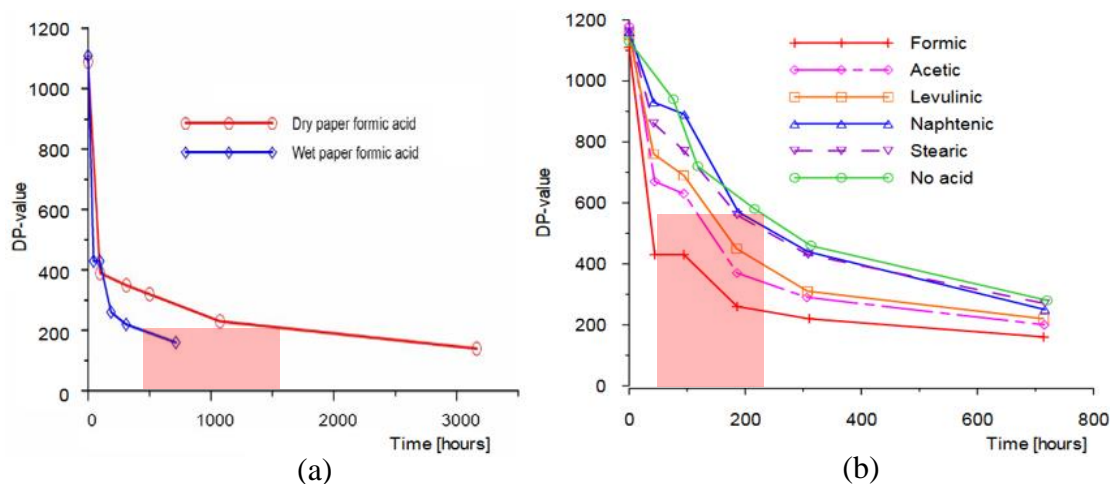


Figure 2.22 Results reproduced from [24] on the effect of acids on the ageing rate of transformer paper insulation (Kraft paper). (a) effect of acid with (2.4%) and without (0.75%) added moisture; (b) comparison samples all with an initial 2.4% of moisture in paper.

While the results above provided clear evidence of the catalytic effect of LMA in paper ageing, no measured acidities in the oil and paper samples were given for different ageing durations. No further quantitative correlation can be performed on the acidity of oil or paper with the DP under different conditions. More tests on the role of LMA in transformer paper ageing were performed in 2008 [14] with more moisture levels used. From Table 2.3 it can be seen that water and acids have a multiplication effect on the acid catalysed ageing of paper insulation. This multiplication effect is quantized by the ratio of reaction rates with reference to that without acid or moisture added. The reaction rate is calculated as the gradient of the chain scission curve as a function of time. Formic is twice active in comparison with acetic acid. With the introduction of moisture, the rate of reaction is approximately doubled.

Table 2.3 Accelerated multiplication effects of moisture and LMA [14] on the initial ageing rate in comparison with dried paper and oil. (dry 0.75%, wet 2.4% of moisture)

Acid type	Formic	Acetic	Levulinic
Dry cond.	5.6	2.6	1.6
Wet cond.	11.6	4.4	3

A post mortem study on retired transformers was performed in [64]. The tensile index of the papers, measured on the bottom part of the HV winding of a 37-year-old 275/66 kV, 180 MVA transformer, changes from 20 Nm/g for the near-oil paper layer to 70 Nm/g near the current carrying conductor. The LMA content varies from 7 mg KOH/g near the oil to 3 mg KOH/g near the conductor among the multi-layer paper insulation around the winding. Laboratory tests were also performed with Gemini X (mineral oil) at 110 °C under dry (0.5% weight) and wet (3% weight) conditions and with and without added acids (formic and stearic acids). The ageing of oil and paper (200 ml : 2 g of paper) was conducted in containers sealed with PTFE screw caps. The initial acidity level in oil is between 0.2 – 0.35 mg KOH/g for LMA and 0.16 – 0.24 mg KOH/g for HMA. Both acidity levels were lower than the typical values measured from real transformers (37 years old). Similar to the conclusions drawn in [24], HMA added to the oil hardly affect the degradation of paper, as shown in Figure 2.23. Under wet conditions (3% moisture in paper) the paper ages much faster. However due to the large

scattering in the measurement results a quantitative description of the effect of the moisture and LMA is challenging.

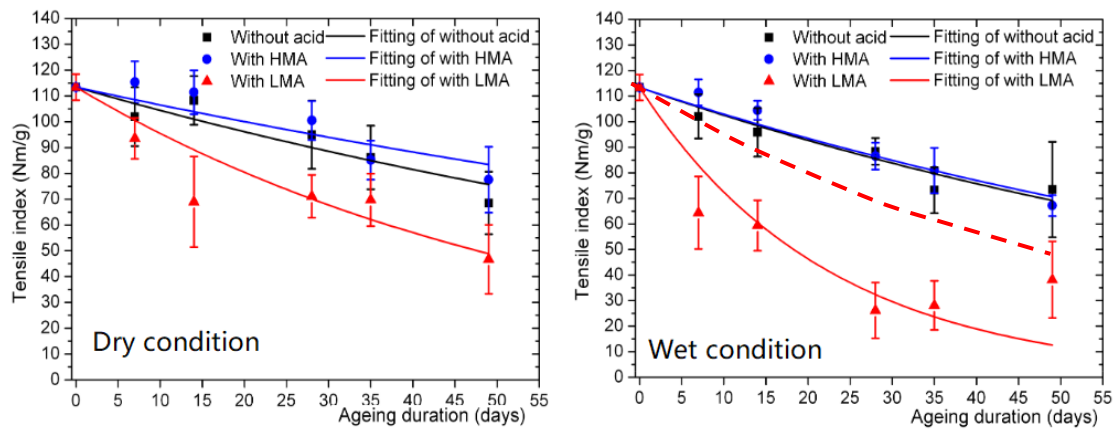


Figure 2.23 Results from [64] on the catalytic effect of acids in transformer paper ageing at 110 °C. The initial tensile index of the paper is 113 Nm/g. The broken line is the trend line for dry condition with LMA.

More recently, the total acidity in ester fluids during the ageing process of Kraft paper with a density of 1.08 g/cm³ and thickness of 0.3 mm at 130 °C using sealed stainless steel containers was measured [98]. The natural esters used in the experiment contain stearic, palmitic, oleic and linolenic acids with different concentrations. Three LMA (formic, acetic and levulinic acids) were added to the liquid to obtain a target acid number of 3 mg KOH/g as the initial condition for ageing. Apart from the result that the acidity number increases substantially within 50 hours at 130 °C, interpretation of the results is difficult because the initial content of different acids were not given, especially those that can potentially affect the ageing of the paper.

The generation of acid by-products is generally understood to be due to hydrolysis of the cellulose molecular chains. In [12], it describes that some molecular degradation reactions which can lead to generation of LMA. The hydrolysis reactions will produce two main types of furanic compounds. They are 2-FAL and 5-HMF. 5-HMF is not stable and can dissociate to form levulinic acid and formic acid. However, these acids might not be stable and can lead to the production of other by-products. Formic acid can further decompose to produce carbon monoxide and water. For levulinic acid, it

can polymerise under certain conditions to form “caramel”, which is an acidic polymer found in sludge [12].

Table 2.4 was constructed based on results from [26], showing results of extraction of in-service aged hydrophilic acids from oil using the water extraction method. The most apparent feature in the results is that water based extraction of the LMA leads to a loss of the total acidity measured. This means the sum of Column 3 and Column 4 is less than Column 2. The separation of the LMA from the oil results in an efficiency between 87% - 100% for the total acidity. The actual amount of LMA that was obtained by water extraction (Column 4) is significantly lower than the amount of acids removed from the liquid by water extraction, which is supposed to be LMA (Column 7 = Column 2 – Column 3). The LMA extraction efficiency ranges from 28.6% to 98.4% (Column 8). The percentage of LMA out of all acids in the service aged oil is mostly 13% on average with a highest value of 28%. Therefore in oil, LMA form a minority group.

Table 2.4 Measurement of TAN and LMA of service aged oils (mg KOH/ g) [26].

Column 1	Column 2	Column 3	Column 4	Column 5	Column 6	Column 7	Column 8
Oil sample	TAN in original oil	TAN in oil after water extraction (HMA)	In water after extraction (LMA)	Percentage of TAN detected using water extraction (LMA+HMA)	Percentage of LMA out of all acids, removed from oil by water extraction (%)	LMA removed by water extraction mg KOH/g	Percentage of LMA detected using water extraction (%)
A	0.076	0.066	0.007	0.960	13.2	0.010	70.0
B	0.156	0.135	0.006	0.900	13.5	0.021	28.6
C	0.195	0.170	0.017	0.960	12.8	0.025	68.0
D	0.259	0.227	0.026	0.980	12.4	0.032	81.3
E	0.369	0.308	0.060	1.000	16.5	0.061	98.4
F	0.566	0.408	0.084	0.870	27.9	0.158	53.2
G	0.150	0.130	0.012	0.950	13.3	0.020	60.0

Results in [26] also show that water and LMA exhibit very similar behaviour in their partitioning between transformer liquid and paper. The ratio in oil and paper is around 1: 100 at 130 °C. It was also found that the LMA acidity of paper measured with the water extraction procedure adopted in their work was on average 20% below the true value derived from mass balance. The extraction rate is in particular low for formic acid in dry paper, which is probably because the relatively low acidity and the volatile nature of the formic acid.

Another important observation that can be made from Figure 2.24 which is from [64] is that the correlation between the mechanical strength of the insulation paper and the measured LMA concentration in paper, whether from laboratory based test or field transformers, shows a clear trend that LMA concentration is affected by the ageing state of the transformer paper. For retired transformers, the sampling process and measurement of LMA takes time and the measurement method may not be accurate because LMA are volatile. It is also an issue that the location of sampling may cause the scattering in data. The LMA may also be affected by the services carried out on the transformer when oil is reclaimed and purified. Therefore, more research is needed on the potential of LMA in oil as an ageing marker for transformer insulation paper.

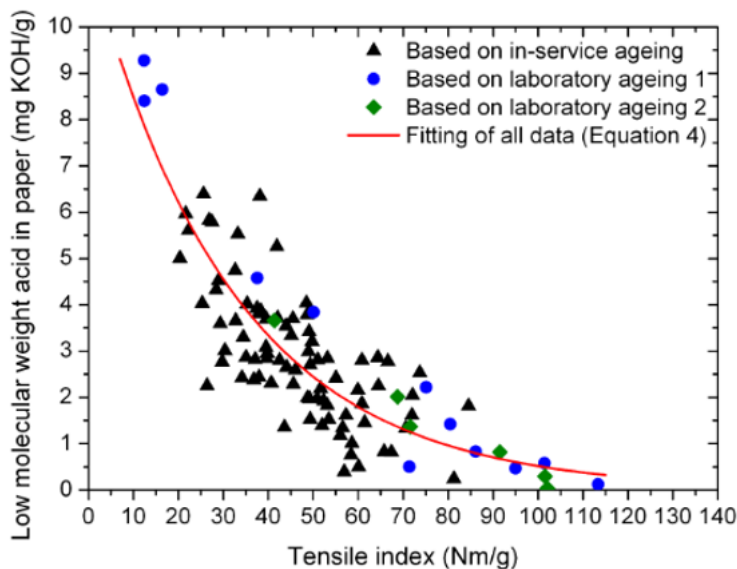


Figure 2.24 Results from [64] showing the correlation between the concentration of LMA in paper and the mechanical strength of the insulation paper. Equation 4 in the legend of the diagram is $LMA_{\text{paper}} = 11.6\exp(-0.03TI)$ where LMA_{paper} is the LMA concentration.

2.8 Summary

The literature review carried out in this chapter shows that much understanding on the insulation ageing process of power transformers has been gained over the past 60 years. Hydrolysis and oxidation play a more important role in the paper degradation process than pyrolysis in normal operations of transformers. The latter only becomes important

when severe overheating occurs, such as under heavily loaded or fault conditions. The following can be stated based on the review of existing work:

- Dissolved gas analysis and furan measurement in oil are the most commonly used means for transformer paper insulation monitoring.
- Methanol is directly related to the ageing of transformer insulation paper and the trend of increase with the decrease in paper mechanical strength is clear from test results. There is good correlation at the initial ageing stage.
- LMA are directly related to the ageing of transformer paper insulation, but no conclusion can be drawn on its potential as transformer paper ageing marker since there is a lack of baseline data.
- Huge fluctuation (scattering) in data (furan and methanol in oil) obtained from field transformers (active or retired) was observed by different researchers. This scattering may be related to the sampling location and further influenced by the treatment of oil during transformer maintenance. More research is needed.
- It was reported that only 80% of the LMA in paper could be detected due to the lack of a standard on LMA measurement. In certain work, there was evidence that only 35% of the LMA were detected. Therefore, there is a pressing need to develop an LMA measurement method that is sufficiently accurate for measurement of LMA in transformer oil and in paper.

CHAPTER 3

3 EXPERIMENTAL METHODOLOGY

3.1 Introduction

This chapter is to provide an organised description of the ideas, strategy, design and procedure carried out in the laboratory ageing experiments. A flowchart is shown in Figure 3.1 summarising the systematic approach of the experimentation in this and the following chapters.

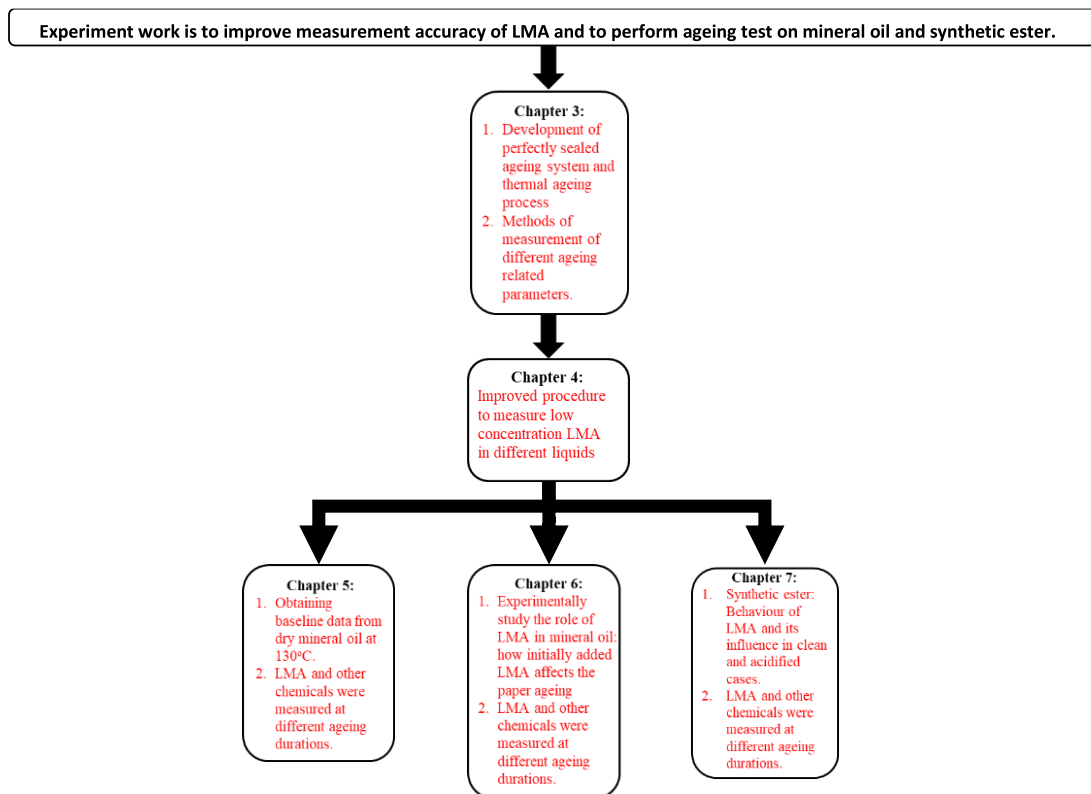


Figure 3.1 Flowchart of methodology for experimental work in the corresponding chapters

The thermal ageing environment is first considered and determined based on the literature review in Chapter 2 and according to the objectives of this project. The basic properties of the liquid and paper insulation mediums are introduced. Then, the conditions of ageing are discussed and set for the purpose of this research. The experimental procedures for ageing and measurement of different parameters are

afterwards developed. This is followed by the description of the measurement system for different parameters, such as the Degree of Polymerisation (DP) of paper, moisture level and acidities in paper and liquid, 2-FAL and methanol in liquid. Attention is also paid to the accuracy of the measurement so adequate confidence can be invested in the results in the following chapters.

3.2 Thermal Ageing Environment

Laboratory based thermal ageing is an effective method of studying and analysing the ageing of transformer liquid and paper insulation. It experimentally simulates the degradation of transformer oil and paper through the use of a controlled thermal environment. An air circulating oven is normally used to create and control this thermal ageing environment. The natural ageing process of solid transformer insulation is extremely slow with a typical time scale of approximately 20 years [99]. Accelerated thermal ageing aims to obtain ageing data on a much shorter time scale yet these data bear similarity to the data from naturally aged insulation mediums. Laboratory ageing can therefore be used to test the potential of ageing markers for condition monitoring of power transformers.

As explained in Chapter 2, transformer paper ageing is a process involving complicated chemical reactions. In theory, each chemical reaction has its time constant which is determined by the reaction rate coefficient. A large rate coefficient means a smaller reaction time constant. It is well known from fundamental chemistry that the rate coefficient is directly related to the activation energy of the reaction and the energy available for reactions. For a thermal equilibrium system, its energy is controlled by the temperature. Therefore increasing the temperature elevates the reaction rate coefficients and accelerates the chemical reactions and thus the ageing process.

The ageing process of in-service transformers takes place within a temperature limit of 95 °C and 105 °C, corresponding to a winding temperature rise of 55 °C and 65 °C at a maximum environment temperature of 40 °C. These temperature limits are not frequently reached during the operation of a transformer. The ageing process is exponentially accelerated with rise in temperature (Figure 3.2).

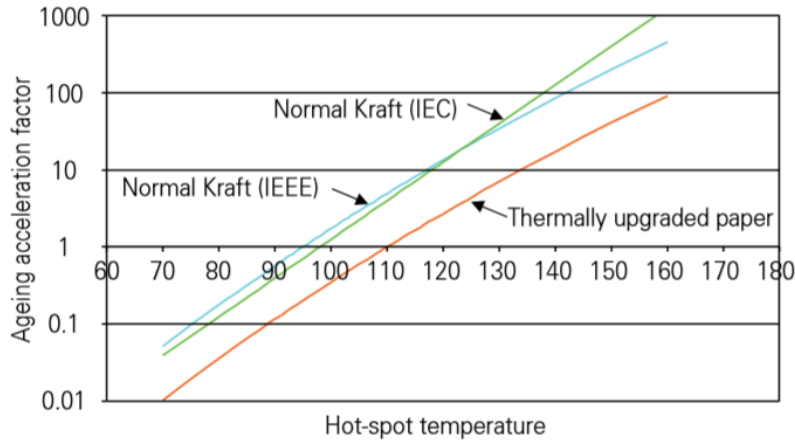


Figure 3.2 Diagram indicating the trend of acceleration of paper ageing with rise in temperature [100].

The temperature of the laboratory based thermal ageing was determined based on the trial tests and also results reported in the literature. A temperature of 130 °C was used considering the data obtained earlier in the same group [101] that the DP of Kraft paper decreased to around 200 in less than 75 days in the laboratory environment at 130 °C and also that using an acceleration factor of 35 from Figure 3.2, 75 days is equivalent to around 7 years of life expectancy of a transformer at, constantly, the upper operational temperature limit which is 98 °C.

To obtain the variation of the parameters associated with transformer liquid and paper as a function of ageing duration, samples placed in the oven at the same start time are taken out on different days. The different durations are determined to achieve maximum resolution of the variation of the parameters, such as the data points shown in Figure 3.3. It is known that the DP of Kraft paper decreases quickly at the initial stage of ageing. It is thus necessary to have more data points within the first 10 days. The schedule of sampling in the present work is detailed in Table 3.1.

Table 3.1 Schedule of sampling of aged transformer liquid and paper

Number of samples placed in oven	24-30								
	Complete Days of ageing	0	1	2	4	7	10	20	40
Sampling order	0	1	2	3	4	5	6	7	8
Number of samples taken out	N/a	3	3	3	3	3	3	3	3

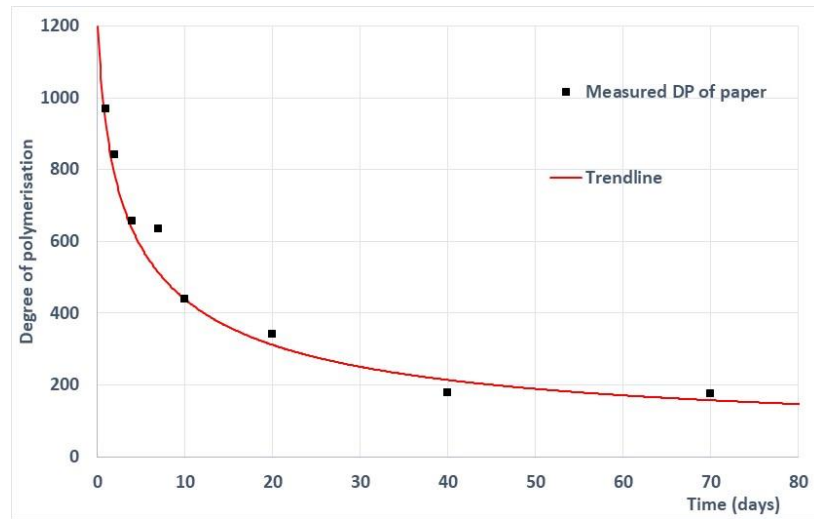


Figure 3.3 Example of sampled ageing data (degree of polymerisation) obtained in the present work at a temperature of 130 °C. This example is for Blank Gemini X without initially added acids.

Since the ageing tests for multiple samples were carried out, it is necessary to have nearly identical, if not perfectly the same, ageing environment for all samples. In this research the ageing environment is created in an air circulated oven (Brand: Binder) which has two levels to place the trays holding the samples (Figure 3.4). The following guidelines are followed to create uniform ageing environment for different samples:

- Sufficient space is maintained between the samples (Figure 3.4) to allow the heated air to circulate at speed to create uniform temperature field in the oven. This is because convection is more effective than thermal conduction in space with negligible temperature gradient.
- Samples are placed a certain distance (>2 cm) away from the oven wall to minimise the effect of the temperature gradient closer to the wall.



Figure 3.4 External and internal appearance of the Binder oven used for thermal ageing of the transformer insulation oil and paper.

Figure 3.5 shows the planned layout of the samples in the oven. The green colour in (a) indicates the possible location of the ampoules on the tray and red are empty locations. This arrangement is chosen to allow the heated air flow to be more evenly distributed around all the ampoules rather than that in a compact arrangement. This should minimize the possibility of hotspot regions occurring. In (b) the intended age of the ampoules arranged in the formation are approximately indicated.

Aged samples are to be removed at a certain period of time. The samples closer to the door were removed first to reduce the interference time of ageing for the other samples. This will make the process of sampling smoother. The samples were labelled with a special code to indicate ageing type, ageing liquid, temperature, time, and sample number (as seen in Figure 3.5 (c)).

Given the length of the ageing and the measures to maintain a uniform temperature distribution in the oven, it is justifiable to state that the ageing takes place in thermal equilibrium conditions. Relevant theory developed under thermal equilibrium can thus be used to interpret the experimental results.

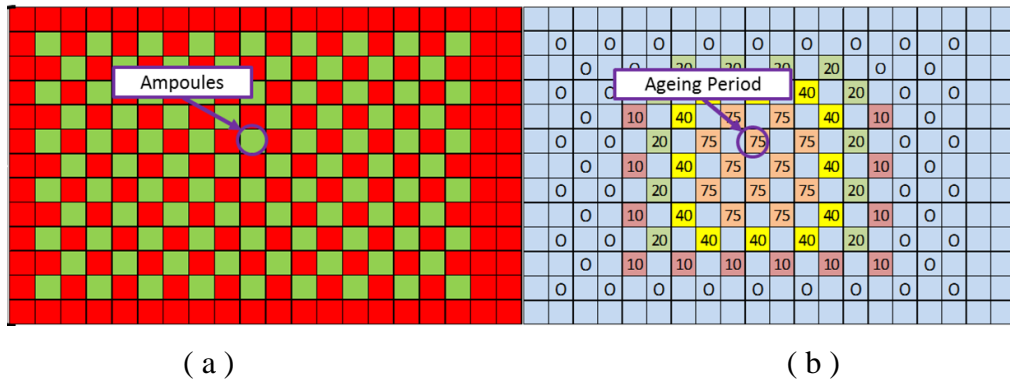


Figure 3.5 Example of ampoule configuration for the tray on each level in the air circulated oven. (a) space for air circulation around samples and (b) layout of samples intended for different ageing durations. (c) sample labelling code where A is ageing type, B is ageing liquid, C is temperature, D is time, and E is sample number.

3.3 Selection of Liquid and Paper Insulation Materials for Ageing Experiment and their Pre-treatment

Kraft cellulose paper was used for solid insulation in liquid filled transformers. It is in fact the most common type of paper insulation found in transformers in the UK power networks [2]. The transformer liquids that were used are: Gemini X (an inhibited transformer mineral oil) and MIDEL 7131 (a synthetic ester). They represent, respectively, the most commonly used traditional transformer oil and the newer biodegradable insulation liquid that has gained fast growth in the past decades [24].

As-received liquids were pre-processed to eliminate the effects of any unexpected contaminations. Gemini X was first filtered using nylon membrane filters of pore size 0.2 μm . This process can take up to 3 hours to filter a litre of oil. Next, it was dried in the vacuum oven at 85 °C for 24 hours at a pressure of 5 mbar. MIDEL 7131 was also filtered using the same size filter as the mineral oils. It was dried at 85 °C for 72 hours. The drying of synthetic ester is longer than the mineral oil because of its higher affinity for water. The water content of the insulation liquids should be around 10 ppm for

mineral oil and 20 ppm for synthetic ester in order to perform expected thermal ageing experiments.

Kraft paper must be dried before it is used in the thermal ageing experiments. The Kraft paper was first cut into strips of 48.5 cm length to achieve a paper to oil ratio of 20:1 for the ampoules used, as shown in Figure 3.6. Care has been taken to not contaminate the paper in the handling process. The strips are then rolled up, fastened and placed in the air circulating oven for 24 hours at 105 °C. After that, they are impregnated with dried mineral oil or synthetic ester and the liquid-paper sample is again dried in a vacuum oven at 85 °C for a further 24 hours. The moisture content of the paper after treatment should be around 0.5 % (in mass).



Figure 3.6 Cut Kraft paper that was ready to be dried in oven

3.4 Determination of the Initial Conditions for Ageing

To study the ageing behaviour of the paper-liquid system, it is important to define the initial conditions of the ageing process. Apart from the ageing environment that is discussed in Section 3.2, the initial conditions of the paper and liquids need to be defined. In the present work, one important objective is to study the role of acids, especially the low molecular weight acids (LMA). One of the options is to set a different initial acidity level for the acids to find out how sensitive the ageing process is to the initial presence of the acids. As mentioned in Chapter 2, four types of LMA have been identified in the ageing process of transformer paper insulation, which are: formic acid,

acetic acid, propionic acid and levulinic acid. The basic properties of the LMA and HMA acids are shown in Table 3.2.

Table 3.2: Basic physical properties of the acids that are present in the ageing process of transformer paper insulation [2, 23, 50].

Acid	Mr (g/mol)	pKa	T _{boil} (°C)	Water solubility (at 25 °C) (mg/L)	Flash point (°C) (closed cup)
Formic	46	3.75	101	1,000,000	69
Acetic	60	4.75	118	1,000,000	39
Propanoic	74	4.87	141	1,000,000	52
Levulinic	116	4.64	245.5	5,238,000	98
Stearic	284	10.5	350	0.597	196

Formic, acetic, propanoic, and levulinic are carboxylic acids (containing the COOH group). The molecular weight, M_r , of the LMA are from 46 to 116 g/mol. Heavier acids, such as stearic acid (284 g/mol), are considered HMA. The pKa is the negative value of the logarithm of the acid dissociation constant [102]. It is a measure of the level of difficulty for the dissociation of the acids to form hydronium ions. A high pKa will result in weak dissociation of the acids and vice versa for a low pKa. The boiling temperature follows the M_r closely. As the M_r increases, the boiling point of the molecules also increases. The water solubility of the LMA are many orders of magnitude higher compared to that of the stearic acid. This property is highly relevant to the present work and due to this property water was used to extract the LMA from the transformer liquid. The flash point may not be directly linked to the ageing experiment results, but it is an important factor to be considered for experimental safety. The closed cup point is obtained in an environment closed off to the atmospheric air and an ignition source is available to ignite the vapour. Due to their low concentration, the risk to catch fire by the acids is low. The samples used in the ageing experiments have different initial conditions of acid and water content. The typical initial conditions are summarised in Table 3.3.

Table 3.3: Typical initial conditions used for the ageing samples

Liquid	Acids	Dry (low moisture)	Blank (no added components)	Added LMA
Gemini X	Formic	Yes	Yes	Yes
MIDEL 7131	Formic	Yes	Yes	Yes

3.5 Consideration of Samples and Issues Associated with Sample Preparation

There will be at least two samples intended for each ageing condition. This will help establish the repeatability of the results. Taking into account the number of insulation liquids and LMA, it would mean for the dry condition there would be approximately 128 ampoule samples.

Glass ampoules are used to contain the mixed liquid, paper or LMA samples. After the measurement of each element, they will be sealed together using a micro flame burner around the neck and then placed on trays for thermal ageing.

One of the limitations in existing thermal ageing experiments is that the samples were contained in bottles that were sealed by screw caps. Although, it was performed with care but the system was not perfectly sealed and over the long period of the thermal ageing there was a possibility that the volatile species produced during the ageing process escaped from the container, leading to inaccuracies in the measurement results. The use of flame sealed ampoules to contain the samples during the thermal ageing process completely eliminates the possibility of mass exchange between the samples and the environment. This allows stricter ageing conditions to be set and contamination of the samples by air ingress is no longer a concern. Work in Chapters 5, 6, and 7 will be carried out using this perfectly sealed system for thermal ageing experiments.

Having an acceptable repeatability of the experimental results is crucial to the accuracy and credibility of the work. At least three samples aged under the same conditions for the same period of time and measured using the same technique are expected to produce results that are close to each other within the estimated measurement uncertainty. At

least two samples are selected due to the time constraints for preparation of samples, space of the oven, and availability of equipment use.

An improved method of controlling added acidity and distribution of acidity in transformer liquid was developed.

One of the main difficulties during experiments of previous work was the addition of LMA and HMA into the insulation liquid. Formic acid is a strong LMA and small amounts of less than 0.1 ml can cause a significant difference in the TAN measurement. There was difficulty in controlling the addition of LMA to such a high degree of accuracy due to the limitations of equipment. The hypodermic syringe had an uncertainty of 0.5 ml, which was far off the accuracy range required. Thick safety gloves hindered the control further. The measurements were not very stable and it was difficult to reproduce the same TAN measurements. In this project, more advanced equipment is introduced in order to solve the problem of the accuracy and stability of TAN measurements for the addition of LMA to liquid insulation. A 500 μL gas tight syringe with a hypodermic needle is used which has an uncertainty of 0.5 μL . Tight safety gloves were also introduced to allow better control of the syringes.

Below are acid stability measurements for formic acid that have been done with the more advanced equipment. The results can be seen in Figure 3.7. Samples were taken from the bottom and top of the mineral oil mixture in the bottle of 200 ml Gemini X. This was done to check whether the distribution of formic acid was uniform in the liquid mixture. Approximately 30 μl of formic acid was added to the Gemini X. The mixture was then left to mix overnight on a magnetic stirrer with no heat added. After 24 hours the acidity of the samples was measured.

From Figure 3.7, it can be seen that good repeatability and uniformity in the measurements taken. The red dot represents an anomaly and it is judged to be a result of the sample being taken too close to the top boundary layer of the mineral oil mixture. A different colour in the legend key of the graph represents a different sample prepared in a different bottle and the values by the coloured diamonds are the added formic acid mass (g) to a bottle. The average TAN value is calculated to be 0.243 mg KOH / g oil.

The standard deviation is calculated to be 0.00732, which is quite small and satisfactory for the level of accuracy required for the experiments.

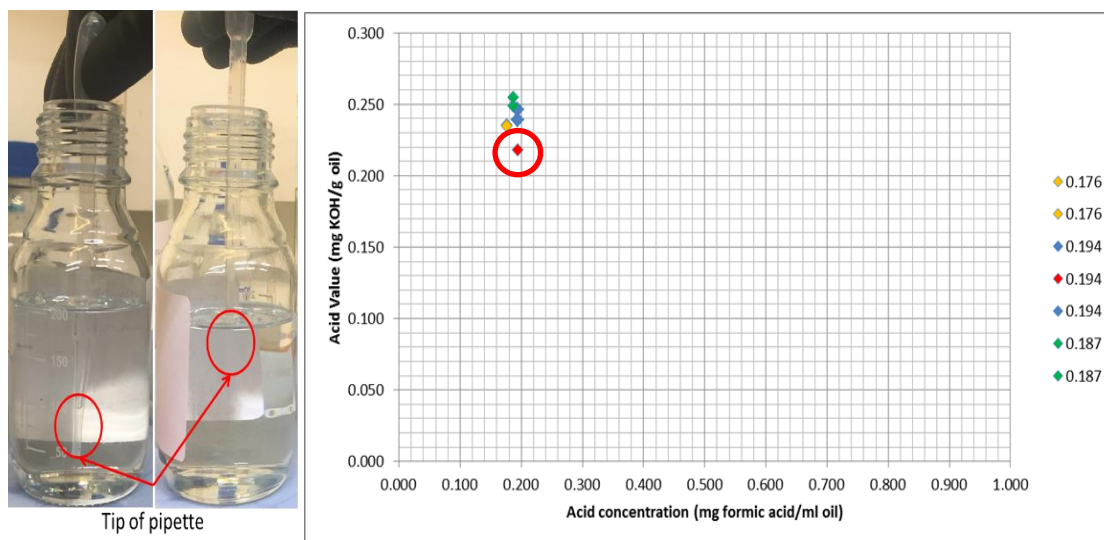


Figure 3.7 Location in bottle where samples are taken and results showing the stability of formic acid measurements. Red diamond point was from a sample taken on the top interface of the oil.

The solubility of acids needs to be determined in order to control the initial acidity of the ampoule samples for the thermal ageing experiments. LMA acids also need to be tested with the different insulating liquids. Figure 3.8 shows the experimental results for the dissociation of formic acid in filtered and dried Gemini X.

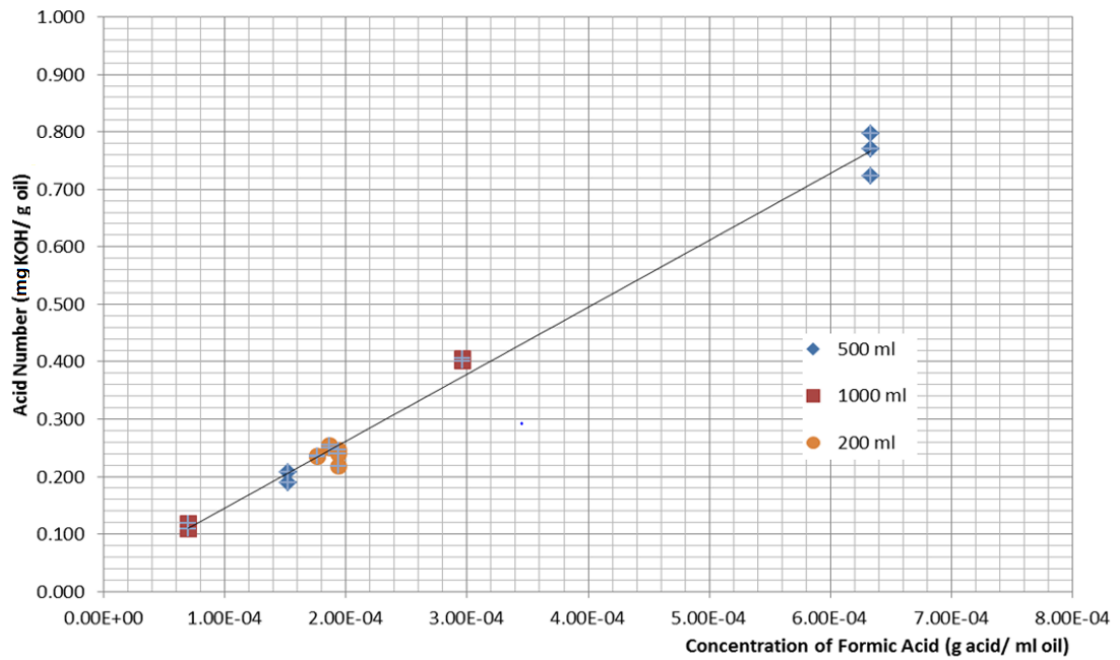
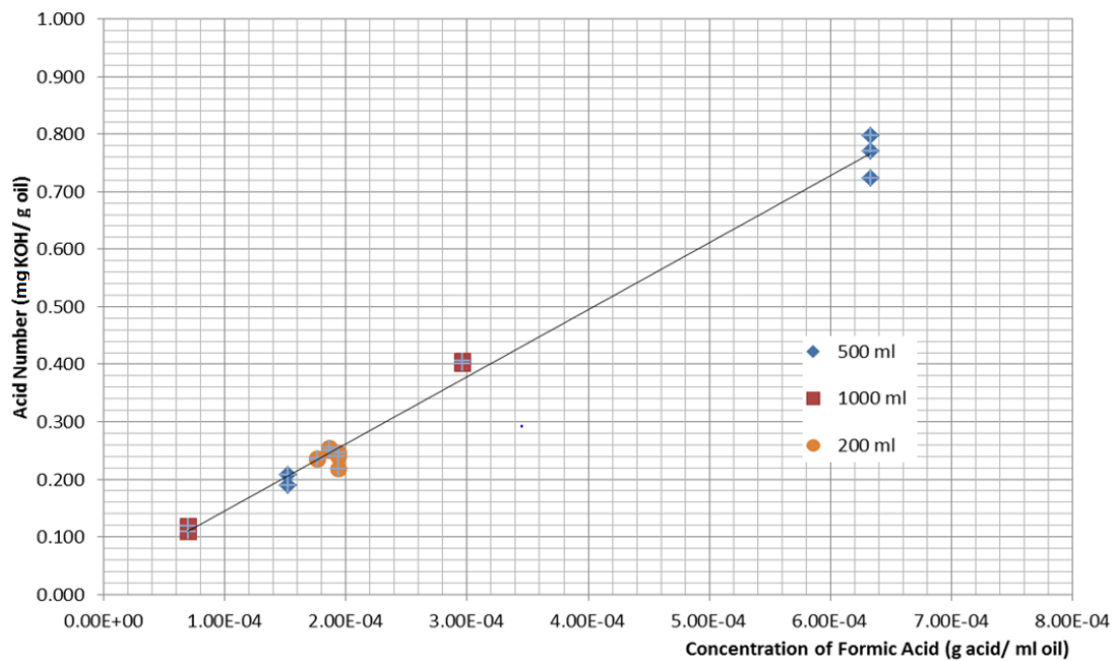


Figure 3.8 Relationship between the total acidity number and the amount of formic acid added to Gemini X.

Formic acid of different mass was added to 200 ml, 500 ml or 1000 ml of Gemini X.

The values in the x-axis in Figure 3.8



was calculated via Equation (3.1) below

$$\text{Concentration (g acid per ml oil)} = \frac{\text{mass of acid added (g)}}{\text{volume of oil (ml)}} \quad (3.1)$$

The results show a good linear correlation and range of acidities tested (acidity values in the range of 0.1 to 0.8). The different volumes of acid used are within the range and sufficient quantities used for experiments in this project. Each sample was measured twice and the acidity values are almost the same so the average standard deviation for the different volumes of oil is 1.17×10^{-04} . The results have excellent repeatability.

Figure 3.9 shows the experimental results of the stearic acid being added to Gemini X. The concentrations were worked out using Equation (3.1). The results show good linearity for the range of acid numbers between 0.01 to 0.5 mg KOH/g Oil.

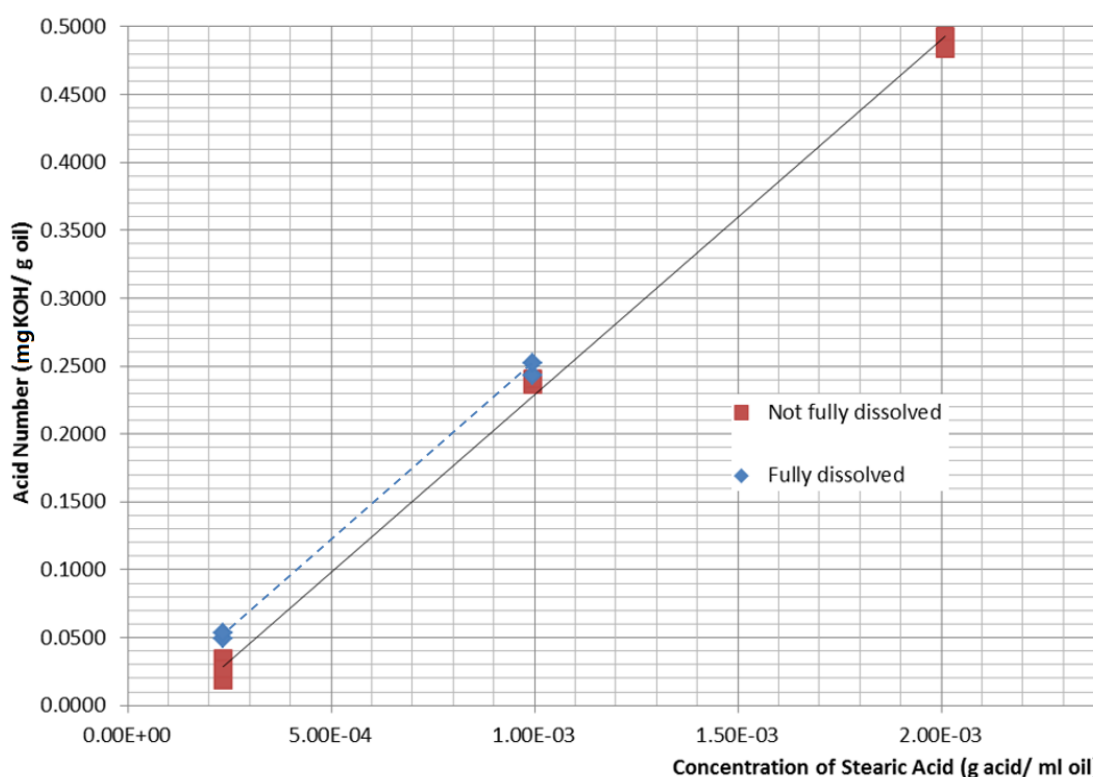


Figure 3.9 Relationship between the total acidity number and the amount of stearic acid added to Gemini X. The volume of Gemini X is 500 ml.

Different masses of 0.498 g, 0.1174 g and 1.0043 g of solid stearic acid were added to 500 ml of Gemini X. The acids were then mixed by a magnetic stirrer which had heating capability for 24 hours. The stearic acid samples were initially stirred without heat. Due to the poor solubility of stearic acid there was a suspension of acid granules, this can be seen in Figure 3.10. Afterwards, heat was added to try to fully dissolve the stearic acid. After three hours of stirring with stearic acid at 85 °C, the acid was fully dissolved in

Gemini X with no suspension of granules visible. From Figure 3.9, it can be seen that with the addition of heat the stearic acid has a slightly higher TAN value. The difference is contributed to the poor dissociation properties, i.e. large pKa value, that stearic acid has (Table 3.2).

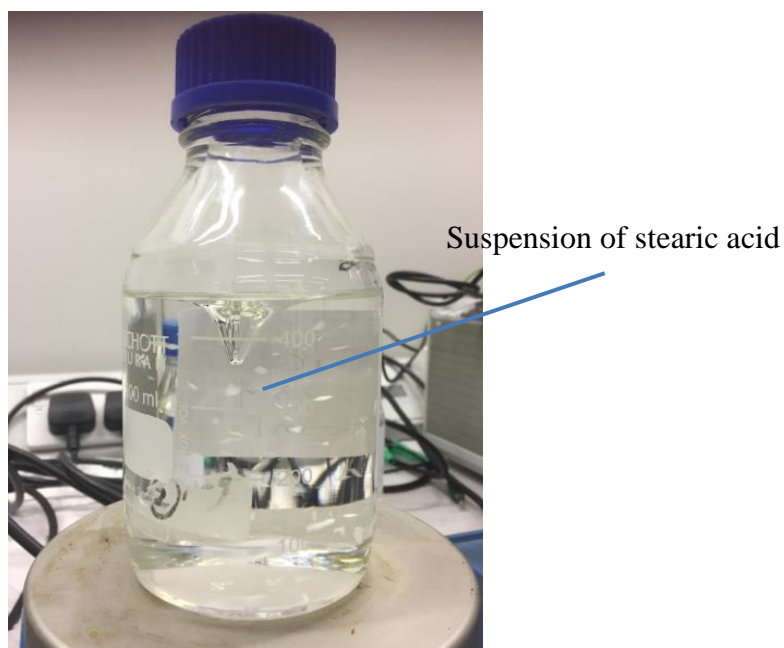


Figure 3.10 – Magnetic stirring being applied to the mixture where stearic acid was not fully dissolved.

Formic acid is a volatile LMA. A basic experiment was done to investigate whether there were any leakages of the acid escaping from the liquid into gas, as shown in Figure 3.11. pH litmus paper was placed on the top of an open bottle of sample, which has formic acid and Gemini X. Photos to capture the pH change were taken. It can be seen that the litmus paper changed from yellow to pink after 2 days. This corresponds to the pH of formic acid which is 2.2 at 20 °C. In the ageing test reported in Chapters 5-7, the samples are well sealed and no LMA will leak out.

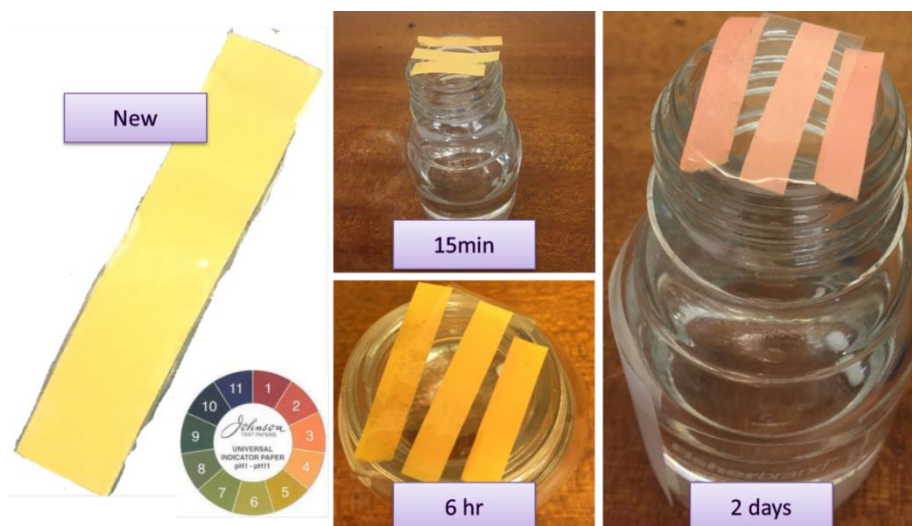


Figure 3.11 Change of the colour of the litmus paper to show formic acid vapour leakage.

3.6 Measurement Methods, Operational Requirements and Estimation of Measurement Accuracy

Previous literature work did not leave samples long enough before sampling and this may cause inaccurate results when sampling at room temperature due to the partitioning equilibrium [103]. Therefore, aged samples were placed in room temperature for at least three months before they were tested. This allowed the molecules in the samples to reach equilibrium and partition completely. At room temperature and in the sealed environment no ageing effect is expected to take place before the acidity and other parameters were measured.

3.6.1 Selection of Standard for Acidity Measurement.

Historically, the standard procedure used in the laboratory at the University of Manchester was the ASTM D664-07 (2001), which is complex and some of the chemicals that it uses are carcinogenic and hazardous. The IEC 62021-1:2003 and 62021-3:2014 standard did not have these problems and therefore they were used to perform acidity measurements in the present work. Table 3.4 presents a comparison of the key points in both standards.

Table 3.4 Comparison between IEC and ASTM standards for acidity measurement.

Each row compared the corresponding requirements in each standard.

IEC 62021	ASTM D664-07									
For acidic constituents in unused and used electrical mineral or non-mineral insulating liquids.	For acidic constituents in petroleum products and lubricants.									
Titration solvent: 2-Propanol (pure)	Titration solvents: Propan-2-ol (anhydrous; less than 0.1% H ₂ O), Toluene and Water.									
N/a	Dissociation constants (K _a) in water needs to be larger than 10 ⁻⁹ . Formic acid – (1.77 x 10 ⁻⁴); Acetic acid – (1.76 x 10 ⁻⁵); Propionic acid – (1.34 x 10 ⁻⁵); Levulinic acid – (2.29 x 10 ⁻⁵); Stearic acid – (3.16 x 10 ⁻¹¹) (approximate)									
N/a	Range: 0.1 mg/g KOH to 150 mg/g KOH									
5g of sample and 20ml of solvent	Recommended size of test portion for sample mass based on 125ml of solvent.									
More accuracy for blank titrations. Two consecutive titrations differ by no more than 0.005 ml based on the 20 ml solvent. More accurate sample titrations: mineral oil 5 g ±0.1(measured to 0.01 g), 20 ml ±0.1 ml solvent).										
	<table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: center;">Acid Number</th> <th style="text-align: center;">Mass of Test Portion (g)</th> <th style="text-align: center;">Accuracy of Weighing (g)</th> </tr> </thead> <tbody> <tr> <td style="text-align: center;">0.05 - < 1.0</td> <td style="text-align: center;">20.0 ± 2.0</td> <td style="text-align: center;">0.10</td> </tr> <tr> <td style="text-align: center;">1.0 - < 5.0</td> <td style="text-align: center;">5.0 ± 0.5</td> <td style="text-align: center;">0.02</td> </tr> </tbody> </table>	Acid Number	Mass of Test Portion (g)	Accuracy of Weighing (g)	0.05 - < 1.0	20.0 ± 2.0	0.10	1.0 - < 5.0	5.0 ± 0.5	0.02
Acid Number	Mass of Test Portion (g)	Accuracy of Weighing (g)								
0.05 - < 1.0	20.0 ± 2.0	0.10								
1.0 - < 5.0	5.0 ± 0.5	0.02								

From Table 3.4, it can be seen that the IEC standard has a number of advantages. They are for electrical insulation materials including emerging materials (synthetic and natural esters); they use a much safer titration solvent (2-propanol); the time taken to prepare the solvent is shorter (a few minutes); they are able to measure acids with dissociation constants less than 10⁻⁹ such as HMA (stearic acid with a dissociation constant of 3.16 × 10⁻¹¹).

In addition, for the IEC standard the sample size used are consistent. For the ASTM standard it depends on the acidity value range that will be measured. This is sometimes difficult to determine without previous experimental experience and in some cases could be relatively large. The IEC standard will allow better planning for experimental sample sizes during processing and reduce waste materials.

3.6.2 Acidity Measurements in Transformer Oil by Titration

Volumetric titration is a well-developed and proven experimental technique used commonly in the fields of chemical analysis to monitor: water purity, blood composition, food quality, etc [86]. In the discipline of power systems it is used to analyse the chemical properties of insulation materials used in high voltage equipment.

A specific type of volumetric titration is the potentiometric titration. In this research project, it is used to measure the acidity of electrical insulating liquids in petroleum and non-petroleum products. The methodologies are standardized internationally and described in the standards IEC 62021-1, IEC 62021-3 and ASTM D664-07 [8, 28, 104]. Potentiometric titration measures the potential between an indicator electrode and a reference electrode as a function of the added titrant in order to determine the concentration of a solute in a given solution. The acidic solutes are quantified using (3.2) to calculate the total acidity number (TAN) with the unit of mg KOH / g oil. The total acidity number is one of the core parameters in the study of liquid and paper insulation ageing.

$$\text{TAN, mg KOH g}^{-1} = (V_1 - V_0) \times M \times \frac{56.1}{m} \quad (3.2)$$

where V_1 is the volume of alcoholic KOH solution used to titrate the test portion; V_0 is the averaged volume of alcoholic KOH solution used for blank titration; M is the molarity of alcoholic KOH solution, usually 0.1; 56.1 is the molecular weight of KOH and it remains a constant; m is the mass of the test portion used; and TAN is the acidity number.

Traditionally, a typical titration would have involved an indicator (e.g. a water soluble dye) being added to an analyte to find the stoichiometric point, as shown in Figure 3.12. By definition, the stoichiometric point is where the volume of the titrant added is the required amount determined by the stoichiometric equation of the titrant and analyte. Modern day titrations involve the use of automatic potentiometric machinery to improve experimental accuracy and efficiency. A description of the equipment system that was used is shown in Figure 3.13 and Figure 3.14. The equipment used is an

automatic potentiometric titration machine, supplied by Metrohm, known as the “848 Titrino Plus”.

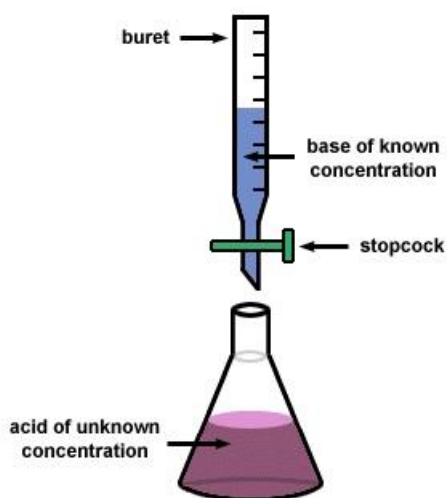


Figure 3.12 Example of traditional titration setup [105]

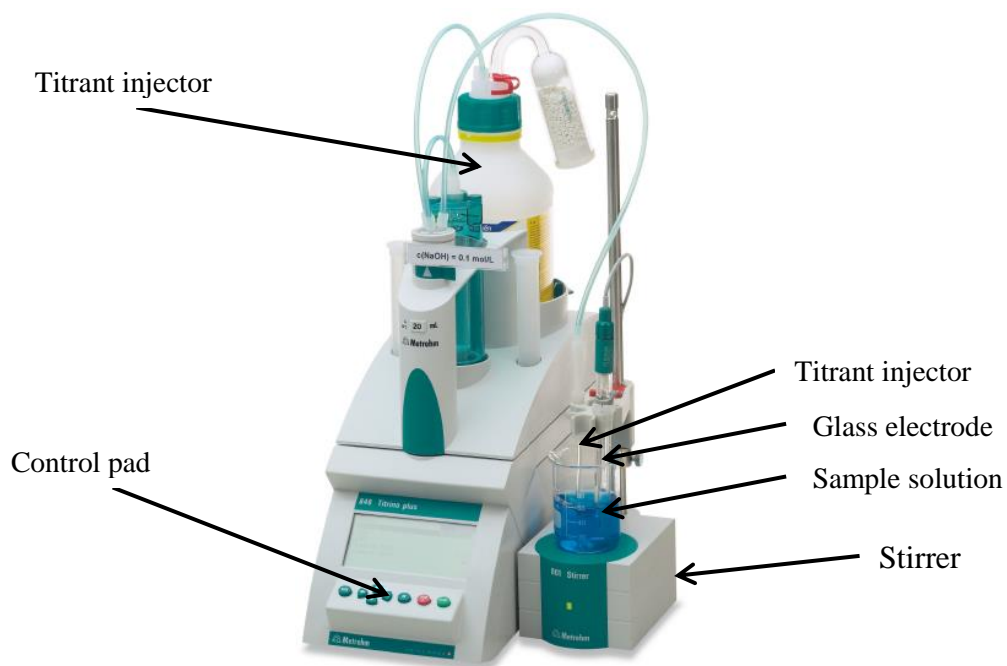


Figure 3.13 Overall structure of the 848 Titrino Plus used to measure the acidity of liquid samples. Its main components are the titrant injector, 10 mL burette, control pad, magnetic stirrer, and Solvotrode easyClean glass electrode.

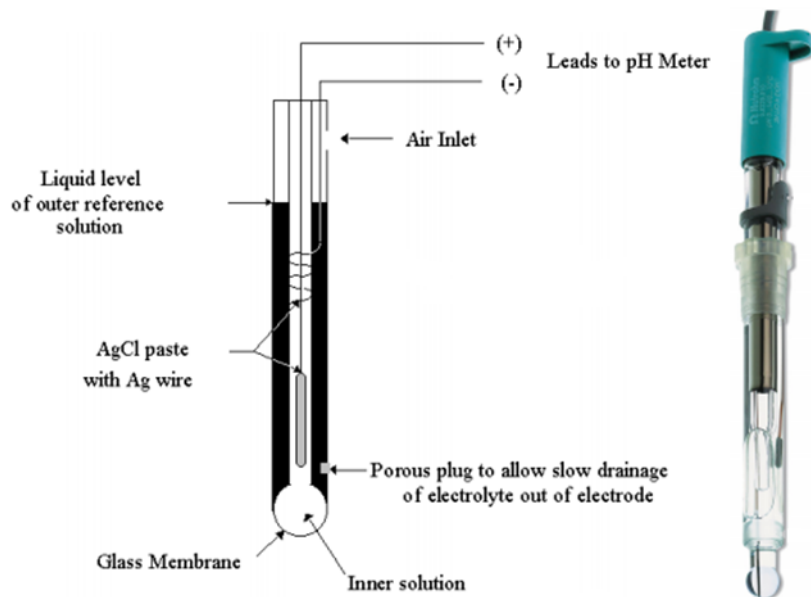


Figure 3.14 – Description of glass electrode, Solvotrode easyClean

The following reagents were used:

- Potassium hydrogen phthalate (KHP), p.a.
- 2-propanol (IPA) anhydrous, p.a.
- Toluene, p.a.
- CO₂ - free H₂O

The solutions used for titration were:

- Titrant – KOH in IPA; $c(\text{KOH in IPA}) = 0.1 \text{ mol / L}$ bought from Fisher Scientific
- Solvent – 500 mL toluene + 495 mL IPA + 5 mL CO₂ - free H₂O; this will later be changed to 1L IPA
- Electrolyte for electrode – Lithium chloride, $c(\text{LiCl}) = 2 \text{ mol/L}$ in ethanol

A potentiometric titration mode known as dynamic equivalence point (DET) was selected. The main significance of the DET mode is that the titrant will be added in variable volume steps. These volume steps vary as a function of slope of the titration curve. The range of these steps are set to be between 50 μL to 0.5 mL. Table 3.5 shows the parameters of the standardization of alcoholic potassium hydroxide solution (titer), the blank titration and sample titration.

Table 3.5 Parameters for titer, blank titration and sample titration

	Titer	Blank Titration	Sample Titration
Mode	DET U	DET U	DET U
Meas. point density	4 (standard)	4 (standard)	4 (standard)
Min. increment	50 μ L	10 μ L	50 μ L
Max. increment	100 μ L	50 μ L	0.5 ml
Signal drift	60 mV/min	60 mV/min	60 mV/min
Max. waiting time	60 s	60 s	60 s
EP Criterion	10	5	5
EP Recognition	Greatest (only EP with greatest ERC value recognized is compared with EP criterion)	All (All Eps are recognized)	Last (only the last EP is recognized.)

In Table 3.5, the measuring point density refers to the size of the volume increment added to the solution under analysis. The values range from 0 to 9 and a small value will mean small volume increment. So it is to be noted that the value to be set is not proportional to the measuring point density, instead it is proportional to the volume increment. The minimum increment refers to the smallest possible dose of titrant. This dose takes place normally at the beginning of the titration and during the steep section of the titration curve. Small dosing is needed if the volume of titrant used is known to be small and where higher accuracies are needed e.g. for cases of drug titrations. A low minimum increment will cause unwanted equivalence points. The 10 μ L for blank titrations were used because of a higher requirement for accuracy. The maximum increment is the opposite of the minimum increment.

The signal drift and maximum waiting time refers to the measurement of the incremental doses. Measurement was taken for an increment after an equilibration time which is controlled by the drift. The EP parameters refer to the equivalence point of the titration. The equivalence points are evaluated with an algorithm which is based on the differential methods proposed by Fortuin [106] and is adapted by Metrohm. The

equivalence recognition is set to 'Last' for measurements which require to determine the sum of different components, such as acidity in the case of this project.

Titration is sensitive to changes in samples, therefore it is always extremely important to make sure the measurements of blanks are done to the required degree of accuracy (difference between two consecutive measurements is within 0.005 ml) at the beginning of experiments. Measuring the blanks accurately allows one to confirm whether the equipment is in good working condition. This will build confidence in the results measured on a particular day and confirm that they are accurate and precise. Additionally, calibration with acidic buffer solutions of pH 4, 7 and 11 were done as well at the beginning of each day to further increase confidence in the accuracy of the results.

External interactions with the tip of the glass electrode should be avoided before measurements because this could change the results significantly. The placement of the glass electrode in the sample is very important. To make sure that the results are consistent and repeatable, the glass electrode needs to be placed to the side away from the vortex that is created by the magnetic stirrer and avoid being too close to the walls of the container. Placement of the glass electrodes in random places for each titration could cause a difference in the acidity values. It is also necessary to make sure measurements are done as quickly as possible once the 5 g of sample is prepared, to avoid leakage of acidic constituents to the atmosphere as shown in Figure 3.11. Finally, it is always advised to take samples from the bottom to middle part of the liquid sample bottle. Samples taken from this area will have the most stability and repeatability in the measurements.

Potentiometric titrations are very sensitive to external changes to the system, e.g. a change of temperature of the atmospheric environment. To maintain a high accuracy and precision for the measurements standardized titrations of the titrant and blank titrations are performed. Additionally, two titrations must be performed consecutively in which the values measured must be similar to an uncertainty of 0.005 ml of titrant.

There are four factors which could affect the accuracy of the measurements. They are:

- Cell configuration

-
- Stirring
 - Positioning of end-point detector and of injector of titrant
 - Temperature of experimental system

Cell configuration refers to the setup of the reference electrode, burette, sample solution and magnetic stirrer. The setup must be the same otherwise the results will differ. The size and positions of the glass beaker, glass electrode, magnetic stirrer and its bar all require consistency in different tests. The positioning of the end-point detector and input of titrant with reference to the magnetic stirrer bar in the glass sample beaker is shown in Figure 3.15.

Occasional maintenance and frequent calibration of the equipment are required to ensure the results obtained are accurate and of professional standard. The maintenance and calibration procedures for the experiments are in the IEC 62021 standards.

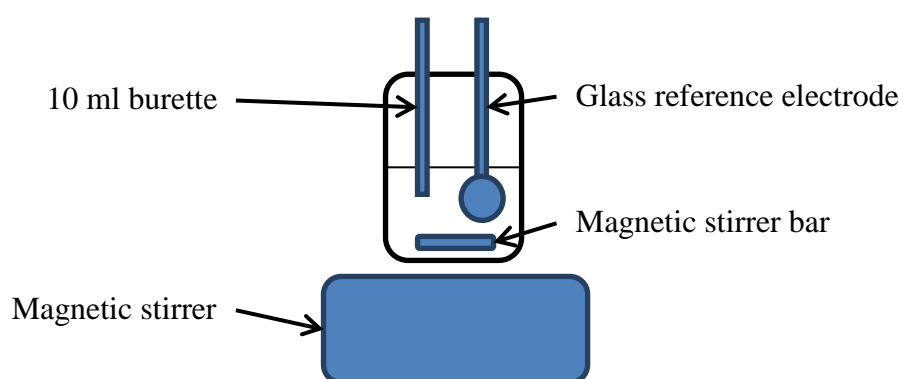


Figure 3.15 Layout of the test sample on the stirrer and the positioning of the glass electrode.

3.6.3 Measurement of DP of Paper

The method of DP measurement in this project is the well-established method for obtaining the “average viscometric degree of polymerisation” (DP_v) that is commonly used in power industry to measure new and aged cellulosic insulating materials. The method is according to the standard ASTM D4243-99, which follows the IEC standard closely. The IEC 60450: 2004 standard was also looked at for comparison. This method aims at measuring the specific viscosity of a Cuen solution with paper and then using it

to calculate the DP_v value. Details of its working principles can be found in [14]. The basic principle is that the Cuen solution will be sucked up from the low reservoir to the level where the upper reservoir is and then count the time difference when the liquid passes M_1 and M_2 in Figure 3.16 [54].

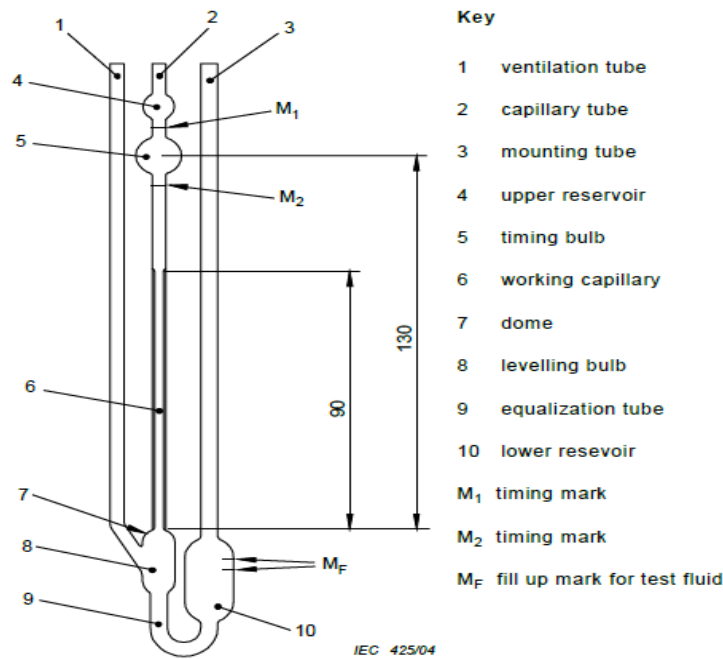


Figure 3.16 Ubbelohde viscometer tube used for DP measurement [54]

When calculating the DP_v value, the specific viscosity, v_s , is obtained first by Equation (3.3):

$$v_s = \frac{t_s - t_0}{t_0} \quad (3.3)$$

where t_s is the mean efflux time of the solution, and t_0 is the mean efflux time of the solvent only. The specific viscosity is converted into the intrinsic viscosity, v , using Martin's formula. [54] shows values of the product of the intrinsic viscosity, v , and concentration, c , as a function of the specific viscosity, v_s . \overline{DP}_v is finally determined by using Equation (3.4) below:

$$\overline{DP}_v^\alpha = \frac{[v]}{K} \quad (3.4)$$

where, α is 1, and K is 7.5×10^{-3} .

Table 3.6 Intrinsic viscosity and concentration as a function of the specific viscosity, according to Martin's Formula [54]. η_s is specific viscosity, η is intrinsic viscosity and c is concentration.

	η_s									
η	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0.0		0.010	0.020	0.030	0.039	0.049	0.059	0.068	0.078	0.087
0.1	0.097	0.106	0.116	0.125	0.134	0.143	0.152	0.161	0.170	0.179
0.2	0.188	0.197	0.206	0.215	0.223	0.232	0.241	0.249	0.258	0.266
0.3	0.275	0.283	0.291	0.300	0.308	0.316	0.324	0.332	0.340	0.349
0.4	0.357	0.365	0.372	0.380	0.388	0.396	0.404	0.412	0.419	0.427
0.5	0.435	0.442	0.450	0.457	0.465	0.472	0.480	0.487	0.495	0.502
0.6	0.509	0.516	0.524	0.531	0.538	0.545	0.552	0.559	0.566	0.574
0.7	0.581	0.588	0.594	0.601	0.608	0.615	0.622	0.629	0.636	0.642
0.8	0.649	0.656	0.662	0.669	0.676	0.682	0.689	0.695	0.702	0.708
0.9	0.715	0.721	0.728	0.734	0.740	0.747	0.753	0.759	0.766	0.772
1	0.778									
η_s	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
1	0.78	0.84	0.90	0.96	1.01	1.06	1.12	1.17	1.22	1.26
2	1.31	1.36	1.40	1.44	1.49	1.53	1.57	1.61	1.65	1.68
3	1.72	1.76	1.79	1.83	1.86	1.90	1.93	1.96	2.00	2.03
4	2.06	2.09	2.12	2.15	2.18	2.21	2.24	2.26	2.29	2.32
5	2.35	2.37	2.40	2.43	2.45	2.48	2.50	2.53	2.55	2.57
6	2.60	2.62	2.64	2.67	2.69	2.71	2.73	2.76	2.78	2.80
7	2.82	2.84	2.86	2.88	2.90	2.92	2.94	2.96	2.98	3.00
8	3.02	3.04	3.06	3.08	3.10	3.11	3.13	3.15	3.17	3.19
9	3.20	3.22	3.24	3.26	3.27	3.29	3.31	3.32	3.34	3.36
10	3.37									

3.6.4 Measurement of Water Content and Concentration of Other Chemical Species in Liquid and Paper

The water content or moisture as a general term is an important parameter in the study of transformer paper ageing. It is an initial condition for paper ageing, a product of the ageing process, and a parameter that is needed in the calculation of the DP of the paper.

The water content in oil and paper was measured with a Coulometric Titrator (Metrohm KF 831) and a Thermo Prep oven (KF 832) according to BS EN 60814 standard [107]. 3 ml of oil placed in a headspace vial was heated up to 140 °C in the oven so moisture could be extracted. Dry air was used to purge the extracted moisture into the container for titration. For paper, a sample of about 10 – 20 mg was placed in a headspace vial and the rest of the measurement procedure was the same as that for oil. The recommended measuring range is 10 µg - 200 mg absolute water content. The whole measurement process gives an uncertainty of 5% at 10 µg -100 µg, 3% at 1 mg/g and 1% at above 10 mg of water.

Apart from the acids, other chemical species e.g. furanic compounds and alcohols are also produced during the ageing process of transformer paper and liquid. The measurement of these species provides a fuller picture of the reaction environment and products during the course of paper ageing.

2-FAL in the transformer oil was measured by high performance liquid chromatography technique following either the BS EN 61198 standard or the ASTM D5837 standard [108, 109]. Previous work [101] confirmed that the direct injection method according to the ASTM D5837 standard, which has a lower detection limit of 0.01 mg/kg, has much better accuracy when measuring the 2-FAL content in synthetic ester (MIDEL 7131) and similar accuracy for mineral oil, in comparison with the indirect injection method according to BS EN 61198 standard that has a detection limit of 0.05 mg/kg. The poorer performance of the indirect injection method is possibly linked to the polar nature of the synthetic ester. Therefore in the present work the direct injection method was used for the measurement of 2-FAL concentration in transformer liquid. Trial tests in [101] showed that the direct injection method has an accuracy better than 90% for both mineral oil and synthetic ester.

The content of methanol was measured using a headspace gas chromatography and mass spectrometry system, based on the method developed in [110]. The following steps were followed to obtain the measurement:

- Extraction of methanol from the liquid sample using a sampler.
- Separation of the species through gas chromatography.
- Identification and quantification of the species using mass spectrometry.

An automatic sampling unit is firstly needed (CTC Combi Pal). It has a gas tight headspace configuration (sample vial with a crimp cap to seal) with a volume of 20 ml. 10 g of liquid was used and heated up to 90 °C in an oven for 40 minutes to extract the volatile compounds. This duration was optimised so a sufficient amount of methanol can be extracted while minimising the extracted amount of other unwanted compounds.

In the second step, a 1 ml gas-tight syringe was used to move the gas species in the headspace into the gas chromatography unit (Varian CP 3800). The temperature of the syringe unit is set slightly above the heating temperature to avoid the sample

condensation in the syringe [111]. This temperature is 91 °C. The gas chromatography unit includes an injector unit, a flow control system and a gas chromatography column placed inside an oven. A 60 m VF624ms column with an internal diameter of 0.25 mm was used to separate the species. A special solid phase material was present in the tube as a film of 1.4 µm in thickness to actually separate methanol from other volatile compounds [110]. The split ratio of the injector is 20:1 and the injector temperature was set to 150 °C to ensure a reasonable peak height for lower concentrations. The wanted species were separated at 40 °C (by setting the oven temperature) with a column flow rate of 1 ml/min.

The mass spectrometer (Varian Saturn 2200) was a quadrupole ion-trap type. At high concentration methanol ions in the ion-trap unit of the spectrometer could react with methanol molecules to produce high m/z ratios such as 33 and 47 [112], which could distort the mass spectrum and lead to errors in the measurement process. Reducing the number of methanol molecules can minimise the distortion but it also affected the detection limit. Thus, the injection volume of the sample and the split ratio needed to be carefully chosen. The ionization current used in the process was 20 µA and the temperature of the ion-trap was 150 °C.

Calibration was an important step in the measurement process because the absolute concentration was obtained based on calibration. Extra dry methanol (99.9% purity with water content less than 50 mg/kg, manufactured by Acros Organics) is used to prepare the calibration samples. Gas-tight syringes were used to prevent any loss of the analytes during the calibration process. A large syringe (100 ml) was used to hold the liquid sample and small syringe (50 µl) was used to inject methanol or ethanol into the large syringe containing the sample. The calibration samples were obtained by further diluting a portion of the mixture prepared in the large syringe.

The internal standard calibration technique was selected for the measurement of methanol concentrations because any loss of the species during the ageing process can be taken into account. This technique involves the use of a compound that is not consumed or produced during the ageing process. Following [110], ethanol d-6 (with 99.5% purity from Sigma Aldrich) (CD₃CD₂OD) was selected. A stock solution of ethanol d-6 was prepared in a sealed container by mixing ethanol d-6 and the liquid

under measurement for a target of 2250 mg/kg. 5 μ l of this solution was then added with a 10 μ l gas-tight syringe into the calibration samples and also into the liquid samples to be measured. The final ethanol d-6 concentration should be kept at 1 mg/kg in the liquid. The peak height at m/z ratio of 33 was used as the representative peak height of ethanol d-6. The peak height ratio between methanol and ethanol d-6 was used for the determination of the concentration. The experimental results showed that the accuracy is typically 90% (the uncertainty is 10%).

The ion count related to m/z ratio 31 was used to quantify ethanol as it is the m/z ratio of the highest abundance. Previous tests [101] have shown that the chosen peaks for ethanol (2 mg/kg, 5 mg/kg and 10 mg/kg) and ethanol d-6 (1 mg/kg) do not interfere with each other so ethanol d-6 can still be used as the internal standard for calibration. The linearity and repeatability of the calibration data suggest that the measurement accuracy is better than 90%.

3.7 Usage of Aged Samples for Different Measurements

It is practically important to plan for the use of aged samples in an efficient way since multiple parameters need to be measured from a limited number of samples. The quantity (volume or mass) of each sample needs to be sufficient to ensure adequate measurement accuracy yet minimal to allow the determination of necessary parameters such as the DP, LMA and HMA concentration, moisture, 2-FAL, and methanol concentrations.

The aged samples of transformer liquid and paper are contained in gas tight ampoules with a volume of 25 ml. Each sample contains 10 ml of liquid and 0.5 g of paper. After the completion of the ageing test, the samples were placed in room temperature for 3 months to allow equilibrium to be reached between paper and liquid.

There are normally 3 samples aged under identical conditions. All the liquid (10 ml) in one of the samples was used to measure the LMA content in liquid. The paper from the same sample was used for a single measurement of paper moisture (20 mg), a single measurement of DP (<250 mg) and a single measurement of paper LMA (<230 mg).

The paper moisture level is needed for the determination of the DP. The allocation of the sample is illustrated in Figure 3.17.

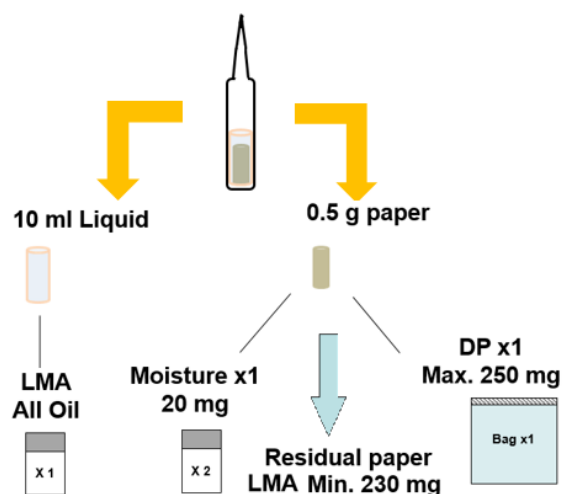


Figure 3.17 Split use of the aged sample for moisture, LMA and DP measurement.

Another sample was used for the measurement of 2-FAL, methanol and ethanol content in the liquid. Only a small amount (1 ml) of the sample liquid was needed for the measurement of 2-FAL. 8 ml was needed for the measurement of methanol using gas chromatography. The paper sample was used to perform another 2 DP measurements (each with <250 mg) and 2 paper moisture level measurements (each with <20 mg). The split of the sample for this group of tests is illustrated in Figure 3.18.

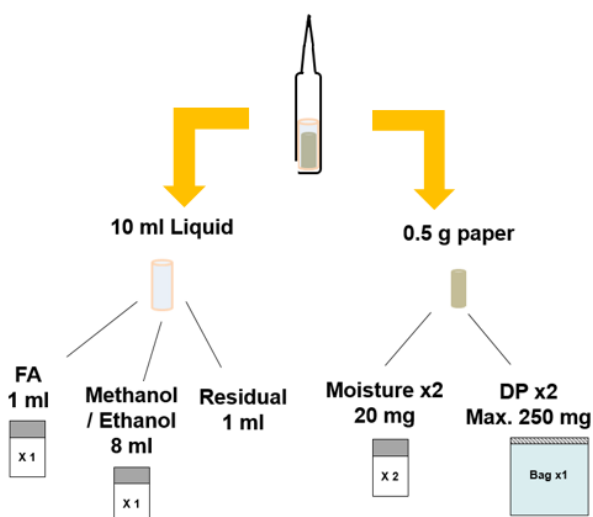


Figure 3.18 Split use of the aged sample for moisture, 2-FAL, methanol and DP measurement.

3.8 Summary

The ageing test strategy and measurement methods of different parameters were introduced in this chapter. The first feature of the ageing test is that the samples were contained in gas tight ampoules during the ageing process with a headspace of about 15 ml. The second feature is that the samples were left to reach equilibrium before they were tested. The acidic sample preparation and measurements were controlled with high repeatability. The ampoules were arranged in a pattern that allowed maximum uniformity in temperature inside the oven.

CHAPTER 4

4 MEASUREMENT OF LOW MOLECULAR WEIGHT ACID IN TRANSFORMER AGEING ENVIRONMENT LIQUID PAPER INSULATION

4.1 Introduction

Following the presentation in Chapter 3 of the overall ageing experimental setup and methodology, the measurement methods for low molecular weight acids (LMA) in transformer liquid paper insulation are to be further developed and verified in this chapter. This is needed to obtain the results in following chapters.

As mentioned in Chapter 2, numerous acids are produced in the ageing process of transformer paper and liquid insulation. Among these acids, LMA are particularly important because of their catalytic effect in accelerating the ageing of paper insulation [14]. Therefore, their presence as a key indicator of the ageing environment needs to be quantified and furthermore this has to be done in a mixture where both LMA and high molecular weight acids (HMA) exist. To measure the LMA, they have to be separated from the HMA. The measurement of low concentration LMA (<0.1 mg KOH/g) in transformer liquid is in particular an issue that needs to be addressed, since there has not been an international standard established for this purpose.

The objective of the work in this chapter is to further develop and test a reliable method of LMA concentration measurement based on water extraction method based on a previous method [14], targeting a measurable LMA concentration level significantly below 0.1 mg KOH/g. This threshold value was chosen because there has been no detailed work on the measurement of such low acidities and the majority of in-service healthy transformers will have total acidities of less than 0.1 mg KOH/g. For example, the neutralization numbers measured in several free-breathing transformers in the field were around 0.2 mg of KOH/g of oil after 35 years of service and around 0.5 mg of KOH/g of oil after 50 years of service [113]. It has also been found that within the total acidity in transformer liquid, the acidity of LMA is always in lower proportions

compared with the HMA [24]. The LMA acidity can thus be much less than 0.1 mg KOH/g.

LMA are volatile and their accurate measurement requires effective separation from the other acids while maintaining negligible loss (such as evaporation from the stirring process) during the measurement process. To this end, the effectiveness of different measurement configurations is investigated. These include the use of beakers, Erlenmeyer flasks (EF) and gas tight syringes (GTS) as an extension of previous work [12, 90]. Two types of transformer liquids were investigated: a commonly used transformer insulation oil (Nytro Gemini X, an inhibited mineral oil) and an alternative liquid which has been increasingly used in power transformers, the synthetic ester (MIDEL 7131). The LMA are represented by the formic acid and the HMA are modelled by the stearic acid. This is because formic acid is a weak carboxylic acid and a typical LMA. They are readily available to purchase and, more importantly, they are produced in the ageing process of transformers [12].

The method and procedure for the measurement of the LMA (formic acid) will be presented first in Section 4.2. Considerations will be given to the choice of the key component, i.e. the container that facilitates the separation and measurement of the LMA. This will be followed by the procedure for transformer liquid pre-treatment and ageing sample preparation in Section 4.3. Results that demonstrate the effectiveness of the measurement configurations are given in Section 4.4 together with an analysis on the influences of key parameters, such as the stirring speed, stirring duration, and the total volume of transformer liquid and water used in the separation process. Finally, a summary is given in Section 4.5.

The major achievement of the work in this chapter is the proposal and verification of the effectiveness of a detailed approach of LMA measurement based on a sealed hardware configuration. It is simple, cost-effective and sufficiently accurate. The lower limit of the LMA measurement range has been successfully extended to 0.017 mg KOH/g with an extraction rate of >80%.

4.2 Method and Procedure of Measurement of LMA in Liquid

LMA have short molecules (up to 5 carbon atoms) and are volatile by their nature. A key factor affecting their measurement accuracy is the loss of LMA in the extraction process. An understanding of the extent of this loss is essential to the development of cost-effective techniques for LMA measurement. For the comparative study in this chapter, one loosely sealed container and two tightly sealed containers are used in the extraction process.

The LMA in the transformer liquids was measured through the procedure shown in Figure 4.1. It follows the proposed sequence of

- acquiring sample and producing sample-water mixture (Step 1 of water extraction)
- enhanced mixing by stirring (Step 2 of water extraction)
- extraction and separation of LMA containing water (Step 3 of water extraction)
- LMA measurement by titration.

The samples of the two transformer liquids were prepared according to a procedure (Section 4.3) because we need to know the content of the added LMA as baseline data for the verification of the extraction efficiency.

Water of analytic grade was used. The sample liquid (whose volume is more than that required for actual measurement) after pre-treatment was originally stored in a glass bottle sealed with a cap. Part of this liquid (25 ml by default) was moved into a cleaned measurement sample container (those shown in Figure 4.2) with a magnetic stirrer placed in it. Water was then added to make a total volume (50 ml for example). The stirring speed for the Erlenmeyer Flask (EF) was determined by trial tests [71] whilst for Gas Tight Syringe (GTS) this was based on the physical limitation (space). The stirring durations were also from [71]. Afterwards, they were left for a certain duration to separate into two layers. Following a set period of stirring and a period of settling and extraction, the LMA was expected to move from the transformer liquid into the water and the transformer liquid physically separated from the water and merge to form a cluster on top of the LMA containing water in the measurement sample container.

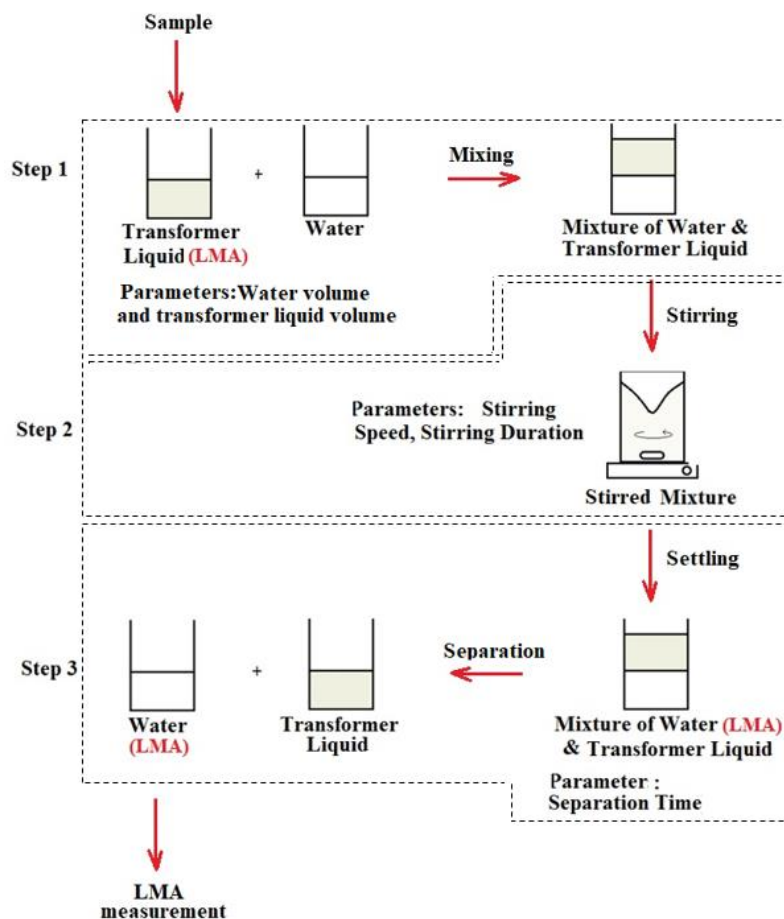


Figure 4.1 Procedure to separate LMA from transformer liquids using water extraction technique.

After the removal of the water into another container, the concentration of the LMA in the water was measured using potentiometric dynamic endpoint titration according to IEC 62021-1 [27] for mineral oils and IEC 62021-3 [114] for synthetic esters. The measurement was executed using Metrohm 848 Titrino Plus with a Solvotrode easyClean glass electrode. Three-point calibration of the pH (4, 7, and 11) was carried out before every group of measurement to ensure the accuracy and validity of the results. The Endpoint mode was used to measure the acidity with an end point pH of 11.5. This value was selected based on industrial common practice for comparison of results between different organisations [104].

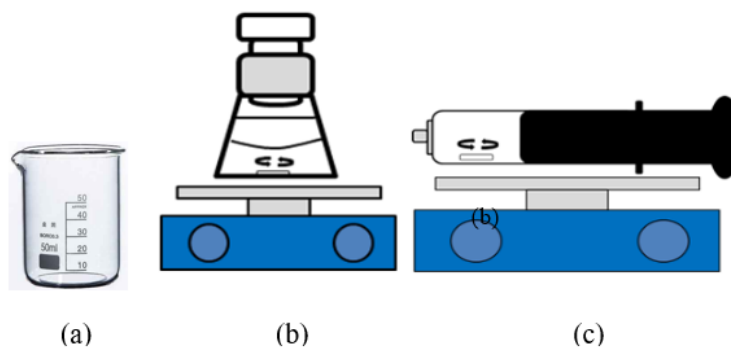


Figure 4.2 Structure of containers used in LMA extraction based on water separation, (a) Beaker, (b) EF and (c) GTS, with the stirring arrangement also shown.

The overall acidity measurement uncertainty originates from a number of sources including the preparation of the titrant, the accuracy of control of the titrant dosing, the time for the titrant dose to uniformly distribute in the solution and react with the sample and the calculation of the total amount of titrant corresponding to an end point of 11.5 in pH. The position of the sensor tip in the solution may also be a factor. From a set of specially designed tests, the overall uncertainty achieved is within 15% at low concentration (0.06 mg KOH/g) and 8% at high concentration (0.5 mg KOH/g).

In terms of hardware configuration, three containers were used and they differ in volume, geometry and level of seal. Their choice was based on availability, reactivity with acid, effective volume and ability to be tightly sealed. A summary of their main features is given in Table 4.1. The beaker as shown in Figure 4.2 represents a loosely sealed environment where the LMA under test is able to evaporate and lost to the atmosphere. The other two containers can be sealed tightly to minimise the loss of LMA.

Table 4.1 Properties of chosen water and transformer liquid containers for LMA extraction from transformer liquid.

Features	Beaker	Flask (EF)	Syringe (GTS)
Volume	50 ml	50 ml	50 ml
Mixing method	Large magnetic stirrer	Mini magnetic stirrer	Mini magnetic stirrer
Sealing	Loose seal with kitchen cling film	Sealed tightly	Tight seal by design

Altogether 4 experiments (A, B, C and D) were performed in this chapter. Experiment A was with the beaker to measure high LMA concentration. The other 3 experiments were carried out to measure the low LMA concentration. The key parameters relating to the water extraction based process to extract LMA are given in Table 4.2. The values may be different from the reference values for specific samples, which is also indicated in Table 4.2.

Table 4.2 Parameters for LMA extraction and separation process

Controlled Parameters	Reference method	Variations
Transformer liquid (ml)	25	8
Water (ml)	25	-
Stirring Speed (rpm)	650	300, 650 and 1000
Stirring Duration (hours)	3	1, 3, 5, 7 and 12
Separation Time (hours)	3	0.25, 0.5, 1 and 3
Temperature (°C)	23	-

Experiment B was on the efficiency of the containers of different structures (EF and GTS) to separate low concentration LMA from the transformer liquids. A total of 3 samples for each concentration (2 concentration levels) were prepared. For 2 types of liquids, a total of 12 samples were needed. By default, 25 ml of analytical grade water was added into 25 ml of transformer liquid. They were mixed by the magnetic stirrer for 1 hour and then left to separate for another hour into two distinctive layers. The

parameters for Experiment B are given in Table 4.3. The two liquids were then separated and the acidity measured.

A magnetic stirrer was added to each sample container. Mixing was then carried out according to conditions given in Table 4.3. After the separation time given in Table 4.3 lapsed, samples were left still for further one hour to allow the separation of water and oil layers. Then each layer was extracted using a syringe and the acidity was immediately measured using titration (details are given in Chapter 3).

Table 4.3 Stirring and separation conditions for the water extraction method used

Controlled Parameters	Values used in different experiment
Transformer liquid (ml)	25 (B, C), 25 (D), 8 (D)
Water (ml)	25 (B, C), 10 (D), 10 (D)
Stirring Speed (rpm)	650 (EF), 300 (GTS)
Stirring Duration (hours)	1 (Gemini X), 3 (MIDEL 7131)
Separation Time (hours)	1
Temperature (°C)	~23° C (Room Temp.)

Experiment C was on the extraction of low concentration LMA from mixtures containing LMA and HMA using the Erlenmeyer flasks. The flasks were used because from the results of Experiment B it was found that the acidities of the separated LMA were similar with both the flasks and gas tight syringes, however the flasks were more convenient to use and more cost-effective. This experiment was designed to show that the presence of HMA would not influence the extraction of LMA at low acidity levels. The separation conditions were indicated in Table 4.3.

Experiment D was to acquire information on the feasibility of minimising the sample volume used in the measurement while retaining adequate extraction efficiency. This issue is practically important because multiple measurements for different parameters (acidity, moisture, 2-FAL, etc) need to be performed from a single aged sample. Minimising the required sample volume means least disturbance to the operation of the transformer if real time sampling is to be carried out. Additionally, this is especially

important for the ampoules used for ageing as they were very small and therefore can only contain small volumes of transformer liquid. The volumes for the transformer liquids and water are listed in Table 4.3. The minimum volume of the sample used is 8 ml and the minimum volume of the water is 10 ml. As a guidance, the amount of water added should be sufficient to dissolve the LMA present in the transformer liquid but not too much to reduce the LMA acidity in the water after extraction.

4.3 Pre-treatment of Test Objects and Sample Preparation

The liquids for testing (Nytro Gemini X and MIDEL 7131) have to be pre-treated to ensure their purity. The treatment involved the following procedure:

- a. Filtration. The transformer liquids were filtered first using a nylon membrane of pore size 0.2 μm ;
- b. The filtered liquids were then dried using nitrogen purging for 3 hours at room temperature;
- c. The dried liquids were degassed under vacuum (~ 5 mbar) at room temperature for 1 hour to remove the nitrogen gas. They were then sealed tightly with a cap in glass bottles;
- d. To save time and reduce the complexity, steps b and c can be replaced by drying under vacuum (~ 5 mbar) at 85 °C. The drying time is 24 hours for the mineral oil (Nytro Gemini X) and 72 hours for the ester (MIDEL 7131). The latter is polar and naturally takes longer time for water molecules to separate and escape.

Since the work in this chapter is to test the proposed LMA measurement procedure when HMA are present, knowledge of the concentration of the added LMA (and HMA when HMA is present) in the samples must be known as reference values to work out the extraction efficiency. It is inevitable that the fresh liquids may already contain a tiny amount of acids, which has to be taken into account. The term “inherent acidity” is used here to refer to the acidity exhibited by the fresh transformer liquids after pre-treatment. “Added acidity” refers to the acidity as a result of the added LMA or HMA. Therefore the measured total acidity is the sum of the inherent acidity and the added acidities.

The inherent acidity in the pre-treated transformer liquids was studied first. A known amount of formic acid was added to a certain volume of the transformer liquid and well mixed. Its acidity was then measured using the titration method. The results are presented in Figure 4.3. The titration method gives the total acidity, including the inherent acidity and the added acidity. Taking into consideration of the possible experimental errors (typically 8%), the measured total acidity follows a linear relationship with the amount of added acid. The inherent acidity of both transformer liquids is approximately 0.035 mg KOH/g, as seen as the intercept in Figure 4.3. This value is close to the value given by the manufacturer for MIDEL7131 but is higher than the manufacturer given value of 0.01 mg KOH/g for Gemini X.

It is not clear what chemical species actually contribute to the inherent acidity. For the work in this thesis, it is important to find out if any acids contributing to the inherent acidity can be separated based on the water extraction method. To this end, samples identical to those directly measured using the titration method were also tested using the water based extraction method for acidity. It has been found that the acidity of the separated water was below the detection limit, providing clear evidence that the acids in the original transformer liquids cannot be moved to water and do not contribute to any increase in acidity in the water.

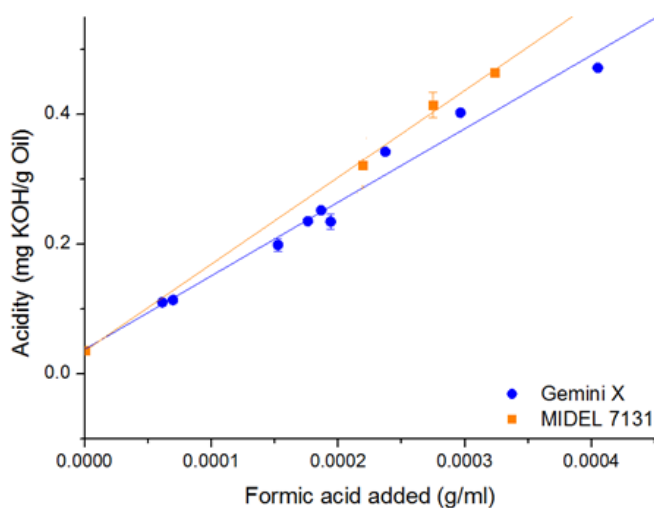


Figure 4.3 Acidity measurement results using direct titration for Gemini X and MIDEL 7131. No water was used in the measurement.

A procedure is thus needed to control the concentration of the added acids. To achieve an expected added acidity value for a sample, the amount of acid, either LMA or HMA, needs to be decided first. In the present work, this was realised by the construction of an empirical relationship between the measured added acidity of the calibration samples and the actual amount of the acid. The empirical relationship is presented in Figure 4.4. A linear relationship was assumed when additional test samples were prepared based on the results from the first set of calibration samples. Each linear function derived and shown in Figure 4.4 was obtained based on at least 10 samples.

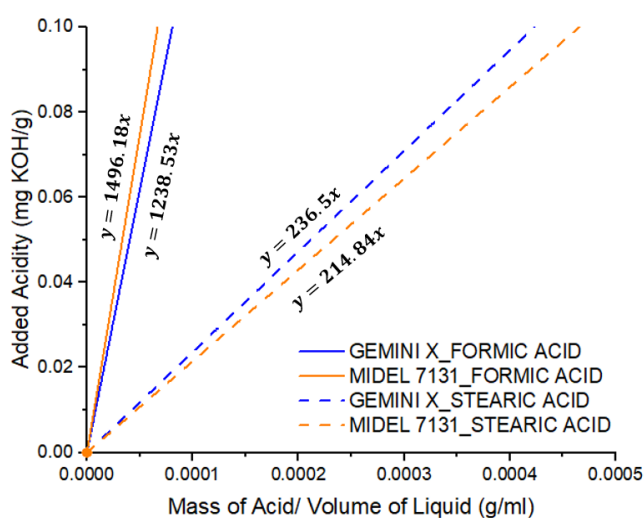


Figure 4.4 Relationship between the added acidity and the mass of formic or stearic acid added to Gemini X and MIDEL 7131.

Formic acid and stearic acids, both of >98% purity from Sigma Aldrich, were used to represent the LMA and HMA. Knowing the volume of the transformer liquid, the mass of the acid can be determined from Figure 4.4. For LMA, the formic acid was injected using a 500 μ l SGE gas tight syringe (Sigma Aldrich) into 200 ml, 500 ml or 1000 ml of transformer liquids.

4.3.1 Sample Preparation for Experiments using a Beaker (High LMA Acidity Measurement)

Three 500 ml bottles for each type of transformer liquid were prepared at room temperature and then injected with the appropriate mass of formic acid, according to Figure 4.4, using 500 μ l gas tight syringes. Added acidities of formic acid of

approximately 0.1, 0.3 and 0.5 mg KOH/g Oil were prepared for each type of transformer liquid for experiments with the beakers. The samples were then left to mix on a magnetic stirrer overnight (12 hours). The final acidity values obtained for each transformer liquid were measured by titration and are shown in Table 4.4, serving as the reference values. No HMA has been added.

Table 4.4 Initial acidities of transformer liquid samples (high acidity samples)

Liquid Type	Manufacturer given inherent acidity in new liquid (mg KOH/g Oil)	Measured inherent acidity in new liquid (mg KOH/g Oil)	Added acidity (mg KOH/g Oil)		
			0.10	0.34	0.51
Gemini X	<0.01	~0.035	0.10	0.34	0.51
MIDEL 7131	<0.03	~0.035	0.11	0.31	0.50

4.3.2 Sample Preparation for Experiments using EF and GTS (Low LMA Acidity Measurement)

Samples of “added acidity” of formic acid approximately 0.017 mg KOH/g and 0.06 mg KOH/g for both Nytro Gemini X and MIDEL 7131 were prepared. Both values are lower than 0.1 mg KOH/g, aiming to test the validity and accuracy of the proposed extraction method for low acidities. The true acidities of the samples with only LMA added are given in Table 4.5, serving as the reference values. The values were averaged from the measurements of 4 samples. The standard deviation is provided to indicate the controllability of the acidity in the samples.

Table 4.5 Initial acidities of transformer liquid samples (low acidity samples)

Liquid Type	Added Acidity (mg KOH/g)			
	Average Low Acidity	Std. Dev.	Average High Acidity	Std. Dev.
Gemini X	0.0172	0.0015	0.0637	0.0016
MIDEL 7131	0.0168	0.0014	0.0598	0.0013

Samples with both LMA and HMA (stearic acid) were also prepared. The Gemini X samples achieved a formic acid acidity of 0.0561 mg KOH/g and Stearic acid acidity of 0.0863 mg KOH/g. The synthetic ester samples (MIDEL 7131) have a formic acid acidity of 0.0741 mg KOH/g and stearic acid acidity of 0.1265 mg KOH/g. The LMA was then separated using water and the acidities of the separated water and transformer liquid were measured separately.

4.4 Experimental Results & Discussions

4.4.1 Influence of Process Parameters

The effect of stirring speed on LMA percentage extracted was studied first and shown in Figure 4.5. The sample contains both LMA and HMA and the initial total acidity was 0.5 mg KOH/g in two transformer liquids. A beaker was used. The percentage of LMA extracted is defined by (4.1)

$$\eta = \left[\frac{A_2}{A_1} \right] \times 100\% \quad (4.1)$$

where η is the percentage extracted (%), A_1 is the initial added LMA and A_2 the extracted LMA.

From Figure 4.5, an optimum stirring speed of 650 rpm was clearly identified for Gemini X. A decrease in the percentage extracted was seen at both 300 and 1000 rpm. This could have occurred due to a slower rate of diffusion at the lower stirring speed and evaporation of formic acid at higher stirring speed as a result of its volatility. For MIDEL 7131, there is a negligible change in the LMA percentage extracted when the stirring speed increases from 300 to 1000 rpm. This phenomenon might be a result of MIDEL 7131 being a more polar molecule and mixing well with the water during the 3-hour stirring period. Experiments conducted using transformer liquid samples with acidities of 0.1 and 0.3 mg KOH/g oil gave similar results and will not be repeated here.

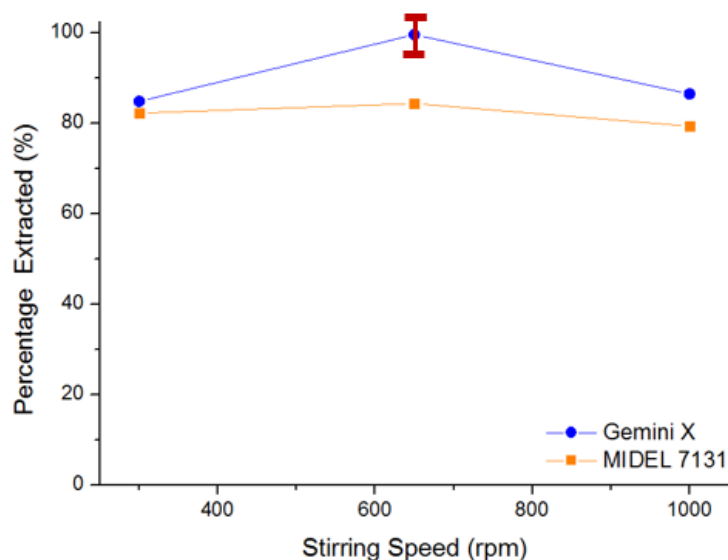


Figure 4.5 Percentage extracted against the stirring speed for Gemini X and MIDEL 7131 with an initial acidity of 0.5 mg KOH/g Oil. A beaker was used.

The effect of stirring duration on LMA extraction was assessed while maintaining other parameters as listed in the reference method given in Table 4.2. The experiment was conducted at 650 rpm with an initial acidity of 0.5 mg KOH/g Oil. The stirring duration of the samples was varied from 1 to 12 hours. Figure 4.6 shows the results and it is clear that for the mineral oil (Gemini X) the extraction process is completed within the first hour, whereas for the synthetic ester this takes approximately up to three hours. The shorter period of time for extraction from the mineral oil is most likely due to its non-polar nature. The polar LMA molecules are more likely to diffuse into water, which is also polar, rather than staying in oil. For MIDEL 7131 the attraction between the LMA molecules and ester can be stronger than in the case with the mineral oil due to their polar nature, which is probably why it takes longer for the LMA to be extracted into water from the synthetic ester. In addition, a residual amount of LMA was found in MIDEL 7131 even after 12 hours of stirring. This means that there will be a small amount of LMA that cannot be separated using water, which is trapped by the polar synthetic ester molecules via hydrogen bonding.

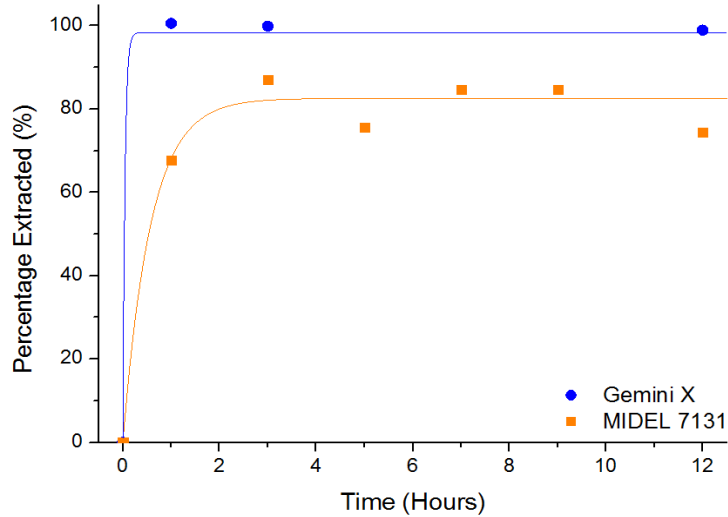


Figure 4.6 Percentage of acidity extraction against stirring time for Gemini X and MIDEAL 7131 stirred at 650 rpm with an initial acidity of 0.5 mg KOH/g Oil. A beaker was used.

While 3 hours of stirring time is sufficient, an overall faster measurement procedure is always preferred. Hence, the effect of separation time was investigated to determine the possibility of shortening the overall measurement duration. Transformer liquid samples prepared with 0.5 mg KOH/g oil added acidity were stirred at 650 rpm for 3 hours and left to separate for different durations from 0.25 to 3 hours. Figure 4.7 shows the percentage of extracted LMA in water at different separation times. It can be seen that the extracted acidity is constant and does not change when the separation time varies from 0.25 to 3 hours for the two types of transformer liquids. This suggests that the LMA has diffused into the water during the stirring period and the separation time could be reduced to 0.25 hour (15 minutes) if desired.

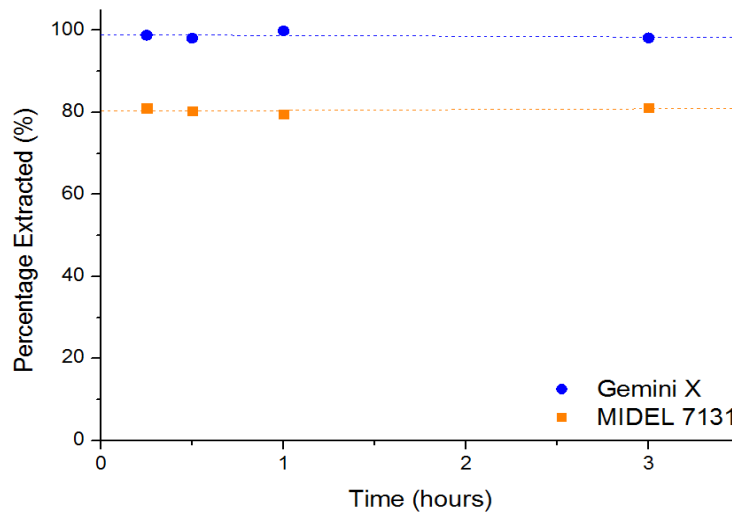


Figure 4.7 Acid extracted to water against separation time for Gemini X and MIDEL 7131 stirred at 650 rpm with an initial acidity of 0.5 mg KOH/g Oil. A beaker was used.

The effect of initial concentration on LMA extraction is shown in Figure 4.8 where the amount of extracted acids in water against the injected LMA acidity at three initial acidity levels was obtained using the reference method in Table 4.2. For the investigated acidity range, the results show that more than 90% of the added LMA can be extracted from the mineral oil. However, for synthetic ester, extraction efficiency is lower than the mineral oil. The residual LMA plus the lost LMA is higher in ester liquids, approximately 0.042 mg KOH/g Oil (the value at which the fitted line intercepts with the horizontal axis). In contrast, the residual amount of Gemini X plus the loss is much lower and close to 0.007 mg KOH/g Oil.

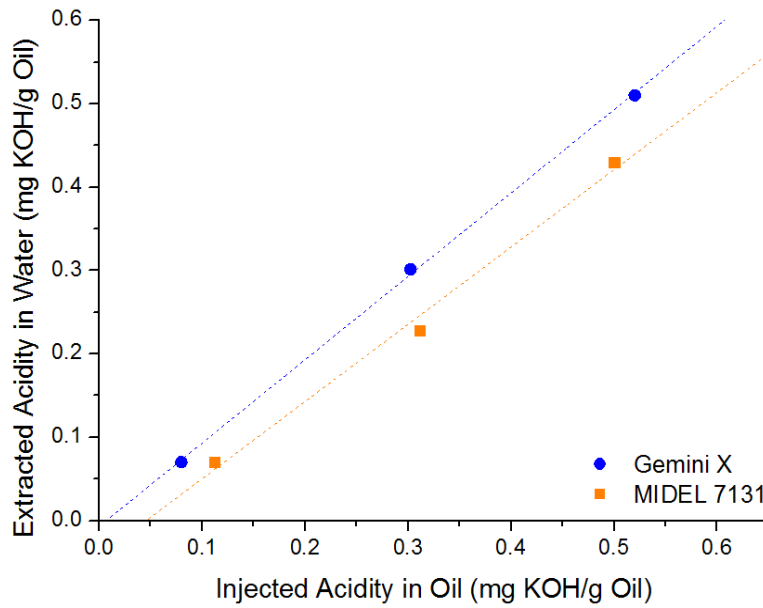


Figure 4.8 Acidity of extracted LMA for different added LMA acidities in Gemini X and MIDEL 7131. Injected acidity here means the added acidity. A beaker was used.

The results in Figure 4.8 also show excellent linearity considering an experiment error of 8%. The fitted lines can thus be used to construct a correction scheme to derive the actual LMA (formic acid) in the samples of the transformer liquids. Two equations were obtained; one for Gemini X (4.2), and one for MIDEL 7131 (4.3), as below:

$$A_{Gi} = 0.007 + A_{GW} \quad (4.2)$$

$$A_{Mi} = 0.042 + 0.927A_{MW} \quad (4.3)$$

where A_{GW} is the acidity, in mg KOH/g Oil, of LMA actually extracted from Gemini X; A_{MW} is the acidity, in mg KOH/g Oil, of LMA actually extracted from MIDEL 7131; A_{Gi} is the derived added acidity in Gemini X and A_{Mi} is the derived added acidity in MIDEL 7131.

The work reported in this section provides important evidence towards the selection of test conditions and parameters. Results also shown that using a beaker is not the best choice for water based LMA extraction from transformer liquids. The results can be summarised as

- A stirring speed of 650 rpm leads to maximum extraction of the LMA from the transformer liquids;

-
- It requires 1 hour of stirring time for GEMINI X and 3 hours for MIDEL 7131 to ensure maximum extraction of the LMA from the transformer liquids;
 - It takes 15 minutes for the water and transformer liquids to separate after stirring. A one hour separation time is recommended to ensure complete separation.
 - Chemicals contributing to the inherent acidity of the transformer liquids will remain in the liquids during the water based extraction process.

4.4.2 Discussions

The results presented in Chapter 4 were obtained from three types of samples, as described below:

- 1) Blank transformer liquid. The samples were used to obtain the inherent acidity levels (Figure 4.3) by titration and the inherent acidity levels were then used to determine the added acidity level (Figure 4.4) in the transformer liquids. Water based extraction was also applied to these samples and the results confirm that no meaningful amount of acid can be extracted from the blank transformer liquids. It is thus highly likely that the inherent acids are HMA.
- 2) Transformer liquid mixed with formic acid only. These samples were used to assess the efficiency of LMA extraction based on water separation for different container structures used in the extraction process. The lowest extraction efficiency is 90% for Gemini X with EF and 82% for MIDEL 7131 with EF. At higher acidity levels around 0.05, the extraction percentage becomes nearly 100%. Beaker is not fit for low level LMA extraction from transformer liquids.
- 3) Transformer liquid added with formic acid and stearic acid. These samples were used to confirm the influence of the presence of the stearic acid on the extraction efficiency of the formic acid. Results confirm that the extraction of the formic acid is not adversely affected by the presence of the stearic acid.

The estimated total measurement uncertainty is around 8%. The acidity values presented in this chapter are those averaged from at least three samples. Figure 4.9 shows the amount of extracted acids into water against the injected acidity in transformer liquids measured. The results show that for added acidities higher than 0.017 mg KOH/g, more than 90% of LMA can be extracted from the mineral oil. This confirms the validity of the measurement method based on water extraction for LMA

in mineral oils. For synthetic esters, the extraction was lower than the hydrocarbon oils and at an acidity level of 0.017 mg KOH/g the extraction reaches 80 % or above with the sealed system. From the trend of low acidity measurement it can be seen that using sealed flasks the measurement accuracy is much higher than that based on a beaker, especially for low level acidity. The sealed system will be used for measurement presented in Chapters 5, 6 and 7.

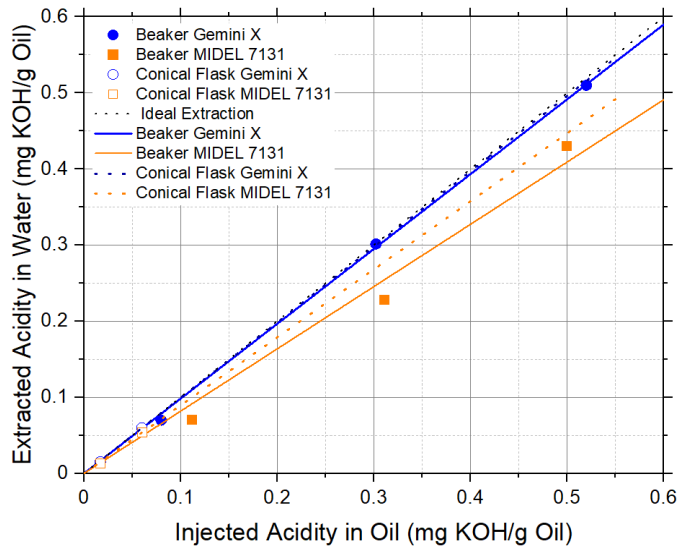


Figure 4.9 Summary of extracted acidity for Gemini X and MIDEAL 7131 at different acidity concentrations and with different mixing and separation container arrangements. The samples do not contain stearic acid.

4.5 Summary

The details of a proposed approach for effective LMA measurement based on water extraction is presented. Results show that it is able to extract at least 90% of the LMA in non-polar transformer liquid and more than 80% for polar transformer liquid such as MIDEAL 7131. The key element is the gas tight Erlenmeyer flask which offers a cost-effective solution and advantage of easy use. This approach can be applied to an acidity level as low as 0.017 mg KOH/g and in the case where HMA are present in the liquids. Results obtained using a beaker implies that it is not suitable for extracting low level of LMA.

The conditions for reliable LMA extraction were also identified in this chapter, i.e. a stirring speed of 650 rpm, stirring duration of 1 and 3 hours for Gemini X and MIDEAL 7131, respectively, and a minimum separation time of 15 minutes.

The presence of HMA (stearic acid for this chapter) does not affect the effectiveness of the water extraction based measurement of LMA, from either mineral oil or synthetic ester, even at a low acidity level of 0.017 mg KOH/g. A residual of acids was also noticed during the extraction of LMA from the synthetic ester. The new approach established and verified in this chapter will be used to obtain results in Chapters 5, 6 and 7.

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CHAPTER 5

5 INHIBITED MINERAL OIL AND KRAFT PAPER THERMAL AGEING IN SEALED AMPOULES

5.1 Introduction

Following the establishment of the experimental strategy and setup of “perfectly sealed” glass ampoule based ageing system in Chapter 3, and the development of the Low Molecular Weight Acid (LMA) measurement technique in Chapter 4, this chapter presents the first major group of thermal ageing results of transformer liquid and Kraft paper using sealed glass ampoules. As mentioned in Chapter 3, the sealed environment is designed to minimise the interference of the environment to the ageing process, especially the exchange (loss) of chemical species with the environment. This includes the potential ingress of air into the oil and the leakage of volatile matters into the atmosphere.

The accelerated ageing process of an inhibited mineral oil and a Kraft paper is reported in this chapter as a set of baseline data for comparison in Chapter 6 and Chapter 7. The insulation system (mineral oil Gemini X and ordinary Kraft paper) without added moisture or acids after the oil and paper are dried is referred to as the ‘blank’ system. The tests were carried out at 130 °C in an air circulating oven with two internal levels, as detailed in Chapter 3 (Section 3.2). Each level contains grid-like holders in which the ampoule samples are held and aged in a particular array to allow even distribution of air and heat flow. Aged in such a way, after a particular period of time the samples were taken out and left for at least 3 months. This allows a molecular equilibrium to develop at room temperature and means that the molecules reached a stable partitioning between different mediums. An equilibrium partition ensures consistency in measurement results, which is achievable using the present ‘perfectly sealed’ ampoules. The samples were tested to obtain the parameters in particular groups so the parameters can be compared directly because they come from the same sample. As stated at the end of Chapter 3, one ampoule is opened and tested for 2-FAL, methanol, paper moisture, and DP. Another ampoule is opened for liquid LMA, paper moisture, paper

LMA and DP. The tests were conducted following the standard testing procedures introduced in Chapter 3.

Section 5.2 first introduces the moisture of the aged paper as a function of time. Then Section 5.3 and Section 5.4 show the test results of the conventional ageing parameters (such as Degree of Polymerisation (DP), 2-FAL and methanol) plotted against time. The results are further processed to study the effects of ageing on the mechanical strength of the Kraft paper through DP. The graphs plotted show the chain scissions per monomer for DP and the kinetic degradation rate of the DP. Through the study of the DP, other comparisons are made between the various ageing parameters. Afterwards, Section 5.5 reports the results of LMA, as the latest type of potential paper ageing indicator. The LMA of paper and transformer liquid are first plotted with time. Then the effects of LMA partitioned between the paper and liquid is studied and LMA is plotted with other ageing parameters to investigate any relationships between them. Section 5.6 assesses the correlation between the different ageing parameters. Finally, a summary is given in Section 5.7.

5.2 Variation of Moisture Level in Kraft Paper

A photo of the oil-paper samples in sealed ampoules with different ageing times is shown in Figure 5.1. As discussed in Section 2.3.3, the presence of moisture in transformer oil and paper, especially at the early stage, has deterministic effect on the ageing speed of the paper through hydrolysis [12]. It is also produced during the ageing process [50] of the transformer oil paper insulation system. Therefore, the moisture concentration reflects an important aspect of the ageing environment.

The initial amount of oxygen contained in the ampoules can be estimated. The ampoules have a volume of 25 ml. The oil takes 10 ml and 0.5 g of paper occupies approximately 0.4 ml. The oil to paper weight ratio is 17.4. The headspace air volume is therefore 14.6 ml. The amount of oxygen is 4.38 mg based on a density of 1.4289 g/l and assuming 21% of oxygen in air. In theory, when all oxygen atoms are used to form water molecules, the maximum amount of water that can be produced is 4.9 mg, corresponding to 1% of the paper weight.



Figure 5.1 A photo of the oil-paper samples in sealed ampoules aged for different durations. It is placed in this chapter as a record of the original test samples that may contain information that is needed in future.

The water content of the paper insulation, aged in inhibited mineral oil (Gemini X) at 130 °C, was plotted against time (days) in Figure 5.2 using the average of 5 sets of measurement. At the start of the experiment, the moisture of the paper was less than 0.5% (weight), which is in a typical dry condition. Results indicate that the moisture level increases with a relatively high rate in the initial stage, reaching 0.9% at Day 20. Afterwards, the production of water gradually slows down. By Day 40, the moisture level reaches 1.3% and continues to approach 1.5% by the end of the 75-day ageing period.

The use of sealed ampoules in the present work eliminates the possibility of moisture ingress into the oil, enabling the association of the water content to chemical reactions taking place during the ageing process. The trend of change is clear and certain. Previous work showed that the partitioning ratio of moisture in oil and paper is around 1:100 [12], thus the moisture level in oil will be rather low. Therefore, results in Figure 5.2 show that ageing in this chapter was performed under strictly controlled initial moisture levels.

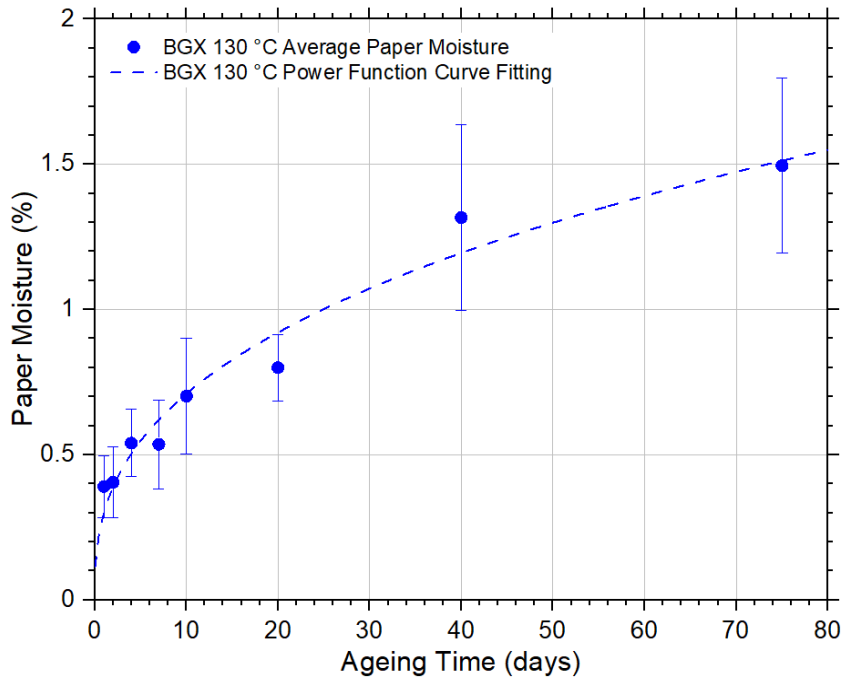


Figure 5.2 Variation of average moisture level in aged Kraft paper impregnated in Gemini X as a function of ageing duration. The error bar indicates the standard deviation from 5 sets of measurement.

5.3 Change in Degree of Polymerisation of Kraft Paper

The degree of polymerisation (DP) and chain scission number are plotted in Figure 5.3 and Figure 5.4, respectively. The chain scission number is defined as

$$\eta = \frac{DP_0}{DP} - 1 \quad (5.1)$$

where DP_0 is the start DP of the paper at time zero and DP is the degree of polymerisation at any time in the ageing process.

The variation of the DP with time follows a relatively smooth trend, as indicated by the blue broken curve in Figure 5.3. The trend follows a shape that is similar to that reported in literature. The difference between the trend line and the measured points are all within the experimental error suggested in the standard.

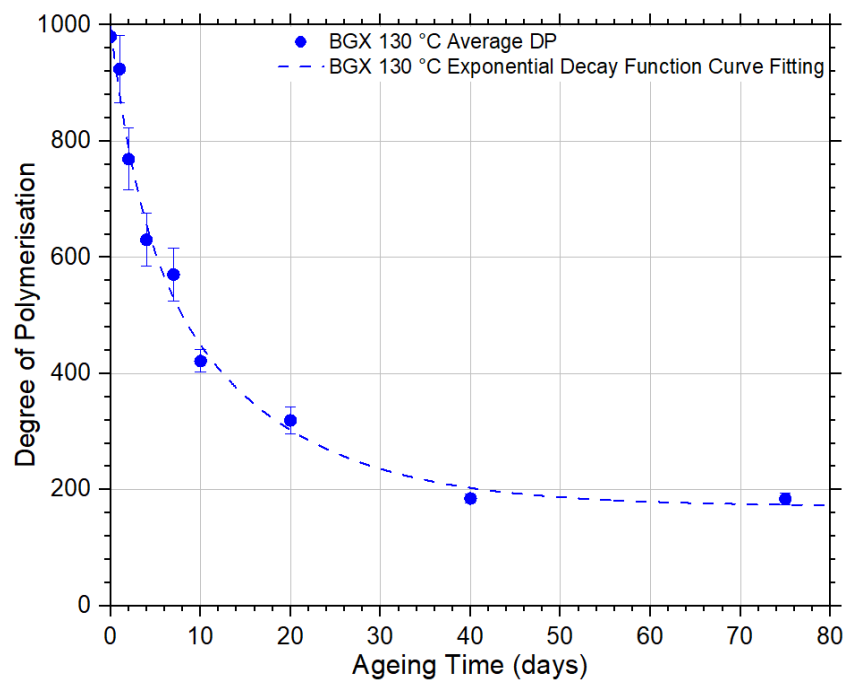


Figure 5.3 DP of initially dried Kraft paper thermally aged in Gemini X without added moisture and acids at 130 °C using sealed ampoules. The error bar is from 12 measurements of two ampoules.

The cellulose structure of the Kraft paper, as described in Chapter 2, contains amorphous and crystalline regions. At the beginning of the ageing process, chemical reactions first favours the breaking of the long molecules at the weak links, which are the amorphous structures. This leads to a rapid initial decrease in the DP as seen in the curve in Figure 5.3 up to Day 10. Once the majority of the easily accessible amorphous regions are gone, the reactions then focus on the crystalline structure which is more difficult to breakdown. Thus the decrease in the rate of degradation after 10 days and the corresponding DP variation gradually slows down, reaching the end of life criteria of the Kraft paper with a DP of around 200.

The chain scission increases linearly in the first 10 days. As shown in Chapter 2, measurement of DP (and thus chain scission number) contains scattering and it may change the local trend of DP change as function of time (such as shown in Figure 2.21), as suggested in [14]. The good correlation of the DP values as reflected by the closeness of the DP points to the fitted line in the present work may partly attribute to the sealed oil and paper samples that completely prevents mass exchange with the environment.

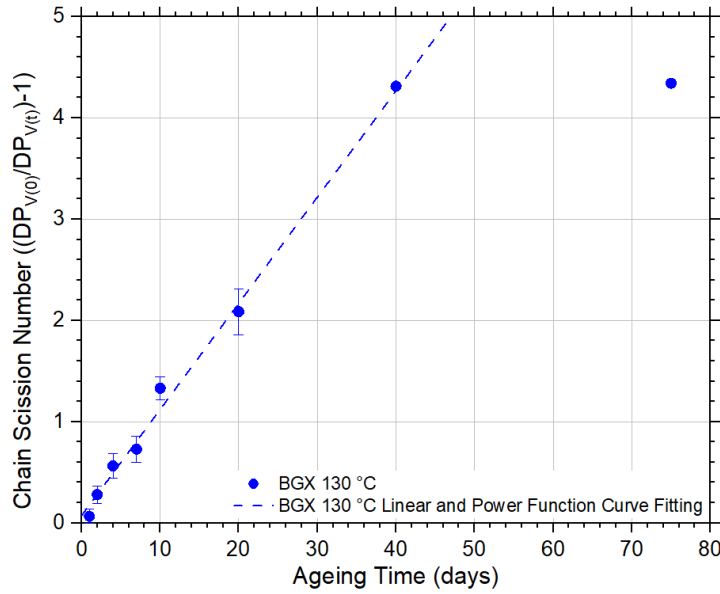


Figure 5.4 Measured polymer chain scission of initially dried Kraft paper that is thermally aged in Gemini X without added moisture and acids at 130 °C using sealed ampoules.

The pseudo-zero order rate law was used in [21] to fit ageing results obtained in different works, as is described in the following equation:

$$\frac{1}{DP} - \frac{1}{DP_0} = kt \quad (5.2)$$

where k is the rate of reaction, or the number of scission per monomer per unit time. The initial reaction rate can be calculated using the following equation:

$$k = \frac{1}{DP_0} \frac{\eta}{t} \quad (5.3)$$

where η is proportional to t in the trend line and the term $\frac{\eta}{t}$ is the gradient of the line approximating the initial increase of the chain scission number as a function of time. In the literature, a unit of time is defined as one hour. Using a straight line fitting to the data in Figure 5.4 between zero and 20 days, a value of 4.72×10^{-6} is obtained. The initial reaction rate obtained in [12] at the same temperature of 130 °C but with non-perfectly sealed bottles to contain the ageing samples is 1.67×10^{-6} . The oil to paper ratio is approximately the same.

5.4 Generation of 2-FAL and Methanol during Ageing of Kraft Paper

During the ageing process, concurrent chemical reactions taking place in the paper and liquid produce chemicals (2-FAL and Methanol) that can be measured. The concentrations of the chemicals that are produced by these concurrent ageing reactions are plotted against time first. Using partitioning coefficients that were obtained in previous work in the same group, the total concentration with reference to the paper is calculated. These data are correlated with other parameters (degree of polymerisation, chain scission) for comparison and better understanding of the ageing of paper. However, due to a lack of knowledge of the exact chemical reactions taking place concurrently, including the reaction path and reaction coefficients, it is still difficult to predict the ageing products in an accurate manner. Experimentally obtained knowledge on the relationship between the measurable chemicals enables the fusion of different measurements to establish a more reliable approach to diagnose the conditions of transformer insulation. The original data of the concentrations of 2-FAL and methanol in transformer oil (Gemini X) are shown in Figure 5.5 and Figure 5.9, respectively.

From Figure 5.5, it can be seen that the variation of 2-FAL concentration follows a clearly increasing trend. The results in the present work show that during the ageing process, the 2-FAL concentration in the transformer oil has gone a significant but smooth change. In the first 8 days, the change is relatively slow, and from day 8 the results exhibit a rather linear increasing trend to reach a value of 25.56 mg/kg at Day 75. This trend is similar to what is seen in literature for 2-FAL generation under similar experimental conditions.

However, it is noted that this is the 2-FAL measured only in oil. 2-FAL is known to partition between the transformer oil and paper insulation. Therefore, the total content of 2-FAL needs to be calculated in order to obtain a more accurate value of the 2-FAL generation from paper ageing. The partitioning relationship is shown in (5.4):

$$P_{2\text{-FAL}} = \frac{2\text{-FAL}_{\text{oil}}}{2\text{-FAL}_{\text{paper}}} \quad (5.4)$$

where $P_{2\text{-FAL}}$ is the partitioning coefficient, $2\text{-FAL}_{\text{oil}}$ is the 2-FAL concentration in oil and $2\text{-FAL}_{\text{paper}}$ is the 2-FAL concentration in paper.

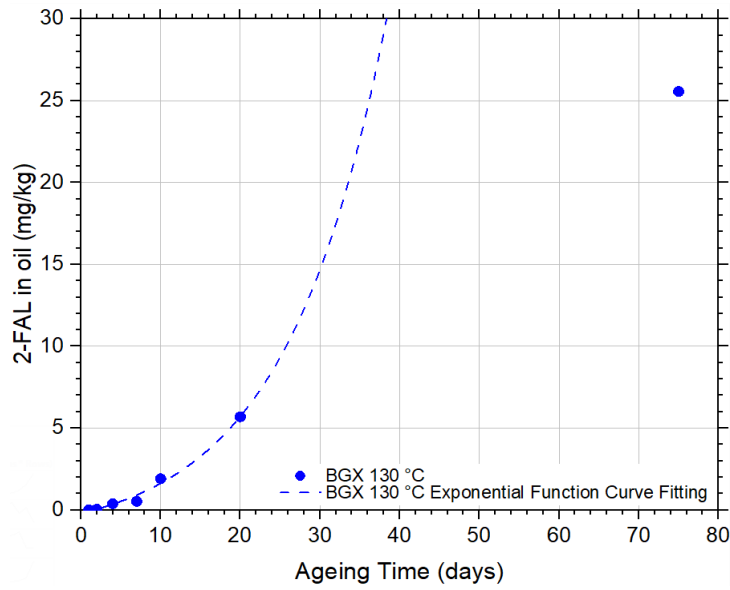


Figure 5.5 Measured 2-FAL concentration in transformer oil during the ageing of Kraft paper in Gemini X without added moisture and acids at 130 °C using sealed ampoules.

Experimental data from [33] is used to find the partitioning coefficient for 2-FAL at room temperature at an initial paper moisture content of approximately 0.4%. The partitioning coefficient is assumed to be the same for the paper throughout the ageing process. The partitioning coefficient is found to be 0.45. The 2-FAL from paper are then calculated using (5.4). To calculate the total 2-FAL from paper (5.5) is used:

$$C_{\text{Total 2-FAL, paper}} = \frac{(2\text{-FAL}_{\text{oil}} \times m_{\text{oil}}) + \left(\frac{2\text{-FAL}_{\text{oil}}}{P_{2\text{-FAL}}} \times m_{\text{paper}}\right)}{m_{\text{paper}}} \quad (5.5)$$

where $C_{\text{Total 2-FAL, paper}}$ is the total 2-FAL concentration from paper, $2\text{-FAL}_{\text{oil}}$ is the 2-FAL concentration in oil, m_{oil} is the mass of oil, $P_{2\text{-FAL}}$ is the partitioning coefficient for 2-FAL derived from [33] and m_{paper} is the mass of paper.

(5.5) is then simplified to:

$$C_{\text{Total 2-FAL, paper}} = \left(\left(\frac{m_{\text{oil}}}{m_{\text{paper}}} \right) + \left(\frac{1}{P_{2\text{-FAL}}} \right) \right) 2\text{-FAL}_{\text{oil}} \quad (5.6)$$

The total 2-FAL concentration from paper is plotted against ageing time as shown in Figure 5.6. It is clear that the variation of 2-FAL follows a clear increasing trend similar

to that seen in Figure 5.5. This is because the concentration of 2-FAL in oil is essentially multiplied by a factor as seen in Equation 5.6.

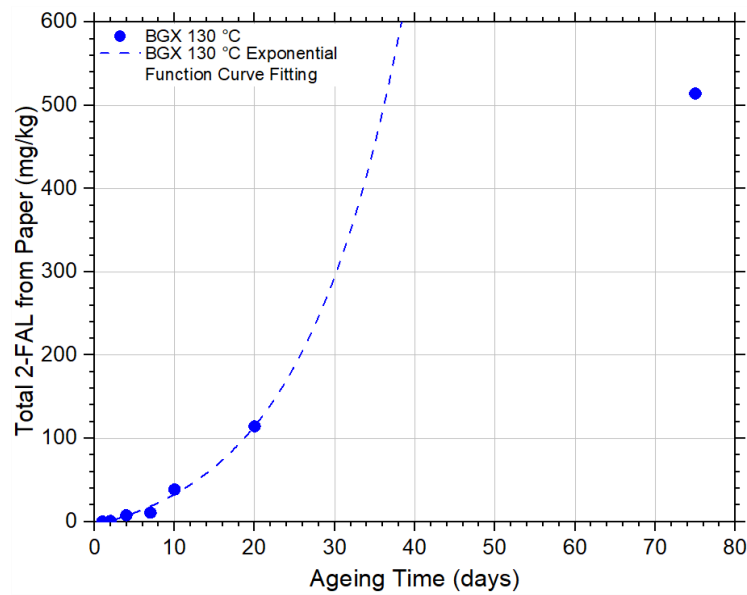


Figure 5.6 Calculated total 2-FAL concentration from paper ageing using partitioning data and ageing time of the paper during the ageing process at 130 °C in sealed ampoules.

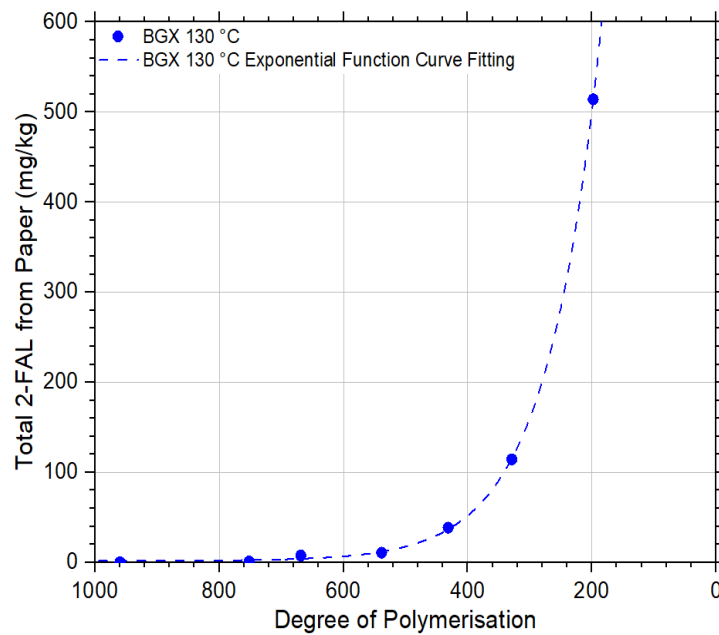
The correlation between 2-FAL and DP is given in Figure 5.7. An exponential trend is clear from the measurements, giving the following relationship:

$$DP = 507 - 222 \times \log(C_{\text{Total 2-FAL, paper}}) \quad (5.7)$$

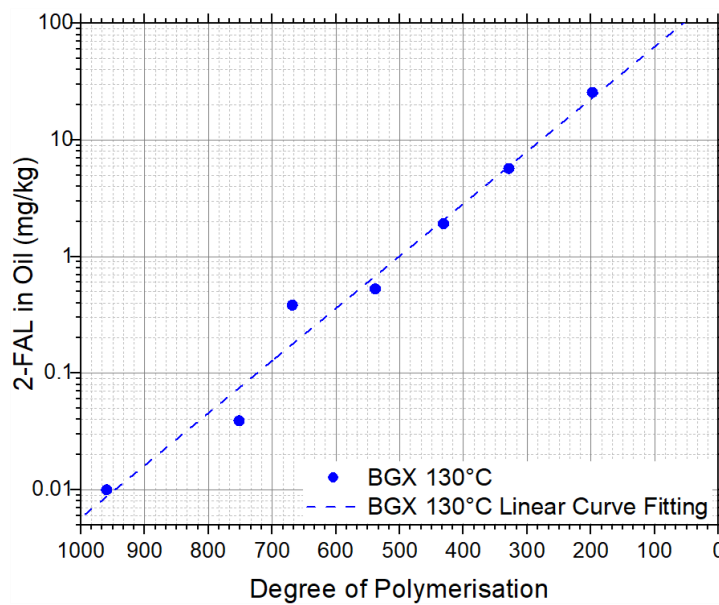
which is a fairly accurate way to describe the ageing process, especially when the DP reduces to below half of the start DP.

2-FAL is considered a late paper ageing indicator as can be seen in Figure 5.7, which follows the expected trend found in literature. The total 2-FAL concentration from paper only starts to increase rapidly below a DP of approximately 540. In reality, the measured 2-FAL concentrations in oil always contain fluctuations, which means if the 2-FAL concentration is used to derive the DP of paper based on an exponential relationship, there will be uncertainties in the derived DP value. From Figure 5.7, it can be shown that the uncertainty in the derivation of DP is around 70 for those points

whose values deviate from the straight trend line. Considering a DP change of 800 in the lifetime of paper insulation in transformers, this level of uncertainty is acceptable.



(a)



(b)

Figure 5.7 Correlation between total 2-FAL from paper and DP of the paper during the ageing process at 130 °C with sealed ampoules. (a) – linear scale; (b) logarithm scale for correlation.

Figure 5.8 shows the relationship between total 2-FAL concentration from paper and the chain scission number with the corresponding DP value. The curve follows a clear

increasing trend, which is more linear compared to Figure 5.7. This suggests Figure 5.8 is a better reference or calibration curve for the correlation curve with 2-FAL as an ageing parameter. From Figure 5.8 it can be seen that the generation of 2-FAL is slow when the chain scission number increases from 0 to 0.8. After the chain scission number of 0.8 the generation begins to rapidly increase. The maximum chain scission number seen is 4 corresponding to a DP of 196. This gives a corresponding total 2-FAL generation of 514.31 mg/kg.

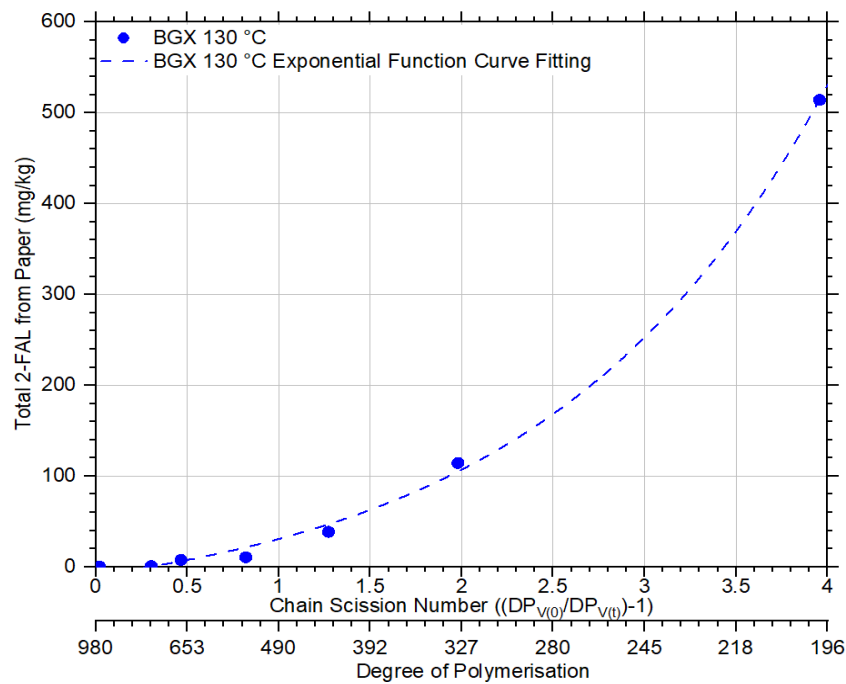


Figure 5.8 Correlation between total 2-FAL in paper and chain scission number for Gemini X measured during the ageing process at 130 °C with sealed ampoules.

The variation of methanol follows a clear increasing trend. The methanol results given in Figure 5.9 show a smooth and close-to-linear variation with the ageing time within 75 days. The value of 1.14 mg/kg is seen at Day 75.

Methanol, likewise to 2-FAL, partitions between the transformer oil and paper. The total content of methanol needs to be calculated in order to obtain a more accurate value of the total methanol generation from paper ageing. The partitioning relationship for methanol is shown in (5.8):

$$P_{\text{Methanol}} = \frac{\text{Methanol}_{\text{oil}}}{\text{Methanol}_{\text{total oil}}} \quad (5.8)$$

where P_{Methanol} is the partitioning coefficient, $\text{Methanol}_{\text{oil}}$ is the methanol concentration in oil and $\text{Methanol}_{\text{total oil}}$ is the total methanol concentration in oil.

Experimental data from [33] is used to find the partitioning coefficient for methanol at room temperature at an initial paper moisture content of approximately 0.4%. The partitioning coefficient is assumed to be the same for the paper throughout the ageing process. The partitioning coefficient is found to be 0.045. The methanol concentration from paper are then calculated using (5.8). To calculate the total methanol content from paper, (5.9) is used:

$$C_{\text{Total Methanol, paper}} = \frac{\text{Methanol}_{\text{oil}} \times m_{\text{oil}}}{m_{\text{paper}} \times P_{\text{Methanol}}} \quad (5.9)$$

where $C_{\text{Total Methanol, paper}}$ is the total methanol concentration from paper, $\text{Methanol}_{\text{oil}}$ is the methanol concentration in oil, m_{oil} is the mass of oil, P_{Methanol} is the partitioning coefficient for methanol and m_{paper} is the mass of paper.

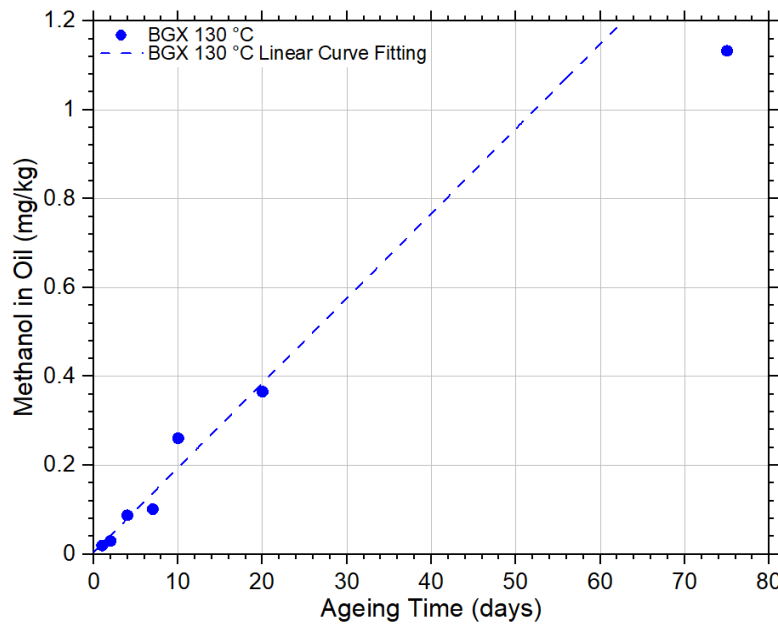


Figure 5.9 Measured methanol concentration in transformer oil during the ageing of Kraft paper in Gemini X without added moisture and acids at 130 °C in sealed ampoules.

(5.9) is then simplified to:

$$C_{\text{Total Methanol, paper}} = \left(\frac{m_{\text{oil}}}{P_{\text{Methanol}} \times m_{\text{paper}}} \right) \text{Methanol}_{\text{oil}} \quad (5.10)$$

The total methanol concentration from paper is plotted against ageing time as shown in Figure 5.10. The variation of methanol content follows a clear increasing trend similar to that seen in Figure 5.9. This is because the concentration of methanol in oil is essentially multiplied by a factor as seen in Equation 5.10.

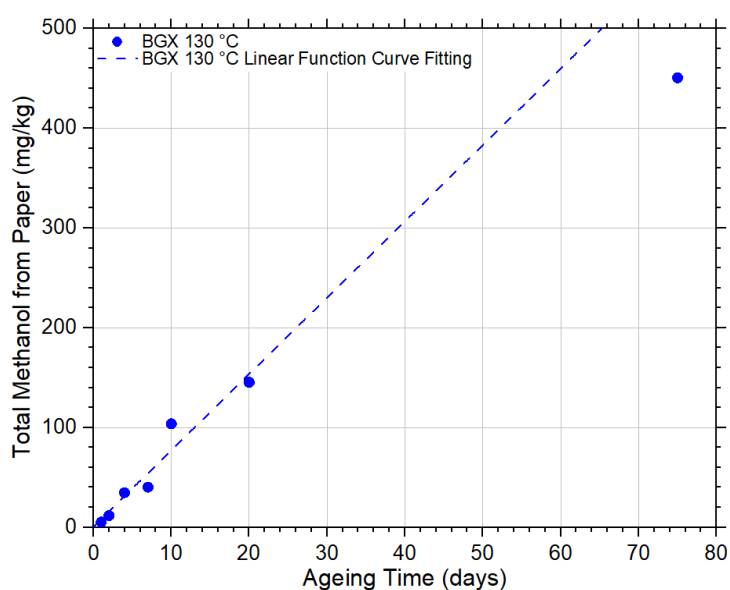


Figure 5.10 Calculated total methanol concentration from paper ageing using partitioning data and ageing time of the paper during the ageing process at 130 °C in sealed ampoules.

To qualify as a paper ageing indicator, a parameter has to be well correlated to the mechanical strength of the paper, such as the DP, instead of time. From Figure 5.11 it can be seen that the total methanol content follows closely an exponential trend with respect to the DP of the paper.

Figure 5.12 shows the relationship between total methanol concentration from paper and the chain scission number. The curve follows a clear increasing trend and it can be seen that the generation of the methanol has almost linear relationship with the chain scission number. The maximum chain scission number seen is 4 corresponding to a total methanol generation of 450.56 mg/kg.

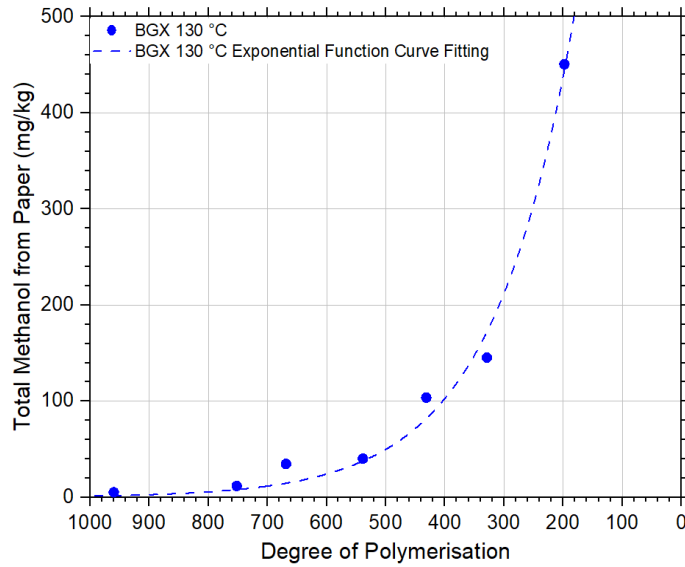


Figure 5.11 Correlation between total methanol from paper and DP of the paper during the ageing process at 130 °C with sealed ampoules.

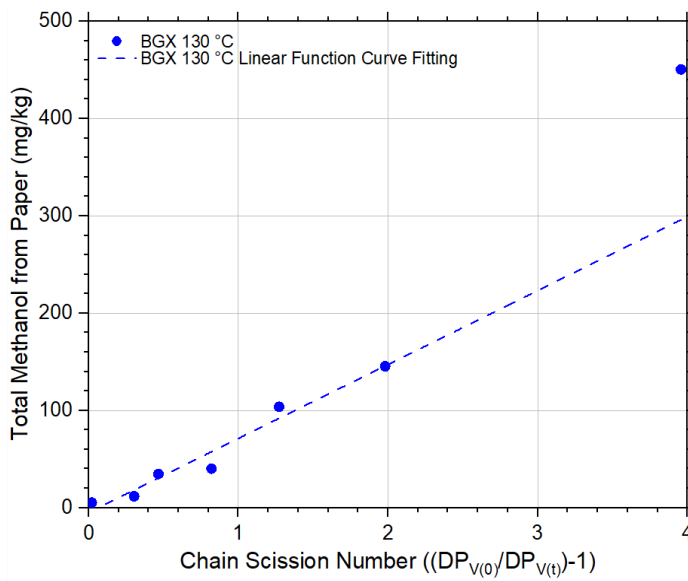


Figure 5.12 Correlation between total methanol in paper and chain scission number for Gemini X measured during the ageing process at 130 °C with sealed ampoules.

The total generation from paper of methanol and 2-FAL are plotted with ageing time in Figure 5.13. The two parameters follow the expected trend in paper ageing that were reported in literature. The total methanol generation exhibits a more linear trend than the total 2-FAL generation. Methanol has been studied for its potential as an early ageing indicator for transformer paper [101]. The present work supports this. It can be

seen in Figure 5.13 that the generation of methanol is clearly higher than 2-FAL until Day 20 (Figure 5.13), corresponding to a DP of 300 (Figure 5.14).

The concentration of 2-FAL overtakes that of methanol at the late ageing stage. Its concentration starts to rapidly increase when DP drops below 300. The final value of the total 2-FAL from paper at Day 75 is found to be 514.31 mg/kg which is 63.75 mg/kg higher than the total methanol generation.

Figure 5.14 shows the correlation between the total methanol and 2-FAL generation and the degree of polymerisation. Both are seen to have exponential trends. The differences in the concentrations as a function of DP mirrors well with the results reviewed in Chapter 2 (Figure 2.19) although the concentrations used in Figure 5.14 are the total generation which can be scaled to the concentration present in oil by dividing by a factor (20 for 2-FAL and 400 for methanol).

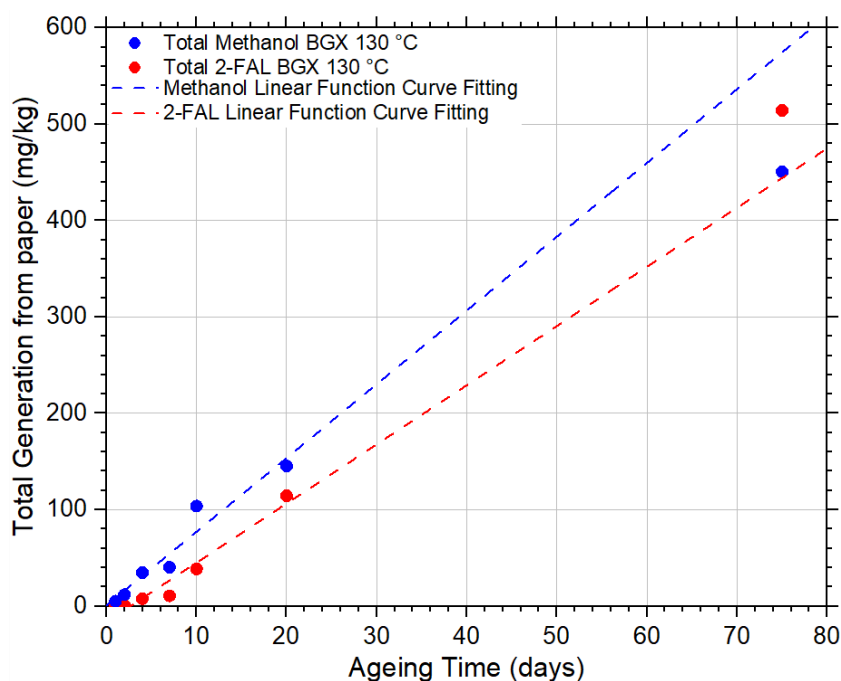


Figure 5.13 Correlation between the total methanol and 2-FAL in paper and ageing time for Gemini X measured during the ageing process at 130 °C with sealed ampoules.

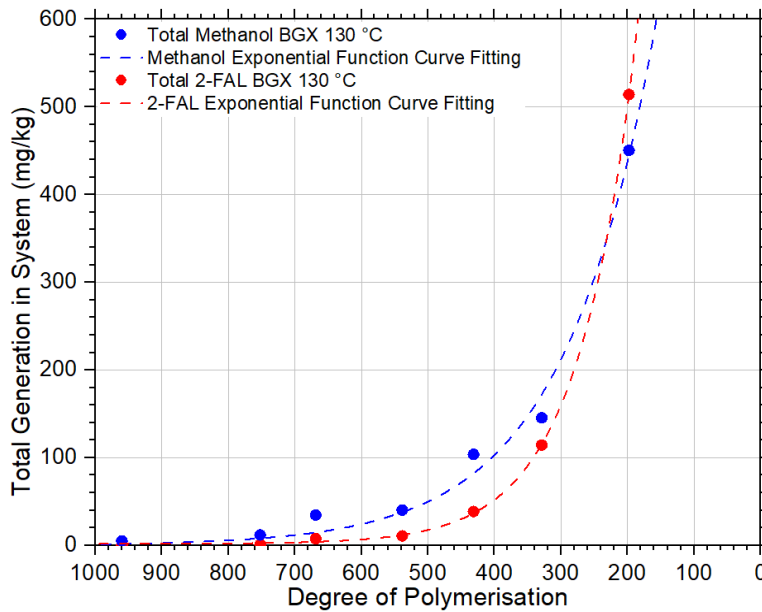


Figure 5.14 Correlation between the total methanol and 2-FAL in paper and degree of polymerisation for Gemini X measured during the ageing process at 130 °C with sealed ampoules. The concentration in oil can be obtained by dividing the total concentration by a factor 20 for 2-FAL and 400 for methanol.

5.5 Acidity Measurement of Aged Samples

One of the focuses in the present work is the investigation of the variation of acid concentrations during the ageing of transformer paper in oil in thermally accelerated ageing tests. Using the method of measurement that has been detailed in Chapters 3 and 4, the baseline data for LMA generation in the absence of added moisture and acids are presented in Figure 5.15 to Figure 5.16.

The LMA mostly stays in paper (Figure 5.15) and increases rapidly in the first 10 days and then slows down. Although there are fluctuations, the trend of increase is clear. Approaching the end of the ageing test, the LMA concentration reaches a value just above 4 mg KOH/g. Figure 5.16 shows the paper LMA concentration correlated with DP. Despite the slightly higher value sampled on Day 2, there is a clear increase in the paper LMA when the DP decreases and the correlation is apparent.

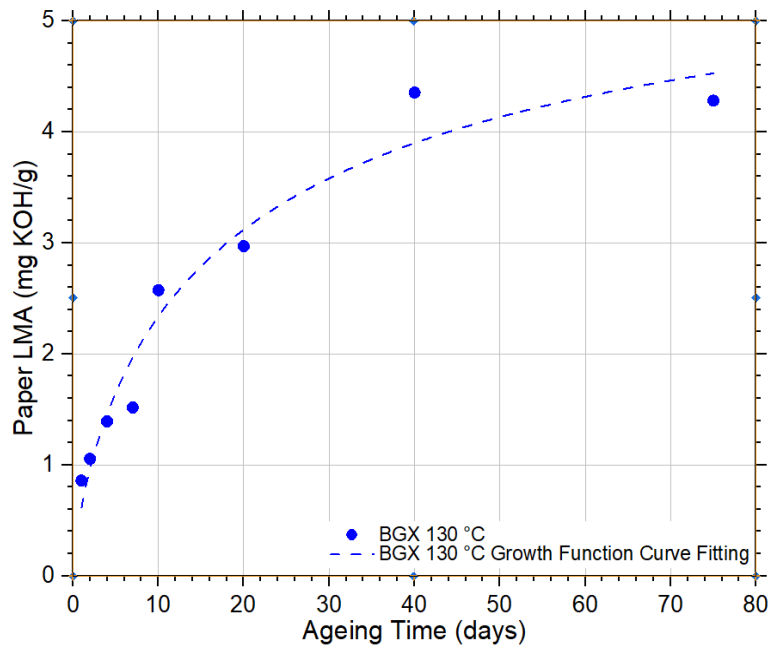


Figure 5.15 Measured LMA in Kraft paper based on water extraction, dried Kraft paper was aged in sealed ampoules at 130 °C.

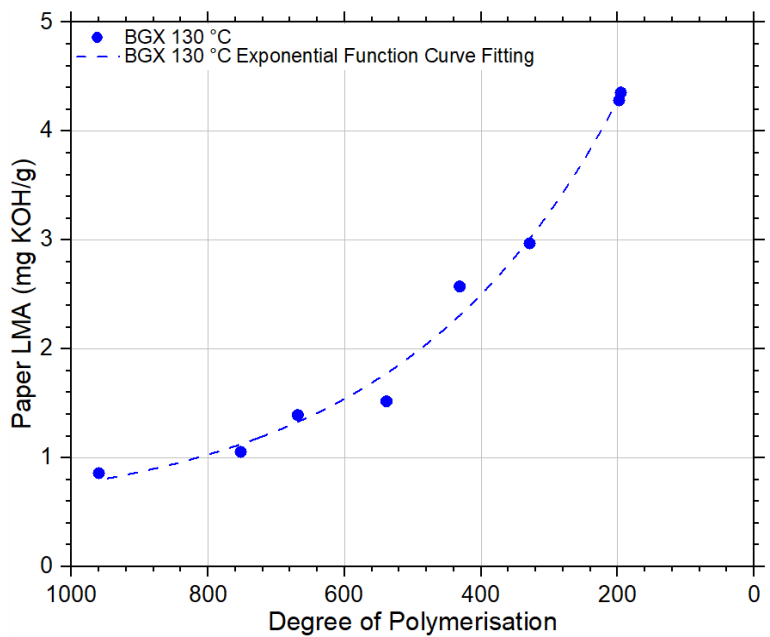


Figure 5.16 Correlation between paper LMA, and DP for Gemini X measured during the ageing process at 130 °C with the sealed ampoules.

Figure 5.17 shows measured LMA, HMA and derived total acidity in Gemini X. The LMA in oil follows a similar trend but with a much lower concentration. Using the values at Day 20 and Day 40, the partition of LMA in oil and paper is estimated to be 0.57% and 0.64%, respectively, in terms of its content. It is to be noted that these two

similar partition percentages were obtained with an oil to paper ratio of 17.3:1 (mass). The LMA concentrations in oil at Day 40 and Day 70 are both higher than 0.025 mg KOH/g, which are well within the range of 0.02 mg KOH/g to 0.1 mg KOH/g that was determined in [24]. For service aged oils the concentration of LMA is 0.03 mg KOH/g and the ratio of LMA in oil and paper was in the range 1:60 to 1: 175 [24]. Using the data at Day 20 in the present work, the ratio of LMA concentration in oil and paper is 1:176, corresponding to the upper limit of the serviced oil and paper insulation system.

On the other hand, the HMA in the aged oil is much higher than that of the LMA, at least 3 times higher from Day 10, as shown in Figure 5.17. The reliability of the measurement was also checked by comparing the directly measured total acidity of the oil with the sum of the LMA and HMA concentrations measured separately in the oil. Figure 5.18 confirms that these two sets of data agree well, giving confidence in the results.

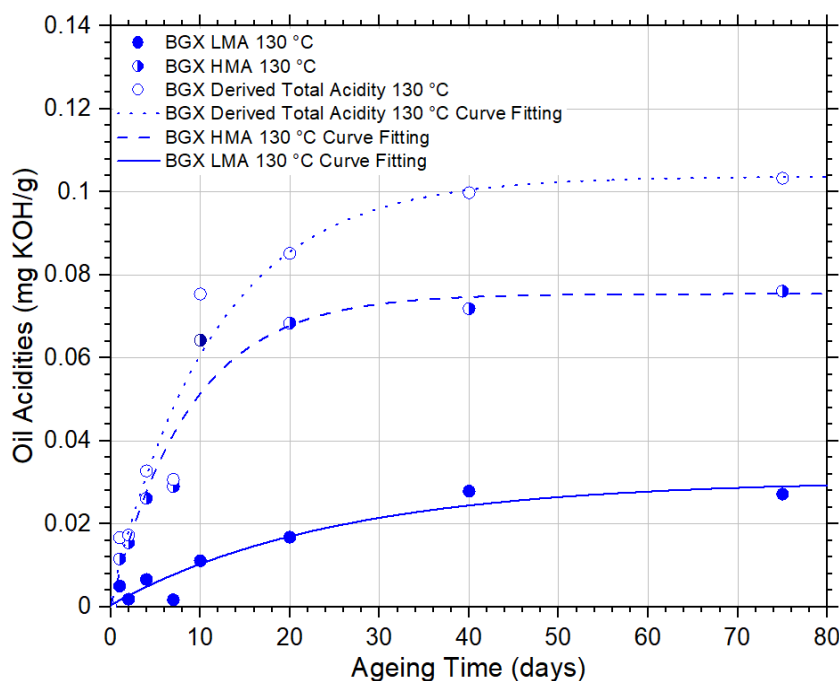


Figure 5.17 Measured LMA and HMAs in Gemini X which was aged together with paper in sealed ampoules at 130 °C.

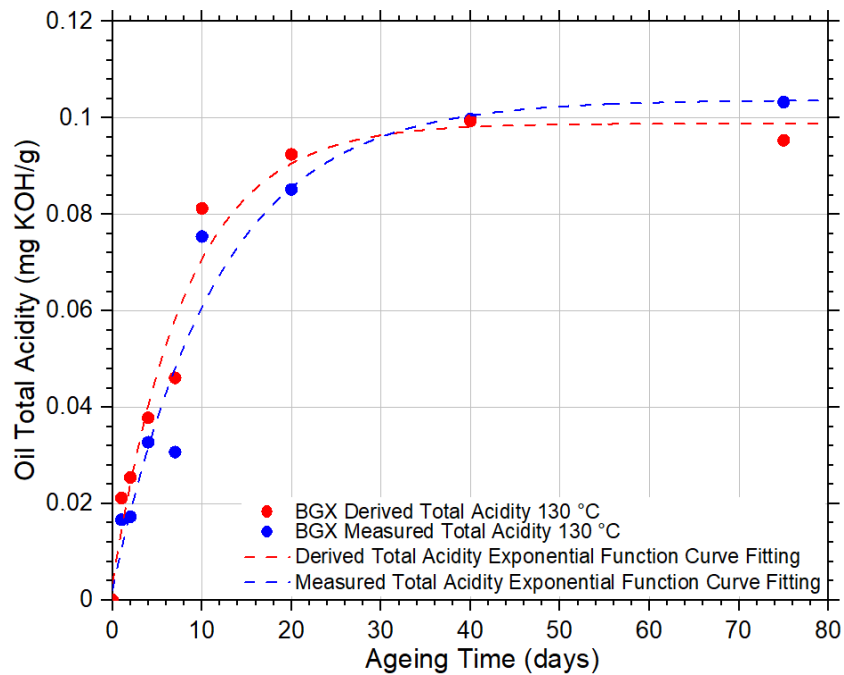


Figure 5.18 Directly measured total acidity and that calculated by adding the measured LMA and HMA concentrations in Gemini X which was aged together with dried Kraft paper in sealed ampoules at 130 °C.

Figure 5.19 shows the correlation between oil LMA concentration and DP. Although there is some fluctuation in the data initially which could be due to the measurement of the very low acidity, an exponential trend can be seen, especially when the DP is below 500.

Figure 5.20 is to assess the correlation between the paper LMA concentration and liquid LMA concentration. Since the paper absorbs most of the LMA, the concentration of LMA in the oil is extremely low in the early stage of ageing. The values are below 0.007 mg KOH/g. In Chapter 4, it has been shown that for LMA concentration down to 0.017 mg KOH/g, at least 90% of the LMA in Gemini X can be detected. Therefore, the uncertainty in the measurement results may contribute towards the deviation of the correlation from the trend line. When the concentration is above 0.015 mg KOH/g, a much stronger correlation can be seen.

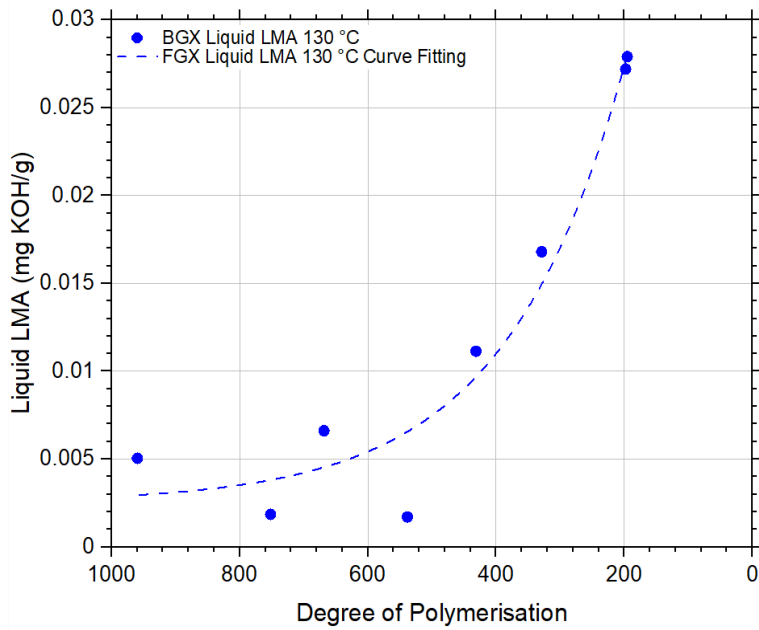


Figure 5.19 Correlation of liquid LMA and DP in Gemini X which was aged together with Kraft paper in sealed ampoules at 130 °C.

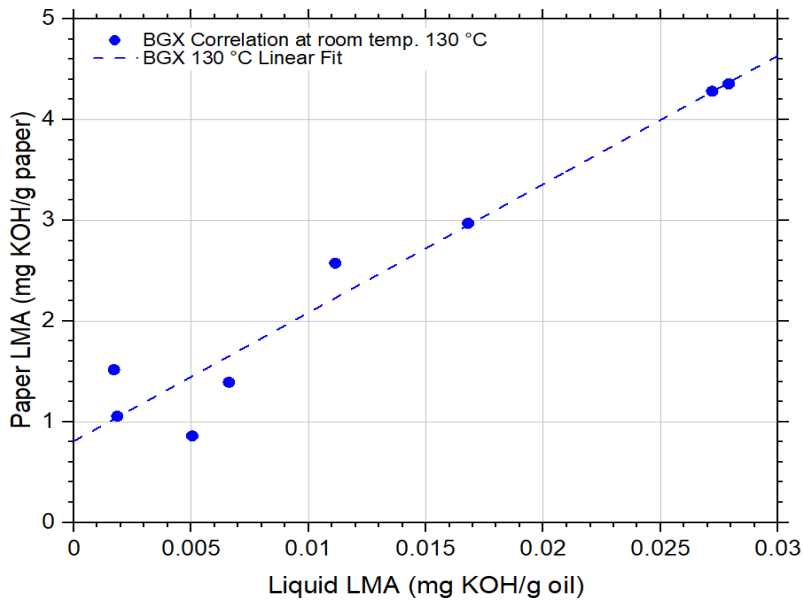


Figure 5.20 Correlation of paper LMA and liquid LMA in Gemini X which was aged together with Kraft paper in sealed ampoules at 130 °C.

The samples after ageing were left at room temperature to reach equilibrium in partitioning between transformer oil and paper. To better understand the effects of LMA generated from the paper insulation, the total LMA generation needs to be calculated. This is calculated via Equation 5.11:

$$C_{\text{Total LMA, paper}} = \left(\frac{(LMA_{\text{oil}} \times m_{\text{oil}}) + (LMA_{\text{paper}} \times m_{\text{paper}})}{m_{\text{paper}}} \right) \quad (5.11)$$

where $C_{\text{Total LMA, paper}}$ is the total LMA concentration assigned to paper, LMA_{oil} is the LMA concentration in oil, LMA_{paper} is the LMA concentration in paper, m_{oil} is the mass of oil, and m_{paper} is the mass of paper.

Equation 5.11 then simplifies to:

$$C_{\text{Total LMA, paper}} = \frac{(LMA_{\text{oil}} \times m_{\text{oil}})}{m_{\text{paper}}} + LMA_{\text{paper}} \quad (5.12)$$

Figure 5.21 shows the correlation of total LMA concentration assigned to paper and degree of polymerisation. Due to the fact that LMA mostly concentrates in paper, this figure has a very similar trend to Figure 5.16. The two points around the DP value of 200 affirms the correlation, i.e. the relationship between LMA generation and DP is not affected by the time. In other words, it is determined by the state of the aged paper.

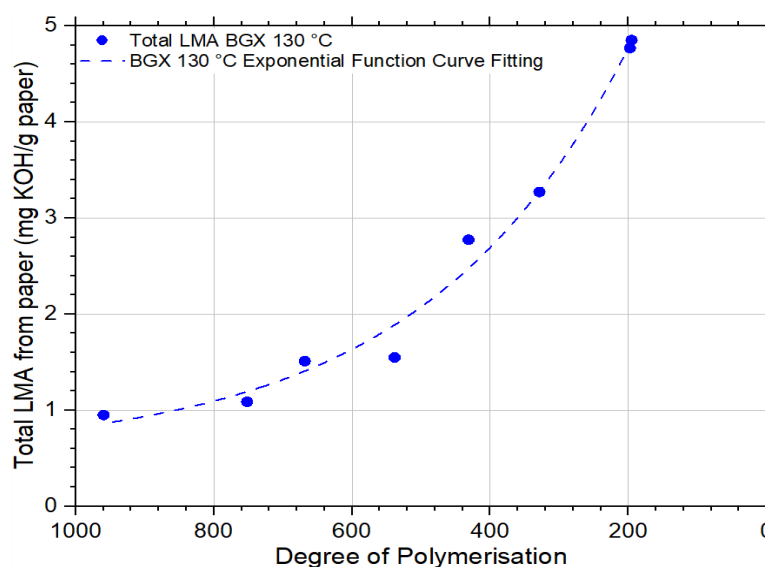


Figure 5.21 Correlation of total paper LMA and DP in Gemini X which was aged together with Kraft paper in sealed ampoules at 130 °C.

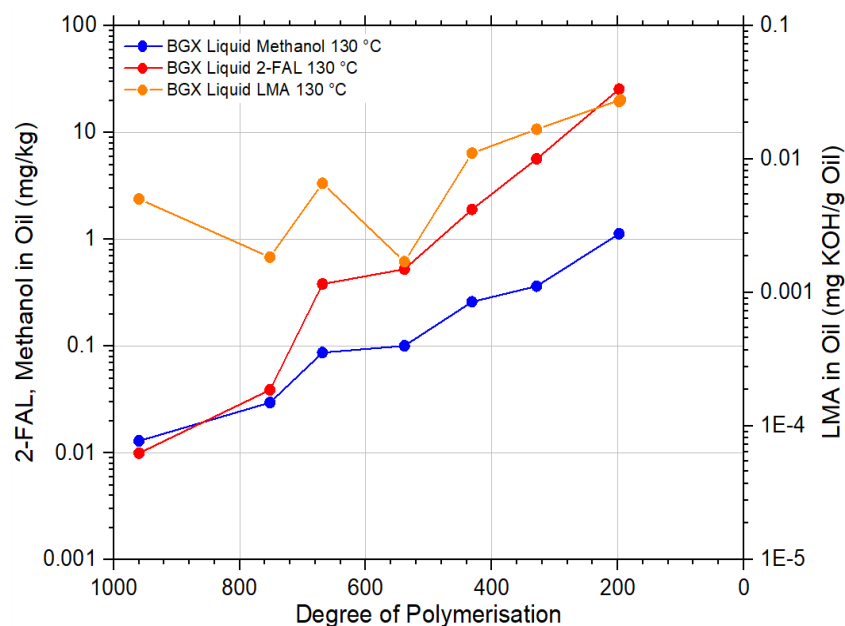
5.6 Correlations between Ageing Parameters

Due to a lack of knowledge of the exact chemical species, such as different types of LMA, chemical reaction paths and the reaction coefficients, it is still difficult to predict the ageing products in an accurate manner. Experimentally obtained knowledge on the relationship between the measurable chemicals enables the fusion of different measurements to establish a more reliable approach to diagnose the conditions of transformer insulation.

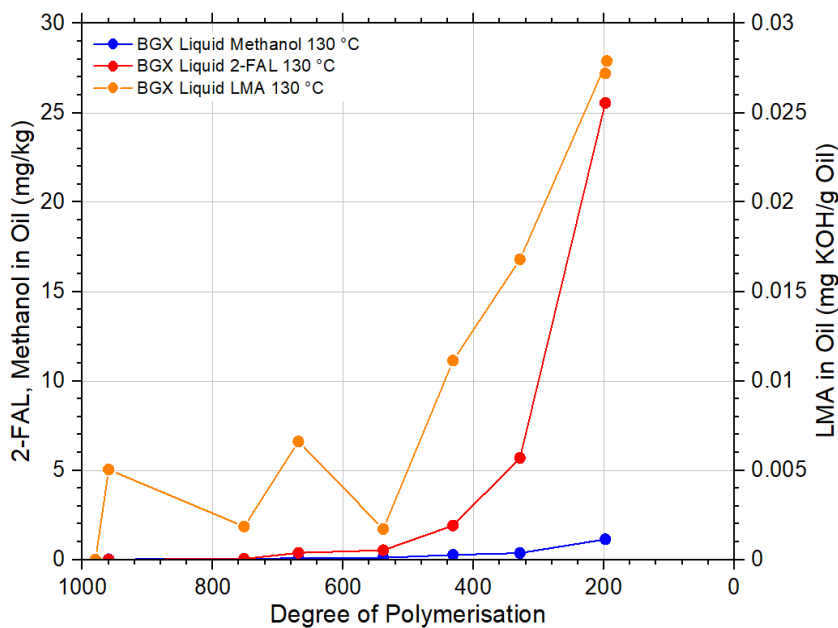
Figure 5.22 presents the variation of 2-FAL, methanol and LMA concentrations as function of paper DP. A comparative analysis shows that when the DP drops below 450, the variation of the three species concentrations follows well exponential trends (Figure 5.22 (a)). Over the whole measurement range, an exponential trend line can still be seen for 2-FAL and methanol concentrations. The relative largeness of the concentration of the three species are given in Figure 5.22 (b). Approaching the end of the ageing process, 2-FAL has a much higher concentration than methanol, by a factor of 17.

Measurement uncertainties are unavoidable in the determination of the concentration of the chemical species. Based on the information from Figure 5.22 (a), the measured 2-FAL and methanol concentrations and the trend line can be used to derive a DP value that differs from the measured DP by a maximum of approximately 80.

Figure 5.23 presents the concentration of 2-FAL, methanol and LMA per paper mass. The values for 2-FAL are obtained using partitioning information from [33]. The values for LMA are calculated by adding the content in oil and paper and divided by the paper mass. It can be seen that the total LMA generation increases monotonically with reduction in DP. The trend of increase is clear in all three sets of data, providing positive experimental evidence for further exploring the possibility of using the three species to monitor the insulation state of transformer paper.



(a)



(b)

Figure 5.22 Correlation between chemical concentrations (2-FAL, methanol and paper LMA) in Gemini X and DP during the ageing process at 130 °C with the sealed ampoules. (a) – logarithm scale for concentration showing trend; (b) – linear scale for concentration showing growth.

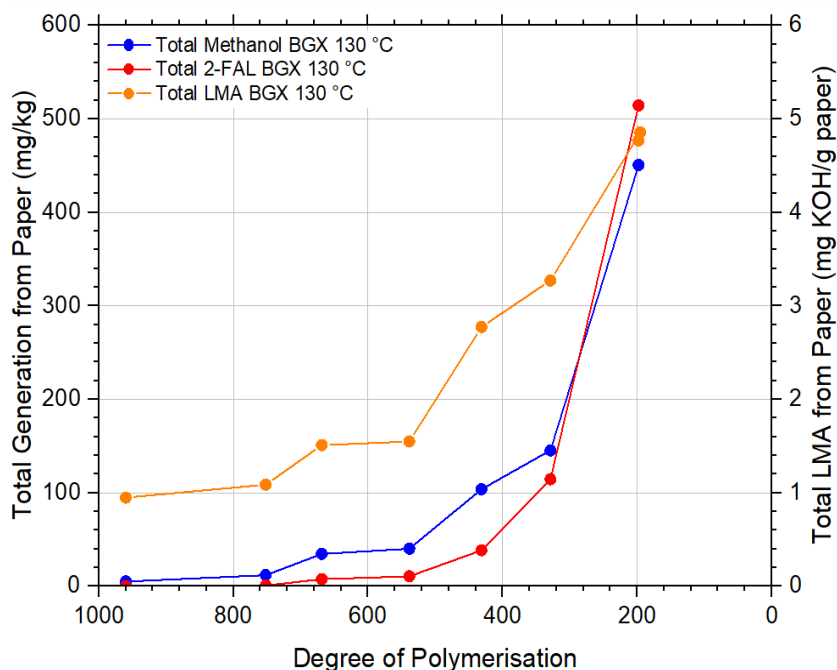


Figure 5.23 Correlation between total chemical concentrations (2-FAL, methanol and paper LMA) assigned to paper and DP during the ageing process at 130 °C with the sealed ampoules.

5.7 Summary

The concentration of LMA, 2-FAL and methanol in a transformer oil (Gemini X) and the moisture level and LMA concentration in aged Kraft paper are reported for thermally accelerated ageing process at 130 °C. The initial moisture level of the paper is around 0.5% (mass) and no acids are added to the ageing system. The oil and paper are both pre-treated by filtration and drying. This corresponds to the conditions of oil and paper in a new transformer. The following features are demonstrated by the results:

- The use of sealed small size ampoules provides a more uniform and isolated ageing environment (apart from heat exchange with the environment) and the measured paper DP, oil 2-FAL, oil methanol and paper LMA results follow closely their respective trend lines, providing a less disturbed ageing system for fundamental research of oil and paper ageing.
- There exist clear correlations between the variation of DP from its starting value and the change of 2-FAL, methanol and paper LMA concentrations. The correlation suggests that the DP of the paper can be derived from the measured concentrations with an uncertainty of approximately 80 in the worst case.

-
- When the oil LMA concentration is higher than 0.01 mg KOH/g, its variation follows linearly the LMA of the paper in logarithm coordinate systems.

The major achievement of the work in this chapter is three-fold: 1) the verification of sealed ampoule thermal ageing as a method to study the degradation of cellulose paper without the interference of excessive oxidation and moisture ingress over long periods of ageing; 2) measurement of LMA as a function of ageing time, which has not been reported in literature; and 3) the work shows that the sealed system allows for a reduced amount of material used for measurement, providing a cost-effective and yet sufficiently accurate ageing technique.

The results in this chapter will be used in Chapters 6 and 7 as baseline data for the comparative studies of the effect of acids on the paper degradation process.

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CHAPTER 6

6 ACIDIFIED INHIBITED MINERAL OIL AND KRAFT PAPER THERMAL AGEING IN SEALED AMPOULES

6.1 Introduction

Important parameters of transformer oil and paper have been measured in well controlled ageing experiments in Chapter 5 for Gemini X, an inhibited mineral oil, in its 'blank' state, i.e. under dry conditions (moisture percentage < 0.5%) without any added acids. These results serve as the reference data in the comparative studies that are to be carried out in this Chapter.

The presence of LMA in service-aged transformer oils and papers, which were also quoted as hydrophilic acids in [24], was confirmed in experiment by a reduction in the neutralization value (NV) of the oil when the oil was rinsed by water. The LMA can account up to 30% of the total acids in the oil [24]. To study the effect of LMA on the ageing process of transformer liquid and paper, LMA such as formic acid were added to the oil sample in [24] with an initial NV of 0.4 mg KOH/g before the paper was immersed in the oil. Only the effect of LMA on the DP was reported in [24] [14] and other parameters like the LMA content in oil and paper as a function of ageing time were not presented. The latter is however essential to study the potential of using LMA concentration in oil as a paper ageing indicator.

This chapter is devoted to a study of the effect of formic acid on the ageing process of oil-paper transformer insulation system. By measuring the important parameters at different lengths of ageing time, such as DP, moisture level, LMA level, and other chemicals, the effect of formic acid as a typical type of LMA will be quantified.

When considering the initial conditions, the inherent acidity of transformer liquids needs to be taken into consideration. It is approximately 0.035 mg KOH/g for the 'blank' mineral oil used. An initial value much higher than 0.035 mg KOH/g needs to be used in order to make a difference to the ageing process. In the present work, a value around 0.4 mg KOH/g was used for the comparative study.

The water content and LMA content in the Kraft paper are key to the initial conditions of the insulation system. Formic acid was added to the samples with the following procedure.

1. The oil was first dried and filtered according to the procedure given in Chapter 3. LMA in liquid form was added to a bottle of oil (500 ml, 250 ml and 100 ml) according to the calibration curve in Chapter 4. This process was kept as soon as possible (a few seconds) and then the bottle was sealed so the possibility of evaporation of LMA is minimal. The bottle was then stirred and left for a few days.
2. The Kraft paper was first dried in air, then dried in well dried oil before it was placed in ampoules. The oil used in this drying process is the same type of oil for ageing. Then the paper was placed in ampoules and temporarily sealed with a rubber stop. Then the oil with added formic acid was added to the paper containing ampoules and temporarily sealed with rubber stops. After all ampoules were ready for the same batch of test, they were properly sealed for ageing.

The work in this chapter is presented in the following order. Section 6.2 briefly describes the variation of moisture level in paper to ensure proper initial conditions. Section 6.3 reports the variation of the degree of polymerization of paper as a function of time and the main features in comparison with the case without added formic acid. Section 6.4 is devoted to the concentrations of 2-FAL and methanol. Section 6.5 is a comparative study on the evolution of the concentration of low molecular acids (LMA) in the ageing process. Section 6.6 provides a brief summary of the major findings in this chapter.

6.2 Variation of Moisture Level in Kraft Paper

In existing work, the measured values of the moisture content in liquid and paper for the ageing process of dry paper show large variation with ageing time [12] [101]. The reasons for this level of variation could not be identified.

In the present work using sealed ampoules, a clear trend of moisture level is shown by the measurement at different ageing times. The initial moisture in the paper is less than 0.5%. The measured value is 0.8% on Day 1. Both in Chapter 5 and this chapter, the moisture measurement on Day 1 has always been slightly larger than but close to the initial moisture value, as shown in Figure 6.1. Compared with the results reported in [12] [101] for dried paper ageing, results in the present work using sealed ampoules have a much clearer trend of change with significantly smaller variation of a random nature.

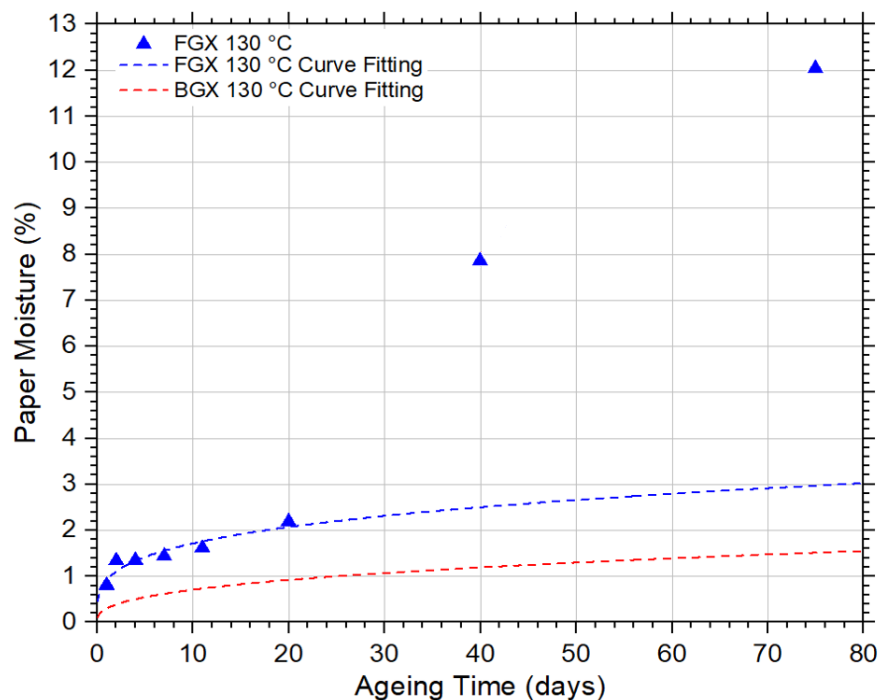


Figure 6.1 Variation of moisture level in aged Kraft paper impregnated in Gemini X as a function of ageing time at 130 °C. Initial moisture level is <0.5 %. BGX means blank Gemini X and FGX means Gemini X with added formic acid.

The measured values at Day 40 and Day 75 seem to be too large to be explained, although no mistakes in the measurement process have been identified. The trend line is therefore based on the data for the first 20 days. In comparison with the moisture results without added formic acid, the moisture concentration is higher, by a predicted factor of about 2. The presence of formic acid and excess moisture in the oil and paper is expected to accelerate the ageing of the Kraft paper.

6.3 Change in Degree of Polymerization of Kraft Paper

The effect of adding formic acid to the oil-paper system is evidenced in Figure 6.2. The decrease in DP in the first 4 days is much faster than in the case without added formic acid. Within the first 4 days, the DP drops to 300 in comparison with a value of 630 without the added acid. The influence is huge. This can be explained by the derived initial reaction rate in the cases. Figure 6.3 shows the corresponding chain scission number plotted with time. From Figure 6.3, the slope of the blue line fitting up to Day 4 is 0.023/hour, which gives an initial reaction rate of 2.35×10^{-5} /hour based on Equation 5.3, which is 5 times the initial reaction rate without added formic acid (4.7×10^{-6} /hour).

Ageing of dried Kraft paper in oil with the same initial formic acid concentration (0.4 mg KOH/g) was also performed in [14] at 130 °C, which gave a value of 2.0×10^{-5} /hour, slightly lower than the value obtained in the present work. The acceleration factor derived in [14] is 5.6 for formic acid, comparing well with the value of 5 in the present work.

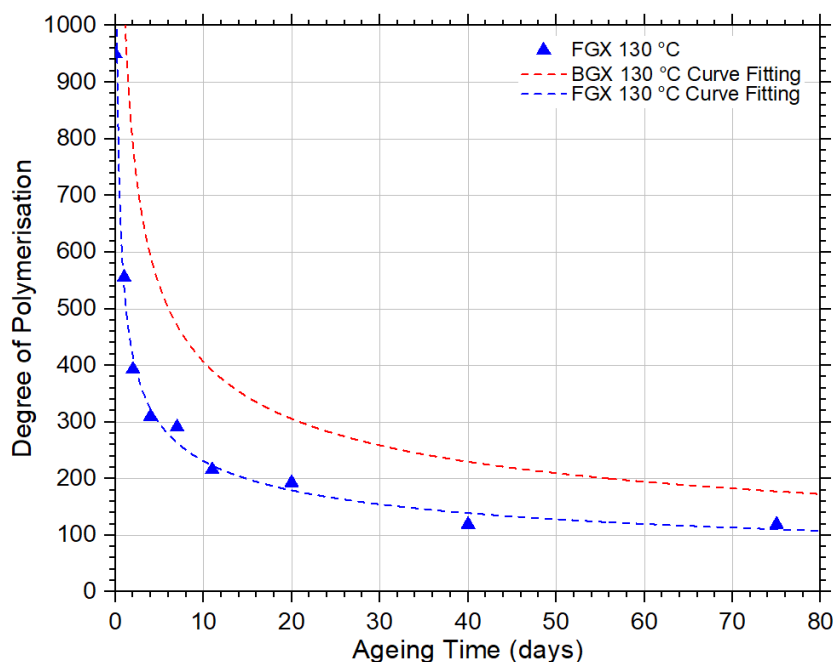


Figure 6.2 Variation of DP as a function of time when the Kraft paper was aged at 130 °C in Gemini X with added formic acid of initial concentration of 0.4 mg KOH/g in oil (before paper was added). BGX means blank Gemini X and FGX means Gemini X with added formic acid.

In interpreting the results from [14], it is to be noted that argon gas was used as a blanket to minimize oxidation and the paper-oil system was aged in large quantities (100 g of paper in large bottles of 2.32 litre) with an oil to paper mass ratio of 18:1. For information, the mass ratio in the present work is 17.4:1.

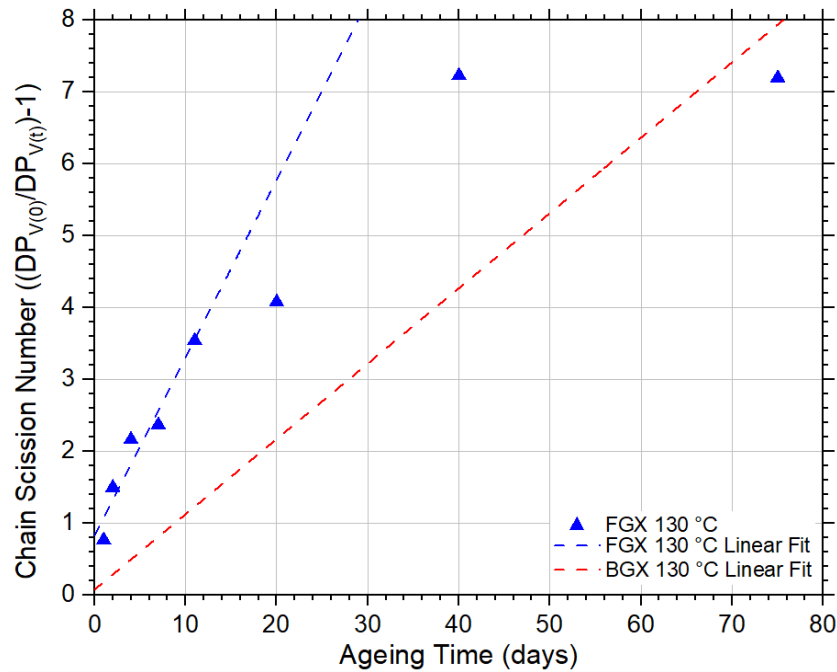


Figure 6.3 Chain scission number of Kraft paper as a function of time when the Kraft paper was aged at 130 °C in Gemini X with added formic acid of initial concentration of 0.4 mg KOH/g in oil (before paper was added). BGX means blank Gemini X and FGX means Gemini X with added formic acid.

6.4 Generation of 2-FAL and Methanol during Ageing of Kraft Paper

It has been found previously that 2-FAL is a common product of transformer paper ageing, as reviewed in Chapter 2. With added formic acid, the concentration of 2-FAL increases much more rapidly following rapid degradation of the Kraft paper, as shown in Figure 6.4. The increase in concentration up to a DP of 220 remains monotonic. The final concentration is also higher by 40% of the blank test case value.

The variation of the 2-FAL concentration with respect to DP with added formic acid follows a different trend line in comparison with the blank test case, as shown in Figure 6.5. The relationship between the concentration of 2-FAL and DP has been suggested

in [76, 79, 80] as described by Equations (2-1), (2-2) and (2-3). Assuming a linear relationship between $\log(2\text{-FAL})$ and DP, the following relationships were obtained based on the data and best fit curve shown in Figure 6.5.

Blank Gemini X:

$$\log(2\text{-FAL}) = 2.287 - 0.00464 \cdot \text{DP} \quad (6.1)$$

Gemini X with added formic acid:

$$\log(2\text{-FAL}) = 1.972 - 0.00282 \cdot \text{DP} \quad (6.2)$$

Reviewing the results presented in Figure 6.5, it is clear that Burton's relationship is close to the data obtained for blank Gemini X and De Pablo's relationship is more applicable to the results with formic acid added. In theory, the same level of DP reduction would result in the same amount of 2-FAL generation. However, the measured 2-FAL concentration in oil might not be the same as illustrated in Figure 6.5. This could be due to the partitioning of 2-FAL between oil and paper and possibly other reactions, which require further studies. Nevertheless, this has shed light to understand the difference among the established 2-FAL-DP equations.

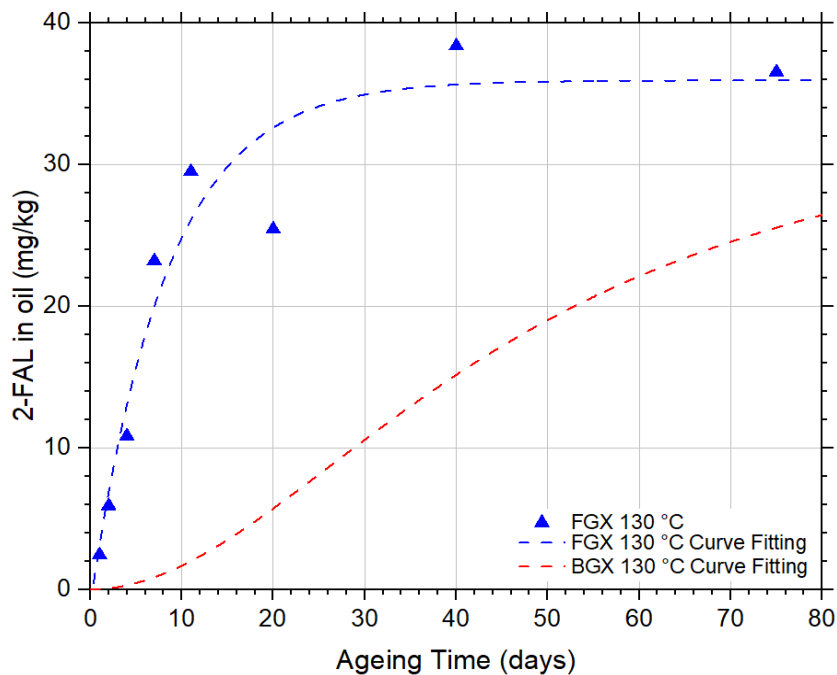


Figure 6.4 Concentration of 2-FAL in oil as a function of time when the Kraft paper was aged at 130 °C in Gemini X with added formic acid of initial concentration of 0.4

mg KOH/g in oil (before paper was added). BGX means blank Gemini X and FGX means Gemini X with added formic acid.

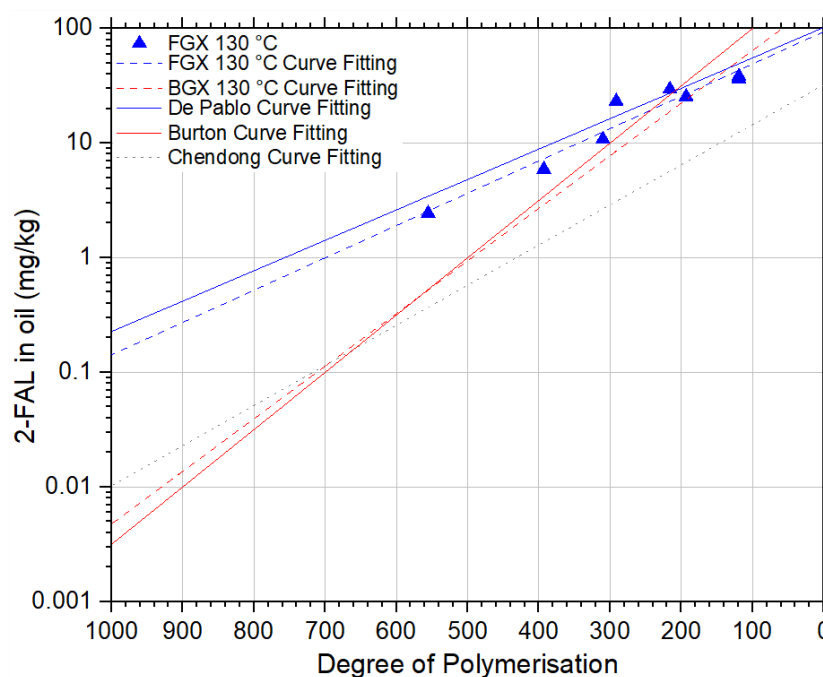


Figure 6.5 Concentration of 2-FAL in oil as a function of DP when the Kraft paper was aged at 130 °C in Gemini X with and without added formic acid of initial concentration of 0.4 mg KOH/g in oil (before paper was added). BGX means blank Gemini X and FGX means Gemini X with added formic acid. Relationships obtained in other works [76, 79, 80] are also plotted.

Methanol as an early ageing indicator has been investigated in [101]. For blank Gemini X, the concentration of methanol increases with a clear trend and reaches 1 mg/kg in oil at Day 75 (Figure 6.6). This trend was also observed in [101] with a value of 2.4 mg/kg at Day 75. However when formic acid was added to the oil-paper system with an initial concentration of 0.4 mg KOH/g in oil, the initial rate of increase becomes much larger. For example, the time that it takes to reach a concentration of 0.8 mg/kg is 44 days without adding acid but it becomes 6 days when formic acid was added.

Another feature from the results is that the concentration of methanol decreases at certain stage in the ageing process. This happens at Day 11 in the case with added formic acid, corresponding to a DP of 220. Without added formic acid, the turning point is around 80 days [101], corresponding to a DP of 300. It thus seems that before the paper DP drops to a value of 300 in the ageing process, the concentration of methanol will experience a continuous increase, as shown in Figure 6.7. In addition, it can be

seen that relationships between Methanol and DP follow the same trend for both blank and formic acid added cases.

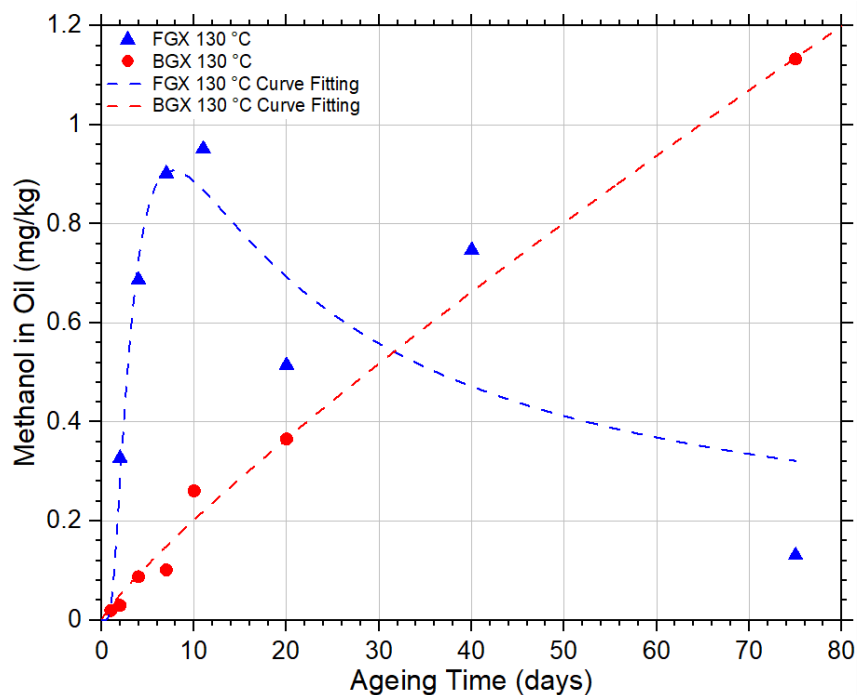


Figure 6.6 Concentration of Methanol as a function of time when the Kraft paper was aged at 130 °C in Gemini X with added formic acid of initial concentration of 0.4 mg KOH/g in oil (before paper was added).

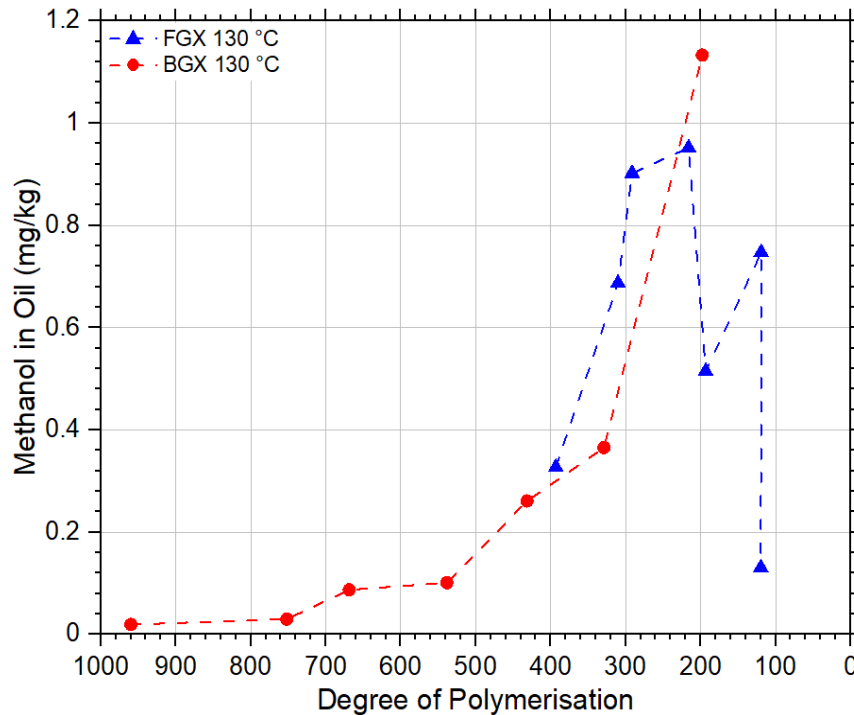


Figure 6.7 Concentration of Methanol plotted against DP when the Kraft paper was aged at 130 °C in Gemini X with and without added formic acid of initial concentration of 0.4 mg KOH/g in oil (before paper was added).

6.5 Variation of LMA Concentration with Initially Added Formic Acid

6.5.1 Comparison with Blank Test Results

To study the feasibility of using the concentration of LMA in transformer liquid as an ageing indicator of transformer paper insulation, such as Kraft paper, it is necessary to gain knowledge on the influence of LMA on the ageing process. Results presented in Chapter 5 (Figure 5.15) show that without added formic acid (the blank test case), the concentration of LMA in paper increases rapidly initially then slows down, which is also shown in Figure 6.8 as the broken red line.

To ascertain the repeatability of LMA measurement in paper, two different measurement samples was taken from the same ageing sample from an ampoule and then tested for its LMA concentration. The two sets of data are shown in Figure 6.8, providing evidence of the excellent repeatability in the measurement.

When formic acid was added to the Gemini X used in the ageing process, the concentration of LMA measured in the paper first stays at relatively low values that are comparable to those in the blank test case (Figure 6.8). It then becomes much higher than in the blank test case after Day 10 when the DP drops to 220. It can be seen from Figure 6.2 that most of the ageing takes place within the first 10 days when formic acid was added with the DP dropping from around 1000 to 220. Towards the end of the 75 day ageing period, the concentration of LMA reaches 4 times that in the blank case.

The LMA concentration in oil follows a similar pattern in the blank and acidified cases, as is shown in Figure 6.9. The trend of increase of the LMA concentration is clear. More analysis is given the sections below.

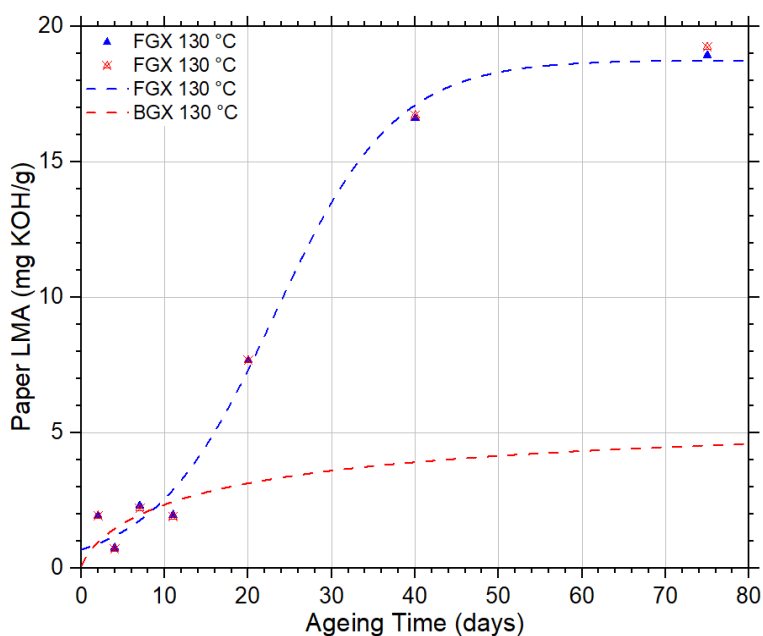


Figure 6.8 Concentration of paper LMA as a function of time when the Kraft paper was aged at 130 °C in Gemini X with and without added formic acid of initial concentration of 0.4 mg KOH/g in oil (before paper was added).

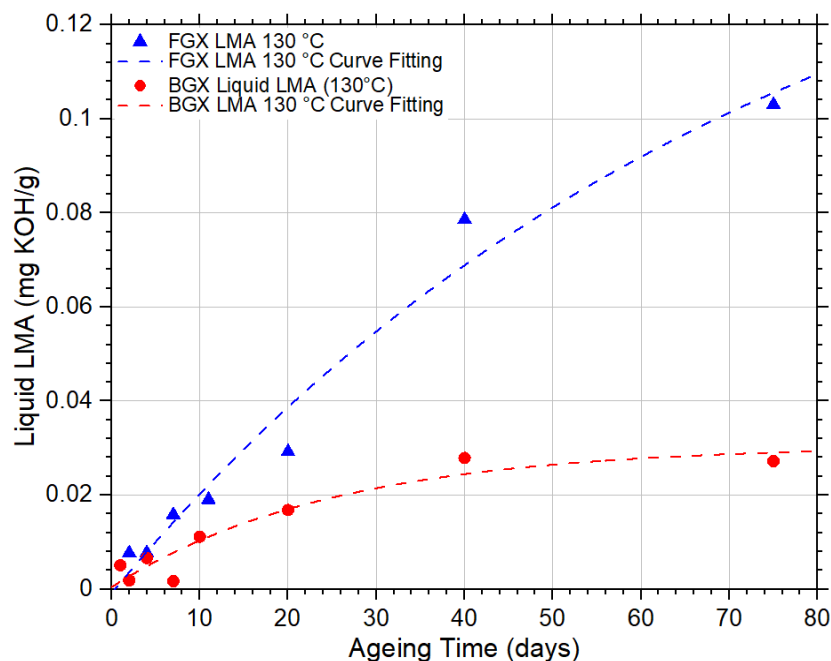


Figure 6.9 Concentration of LMA in oil as a function of time when the Kraft paper was aged at 130 °C in Gemini X with and without added formic acid of initial concentration of 0.4 mg KOH/g in oil (before paper was added).

6.5.2 LMA Concentration at the Initial Stage

If the added formic acid is not consumed at the beginning of the ageing process, the concentration of LMA in paper, corresponding to the initially prepared value of 0.4 mg KOH/g in oil, is expected to have a value around 7 mg KOH/g according to the partitioning test results obtained in [14] at 130 °C where 95% of the formic acid originally added to the oil was removed from the oil when paper was put in the oil. Measurement results in Figure 6.8 however show that this is not the case. The LMA concentration varies between 0.6 mg KOH/g and 2.3 mg KOH/g, much lower than the expected concentration. The LMA concentration of the paper sample was measured twice and the results are also shown in Figure 6.8. The repeatability is better than 5%. Systematic error such as LMA extraction percentage will not lead to the fluctuation exhibited in the first 4 measurement values. Secondly, the fluctuations in both paper LMA and oil match each other, indicating a level of consistency in the results. Thirdly, the paper and oil LMA measurement for all samples in this chapter was performed as a batch job and the measurement procedure was applied consistently, implying that the

random LMA measurement error should not cause such a huge drop. Therefore it is fair to state that the concentration variation shown in Figure 6.8 and Figure 6.9 in the initial stage of the ageing process with added initial formic acid could be related to the chemical processes although the possibility of being caused by uncertainties in LMA measurement cannot be excluded.

As regard the lowered LMA concentration in paper at the beginning of the ageing process, when discussing the partitioning of formic acid between oil and paper, the authors of [14] stated that over the temperature range of 60 °C to 130 °C,

“The acidity of the paper was also checked. The measured value for the LMA content in the paper would on average cover for 50 % of what was lost from the oil (varying between 24 % and 80 %).”

The above comment implies that part of the added LMA were lost through some mechanisms apart from the portion absorbed in paper, and at different temperatures the loss percentage is different. Assuming 76% loss for formic acid at 130 °C (more loss at higher temperature), the detectable LMA in paper shortly after the start of the ageing process at 130 °C would be lower than 24% of the no-loss concentration (7 mg KOH/g), which is 1.68 mg KOH/g. This estimated LMA concentration fits well into the measurement values, which is in fact about the average of the lower and upper limits of 0.6 mg KOH/g and 2.3 mg KOH/g, respectively. For comparison, the LMA concentration in the oil is very low at the initial stage, typically, 0.01 mg KOH/g of oil.

Therefore, results in [14] and in the present work both point to the possibility of immediate reaction of formic acid with new Kraft paper, indicating the reactivity of formic acid. The reaction leads to rapid scission of the polymer molecules and rapid decrease in DP, as shown in Figure 6.2. It is thus fairly safe to say that the availability of LMA at the initial stage of ageing has significant acceleration effect on the ageing of Kraft paper. In addition, the LMA concentration during the rapid ageing process (over the first 10 days) exhibits an oscillatory pattern with the extent of variation much larger than the measurement uncertainty.

6.5.3 Features of Variation of LMA, 2-FAL and Methanol during the Ageing Process

It has been observed that in the first 10 days of ageing with formic acid added, the LMA concentration stays relatively low, below 2.3 mg KOH/g while there was a rapid increase in the concentration of 2-FAL and methanol (Figure 6.4 and Figure 6.6). This is in line with the existing knowledge that 2-FAL and methanol are products of the degradation of paper insulation [101]. The added formic acid accelerated this ageing process, as shown in Figure 6.2.

An interesting feature that appears in the ageing process with added formic acid is the rapid rise in LMA concentration after Day 10 and obvious decrease in the concentration of methanol. This was not observed in the blank test case as reported in Chapter 5. A drop in the concentration of methanol was also observed in [101] after the initial rapid increase. The reasons for this decrease are not clearly understood although there is proposal that it may be linked to changes in the partitioning characteristics when the paper and oil are being aged [115]. A distinct feature that was mentioned in [101] [115] is that the decrease in methanol concentration takes place when the levelling-off degree of polymerization (LODP) of the Kraft paper is reached. A value of 200 was given in [101] as the LODP. This is also true in the present case at a DP value of 210.

One conclusion that can be drawn from the present work is that LMA are able to greatly accelerate the ageing of Kraft paper at the hot spot of new transformers where its temperature is close to 130 °C. LMA thus form an important part of the ageing environment in new transformers. This also implies that LMA should be removed from the transformer oil and paper for newly commissioned transformers as an essential part of the preparation procedure. With negligibly low initial concentration of LMA, there is clear correlation between DP and liquid LMA concentration, especially in the important stage of ageing when DP decreases from 500 to 200 (Figure 5.16 and Figure 6.9). There is plausible evidence to further explore the use of LMA in transformer oil as a paper ageing indicator.

6.5.4 Correlation of Liquid LMA with Paper Ageing

Transformer ageing monitoring relies on indicators contained in the oil. Given that LMA collectively may act as an important ageing indicator when they are removed from the insulation system at the initial stage, the relationship between LMA

concentration in oil and paper becomes important. As shown in Figure 6.8 and Figure 6.9, the change of oil and paper LMA concentrations without added formic acid can be fitted into an exponential function with time. Figure 6.10 and Figure 6.11 show that with the decrease in DP the LMA concentrations in oil and paper do increase.

For blank oil-paper insulation system (without excessive LMA present at the beginning of the ageing process), the concentration ratio of paper to oil is in the range 175-200. For the case with added formic acid, the correlation can also be identified, as shown in Figure 6.12 despite the deviation from the trend line.

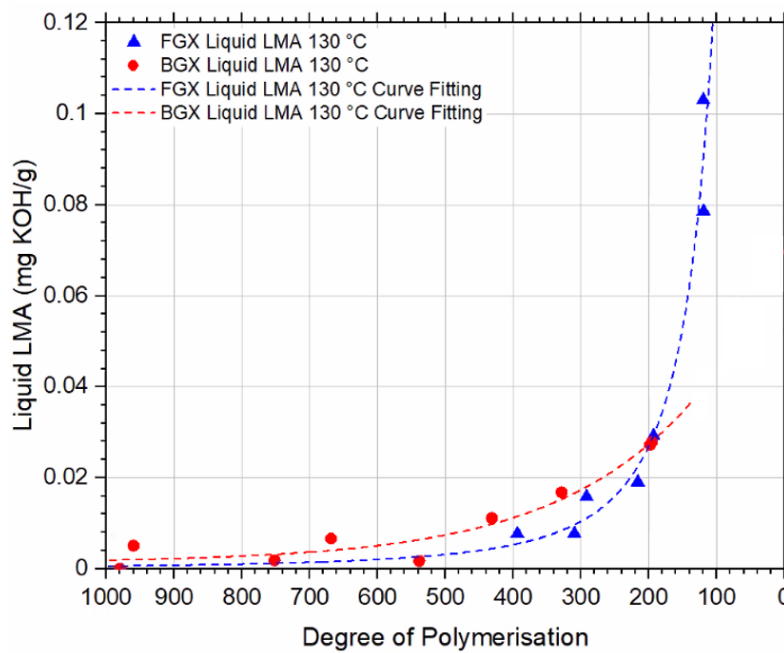


Figure 6.10 Concentration of liquid LMA plotted against DP when the Kraft paper was aged at 130 °C in Gemini X with and without added formic acid of initial concentration of 0.4 mg KOH/g in oil (before paper was added).

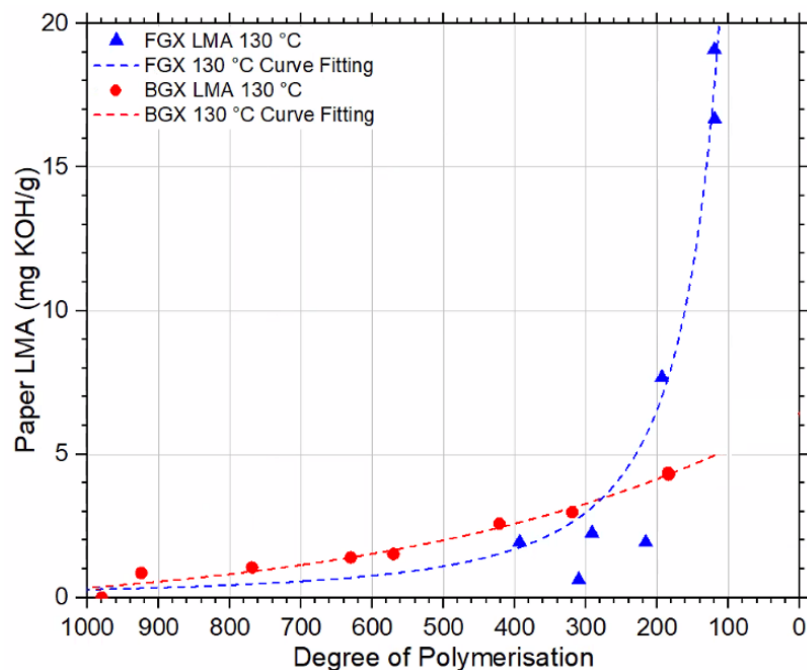


Figure 6.11 Concentration of paper LMA plotted against DP when the Kraft paper was aged at 130 °C in Gemini X with and without added formic acid of initial concentration of 0.4 mg KOH/g in oil (before paper was added).

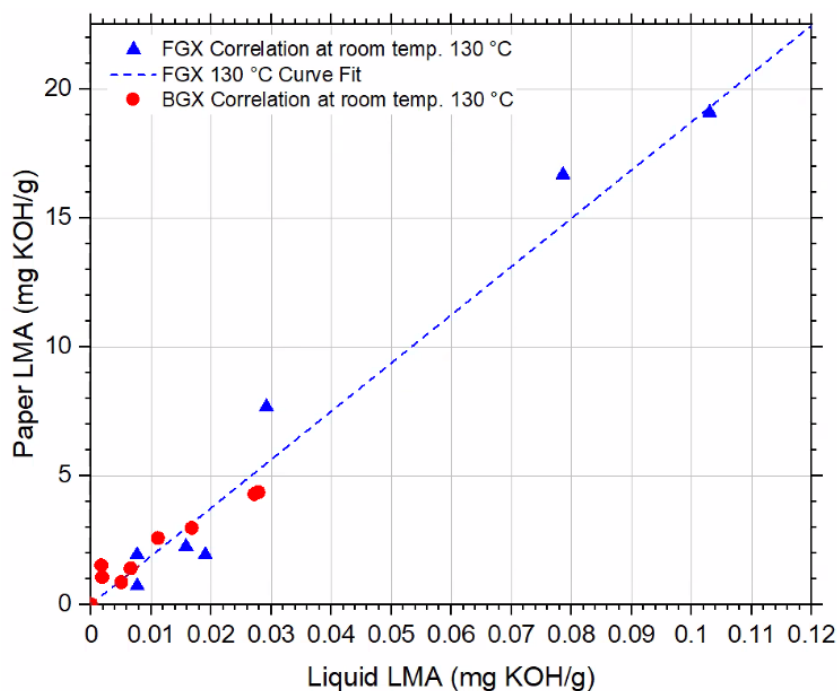


Figure 6.12 Correlation between concentration of liquid LMA and paper LMA when the Kraft paper was aged at 130 °C in Gemini X with and without added formic acid of initial concentration of 0.4 mg KOH/g in oil (before paper was added).

The partitioning between oil and paper for LMA has not been thoroughly investigated in existing work. The ratio has not been given in literature. In fact the use of the term

‘partitioning’ is not appropriate because some of the LMA added to the oil became unaccountable as shown in [101] and also in the present work. In addition, there is suggestion from the results that the concentration of LMA experiences oscillatory changes during the rapid ageing process at the initial stage.

The percentage of the LMA contained in the oil (10 ml) out of the total amount of LMA in oil and paper can be derived from the concentration values in Figure 6.10 and Figure 6.11. It can be shown that during the rapid ageing stage, where the DP experiences significant changes up to the LODP of the Kraft paper (~200), the percentage of LMA in oil out of the total amount of LMA contained in the oil and paper varies between 6% and 17%. Once the DP levels off and becomes stable, the percentage approaches 9%.

Apart from the LMA in the oil, there are also HMA, as shown in Figure 6.13. The HMA concentration in oil up to Day 20 is lower than that in the blank test case. However it overtakes the latter after Day 20. With a significantly higher LMA concentration in the case with added formic acid, the total acidity remains approximately the same with and without added formic acid up to Day 20), but a much higher value was resulted in by the end of the 75 day ageing process. It can be concluded that the total acidity in oil becomes much higher when formic acid is added to the oil-paper insulation system at relatively high temperature, such as 130 °C. The presence of a high concentration of HMA in transformer oil leads to a high total acidity in oil. To use acidity in oil as an ageing indicator, the LMA concentration instead of the total acidity in the transformer liquid should be used to reflect the physical links between the LMA production and paper ageing.

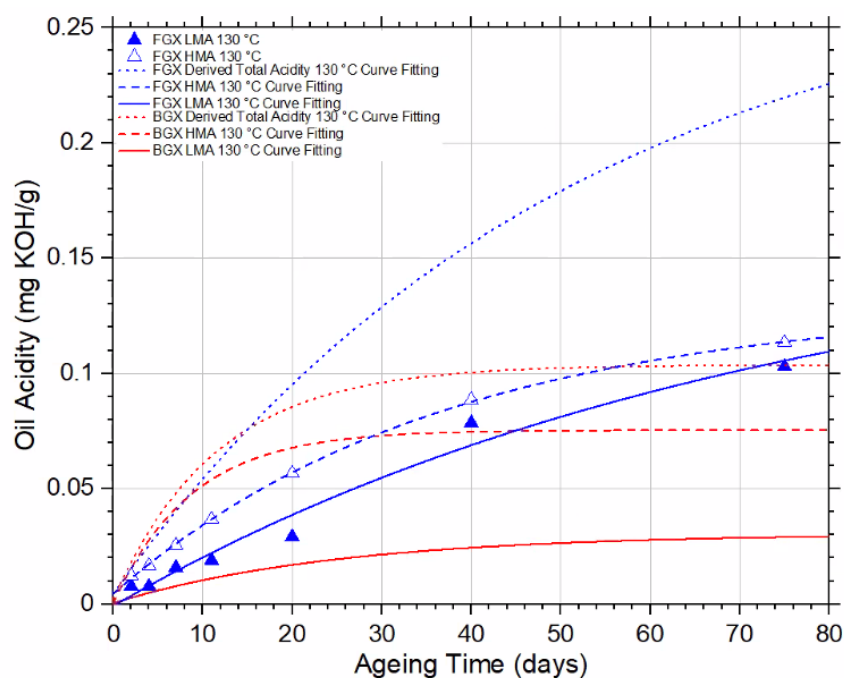


Figure 6.13 Concentration of LMA and HMA in Gemini X when the Kraft paper was aged at 130 °C in Gemini X with and without added formic acid of initial concentration of 0.4 mg KOH/g in oil (before paper was added).

6.6 Summary

Measurement and analysis of the concentrations of ageing products and environment parameters is reported in this chapter for the case with pre-added formic acid in Gemini X. The ultimate objective is to ascertain the influence of LMA in the degradation of transformer paper insulation (normal Kraft paper) and the potential of using LMA concentration in transformer liquid as an ageing indicator. The following can be concluded:

- When LMA are present or added to oil (0.4 mg KOH/g of oil) at the beginning of the ageing process, the Kraft paper will experience a much faster degradation process with an acceleration factor around 5 at a temperature of 130 °C.
- A large proportion of the LMA made available in the oil will disappear into the paper to accelerate the paper ageing or stored in the paper undetected. This loss can reach 80% within 2 days. The exact mechanisms are not clear.
- With the pre-added formic acid, 2-FAL and methanol can still be used as an early ageing indicator because both concentrations increase when the DP decreases from 1000 to 250. The relationship obtained by Burton agrees with

the measured 2-FAL concentrations in the blank test case, i.e. with dried paper and no added LMA in the oil.

- LMA in the oil has the potential to be used as a paper ageing indicator with the assumption that the LMA in the oil and paper are removed before being used in transformers.

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CHAPTER 7

7 THERMAL AGEING OF SYNTHETIC ESTER AND KRAFT PAPER IN SEALED AMPOULES

7.1 Introduction

Synthetic ester as a transformer insulation and cooling liquid is environmentally friendly (bio-degradable) and fire-safer, and has the potential to replace mineral oil in large scale [19]. Since its chemical structure is different from mineral oil, transformer paper impregnated in synthetic ester is expected to behave differently. In fact as shown in [19], its ageing generates more acids (about 4 times higher than mineral oil when aged at 80 °C – 120 °C). Another feature is that ester can hold more water due to its higher water solubility, thus potentially reducing the relative moisture level in paper and slowing down the degradation of paper.

This chapter mainly presents the measurement results of thermally aged Kraft paper that is impregnated in a synthetic ester, MIDEL 7131, at 130 °C. A comparative study of the ageing behaviour of Kraft paper in Gemini X and that in MIDEL 7131 has been carried out. For convenience, the two cases under comparison in this chapter are referred to as BGX (blank Gemini X, without added formic acid) and BM7 (Blank MIDEL 7131, without added formic acid). The synthetic ester and Kraft paper were prepared according to the procedure described in Chapter 3 for filtration and drying. The moisture level in paper was less than 0.4% in the BM7 case. The ageing behaviour of the Kraft paper in MIDEL 7131 with added formic acid is reported in a separate section.

This chapter is organised in the following order. Section 7.2 reports the moisture level measurement during the ageing process in order to have an overall picture of the presence of moisture in the paper. The change of DP and chain scission number in the ageing process as a function of time is reported in Section 7.3. This is followed by the results of 2-FAL and methanol concentration measurement in Section 7.4, and acidity measurement in Section 7.5. The results of paper ageing with formic acid initially added

to MIDEAL 7131 is separately reported in Section 7.6. Finally, a summary is given in Section 7.7.

7.2 Variation of Moisture Level in Kraft Paper

While the moisture concentration in paper in the BGX case shows a clear increasing trend with ageing time as presented in Chapter 5, which is also presented in Figure 7.1 as the broken red line, paper ageing in MIDEAL 7131 behaves differently. In the BM7 case, the measured moisture concentration in paper was low before ageing at 130 °C. During the ageing process, the moisture level fluctuates, as shown in Figure 7.1, and no clear and simple trend of change can be identified. The moisture level does not have the tendency to increase. Results in Figure 7.1 confirms that the ageing process started with a dry condition, so a valid comparison with the results in Chapter 5 for Gemini X can be made.

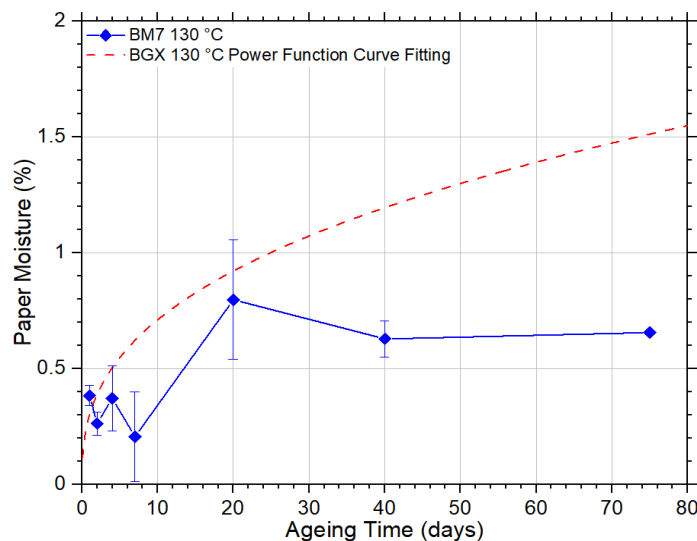


Figure 7.1 Variation of moisture concentration as a function of ageing time in aged Kraft paper that is impregnated in MIDEAL 7131 at 130 °C. This diagram is based on the measurement of 2 samples.

7.3 Change in Degree of Polymerization of Kraft Paper

The moisture concentrations for the two cases of BGX and BM7 are comparable and remain low in the first 7 days. This implies that the starting conditions for paper ageing

are similar in the two cases. Figure 7.2 shows that, in the first 20 days of ageing the DP of the Kraft paper has very similar rate of change. The difference starts to become noticeable after Day 20 when the DP drops below 300. The time to 50% of the starting DP is around 7.5 days in both cases. From the chain scission number given in Figure 7.3 and using Equation 5.3, the initial reaction rates based on the values in the first 8 days are close to each other, with calculated values of 4.72×10^{-6} /hour and 5.31×10^{-6} /hour, respectively, for the BGX and BM7 cases.

The ageing of the Kraft paper in MIDE L 7131 becomes slower at a later stage with DP below 300, which is reflected in both Figure 7.2 and Figure 7.3, especially the latter. This agrees with the expectation that MIDE L7131 helps slowing down the paper ageing. As moisture accelerates the paper ageing, the higher DP of paper aged in MIDE L7131 may be due to that MIDE L 7131 helps keeping the paper drier during the ageing process, as evidenced in Figure 7.1.

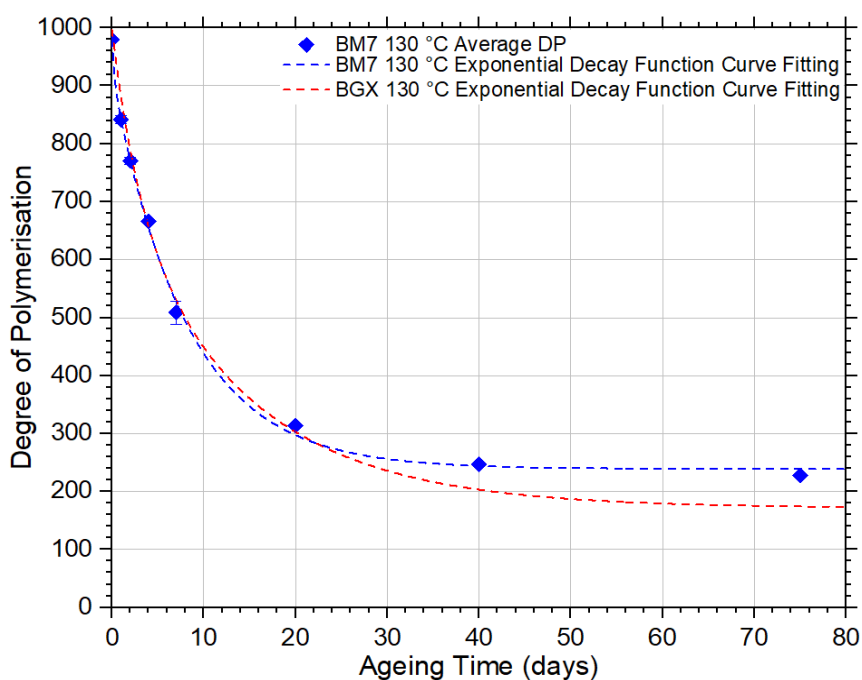


Figure 7.2 DP of Kraft paper as a function of time when dried Kraft paper was aged at 130 °C in MIDE L 7131 with added formic acid. The initial concentration of formic acid is 0.4 mg KOH/g in oil only.

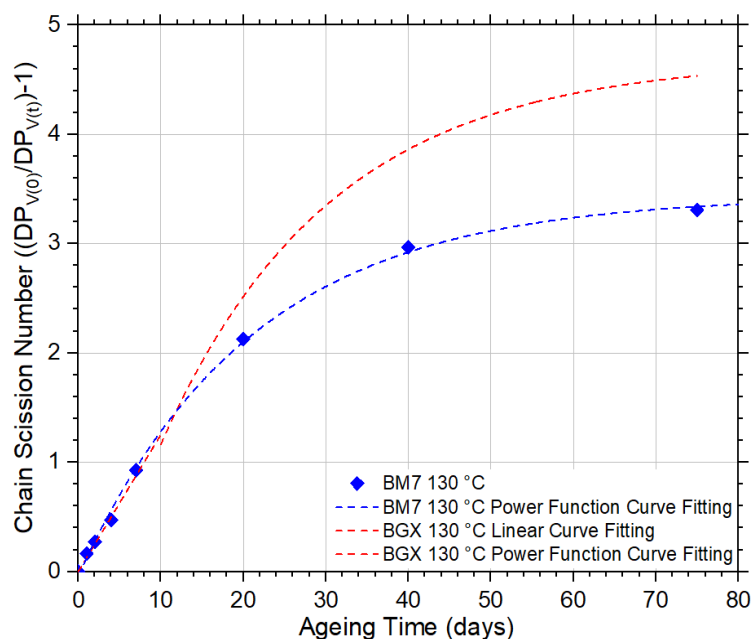


Figure 7.3 Chain scission number of Kraft paper as a function of time when dried Kraft paper was aged at 130 °C in MIDEL 7131 without any initially added acid.

7.4 Generation of 2-FAL and Methanol Concentrations during Ageing of Kraft Paper

The concentration variation of 2-FAL in MIDEL 7131 without any initially added acids behaves in a pattern similar to that in Gemini X. In both cases, BGX and BM7, the change of 2-FAL concentration fits well into power functions, as shown in Figure 7.4 where the trend of increase with ageing time is beyond reasonable doubt. The end concentration of 2-FAL on Day 75 is 20 mg/kg in the BM7 case, 25% lower than that in the blank Gemini X case (~26 mg/kg). The difference between the two cases starts to be seen right from the beginning and grows steadily with ageing time.

The correlation between 2-FAL concentration and DP in the whole ageing process is given in Figure 7.5 using linear scales for both axes, clearly showing that the production of 2-FAL in the majority of the ageing process, with DP change from 1000 to 400, is slow, with an average rate of 4.17×10^{-3} mg/kg per DP decrease. This is in contrast to the generation rate of 1.46×10^{-1} mg/kg per DP decrease over the course of DP dropping from 400 to 220, increasing by a factor of 35.

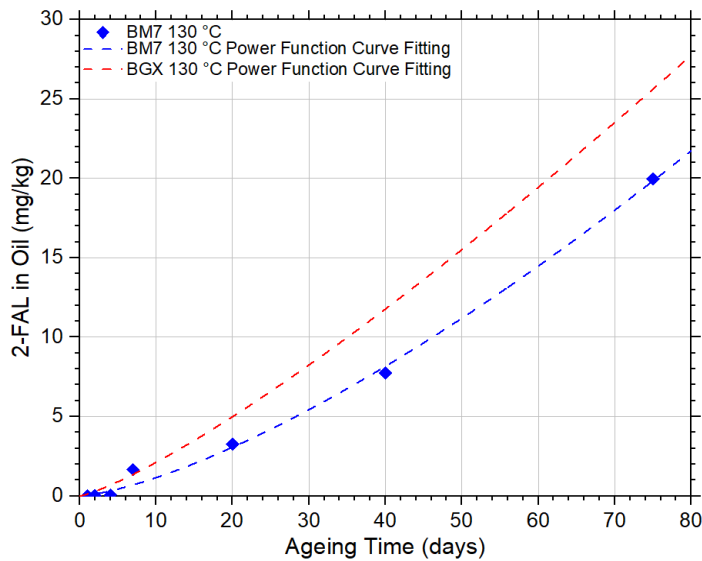


Figure 7.4 Concentration of 2-FAL measured in oil as a function of ageing time when dried Kraft paper was aged at 130 °C in MIDEL 7131 without any initially added acids.

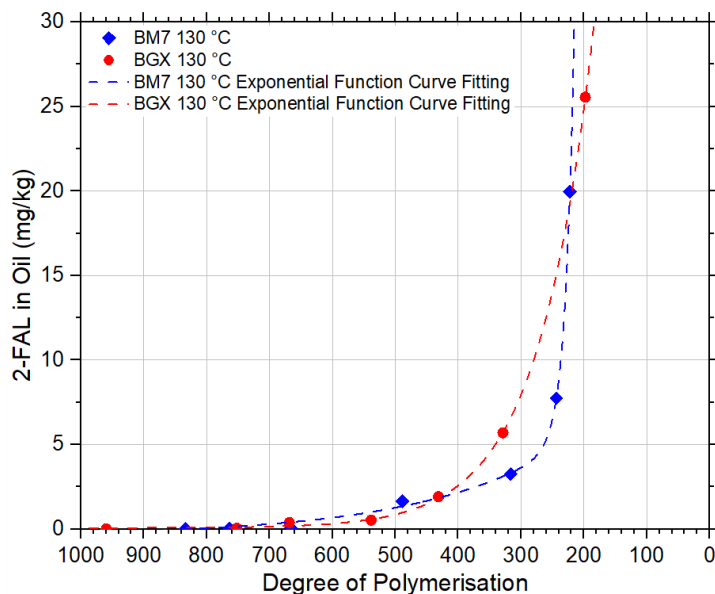


Figure 7.5 Concentration of 2-FAL measured in oil plotted against DP when dried Kraft paper was aged at 130 °C in MIDEL 7131 without any initially added acids.

The relative change of 2-FAL concentration with respect to the drop in DP, $\frac{1}{c_{2-FAL}} \frac{dc_{2-FAL}}{d(-DP)} = \frac{d \log(c_{2-FAL})}{d(-DP)}$, is shown in Figure 7.6. It takes 3 days for the DP to drop from around 1000 to 800 (Figure 7.2). The first 2-FAL measurement was carried out on Day 2. By this time, the 2-FAL concentration reaches 0.01 mg/kg in oil. The information that is missing from Figure 7.5 but clearly manifested in Figure 7.6 is

twofold: 1) during the stage of slow 2-FAL concentration increase (shown in Figure 7.5 over the DP range of 1000 - 400), the change is indeed exponential, or the relative change of 2-FAL concentration with respect to DP is linear; 2) the overall trend of concentration change is exponential and can be described by:

$$DP = 455 - 202 * \log_{10}(2\text{-FAL}) \quad (7.1)$$

which can be compared with the trend line for BGX (blank Gemini X) that is obtained in Chapter 5 and replotted in Figure 7.6 (broken red line) as

$$DP = 507 - 222 * \log_{10}(2\text{-FAL}) \quad (5.3)$$

where a larger value of 222 translates into a smaller gradient in Figure 7.6

Similar to that in Chapter 5, it is informative to give an indication on the potential use of 2-FAL concentration as an ageing indicator, i.e. to estimate the variation of DP based on 2-FAL concentration. Notwithstanding that this is a laboratory based ageing test under conditions that are much more ideal than those in practical transformer operation, results in this work show that by measuring the 2-FAL concentration, it is possible to use the established trend line (broken blue line in Figure 7.6) to estimate the DP value.

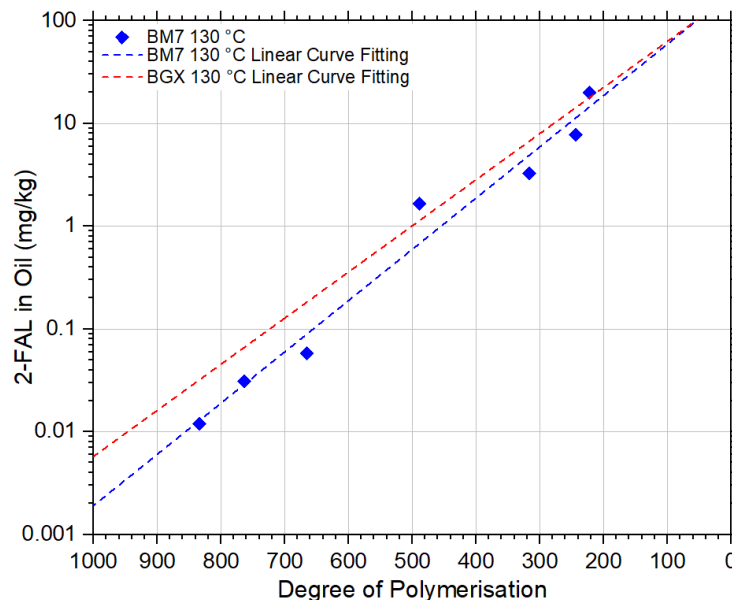


Figure 7.6 Concentration of 2-FAL measured in oil plotted in logarithm scale against DP when dried Kraft paper was aged at 130 °C in MIDEL 7131 without any initially added acids.

Chain scission number is a measure of the relative change in DP, as can be seen from the following expression

$$d\eta = \frac{DP_0}{DP} \left(-\frac{d(DP)}{DP} \right) \quad (5.4)$$

where η is the chain scission number, DP_0 represents a single variable which is the starting DP of the Kraft paper and DP as a single variable is the degree of polymerization of the paper at an instant in the ageing process. At the beginning of the ageing process, $DP = DP_0$ and so $d\eta$ is the opposite of the relative change of DP . When the DP decreases, $d\eta$ represents a magnification of the relative change of DP with a factor of DP_0 / DP . For example, on Day 20 the DP is 300, the ageing of paper starts to slow down with a reduced rate of change in DP , and at this point $\eta = -3.27 \frac{d(DP)}{DP}$. Thus, using chain scission number can be advantageous when the change in DP below the value of 300 is focused. Compared with Figure 7.5, the correlation between the 2-FAL concentration and chain scission number points can be better fitted and comprehended, as shown in Figure 7.7, for both cases, the blank Gemini X and blank MIDEL 7131.

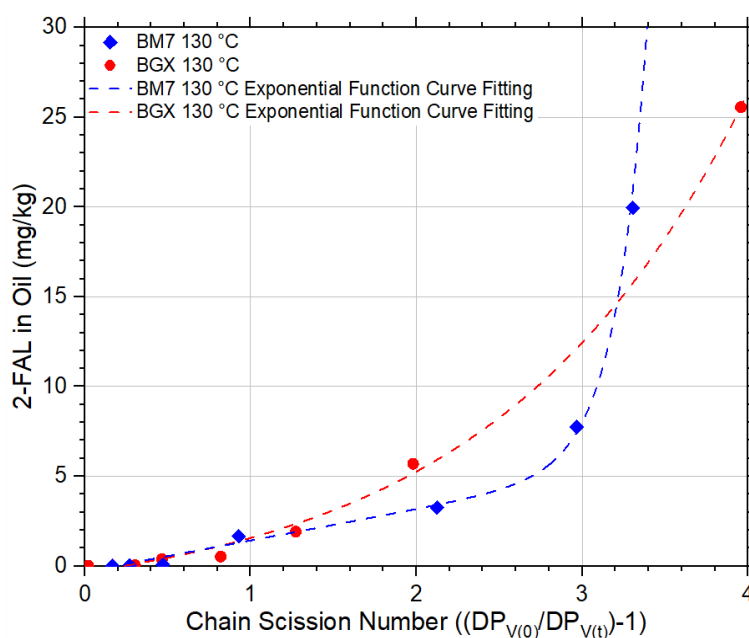


Figure 7.7 Concentration of 2-FAL measured in oil plotted against chain scission number when dried Kraft paper was aged at 130 °C in MIDEL 7131 without any initially added acids.

The measured concentration of methanol in MIDEL 7131 follows a rather different pattern in comparison with the results obtained for Gemini X. As shown in Figure 7.8, when dried Kraft paper is aged in MIDEL 7131 at 130 °C, the methanol concentration in the liquid increases at a much higher rate of 0.26×10^{-3} mg/kg/day in the first 7.5 days until the DP drops to 50% of its starting value, it is much higher than the rate of 0.02×10^{-3} mg/kg/day in the BGX case.

One important difference with MIDEL 7131 is that the concentration of methanol starts to decrease after 20 days when the DP drops below 300. The reduction is likely due to the esterification of methanol and acids in the liquid [19]. It is however still true that the concentration of methanol appearing in the two types of liquid (Gemini X and MIDEL 7131) increases when the DP drops from its starting value to 300 (corresponding to Day 20).

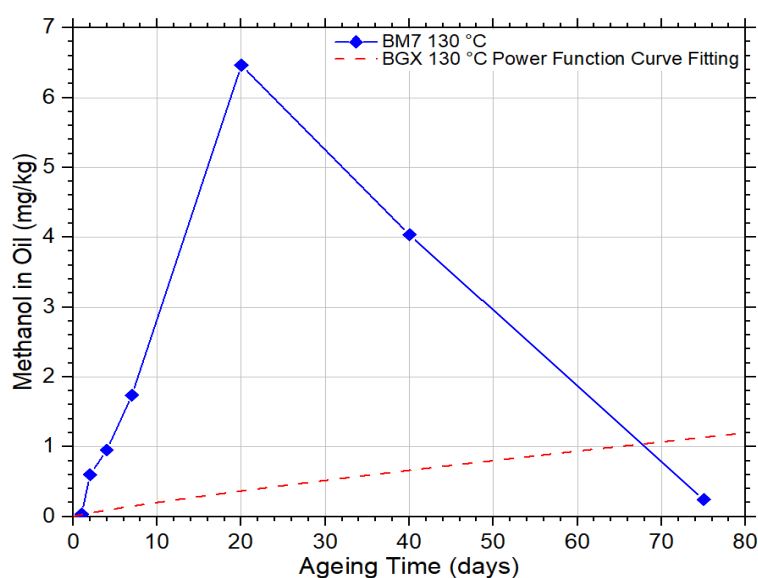
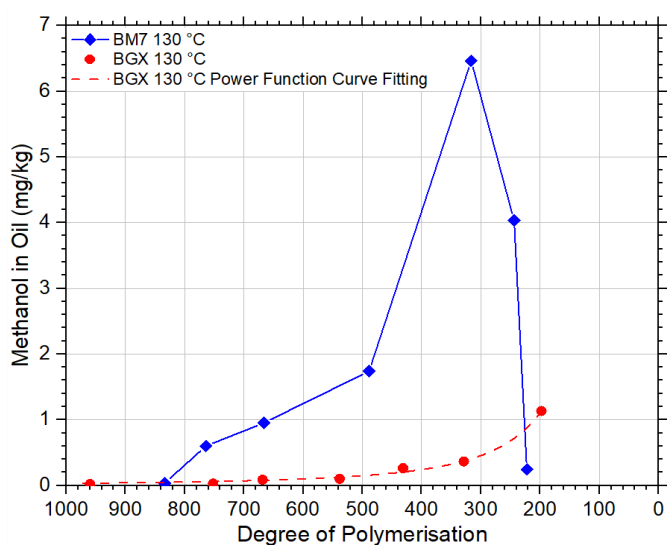


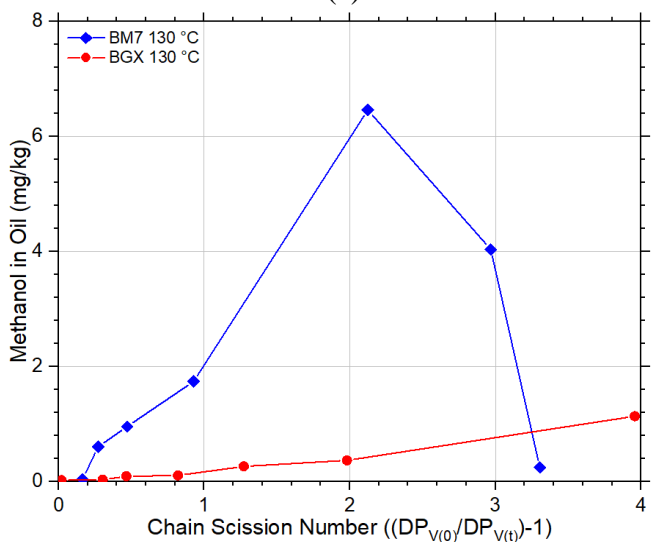
Figure 7.8 Concentration of methanol measured in oil plotted against chain scission number when dried Kraft paper was aged at 130 °C in MIDEL 7131 without any initially added acids.

Over the course of methanol concentration changing and DP decreasing, Figure 7.9 manifests the fact that, in comparison with the BGX case, the concentration of methanol in the BM7 case starts to increase rapidly at a much early stage of paper degradation in terms of the DP. A clear overall pattern of the concentration change cannot be defined, as shown in Figure 7.10. However, over the DP range from 700 to 300 the measurement

falls on an exponential line segment. This is in contrast to the case where the Kraft paper is aged in Gemini X under the same conditions as also illustrated in Figure 7.10. The difference indicates that the partitioning of methanol between Gemini X and Kraft paper is different from that between MIDEL 7131 and paper. At the same DP, the same amount of total methanol is expected to be generated. However due to the more polar nature of MIDEL 7131, more methanol is measured in the MIDEL 7131 after equilibrium.



(a)



(b)

Figure 7.9 Concentration of methanol in oil plotted against (a) DP and (b) chain scission number when dried Kraft paper was aged at 130 °C in MIDEL 7131 without any initially added acids

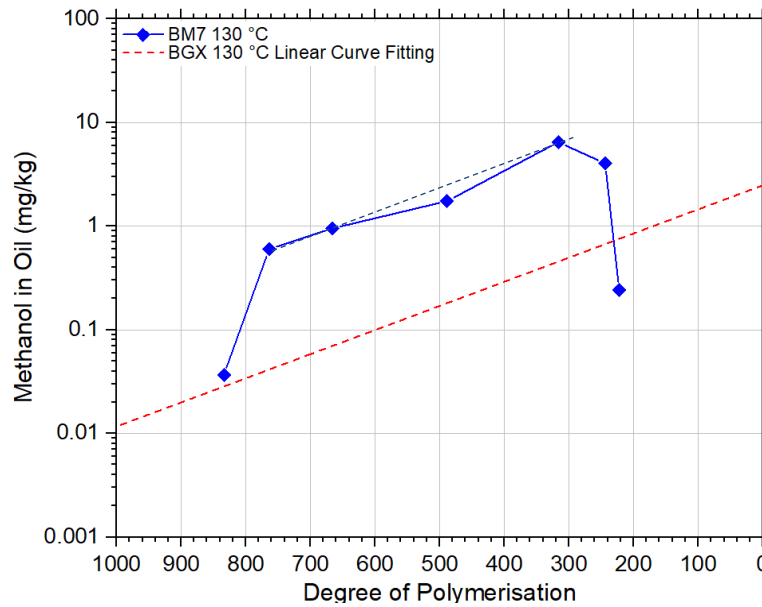


Figure 7.10 Concentration of methanol in oil plotted in logarithm scale against DP when dried Kraft paper was aged at 130 °C in MIDEL 7131 without any initially added acids.

7.5 Variation of LMA Concentration in the Ageing Process of Kraft Paper

7.5.1 LMA Concentration in Paper

The role and behaviour of LMA in transformer paper ageing is one of the focuses in the present work. In the blank case which represents the normal operational conditions for oil-paper insulation in new transformers, results show that the LMA concentration starts with a very low value and increases rapidly in the first 10 days before it slows down. Results in Figure 7.11 show that this pattern of change is applicable to both the BGX and BM7 cases, with the LMA concentration reaching a value of around 5.6 mg KOH/g of paper in the latter case. To ascertain the changes in the BM7 case, measurements were taken from two samples from the same ampoule. The two sets of LMA measurement are very close to each other with a maximum difference of < 5%, demonstrating the very good repeatability of the LMA measurement as described in Chapter 4. The average of the two sets are plotted in Figure 7.11 as the blue diamonds.

The paper LMA concentration is plotted against DP in Figure 7.12. It can be clearly seen that from a DP of 800 down to 300, the correlation between paper LMA

concentration and DP overlaps for the two cases, BM7 and BGX. This provides the first set of evidence that the major stage of paper ageing is not significantly affected by the replacement of the liquid medium around the paper provided that the ageing temperature is the same and the starting moisture level is low without any added acids.

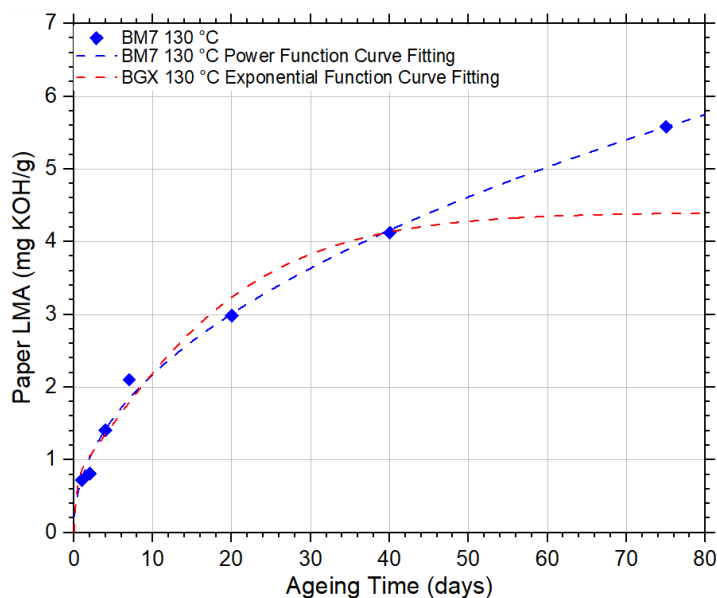


Figure 7.11 Measured paper LMA concentration as a function of ageing time when dried Kraft paper was aged at 130 °C in MIDEL 7131 without added acids. The BM7 data points are the average of two sets of acidity measurement with less than 5% difference.

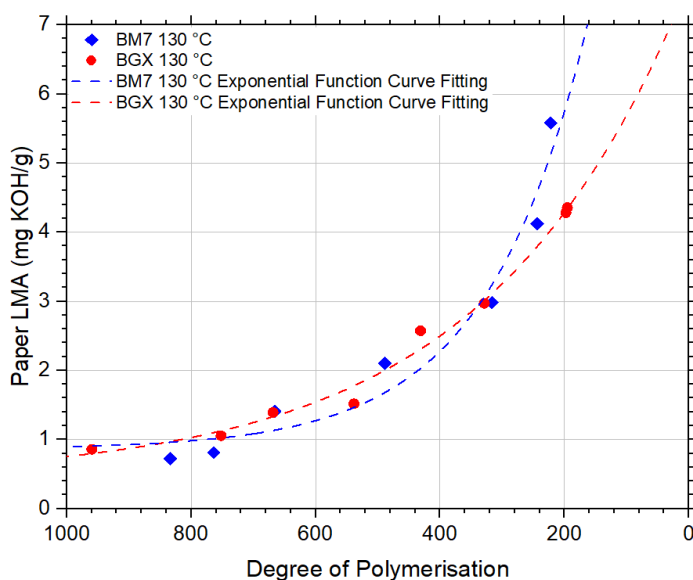


Figure 7.12 Concentration of paper LMA plotted against DP when the Kraft paper was aged at 130 °C in MIDEL 7131 without any initially added acids.

7.5.2 LMA Concentration in Oil and Partitioning Between Oil and Paper

Turning to the LMA concentration in Gemini X and MIDEL 7131 as shown in Figure 7.13, the first feature standing out from the comparison is that the variation of LMA concentration in both liquids is smooth. This is different from the behaviour of methanol concentration in MIDEL 7131, as reported in Section 7.4.

The second feature is that more LMA appear in MIDEL 7131 as compared with Gemini X under identical ageing conditions. The difference manifests itself right from the early stage of ageing.

The higher LMA concentration in MIDEL reflects a difference in the partition of LMA between oil and paper given that the LMA concentrations in paper are close to each other in the BM7 and BGX cases down to a DP of 300 (Figure 7.12). To check this, the LMA concentrations in oil and paper are plotted in Figure 7.14. Three general observations can be made. Firstly, at the same paper LMA concentration, more LMA are partitioned into MIDEL. Secondly, the difference in partition becomes larger when paper LMA increases. Thirdly, for both Gemini X and MIDEL 7131, the LMA content in stored in oil is only a small part of that in paper.

Taking the paper LMA concentration of 3 mg KOH/g at Day 20 as an example (Figure 7.11), it can be seen from the trend lines in Figure 7.14 that the LMA concentration is 0.03 mg KOH/g in MIDEL 7131 and 0.016 mg KOH/g in Gemini X, giving a partitioning ratio of 1 : 100 and 1 : 188. At Day 40, the paper LMA concentration is 4.1 mg KOH/g and the partitioning ratio becomes 1 : 85 for MIDEL 7131 and 1 : 157 for Gemini X.

In the partitioning tests reported in [14], a time scale of 2 weeks is quoted for formic acid to reach equilibrium in oil and paper at room temperature. This time scale tends to reduce when the temperature is higher. From literature, there is no information on the time used for the partitioning test on formic acid at 130 °C and no measurement of the paper DP after the partitioning test. In the current work, the samples were left at room temperature for more than 3 months. There was sufficient time for partitioning equilibrium to be reached.

A variation in DP means a change in the structure and weight of the cellulose molecules in paper. Therefore it is expected that at different DP values, the partitioning ratio changes. It is however to be noted that more work is necessary on the partitioning behaviour of the oils at low LMA concentrations.

Corresponding to the ageing time of Day 20, the ratio of LMA content stored in MIDEL 7131 and paper is approximately 1:5 and that for Gemini X is 1:10.5. At Day 40, the two ratios reduces slightly to 1:4.6 and 1:8.8, correspondingly. This means that the LMA content in the oils is only a small portion of that stored in paper. While the LMA concentration in the oil can be quite different, the paper LMA is not greatly affected.

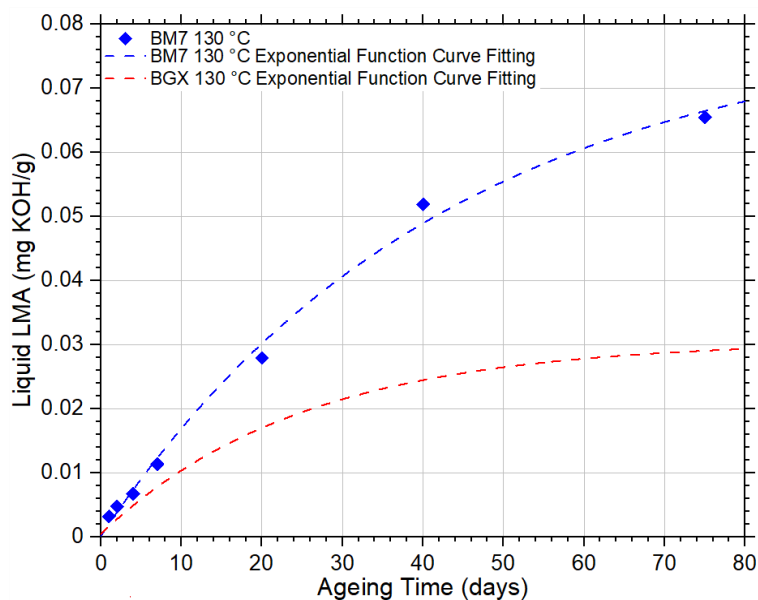


Figure 7.13 LMA concentration in oil as a function of ageing time when dried Kraft paper was aged at 130 °C in MIDEL 7131 without any initially added acids.

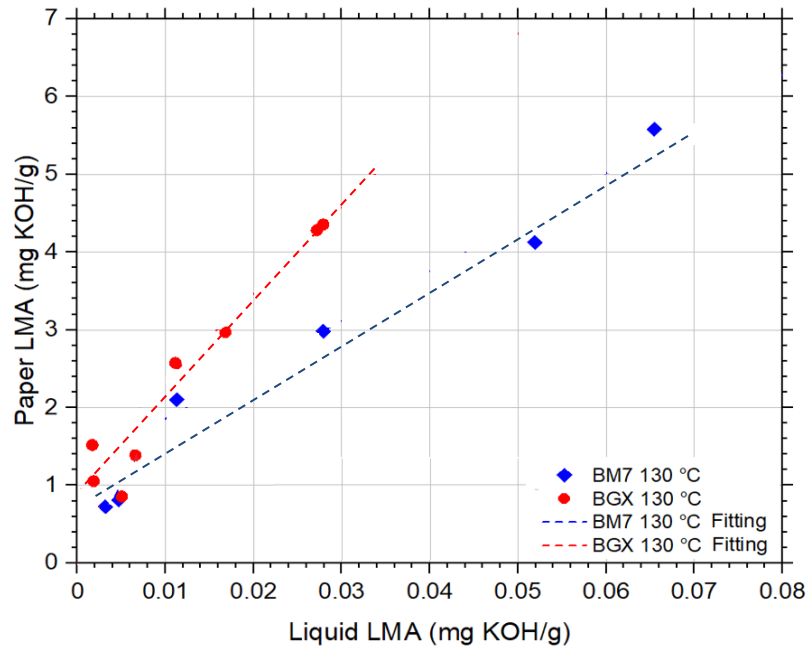


Figure 7.14 Correlation between concentration of liquid LMA and paper LMA when the Kraft paper was aged at 130 °C in MIDEL 7131 without any initially added acids.

7.5.3 Correlation of Liquid LMA with Paper Ageing

The strength of correlation between the total LMA generation and paper ageing index is important because results so far support that LMA generation in the oil-paper insulation system is mainly caused by paper ageing. The total LMA generation can be obtained by summing the LMA content in oil and that in paper. The LMA content in paper or oil can be calculated by multiplying the LMA concentration and the corresponding mass. The total LMA results are given in Figure 7.15.

A striking feature emerging from Figure 7.15 is that, over the important DP range of 850 to 300, the total LMA generations in Gemini X and MIDEL 7131 well overlap each other and both follow a clear increasing trend with the reduction in DP. A good approximation of the rate of generation over the above DP range gives a value of 2.55×10^{-3} mg KOH/g per DP reduction.

Given that a firm statement can be made on the correlation of the total LMA generation and the mechanical strength of the paper over the DP range of 850 – 300, it is thus nature to consider the use of the LMA concentration in oil as a paper ageing indicator.

The relationship between the LMA concentration in oil and the paper DP is shown in Figure 7.16. The variation of LMA concentration in MIDE L 7131 follows closely the trend line. The LMA concentration in Gemini X also follows a well-defined trend line. Therefore, oil and paper LMA measurement results obtained in the present work show clear evidence that the LMA concentration in the oil can be used as a paper ageing indicator in Gemini X and MIDE L 7131 over an important range of paper DP that provides critical information on the deterioration of transformer paper insulation strength.

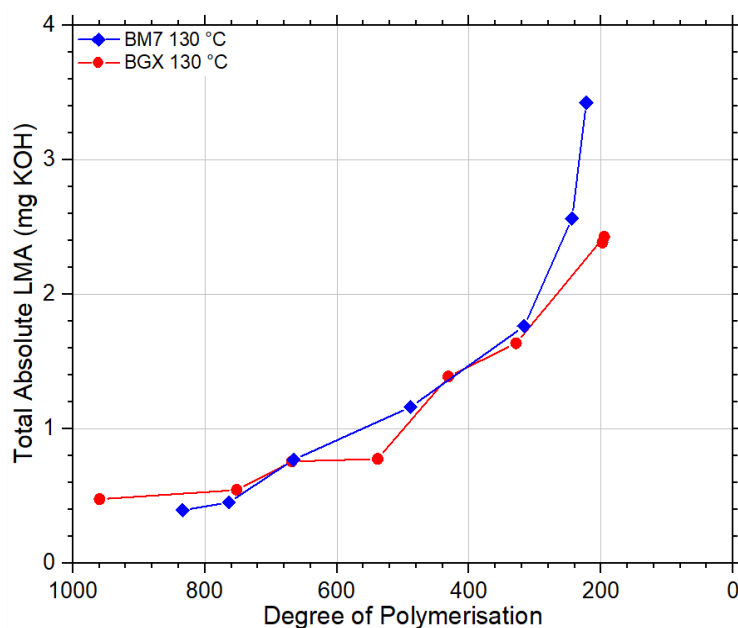


Figure 7.15 Total generation of LMA in oil and paper plotted against DP and chain scission number when dried Kraft paper was aged at 130 °C in MIDE L 7131 without any initially added acids.

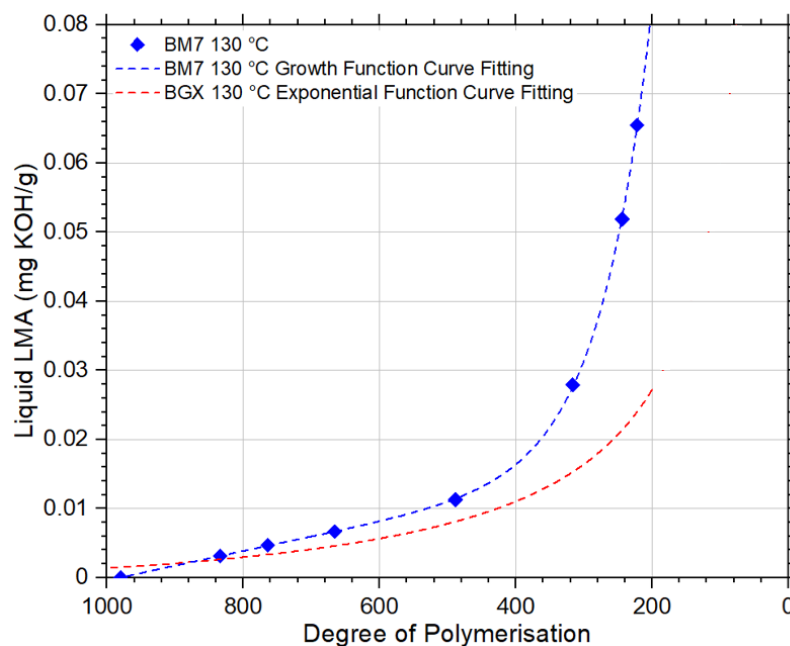


Figure 7.16 Concentration of oil LMA plotted against DP when the Kraft paper was aged at 130 °C in MIDEL 7131 without any added acids.

7.5.4 Concentration of High Molecular Weight Acids (HMA) in Oil

As shown in Chapter 5 (Figure 5.17), ageing of the Gemini X at 130 °C produces HMA that roughly accounts for 75% of the total acidity in the oil. It is generally accepted that HMA are produced mainly by the ageing of the transformer fluid, not from the ageing of paper. At this temperature, HMA are also expected to be produced in the ageing of MIDEL 7131.

The concentrations of HMA in oil are displayed in Figure 7.17 for comparative purposes between Gemini X and MIDEL 7131. Firstly, in both oils the HMA concentration is higher than that of the LMA throughout the aging process. Secondly, the total acidity in Gemini X saturates at Day 10, corresponding to a DP value of 440, whereas in the case of MIDEL 7131 the total acidity keeps increasing after Day 10 and reaches a value of 1.2 mg KOH/g at Day 75. The total acidity at Day 75 in the Gemini X case is only 0.1 mg KOH/g, less than 10% of that in MIDEL 7131. It is thus fair to state that the ageing of MIDEL 7131 controls the total acidity in the fluid. According to [116], ester is produced by reacting carboxylic acid with alcohol and the reverse reaction will produce acids when ester reacts with water. Therefore, the total acidity cannot be used as an indicator for paper ageing.

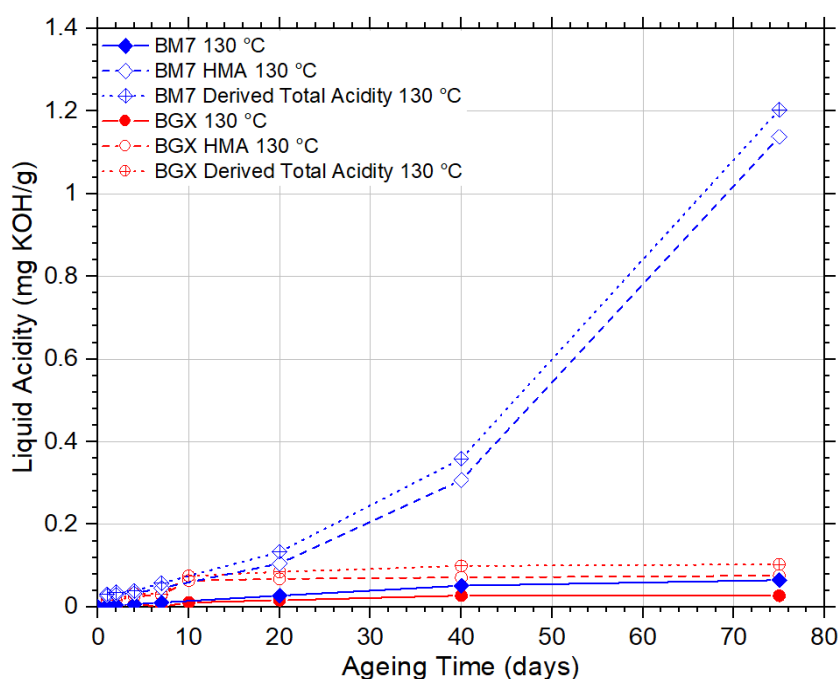


Figure 7.17 Concentration of LMA and HMA in MIDEL 7131 when Kraft paper was aged at 130 °C in MIDEL without any initially added acids.

7.6 Ageing of Kraft Paper in MIDEL 7131 with Initially Added Formic Acid

To further study the effect of LMA ~~low molecular weight acids~~ on the ageing of Kraft paper in synthetic ester, experiment was performed to thermally age the Kraft paper with initially added formic acid. The synthetic ester and Kraft paper were prepared according to the procedure described in Chapter 3 for filtration and drying. A nominal value of 0.4 mg KOH/g of oil was prepared for formic acid. The moisture level in paper was 0.8%. These two conditions were used to create an initial environment where the added formic acid can be dissolved in water to effectively catalyse the ageing process. A similar moisture level of 0.75% was used in [14] [24] to study the ageing of mineral oil impregnated cellulose by acid catalysis.

The paper moisture concentration was monitored during the ageing process. It fluctuates between 0.64% and 1.2% in the first 40 days with an average of 0.9%. At day 75, moisture measurement of multiple samples gives moisture concentrations between 0.2% and 0.7%. The fluctuation in moisture concentration was also observed in other

works such as [12, 101]. The moisture level in MIDEL 7131 varies between 30 ppm and 68 ppm.

The variation of DP as a function of ageing time is presented in Figure 7.18. Compared with the BM7 (blank MIDEL 7131) case, the initial drop in DP is evidently faster in the case where formic acid was added to the oil (which is referred as the FM7 case in this section). For example, the time to reach 50% of the starting DP is 8 days in the BM7 case, whereas with added formic acid this time is reduced to 3.4 days. Both sets of data in Figure 7.18 fit well with exponential trend lines.

The chain scission number for the Kraft paper is given in Figure 7.19. Using equation (5.3), the initial reaction rate is calculated as 5.31×10^{-6} /hour and 1.20×10^{-5} /hour for the BM7 and FM7 cases, respectively.

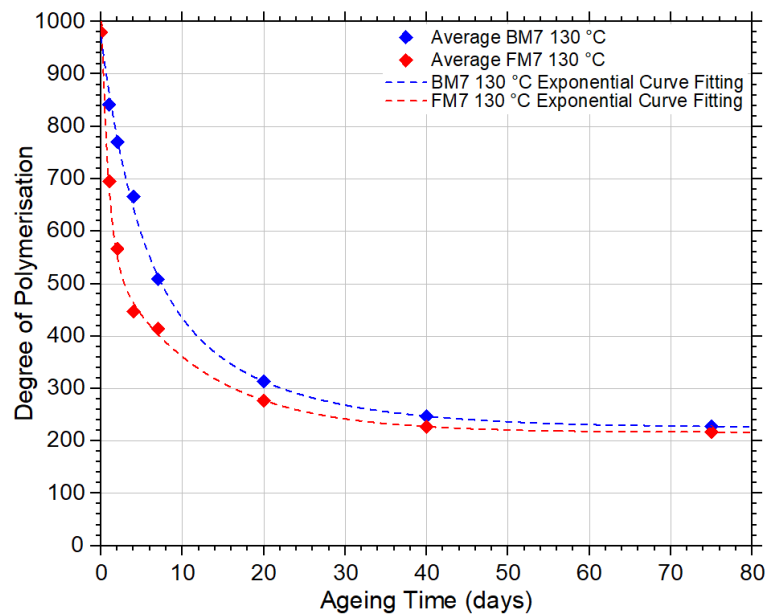


Figure 7.18 DP of Kraft paper as a function of time when Kraft paper was aged at 130 °C in MIDEL 7131 with and without added formic acid. The initial concentration of formic acid is 0.4 mg KOH/g in oil only.

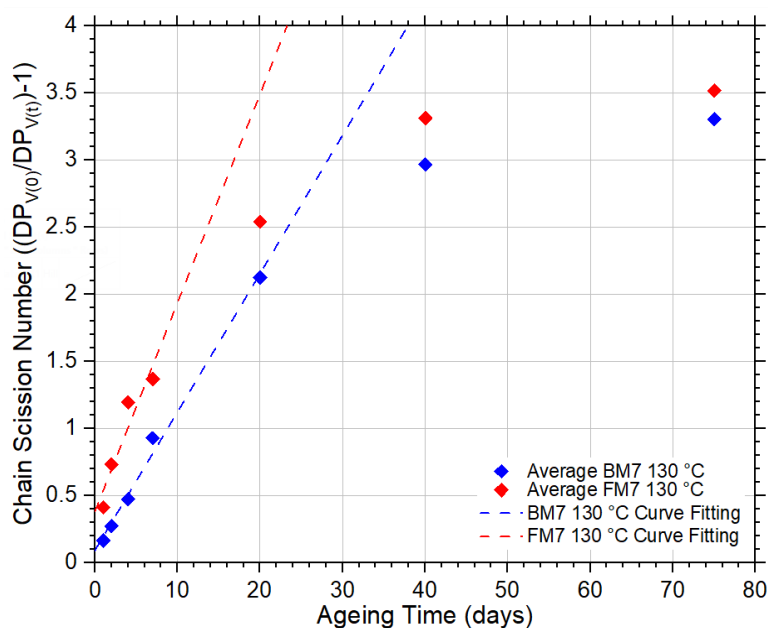


Figure 7.19 Chain scission number of Kraft paper as a function of time when Kraft paper was aged at 130 °C in MIDE L 7131 with and without added formic acid. The initial concentration of formic acid is 0.4 mg KOH/g in oil only.

The concentration variation of 2-FAL in the BM7 and FM7 cases follows clear trends as shown in Figure 7.20, but with different initial rate of rise. The initial rate of rise in the FM7 case is higher but the end values at Day 75 are close to each other (21 mg/kg). In general, the end concentration at Day 75 in the two MIDE L 7131 cases are lower than those obtained in the Gemini X cases (at a value of 25 mg/kg for the BGX case and 35 mg/kg in the FGX case).

The correlation between 2-FAL concentration and DP for MIDE L 7131 is given in Figure 7.21 to assess the overall exponential nature of the change in 2-FAL concentration. It can be seen that most of the 2-FAL concentration values correlate well with the DP, except in the DP range from 400 to 500. The extent of deviation from the exponential trend line can also be viewed in Figure 7.22 using linear scales. The absolute difference for the point of DP = 490 in Figure 7.21 corresponds to a chain scission number of 0.9 in Figure 7.22.

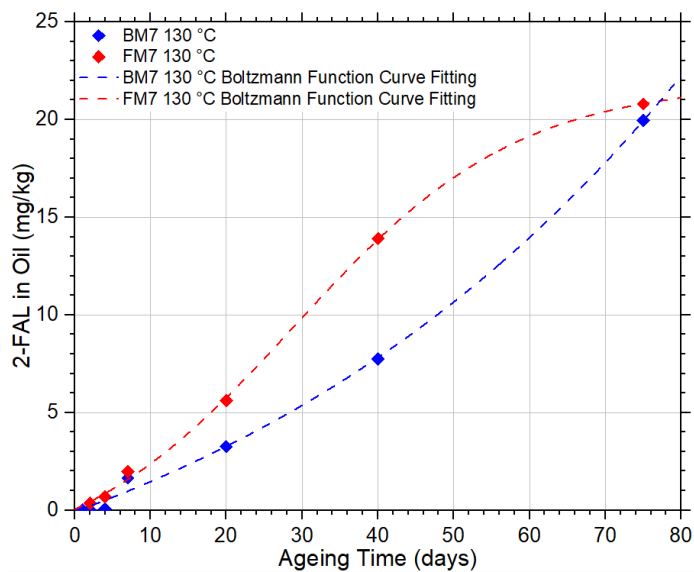


Figure 7.20 Concentration of 2-FAL in oil as a function of time when dried Kraft paper was aged at 130 °C in MIDE L 7131 with and without added formic acid. The initial concentration of formic acid is 0.4 mg KOH/g in oil only. Only one set of data is used in producing the graph.

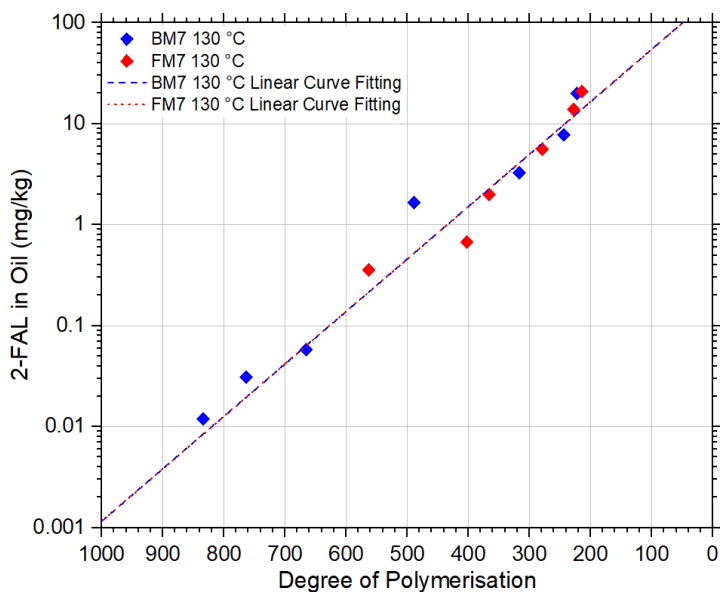


Figure 7.21 Correlation between the concentration of 2-FAL in oil and paper DP when dried Kraft paper was aged at 130 °C in MIDE L 7131 with and without added formic acid. The initial concentration of formic acid is 0.4 mg KOH/g in oil only.

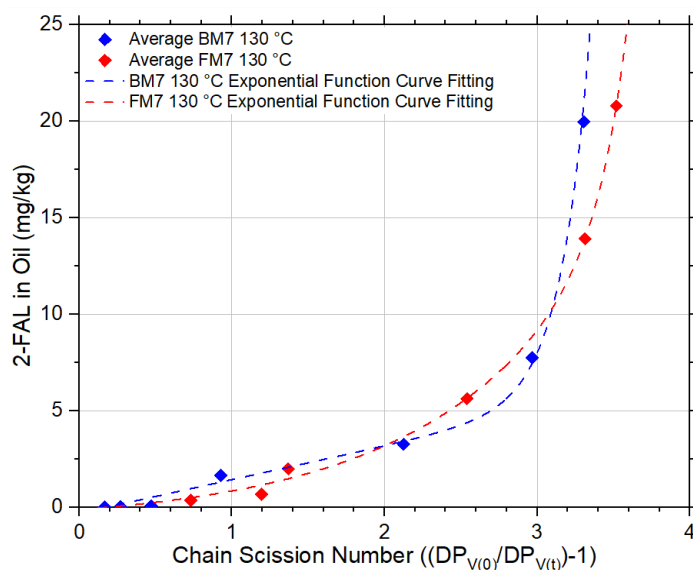


Figure 7.22 Correlation between the concentration of 2-FAL in oil and chain scission number when dried Kraft paper was aged at 130 °C in MIDE L 7131 with and without added formic acid. The initial concentration of formic acid is 0.4 mg KOH/g in oil only.

When formic acid is added to MIDE L 7131, the concentration of methanol increases initially (Figure 7.23) before abrupt changes start to take place at a DP of 500 (Figure 7.24). The BM7 case has a similar behavioral pattern but shows a larger methanol concentration change (up to 6.5 mg/kg in comparison with 3 mg/kg in the FM7 case). Both cases show a drop in methanol concentration towards the end of the ageing period. The results obtained in the present work is consistent with the conclusion drawn in [101] that methanol has the potential to be used as an indicator for the early ageing stage of transformer Kraft paper in MIDE L 7131 as a synthetic ester.

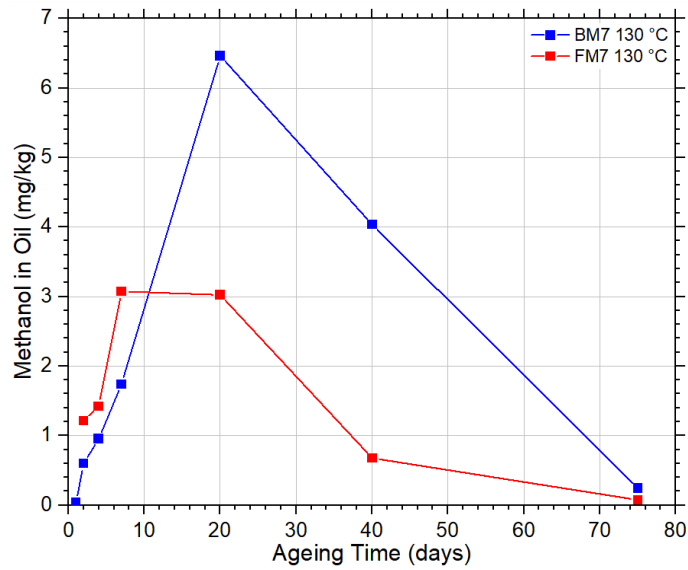


Figure 7.23 Concentration of methanol in oil as a function of time when dried Kraft paper was aged at 130 °C in MIDE L 7131 with and without added formic acid. The initial concentration of formic acid is 0.4 mg KOH/g in oil only. Only one set of data is used in producing the graph.

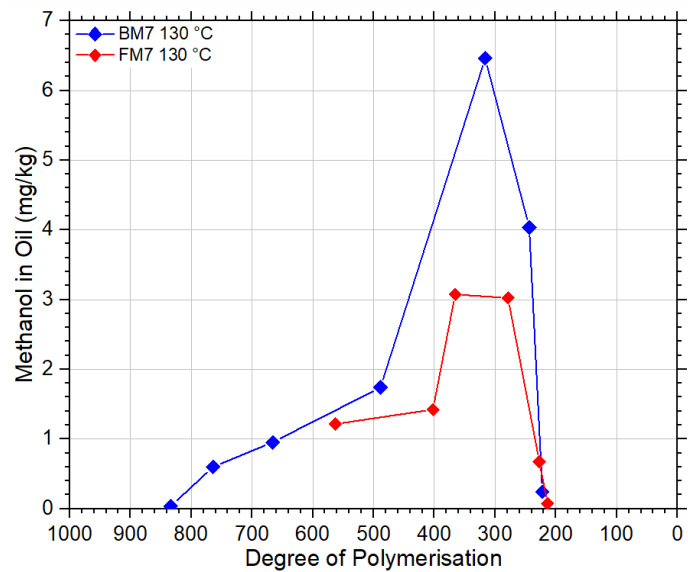


Figure 7.24 Correlation between the concentration of methanol in oil and paper DP when dried Kraft paper was aged at 130 °C in MIDE L 7131 with and without added formic acid. The initial concentration of formic acid is 0.4 mg KOH/g in oil only.

The variation of paper and fluid LMA concentrations when formic acid was initially added to MIDE L 7131 follows a pattern that is not seen in the BM7, BGX and FGX cases. Two sets of data are displayed, obtained from different ampoules with identical initial and ageing conditions. Good repeatability is demonstrated. As shown in Figure

7.25 and Figure 7.26, the concentration at Day 1 is 6.3 mg KOH/g and 0.0513 mg KOH/g in paper and oil, respectively. The oil mass is 9.7 g for 10 ml and the paper mass is 0.5 g. The total KOH equivalence is thus 3.65 mg. The initial LMA density is prepared to be 0.4 mg KOH/g which gives a KOH equivalence of 3.88 mg. This means 94% of the added formic acid is accounted for at a temperature of 130 °C. In contrast, it has been estimated that in the acidified Gemini X case (FGX), only 30% of the added formic acid is accounted for. Considering that the water based LMA extraction efficiency is between 80% and 90% (Chapter 4), it can be concluded with confidence that formic acid in the paper - MIDEL 7131 insulation system can stay relatively stable at a temperature of 130 °C for an initial period of 24 hours before it starts to be involved in the ageing process of paper.

Another important finding is the synchronous drop of LMA concentration in paper and oil in the first 7 days when the paper DP degrades from 980 to 400. The concentration in paper drops 50% from 6.3 mg KOH/g to 3.2 mg KOH/g before it recovers to 6 mg KOH/g by Day 20. The LMA concentration in the oil drops only 25%, showing a change in the partitioning characteristics when the paper DP drops.

By calculating the initial reaction rate and time to half of the starting DP, it can be concluded that the paper ageing speeds in both blank Gemini X and blank MIDEL 7131 cases are similar, however the acceleration factors of initially added formic acid are quite different. As shown in Table 7.1, the MIDEL 7131 is capable of mitigating part of the ageing effect of the added LMA by holding more LMA. As a result, the ageing acceleration factor in MIDEL is only 48% of that in Gemini X.

Table 7.1 Time (day) to reach 50% of the starting DP of the Kraft paper

Test cases	Blank Gemini X	Blank MIDEL 7131	Acidified Gemini X	Acidified MIDEL 7131
Initial reaction rate (/hour)	4.72×10^{-6}	5.31×10^{-6}	2.5×10^{-5}	1.20×10^{-5}
Days to reach 50% of starting DP	6.6	8	1.5	3.4

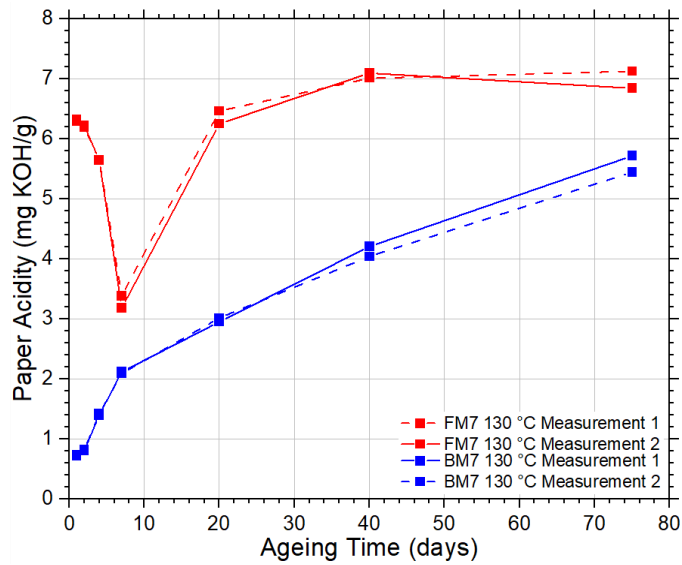


Figure 7.25 Paper LMA as a function of ageing time when Kraft paper was aged at 130 °C in MIDEL 7131 with and without added formic acid. The initial concentration of formic acid is 0.4 mg KOH/g in oil only. The two sets of data are from different ampoules with identical initial and ageing conditions.

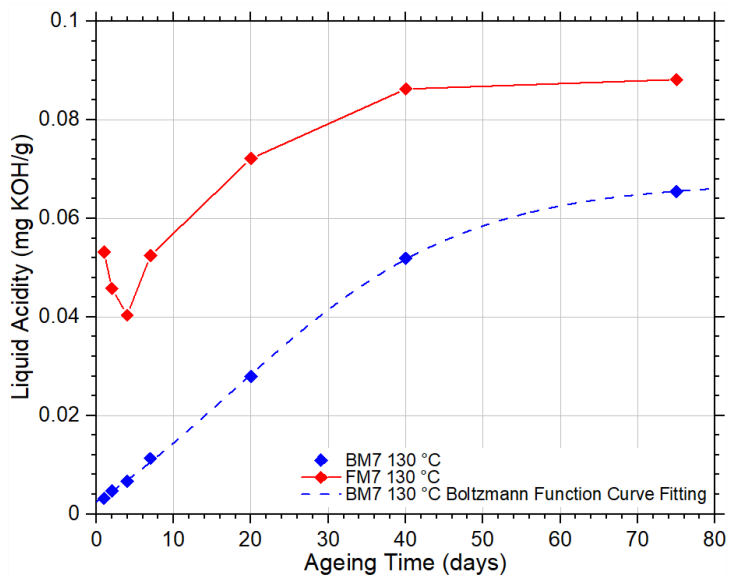


Figure 7.26 LMA concentration in oil as a function of ageing time when dried Kraft paper was aged at 130 °C in MIDEL 7131 with and without added formic acid. The initial concentration of formic acid is 0.4 mg KOH/g in oil only.

7.7 Summary

The ageing behaviour of Kraft paper in a synthetic ester transformer liquid, MIDEL 7131, was investigated in this chapter at a temperature of 130 °C. Two groups of test were performed, one without any initially added formic acid (the BM7 case) and the other with added formic acid at a prepared concentration of 0.4 mg KOH/g of oil (the FM7 case).

In the absence of added LMA (formic acid as representative), dried Kraft paper ages at a very similar speed in Gemini X and MIDEL 7131 up to a DP of 300. By the end of 75 day ageing, the paper DP in MIDEL remains marginally higher than that in Gemini X by a difference of 50.

The total LMA generation in the blank Gemini X and blank MIDEL 7131 cases are very close to each other in the DP range from 850 to 300, proving that LMA generation is mainly due to paper ageing. The concentration of LMA in MIDEL 7131 in the blank MIDEL case increases smoothly when the paper ages, providing strong experimental evidence for LMA being used as an ageing indicator for MIDEL 7131.

8 CONCLUSIONS AND FUTURE WORK

8.1 Summary and Conclusions

Oil filled transformers are complex systems whose operation concerns electrical, thermal, mechanical and chemical processes. The temperature distribution inside the transformer tank is affected by oil flow and transformer loading and also the detailed internal structure. As a result, thermal ageing of paper insulation inside a transformer will not be spatially uniform. With regard to transformer paper insulation monitoring, the challenges lie with the facts that the ageing conditions vary substantially at local scale within the transformer tank and the development of an insulation fault depends not only on the condition of the insulation paper but also on the local electric field. The combination of these two complexities render transformer insulation condition monitoring a difficult subject.

There has been a significant amount of research, since as early as 1960s, to study the ageing phenomena of transformer oil-paper insulation system, and in-depth knowledge has been established. As reviewed in Chapter 2, laboratory based thermally accelerated ageing is the main method of research supplemented by measurement and study on post service transformer insulation. The mechanical strength of the paper is dominated by the structure of the polymer cellulose molecules which can be changed by chemical chain scission, and described by tensile index and degree of polymerization (DP) which are well correlated. The measurement of DP during thermal ageing of paper insulation is mostly performed. Over the past six decades, different aspects of the ageing process have been studied, including 1) the effect of temperature, moisture and oxygen as ageing environment on the paper degradation rate; 2) the chemical mechanisms responsible for the degradation of oil and paper (hydrolysis, oxidation and pyrolysis); 3) chemical ageing products (e.g. acids, furfurals and alcohols) and their correlation with the mechanical strength of the paper; and 4) ageing behaviour of oil and paper in servicing or post service transformers (DP, acidity and chemical concentration measurements).

In most of the laboratory ageing tests, the oil and paper samples were placed in bottles that had relatively large volumes (200 ml – 2000 ml) and were closed with caps. It has been a well-known challenge to ensure the sealing performance of the bottles during the long-term ageing. In some tests, the bottles were even opened regularly during the ageing cycle to take a small amount of oil and paper samples out for measurements before they were returned to the oven for further ageing. This process of sampling might lead to disturbance to the ageing process and make it difficult to interpret the measurement results. In addition, only a small amount of meaningful results have been obtained on the role of the low molecular weight acids (LMA) for paper and oil ageing. No systematic measurement of the LMA concentration in paper and oil has been carried out during the ageing process although the total acidity has been monitored in some studies.

In the present work, the following outputs have been produced that contribute to the knowledge and understanding of the ageing process of the transformer oil-paper insulation system.

- i) A completely gas tight ageing system has been designed and used to study the ageing of Kraft paper in one mineral oil and one synthetic ester liquid (Chapter 3). It completely isolates the ageing samples from the environment to stop any mass exchange through leakage and ingress, enabling trusted ageing conditions to be set. The size of the samples is significantly reduced, down to 10 ml for oil and 0.5 g for paper. Such a system allows better observation and assessment of low molecular weight chemicals in the liquid that are usually volatile. It also allows long-term partitioning of these chemicals between the liquid and solid insulations after the ageing to reach equilibrium.
- ii) An improved approach of liquid LMA concentration measurement based on water extraction has been proposed by using Erlenmeyer flasks (EF). Its extraction efficiency, with and without the presence of high molecular weight acids (HMA) in the oil, has been proven to be better than 80% for MIDEL 7131. The efficiency is better than 90% for Gemini X in cases with a concentration as low as 0.017 mg KOH/g of LMA.
- iii) It is the first time, to the author's knowledge, that the concentration of LMA in paper and in liquid has been systematically measured together with those

of moisture, 2-FAL and methanol during the ageing process where the DP of the paper decreases from 1000 to around 200. This provided multiple sets of baseline data to assess the ageing process from different angles, especially the evolution of LMA concentration during the ageing process and the effect of an added LMA (formic acid) on the ageing of Kraft paper in mineral oil and synthetic ester.

- iv) When the ageing starts with filtered dried oil and dried paper with a moisture level less than 0.5%, Kraft paper ages at the same rate in Gemini X as in a synthetic ester. The moisture level remains below 1.5%, representing a perfectly controlled ageing system. The addition of formic acid with an initial concentration of 0.4 mg KOH/g in oil greatly accelerates the ageing of the paper in Gemini X, by a factor of 5.3. For MIDEL 7131, the acceleration factor is 2.3, demonstrating the ability of MIDEL 7131 in mitigating the effect of LMA on paper ageing.
- v) The variation of the concentrations of 2-FAL and methanol has also shown clear correlation with the change in paper DP under conditions similar to those of new transformers, confirming the findings in previous works that these two chemical species are produced by paper ageing and can be considered as paper ageing indicators.
- vi) Clear evidence has been shown in the present work that, with initially dry conditions for paper and oil, the total LMA generations as a result of paper ageing in the two transformer fluids (Gemini X as a typical mineral oil and MIDEL 7131 as a synthetic ester fluid) follow the same trend line over the DP range of 850 – 300. This DP range is critical to the monitoring of transformer insulation deterioration. The LMA concentrations in paper and in the two types of transformer liquids are also strongly correlated to the paper DP during the ageing process. Thus the present work enables a firm step forward to be made in establishing LMA concentration as an indicator of transformer paper ageing in different transformer liquids.

8.2 Discussions and Future Work

A technical challenge in applying the laboratory based test results to real transformer condition monitoring is the mapping of the measurement results obtained from the transformer oil samples with the paper ageing state at different locations in the transformer tank, especially near the hot spots. The oil is sampled at an outlet on the tank wall and the flow field and temperature of the oil inside the tank has a complex distribution. This mapping will not be possible purely based on measurement or monitoring at single location, which would be still challenging even sampling at multiple locations are made possible.

Future transformer monitoring systems need to be more intelligent, which can be assisted by the use of computer models or verified database developed with computer simulation under different conditions. To enable this, the following sub-models need to be made available.

- Sub-model A: A thermal flow model that is able to predict the temperature and flow field and the transport of chemical species inside the transformer tank.
- Sub-model B: A paper ageing model that is able to describe the accumulative effect with varying thermal and chemical environment, and in turn provides information on the change of the chemical species under consideration.
- Sub-model C: A model to represent the dynamic partitioning of different chemical species between oil and paper, i.e. the exchange of chemical species between paper and oil.

With the above sub-models it is then possible to establish the necessary mapping to obtain spatially resolved paper ageing state based on measurement at discrete locations in the transformer tank (near the tank wall).

The present work focuses on seeking experimental evidences relating to sub-model B and sub-model C. Much work is to be done.

In terms of improvement from the present work, the following aspects may be considered in the future work:

8.2.1 Accuracy and Repeatability of Measurement Results

Reliable conclusions must be based on trustable information on the accuracy of the measurement. Although there are established methods for the measurement of DP, moisture, 2-FAL, methanol and acidity, the accuracy of the results still depends on the operation. A reliable estimation of the absolute measurement error is often difficult. The trend and pattern of variation of the measured parameters in the present work are clear and beyond reasonable doubt. However further conclusions on the detailed change of the parameters in particular at the low concentration region for the chemical species cannot be drawn.

With the proposed completely sealed paper oil ageing system available to better control the ageing conditions, it is therefore suggested that more research can be performed to identify the causes of scattering in the measurement results to improve the measurement accuracy and better quantify the ageing behaviour. Multiple samples should be prepared and aged under identical ageing conditions and measured using identical methods at the same time to obtain statistical evaluation.

8.2.2 Partitioning of Chemical Species between Oil and Paper at Different DP

Information on partitioning of chemical species between oil and paper can only be obtained when the species stay stable in the oil and in the paper, i.e. they do not react or react slowly within the time scale for equilibrium with the materials that they are in contact. Although sufficient time (3 months) was given in the present work to allow equilibrium of partitioning to be achieved before measurement, the important issue is that the DP has been changed due to ageing process and it is necessary to confirm the time to reach equilibrium and the partitioning ratio for the aged paper whose DP can be much lower than the new paper. It is also useful to find out if the presence of other chemical species affects the partitioning of a specific species.

8.2.3 Initial Concentration Variation of Added LMA at Elevated Temperature

As is shown in Chapters 6 and 7, there were two interesting observations that need further confirmation. The first one is that only one third of the added formic acid in Gemini X was accounted in the first 8 days when DP decreases rapidly. With Gemini X, the initial measured LMA in paper and oil accounts for over 90% in the first 2 days before the LMA concentration drop to 3 mg KOH/g in paper (1 mg KOH/g – 2 mg KOH/g in Gemini X in the first few days). The reduced LMA concentration implies that LMA is consumed in the initial stage of paper ageing, i.e. the scission of new and long cellulose molecules. Based on these two observations, further work can be carried out to confirm this initial consumption of LMA and the much rapid consumption speed in Gemini X in comparison with MIDEL 7131.

The proposed future work above will help extend the findings made in the present work and prepare for the next stage of study on transformer paper insulation ageing.

APPENDIX A: LIST OF PUBLICATIONS

INTERNATIONAL CONFERENCE PAPERS

- 1) Yan, Z.W., Matharage, S.Y., Liu, Q. and Wang, Z.D., Extraction of low molecular weight acids from transformer liquids using water extraction technique. In *2018 12th International Conference on the Properties and Applications of Dielectric Materials (ICPADM)* (pp. 198-201). IEEE.
- 2) Yan, Z.W., Matharage, S.Y., Liu, Q. and Wang, Z.D., “Measuring Low Molecular Weight Acids in Mineral and Ester Transformer Liquids”, In *2020, 8th International Conference on Condition Monitoring and Diagnosis (CMD)*, IEEE.

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