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Physico-chemical analysis of transformer oil and stability studies of their blends with synthetic and natural antioxidants.

by

Veresha Dukhi

Dissertation submitted in fulfilment of the academic requirements for the degree of

Master of Science

School of Chemistry, University of KwaZulu-Natal, Westville, Durban

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Co-Supervisors:	Mr Ajay Bissessur
	Prof Nelson Ijumba

March 2012

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This dissertation has been prepared according to Format 3 as outlined in the guidelines from the Faculty of Science and Agriculture which states:

> This is a dissertation in which the chapters are written as a set of discrete research papers with an overall introduction, literature review, a general experimental and conclusions chapters. All the manuscript-formatted chapters have already been submitted in international peer-reviewed journals.

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Name: Prof J. Catherine Ngila

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DECLARATION 1- PLAGIARISM

I, Veresha Dukhi, declare that the experimental work described in this dissertation was carried out at the School of Chemistry, University of KwaZulu-Natal, Westville campus, between March 2010 and December 2011, under the supervision of Mr. A. Bissessur, Prof. J. C. Ngila and Prof. N. M. Ijumba and that:

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2. This dissertation has not been submitted for any degree or examination at any other university.

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DECLARATION 2- PUBLICATIONS

V. Dukhi, A. Bissessur*, J. C. Ngila and N. Ijumba. (2011). Proceedings of XVII International Symposium on High Voltage Engineering (ISH), Hannover, Germany, August 22-26, 2011. E-029, p294.
I performed the research, data analysis and write-up. All other co-authors are my supervisors who provided guidance and were involved in editing the manuscript.

V. Dukhi, A. Bissessur*, J. C. Ngila and N. Ijumba. (2011). Physico-chemical properties of transformer oil blends with antioxidants extracted from turmeric powder., *World Academy of Science and Engineering*. (submitted).
I performed the research, data analysis and write-up. All other co-authors are my supervisors who provided guidance and were involved in editing the manuscript.

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I performed the research, data analysis and write-up. All other co-authors are my supervisors who provided guidance and were involved in editing the manuscript.

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ABSTRACT

This study is focused on the analysis of transformer oil commonly used in South African transformers and the characterisation of the blends of these oils with either synthetic antioxidants or those extracted from natural sources.

The virgin naphthenic based uninhibited transformer oil was shown to have no acidic or saponifiable constituents. Although the oil used in this study is naphthenic based it was found to contain bicyclic compounds identified as tetralin (aromatic) and decalin by GC-MS. The oils were void of typical wear metals and only additive metals/non-metals were present. The blending of transformer oils with synthetic antioxidants was successful as confirmed by ^{1}H NMR, ^{13}C NMR and FT-IR data. The blending showed increased antioxidant activity of the oils as well as thermal stabilities (DPPH assay and TGA respectively). Apparent activation energy for the decomposition reaction was determined by means of the Ozawa, Flynn and Wall (OFW) and Kissinger models. The apparent activation energy for BHT-B, DBP-B and VO were found to be 57.0, 63.7 and 69.3 kJ mol^{-1}, respectively for 10% mass conversion obtained from TGA data (OFW model). The dissipation factor for the oil blends was established to be favourably lower than that of unblended oils; however an undesirable decrease in the dielectric breakdown voltage of the blends was observed (16, 26 and 50 kV for BHT-B, DBP-B and VO respectively).

The blending of transformer oil with synthetic antioxidants is a common practice, however greener approaches are always favoured. In this study, a greener approach was employed by blending the transformer oil with turmeric plant extract in an effort to improve the oil's performance. Turmeric is known for its antimicrobial, antioxidant and anticarcinogenic properties. Solvent extraction of turmeric powder and subsequent blending into transformer oils, revealed the dissolution of 5 components from turmeric into the oil, viz., curcumene, sesquiphellandrene, *ar*-turmerone, α-turmerone and β-turmerone (curlone). In this work, we analysed novel turmeric-oil blends in terms of oxidation and thermal stability in comparison to that of virgin transformer oil. The DPPH assay confirmed that addition of these blends into the oil increased its ability to scavenge the free radical DPPH. Thermogravimetric analysis showed an increase in thermal stability when compared to that of virgin unblended oil. Evidently blending of synthetic antioxidants/turmeric extract has potential to enhance the performance and increase the life-span of transformer oils.

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DEDICATION

This dissertation is dedicated to my family for your love and support.

“You must be the change you wish to see in the world”… Mahatma Gandhi

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LIST OF ABBREVIATIONS

∏	pi
°C	degrees Celsius
AC	alternating current
AO	antioxidant
ar-	aromatic
ASTM	American Standard Testing Methods
ATR	attenuated total reflectance
β	heating rate
BHT	butylated hydroxy toluene
BHT-B	butylated hydroxy toluene blend
C	capacitance
DBP	di-butylphenol
DBP-B	di-butylphenol blend
DPPH	2,2-diphenyl-1-picrylhydrazyl
DSC	differential scanning calomitery
E-OB1	extract oil blend 1
E-OB2	extract oil blend 2
E-OB3	extract oil blend 3
E-OB5	extract oil blend 5
f	frequency
FT-IR	Fourier transform infrared spectroscopy
GC-FID	gas chromatography- flame ionisation detector
GC-MS	gas chromatography- mass spectrometry
HV	high voltage
I	current
ICP-OES	inductively coupled plasma- optical emission spectroscopy
IEC	International Electro- Technical Commission
K	Kelvin
kVA	kilo volt amps
NERSA	National Energy Regulator of South Africa
NMR	nuclear magnetic resonance
OFW	Ozawa, Flynn and Wall
PCB	polychlorinated biphenyls
TA	thermal analysis
tan δ	tan delta/dissipation factor
TGA	thermo gravimetric analysis
TPP	triphenylphosphine

TPPO	triphenylphosphine oxide
TPPS	triphenylphosphine sulphide
UV/Vis	ultraviolet/visible
VO	virgin oil
w/w	weight by weight
α	conversion
ω	angular frequency
Ω	ohm

CHAPTER 1

INTRODUCTION

The basic principle of transformers was initially introduced by Michael Faraday in 1831, however transformers were only developed late in the 19th century [1]. Today, their role in the electricity supply industry is indispensable. The performance of a transformer is crucial to the efficiency of power transference. However the lifetime of a transformer is limited. Fouling of the transformer is more likely due to insulation failure than mechanical wear [2]. Many types of liquid filled transformers are commonly insulated using mineral oil. Mineral oil was first introduced as a dielectric fluid in 1892 [3]. A typical generator step-up (GSU) transformer contains several thousand gallons of transformer oil [4]. Although oils function efficiently as coolants and insulators [5], it suffers the drawback in which it is susceptible to oxidative processes. Ageing of insulation material inevitably leads to insulation failure [6]. This work focuses on a naphthenic based transformer oil, used typically as a dielectric fluid in South African transformers.

1.1 PROBLEM STATEMENT

South Africa is a country that is presently advancing industrially and economically [7]. With the expanding growth of the urban population, demand is placed on everyday ‘necessities’ such as clean running water, electricity, among other social amenities. One of the current issues in South Africa is the energy crisis. As a consequence of urbanization, stress is placed on the service providers (such as those that provide electricity) for more efficient production and delivery. The main electricity supplier in South Africa, Eskom cannot deal with such enormous demands for electricity with the limited number of power stations that are currently in place. One of the solutions to curb the power shortage for Eskom has been frequent power cuts across the country [8]. Currently, consumers are still urged to restrict their use of electricity. The matter has however worsened when the National Energy Regulator of South Africa (NERSA) recently granted Eskom a 24.8% hike in the price of electricity resulting in increased bills for the consumer [9].

In order to increase the production of electricity, one has to improve the efficiency of power generation.

One of the ways to achieve this is by optimizing the performance of the transformer and one of the key components of the transformer is its insulation, in this case the transformer oil. Insulation failure of transformers inevitably leads to high repair costs, long downtime and very real safety risks. Moreover, transformers are too expensive to repair/replace regularly and must be properly maintained to maximize their life expectancy. This can be achieved by improving the stability and performance of its insulation. Oil filled transformers have two aspects in terms of insulation: paper and dielectric fluid. The liquid component of the insulation is transformer oil. Oil serves a dual function in transformers, acting as a coolant and an insulator [5]. However the ageing process is unavoidable and reduced quality of the oil and paper eventually results in transformer failure [10]. Nonetheless it was found that some oils underwent the oxidation process at a slower rate than others. The key question was what was the difference between these oils? Later it was established that oils which managed to retard the oxidation process, contained natural antioxidants [11]. Antioxidants are free radical scavengers in which their general function is to donate hydrogen and thereby terminate the radical chain mechanism [11].

1.2 HYPOTHESIS

The synthetic antioxidants, 2,6-di-*tert*-butyl-4-methylphenol (butylated hydroxy toluene-BHT) and 2,6-di-*tert*-butylphenol (DBP) as well as turmeric plant extracts when blended with transformer oils can extend the lifetime of the oils by increasing their antioxidant activity and therefore their stability.

1.3 AIM OF THE STUDY

The aim of the study was to compare the stability of naphthenic based virgin transformer oils by investigating the physico-chemical properties of uninhibited oil before and after blending with synthetic antioxidants, namely BHT and DBP, and turmeric plant extract.

1.3.1 Specific Objectives of the Study

The specific objectives of the study include:

i. Determination of the physico-chemical properties of uninhibited naphthenic based transformer oil.

ii. To determine the physico-chemical properties of naphthenic oil blends with synthetic antioxidants, namely BHT and DBP and the effect accelerated ageing has on these antioxidants.

iii. Characterisation of the effect that, blending of turmeric powder extract with naphthenic oil has on its physico-chemical and electrical properties.

iv. Thermal analysis of uninhibited oils and their blends with synthetic antioxidants so as to determine the kinetic parameters of the decomposition reaction.

1.4 DISSERTATION OVERVIEW

Chapter 1 outlines an introduction on transformers and oil as an insulator. In addition it highlights the problems associated with transformer oils and possible ways to improve its performance.

Chapter 2 reviews the literature on transformers, oil insulators in transformers as well as the effect electrical and thermal stresses have on transformer oils. This chapter also discusses the role of synthetic and plant extract antioxidants, on improving stability of the transformer oils. It also discusses principles of methods and instruments.

Chapter 3 is a general experimental overview to the work that has been carried out in this study. It includes the instrumental methods used for characterisation of transformer oils before and after blending. The chapter also discusses the physico-chemical parameters of virgin transformer oils including viscosity, water content, acid number, iodine value, dissipation factor as well as dielectric breakdown testing, among other properties of oils.

Chapter 4 presents the first published manuscript (Proceedings): C*haracterisation of a naphthenic based uninhibited virgin transformer oil and the use of synthetic antioxidants.* XVII International Symposium on High Voltage Engineering: Leibniz Universität Hannover, Schering-Institut, Hannover, Germany, August 22-26, 2011: E-029 p294. In this manuscript, the physico-chemical properties of the oil blended with synthetic antioxidants, namely BHT and DBP were carried out. The oil blends were also subjected to digestion by exposure to UV radiation, the antioxidant (AO) content was monitored and the AO degradation products were determined.

Chapter 5 is the second manuscript that has been submitted to *World Academy of Science and Engineering Technology*: *Physico-chemical properties of transformer oil blends with antioxidants extracted from turmeric powder.* It details transformer oil blending with extracted antioxidant components from turmeric (*Curcuma longa)* powder. These blends were then characterised in comparison with virgin non-blended oil.

Chapter 6 presents results of the third manuscript: *The determination of kinetic parameters of transformer oil and its blends by thermal analysis,* submitted to *South African Journal of Science.* The study is based on the determination of apparent activation energy of the oil and its blends for the decomposition reaction by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The study highlights the use of thermal analysis for the determination of the kinetic parameters by means of the Ozawa, Flynn and Wall (OFW) and Kissinger models.

Chapter 7 is the conclusion which presents a summary of the major results of this MSc dissertation work. It outlines suggestions and recommendations for further work with respect to dielectrics fluids that are used in transformer insulation.

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REFERENCES

[1] Coltman J. W., The transformer, *IEEE Industry Application Magazine,* **2002**, *Jan/Feb*:8-15.

[2] Verma P., Condition monitoring of transformer oil and paper, Electrical and Instrumentation Engineering, Thapar Institute of Engineering and Technology **2005**, *Doctor of Philosophy*.

[3] Yuliastuti E., Analysis of dielectric properties comparison between mineral oil and synthetic ester oil, Department of Electrical Sustainable Energy, Delft University of Technology **2010**, *Master of Science*.

[4] U.S. Department of the Interior Bureau of Reclamation, Transformers: Basics, Maintenance, and Diagnostics, Reclaimation: Managing Water in the West, **2005**, www.usbr.gov/pmts/client_service/recent/studytransformers.pdf (accessed 27 July 2011).

[5] Heathcote M. J., J & P Transformer Book, Elsevier, **2007**.

[6] Meshkatoddini M. R., Aging study and lifetime estimation of transformer mineral oil, *American Journal of Engineering and Applied Sciences*, **2008**, *4*:384-388.

[7] South Africa: Economy overview, http://www.southafrica.info/business/economy/econoverview.htm (accessed 5 October 2011).

[8] Mail and Guardian Online, Eskom: Power supply 'a serious concern' from 2011, http://mg.co.za/article/2010-03-16-eskom-power-supply-a-serious-concern-from-2011 (accessed 5 October 2011).

[9] Mail and Guardian Online, Nersa grants Eskom 24,8% price rise, http://www.mg.co.za/article/2010-02-24-nersa-grants-eskom-248-price-rise (accessed 4 May 2010).

[10] Jarman P., Wang Z., Zhong Q. and Ishak T., End-of-life modelling for power transformers in aged power system networks, *Cigré*, **2009**, *C105*.

[11] Rudnick L. R., Lubricant Additives: Chemistry and Applications, CRC Press, **2009**.

CHAPTER 2

LITERATURE REVIEW

2.1 AN OVERVIEW OF TRANSFORMERS

In general terms, an electrical transformer is a device that can transfer electrical energy from one circuit to another [1]. However its precise definition is rather more complex than this. The transformer was developed with the aim to allow electricity to transfer from an electrical generator to the consumer [1]. The transformer is required to 'transform' the high current lower voltage output from an electrical generator to a voltage that can be handled by cable direct to the consumer [1]. Power transformers that are rated 500 kVA and larger, are oil filled for insulation and cooling [2]. Transformers rated less than 500 kVA are used for distribution e.g. pole-top transformers [2].

Figure 2.1 Depiction of a typical GSU, three phase transformer [2].

Step-up transformers, receives energy at a generator voltage and increases it to a higher voltage for transmission lines whereas a step-down transformer receives energy at a higher voltage and delivers it at a lower voltage for distribution to various loads [2]. Since the power is constant, step down transformers step up the current and vice versa. Transformers are composed of two sets of windings referred to as primary and secondary, which are linked by a ferromagnetic core. The transference of energy is via the process of electromagnetic induction [1, 3]. One winding (primary winding) of the transformer is energized by an alternating current. This brings about a magnetic field in the core, as a result flux lines circulate the transformer core. The secondary winding is around the same core, consequently the alternating flux lines induce a voltage in the secondary winding (Figure 2.2) [2]. The total voltage induced is equal to the sum of the individual voltages induced in each turn of the windings [2]. As a result in a step up transformer, a greater voltage output is required hence the number of turns in the secondary winding is greater than that of the primary windings; the converse is applicable for step down transformers [2].

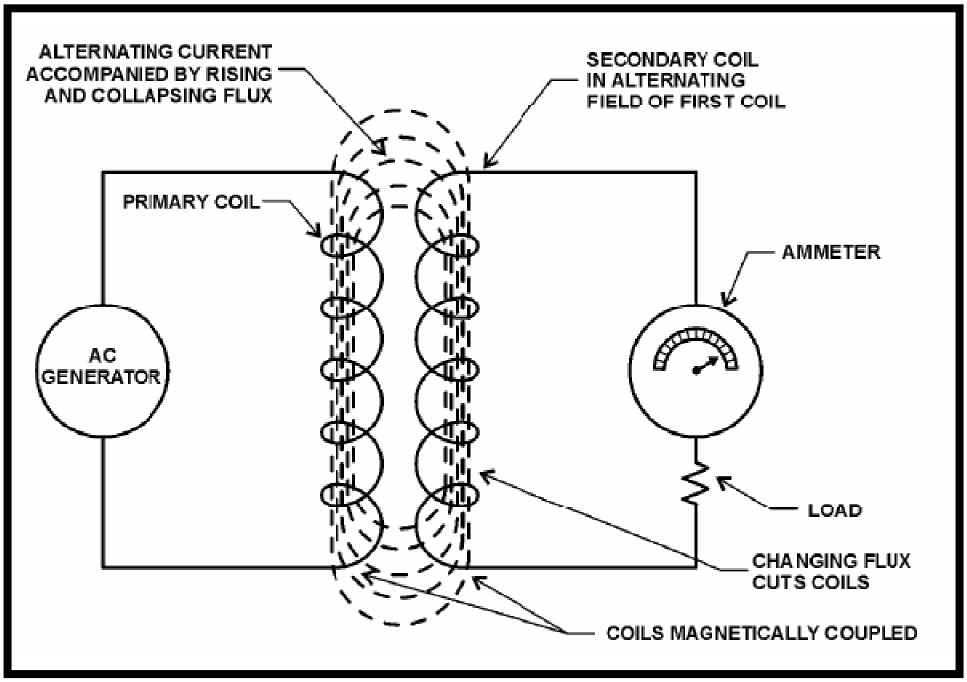


Figure 2.2 Representation of primary and secondary windings of a transformer showing the induction of voltage by electromagnetic flux [2].

2.2 TRANSFORMER INSULATION USING OILS

As previously indicated the insulation of the transformer is crucial to its lifetime. The transformer insulation must be substantial for forty years or more of service [1]. Oil filled transformers have two aspects in terms of insulation: paper and oil.

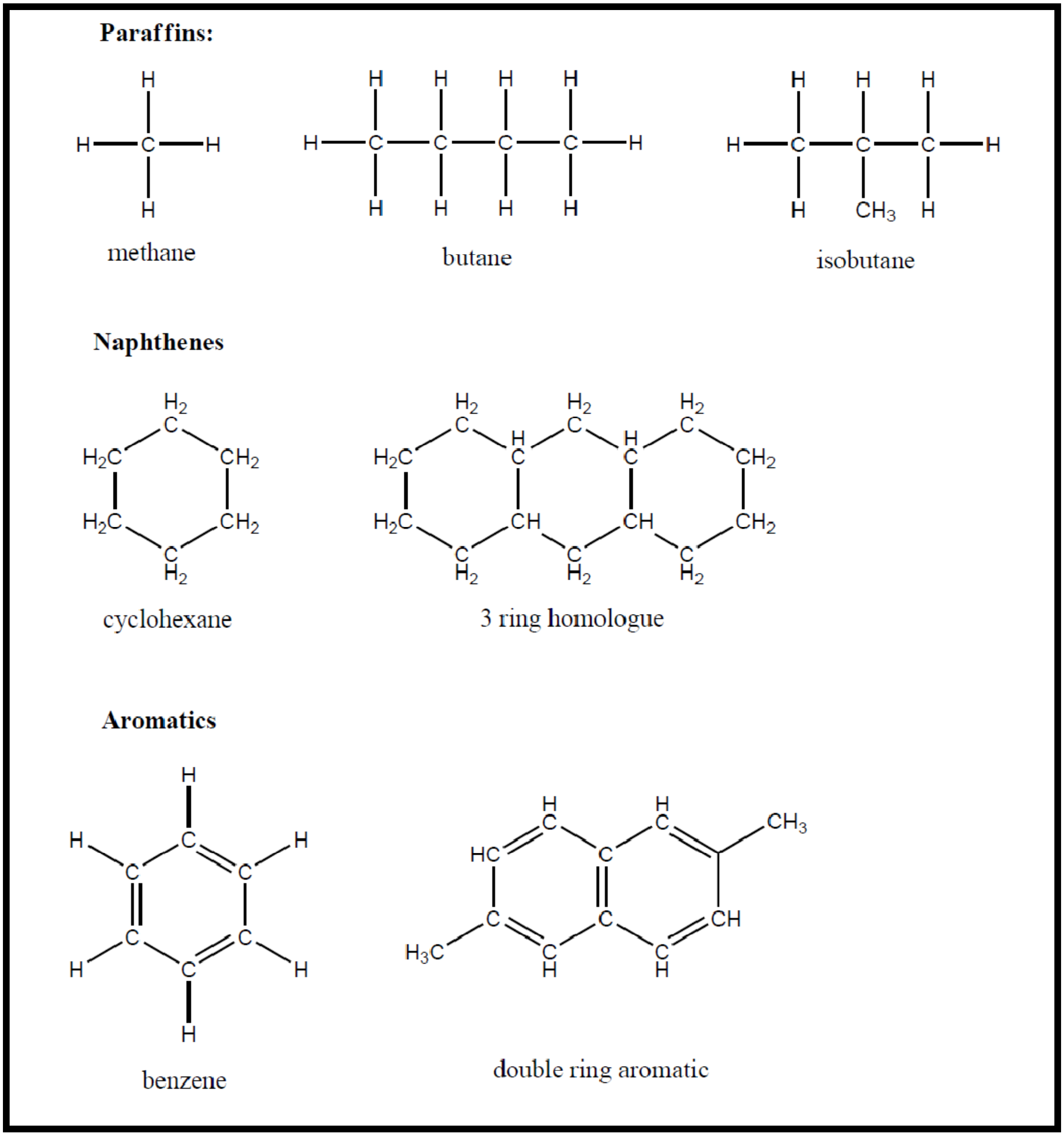
The paper insulation can be divided into: (a) Kraft paper and (b) cotton cellulose [1].

The liquid component of the insulation is transformer oil. Oils in general serves a dual function in transformers, acting as a coolant and an insulator. The basic materials of a transformer include copper and iron. These materials bring about energy losses in the form of heat. This leads to an overall increase in the temperature of the transformer [1]. Since the operation temperature of a transformer is dependent on the paper insulation, it is common practice that the temperature should not exceed 100 °C. Based on this temperature restriction, a medium is required to absorb heat from the system [1]. Mineral oil has been found to be the most efficient medium for absorbing heat from the core and the windings.

In terms of the oil acting as an insulator; a transformer is made up of a number of different parts held at different electrical potentials [1]. Thus a medium is required in order to insulate the different parts from each other.

The oil is also required to aid in the efficiency of the solid insulation (paper) [1, 4]. The oil penetrates the paper and fills the spaces between the wound insulation [1]. Oils are also relatively inexpensive however their flammability restricts the placement of transformer units indoors. Previously polychlorinated biphenyls (PCB's) were employed as insulators, their non flammable nature made them preferential [5]. However PCB's are now known to be toxic and persistent pollutants [5]. Consequently the use of PCB's as dielectrics in transformers have been banned [6].

Currently there are different types of mineral oils that are available for use in transformers. Most mineral oils that are used are obtained from crude petroleum. There are three types of hydrocarbon oils that are used: paraffins, naphthenes and aromatics (Structure 2.1). Other dielectric fluids are available; however this work focuses exclusively on mineral oil that is naphthenic based.



Structure 2.1 Molecular structure of compounds found in hydrocarbon mineral oils [1].

Criteria that should be met in order for an insulating oil to be deemed efficient include:

i. Low viscosity: heat is dissipated in three ways: convection, radiation and conduction. The reliability on convection is found to be the most important. Convection relies on natural circulation that arises due to the difference in densities of hotter and cooler fluids. Thus efficient convection is dependent on the oil viscosity. [1]

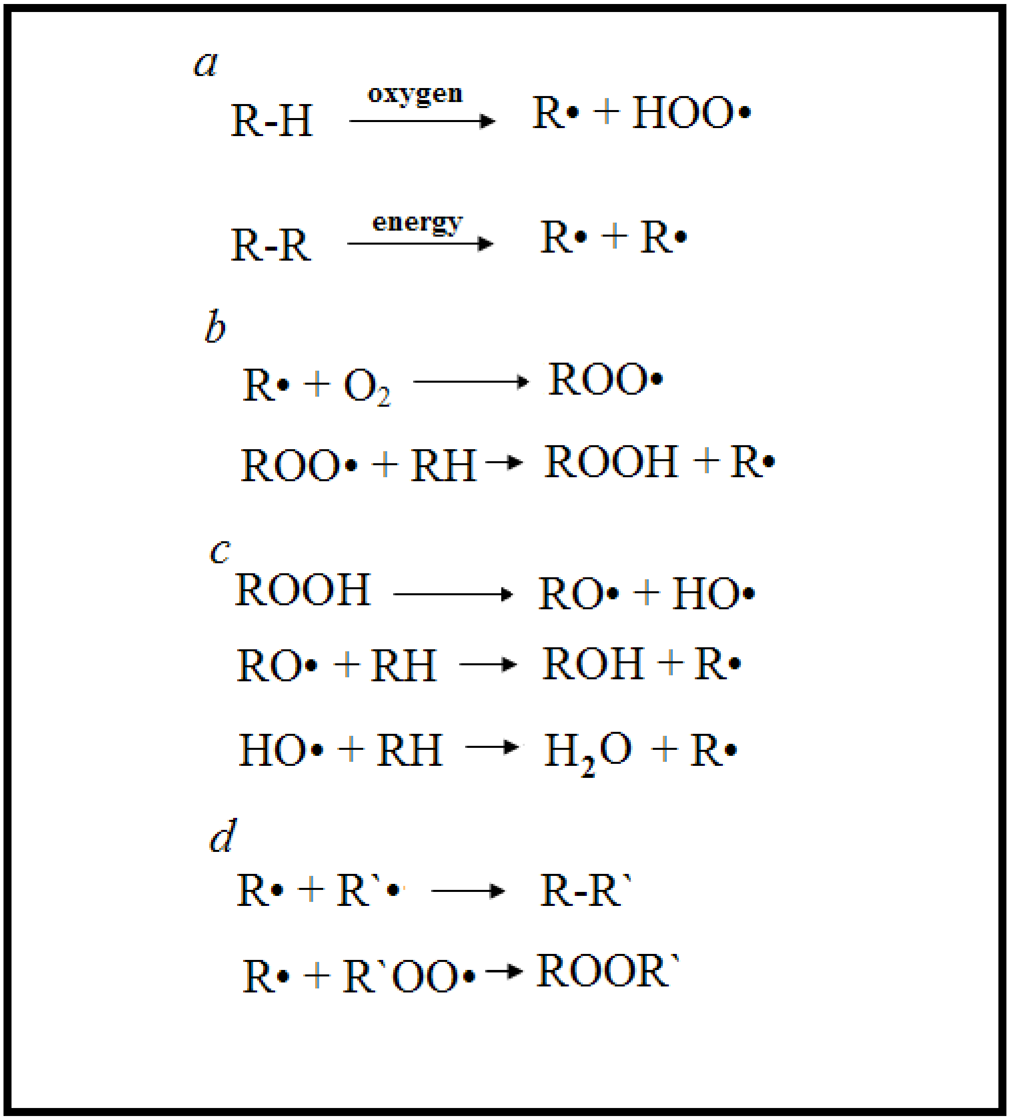
ii. Low pour point: with a decrease in temperature oils become semi solid after which it loses its ability to act as an efficient coolant. [1]
iii. High flash point: the oil should not change drastically in terms of composition due to losses of volatile components. [1]
iv. Excellent chemical stability: formation of sludge and increases in acidity due to oxidation is best avoided. Oxidation processes are accelerated by oxygen, catalysts and elevated temperatures. Even though oxidation reactions are inevitable, oils should provide some chemical stability. [1]

In addition to these properties, the oil should be non-toxic (not listed as a hazardous material), biodegradable, reclaimable and easily disposable [7].

2.3 IMPACTS OF STRESS ON TRANSFORMER OIL

Transformer oils can be subjected to stress under oxidative, thermal and electrical conditions [8]. Such stresses bring about the formation of acidic oxidation products, the occurrence of these products can be catalysed by the presence of metals, oxygen, high temperatures and increases in moisture content [9]. These acidic products eventually lead to the formation of sludge resulting in inadequate cooling of the transformer unit. In addition, primary and secondary breakdown products are known to be able to carry an electrical charge which consequently hinders the electrical properties of the oil [10]. However the formation of carboxylic acids is not only detrimental to the transformer oil but also results in the deterioration of the paper insulation [10]. For most mineral oils it has been found that the rate of oxidation doubles for every 10 °C rise in temperature above 75 °C [11].

The oxidation of lubricating oil can be broken down into different steps: chain initiation, propagation, branching, and termination [12]. Scheme 2.1 illustrates the general outline for oil oxidation reactions.



a

$$\text{R-H} \xrightarrow{\text{oxygen}} \text{R}\bullet + \text{HOO}\bullet$$

$$\text{R-R} \xrightarrow{\text{energy}} \text{R}\bullet + \text{R}\bullet$$

b

$$\text{R}\bullet + O_2 \longrightarrow \text{ROO}\bullet$$

$$\text{ROO}\bullet + \text{RH} \rightarrow \text{ROOH} + \text{R}\bullet$$

c

$$\text{ROOH} \longrightarrow \text{RO}\bullet + \text{HO}\bullet$$

$$\text{RO}\bullet + \text{RH} \longrightarrow \text{ROH} + \text{R}\bullet$$

$$\text{HO}\bullet + \text{RH} \longrightarrow H_2O + \text{R}\bullet$$

d

$$\text{R}\bullet + \text{R`}\bullet \longrightarrow \text{R-R`}$$

$$\text{R}\bullet + \text{R`OO}\bullet \rightarrow \text{ROOR`}$$

Scheme 2.1 A scheme representing auto-oxidation reactions of transformer oil [12].

a) The initiation step (Scheme 2.1*a*) involves the formation of free alkyl radicals. Free radical formation can be induced by oxygen, heat and ultraviolet light. This process is rather slow but can be accelerated by metal catalysts and increases in temperature [12].

b) The alkyl radicals produced in the initiation step reacts with oxygen to form peroxy radicals in what is known as the chain propagation step (Scheme 2.1*b*).

The peroxy radicals then can take on a hydrogen atom from another hydrocarbon molecule, to form a hydroperoxide molecule and another alkyl radical. The chain propagation step is irreversible and extremely fast. [12]

c) In the chain branching step (Scheme 2.1*c*), a hydroperoxide molecule is cleaved and in the process, two radicals are formed viz., the alkoxy radical and the hydroxyl radical.
The formation of these radicals brings about a number of other reactions that these radicals can possibly undergo. These radicals can then abstract hydrogen from other molecules forming more radicals in the process. Primary and secondary alkoxyl radicals that are formed, eventually decompose to form aldehydes and ketones, respectively. [12]

d) Under high temperatures the ketones and aldehydes that are formed, are further oxidized to carboxylic acids. During the oxidation process, the viscosity of the oil increases due to the formation of high molecular weight species, at this time chain termination reactions dominate. Alkyl radicals can combine with each other to form hydrocarbon molecules. In addition an alkyl radical can combine with an alkyl peroxy radical to form a peroxide. This is however unstable and forms more alkyl peroxy radicals and the process repeats itself (Scheme 2.1*d*) [12].

The number of transformers that have malfunctioned due to insultaion failure is substantial and incur alot of expenditure [7]. Considerable research has been conducted with respect to ageing of transformer oils and other related aspects in this field.

Meshkatoddini [9] reported that continuous monitoring of transformer oil is essential, considering the fact that oxidation products (acids and sludge) hinders the performance of the solid insulation as well. Copper, paint, varnish and oxygen are contributing factors that catalyse oxidation reactions and speed up the ageing process [9]. In their study, nine on-site transformers were used, all from the same manufacture and all containing the same naphthenic based oil. The tenth sample was virgin transformer oil. The authors collected the following data with respect to time: dissipation factor, dielectric constant, breakdown voltage, specific resistance, viscosity, flash point, acidity and density. From their results the authors found that density, flash point, permittivity and dielectric breakdown voltage showed poor correlation with respect to service life/degradation, consequently these factors were negated as parameters that can correlate to lifetime estimation.

However the authors did find good correlation to ageing in their dissipation factor and viscosity tests. Nevertheless the best correlation to ageing was found with acid number. Subsequently, the authors then aged oil samples at different temperatures using acid number of 0.3 mg KOH/g oil as the criterion for degradation. The data was then used to verify that the Arrhenius Law was valid for transformer oil.

El-Refaie, Salem and Ahmed [13] also outlined the need for continuous oil monitoring. There are several maintenance tests that can be carried out to determine the progression of ageing [13]. El-Refaie and coworkers investigated six transformer oil samples in order to study the changes of certain characteristics as a function of time (service life). They reported the variance in the type of transformer oil used, as: fresh, purified and changed oil. They monitored breakdown voltage, total acidity, flash point, specific gravity and kinematic viscosity over time. They found that the breakdown voltage of the oils decreased over long periods of time. They also observed that changing or purifying the transformer oil caused the dielectric breakdown voltage to initially increase, but then decrease after long periods of time. They obtained a converse pattern for acid value and kinematic viscosity results, where these values increased over long periods of time but changing or purifying the oil showed an initial decrease in these values.

Neto *et al.* [14] researched the combined effect of metal passivators and antioxidants on transformer oil.

A series of five AO's; viz. 2,6-di-*tert*-butyl-4-methylphenol; tetrakis[methylene(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate)]methane; 2-amino-5-pentadecylphenol; 2,4-diamino-5-pentadecylphenol; and thiodiethylenebis(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate) were used in their study. These AO's were used in concentrations of 500 and 1000 ppm. They also investigated the combined effect of using both, an antioxidant and metal passivator [*n*-(1,2,3-benzotriazole)] in concentrations of 500 and 8 ppm, respectively. Their work involved subjecting non doped oils to ageing in a vessel which was maintained at constant temperature (90, 100, 110, and 120 °C) and oxygen flow in the presence of copper wire. Samples were monitored at regular time intervals by FT-IR. After doping the oils with AO's and the metal passivator, they subjected the oils to accelerated ageing for 164 hours, at a temperature of 100 °C and 1.0 L h^{-1} flow rate of oxygen in the presence of copper. Degradation of the oil was determined by monitoring the region of the carbonyl band (1713 cm^{-1}) in the FT-IR spectrum.

The non-doped oil was found to have an activation energy of 10 kcal mol^{-1}, however the authors did not determine the activation energy of the decomposition reaction for that of doped oil. Their study concluded that antioxidants, which were more sterically hindered, were most effective in preventing oxidation. They also observed that the metal passivator independently did not reduce degradation levels; however AO and passivator blends significantly decreased the rate of oxidation.

Georgiev *et al.* [15] focused their study on the monitoring of transformer oil degradation by using FT-IR, making it possible to identify oxidation products both qualitatively and quantitatively. Although accelerated oxidation studies have been done, it is rather difficult to monitor changes perhaps due to inadequate time. In their study, an extraction technique was developed for the isolation of volatile and total acids. FT-IR spectra were obtained for oxidized transformer oil and oxidized transformer oil doped with antioxidants; 0.38% (w/w) of ionol and piperidone and 0.38% (w/w) piperidone: ionol at a mass ratio 1:1.Their results showed that the absorbance at 1710 cm^{-1} increased with progression in oxidation of the oils. Extracted oxidized transformer oil showed a strong band in the 1710 cm^{-1} region when compared to the spectra obtained without the extraction step. The authors concluded that the use of the extraction method was far more superior to monitor oil oxidation breakdown products.

A great deal of work has also been done on the prediction of lifetime [9, 16]. The basis of lifetime prediction is the Arrhenius equation (Equation 2.1) [17];

$$k = Ae^{\frac{-E}{RT}} \text{ .... } (2.1)$$

where, A is the pre-exponential factor, E is the activation energy and k is the rate constant.

The Arrhenius equation indicates that for reactants to form products there is a minimum amount of energy that is needed by the molecules. Materials that have higher activation energy become more resistant to chemical degradation [16]. Thus the application of the Arrhenius equation to insulating materials plays a crucial role. Meshkatoddini [9] did an effective job in looking at thermal ageing and acid value criteria. However, other work focused on the determination of kinetic parameters of polymers using thermal analysis [17]. Thermogravimetric curves provide adequate information to determine the decomposition kinetic data for oils [17].

The OFW approach has been used in many studies to determine the activation energy by iso-conversional method. This method utilises data in which thermal analysis is carried out for the sample under a range of heating rates (β) [18]. Using Equation 2.2 [16], log β verses 1/T is plotted and the activation energy at different conversion values (α) is obtained.

$$E = \frac{-R}{b}\left[\frac{d\log\beta}{d\frac{1}{T}}\right] \qquad (2.2)$$

where, E is oxidation energy, R is the universal gas constant, b is a constant with a value of 0.457, T is the temperature and β is the heating rate.

Kenar *et al.* [18] presented work on the DSC study of blown soya bean oil. Blown oil is obtained by a process involving a combination of heating and blowing air through vegetable oil. The blowing of oil promotes auto-oxidation. Kenar and co-workers used the OFW model to determine the kinetic parameters of the oil. The authors carried out DSC experiments from a temperature of 25-300 °C at variable ramp rates (β) between 3-20 °C $\min^{-1}$ for the soybean oils [18]. The oil oxidation reaction was found to be exothermic in nature [18]. These workers recorded the onset of degradation temperature and maximum heat flow values from the DSC curves for each β value. They plotted the data of log β verses 1/T to obtain the E_a. Application of the OFW method is not unique to oils but can be related to other polymers as well. Zelic *et al.* [19] studied the kinetic information obtained from TGA of cement. The authors heated calcium hydroxide in the presence of nitrogen from a temperature of 330 to 460 °C at β values of 5, 10, 15 and 20 °C $\min^{-1}$ [19]. However in their study, different conversion values were used, as discussed previously. Their work outlined the dependence of activation energy on conversion. The activation energy was found to decrease with conversion and this tied in with literature for an endothermic reversible reaction followed by a irreversible one [19]. Nguyen and Gu [20] focused their study on lifetime estimation of an acrylate based photopolymer for microfabrication and photonic applications. They used the OFW model to determine kinetic parameters and predicted lifetime of their photopolymer from work described previously by Toop [21].

The OFW model is not the only method that has been used for the determination of kinetic parameters from DSC results. The Kissinger model (Equation 2.3) is an alternate method that can be used for the determination of kinetic parameters and is applied to data obtained from DSC. This method utilizes the signal maxima from the DSC curves [22].

$$\ln\frac{\beta}{T^2} = \ln\frac{AR}{Ea} - \frac{Ea}{RT} \quad \text{..} \quad (2.3)$$

where, T is the maximum heat flow temperature, A, Arrhenius factor, E_a the activation energy and β, the heating rate.

2.4 ANTIOXIDANTS/ADDITIVES[1]

For many years oils were known to undergo oxidation [12]. However those that managed to retard the oxidation process contained natural antioxidants [12]. Antioxidants are free radical scavengers in which their general function is to donate hydrogen and thereby terminate the radical chain mechanism [12].

There are a vast number of oil soluble organometallic and organic antioxidants/additives that are available. These can be placed into the following categories: sulfur compounds, sulfur–nitrogen compounds, phosphorus compounds, sulfur–phosphorus compounds, aromatic amine compounds, hindered phenolic compounds, organo–copper compounds and boron compounds [12].

---

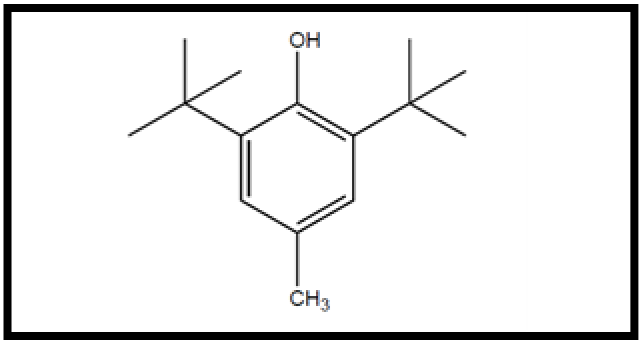
[1] *In view of the large number of antioxidant groups that are available, my MSc study will focus on those with relevant importance to this work.*

Oils are characterised as uninhibited, that is, they contain no antioxidants, or inhibited oils that contain antioxidants [23]. A new oil is classified by the American Standard Testing Methods (ASTM) into two categories: Type I oil that has 0.08% of oxidation inhibitor and type II oil that contains 0.3% of inhibitor [23].

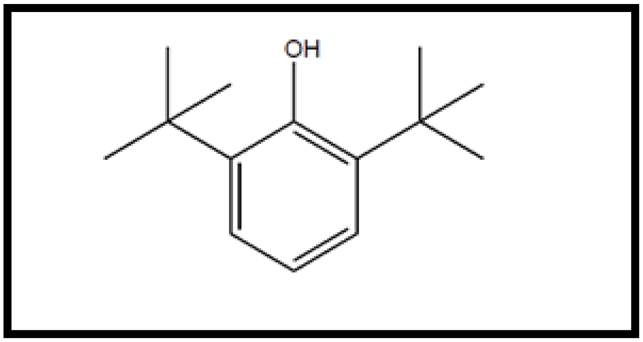
Sulfur compounds: Earlier, mineral oil was heated with elemental sulfur to produce a non-oxidizing oil.

However, the limitation in the addition of sulfur is that it leads to an increase in the corrosivity of copper in the transformer unit. Phosphorus containing compounds have also been used as a common additive. The addition of elemental phosphorus is known to reduce sludge formation in oils. However the addition of elemental phosphorus leads to problems associated with corrosivity with respect to alloys and non-ferrous metals [12]. Consequently elemental phosphorus is avoided and alternatively oil-soluble organic compounds of phosphorus are preferred [12].

Sterically hindered phenols are extensively used in lubricating oils. This work focuses on the hindered phenolic compounds that are most commonly used in oils filled in South African transformers. Currently the antioxidants that have been used include BHT (butylated hydroxy toluene) (Structure 2.2) and DBP (dibutylated phenol) (Structure 2.3) and are expected to be in the range of 0.25 to 0.35 (w/w) % [23].

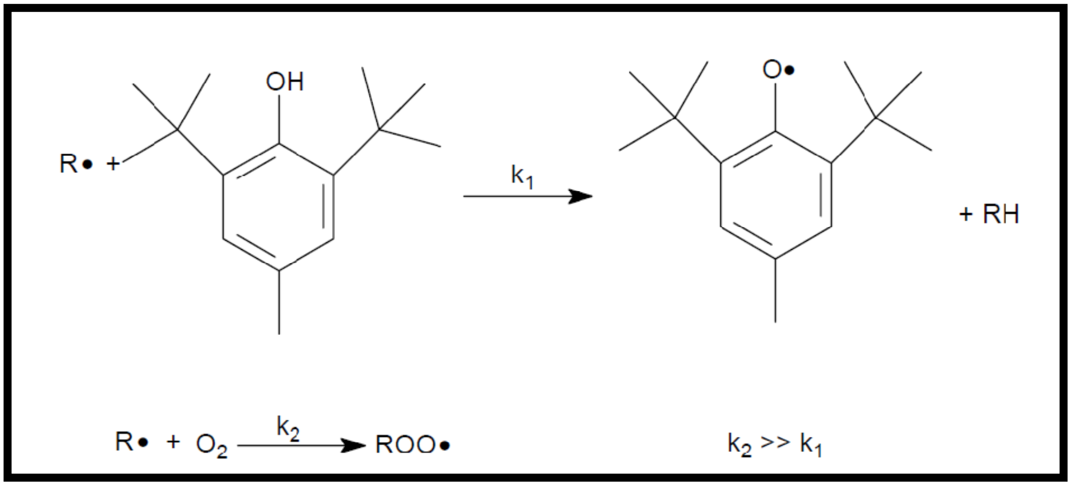


Structure 2.2 Structure of 2,6-di-*tert*-butyl-4-methylphenol (BHT).



Structure 2.3 Structure of 2,6-di-*tert*-butylphenol (DBP).

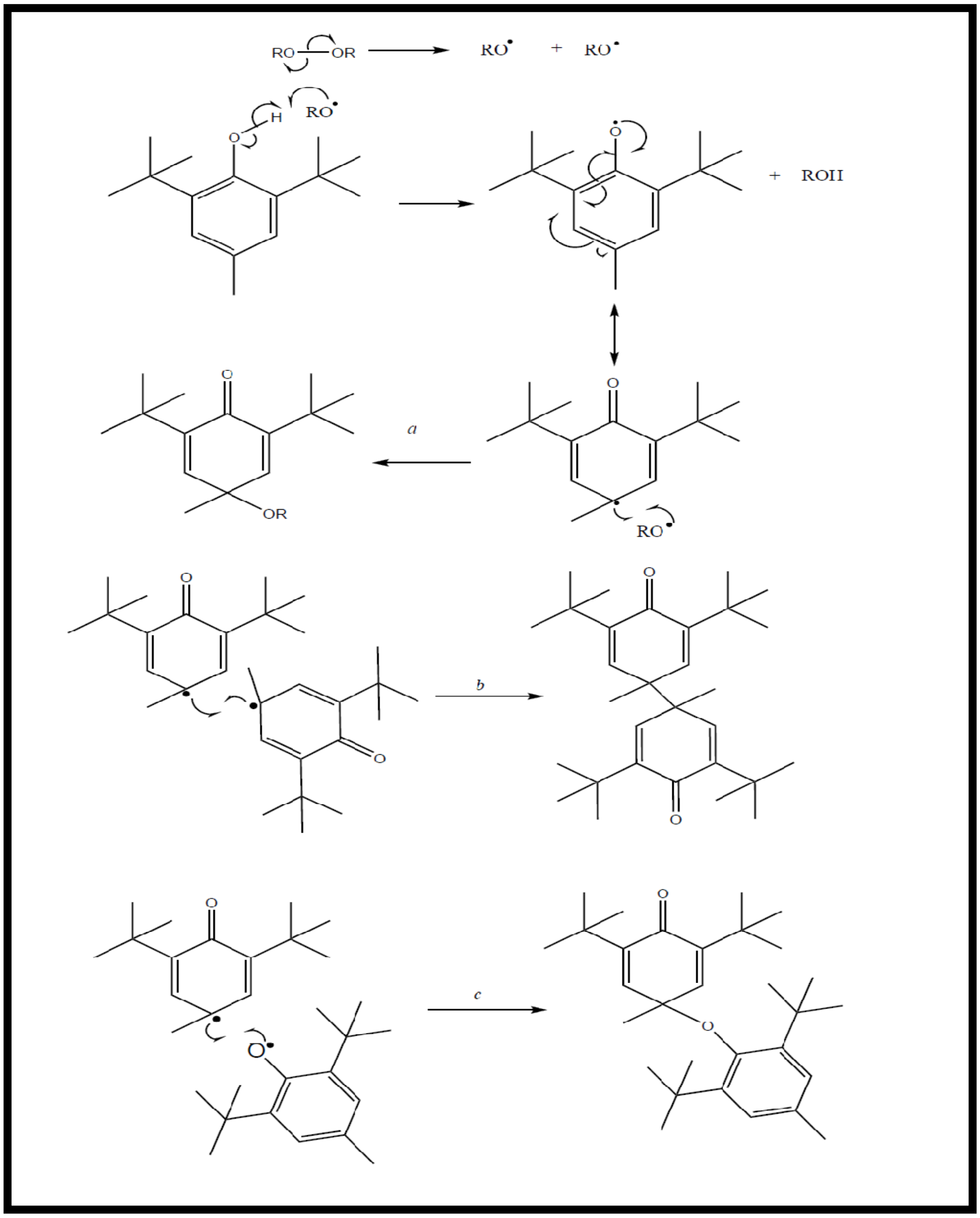
BHT is a representative example of a sterically hindered phenol. Scheme 2.2 represents the reactions of an alkyl radical with O_2 and an alkyl radical with BHT. The reaction rates are k_2 and k_1 respectively, where $k_2 > k_1$ [12].



Scheme 2.2 Reactions of alkyl radicals with BHT and oxygen [12].

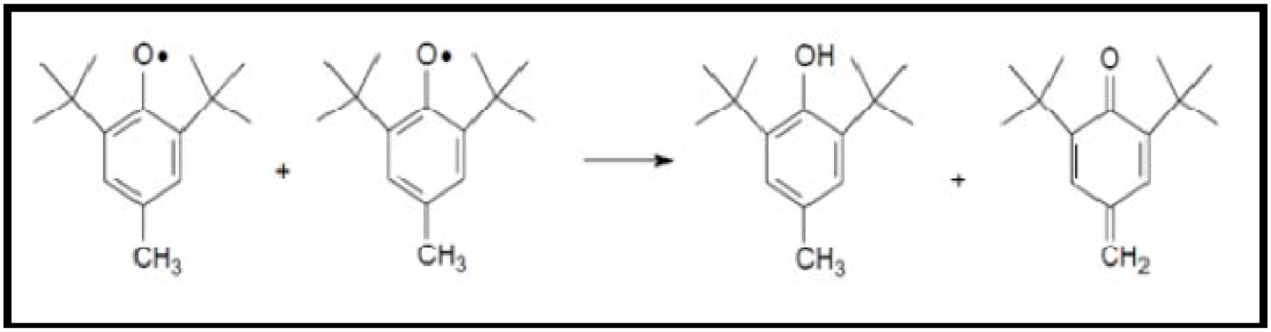
Since $k_2 > k_1$, the likelihood of the alkyl radical reacting with BHT is rather low. However during the progression of oxidation, alkyl radicals are converted to peroxy radicals [12]. It is at this point that the addition of BHT takes effect. BHT donates a hydrogen atom to the peroxy radical to form hydroperoxides, BHT in turn is converted into a phenoxy radical (2,6-di-*tert*-butyl-4-methylphenoxy radical). This radical is stabilised through steric hindrance and resonance [12] (Scheme 2.3*a*). However the phenoxy radicals can react with each other (Scheme 2.3*b*);

alternatively with other radicals formed by resonance (Scheme 2.3*c*) to form different BHT oxidation products.



Scheme 2.3 (*a*) Reaction describing the conversion of BHT into a phenoxy radical that is stabilised by steric hindrance and resonance. Alternate pathways of the radical reaction is also outlined in *b* and *c* [12].

Without resonance an alternate pathway is followed. The termination reaction is represented in Scheme 2.4. The phenoxy radicals react with each other. A hydrogen atom is donated from one phenoxy radical to the other, forming a BHT molecule and one methylene cyclohexadienone molecule [12]. Under the influence of high temperatures, the reaction product of Scheme 2.3*a* (cyclohexadienone alkyl peroxide) becomes unstable and decomposes to eventually form 2,6-di-*tert*-butylcyclohexa-2,5-diene-1,4-dione [12] [benzoquinone] (Structure 2.4*d*).

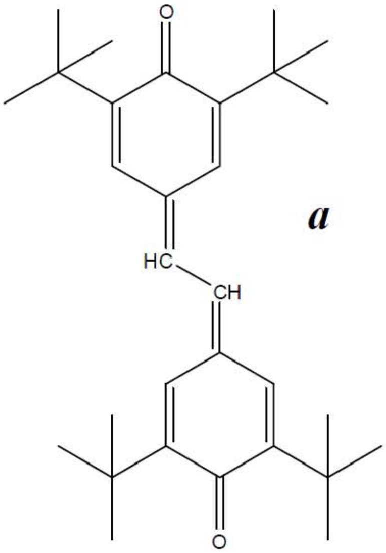


Scheme 2.4 Reaction showing the chain termination step, upon which BHT and methylene cyclohexadienone are formed [12].

Studies related to the degradation of BHT and DBP has been previously carried out. Cook [24] reported that the oxidation of hindered phenols most commonly leads to the formation of dimeric products. Foley and Kimmerle [25] researched the use of pulse voltammetry for the determination of BHT in transformer oils. The following compounds, 4,4′-(ethane-1,2-diylidene)bis(2,6-di-*tert*-butylcyclohexa-2,5-dienone) [Stilbene quinine] (Structure 2.4*a*) and 4,4′-(ethane-1,2-diyl)bis(2,6-di-*tert*-butylphenol) [dimer] (Structure 2.4*b*) are generally found in used oils [25]. Under more wet oxidative conditions 3,5-di-*tert*-butyl-4-methylbenzaldehyde [benzaldehyde] (Structure 2.4*c*) and 2,6-di-*tert*-butylcyclohexa-2,5-diene-1,4-dione [benzoquinone] (Structure 2.4*d*) are the major products. The oxidation products of BHT are dependent on the nature of the media. In brief, in acidic media an ionic pathway is followed however in neutral media a radical reaction pathway is followed [25].

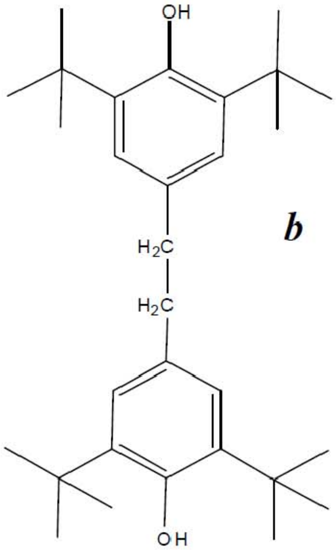
Hassanein *et al.* [26] focused on the auto-oxidation of DBP catalyzed by 5,10,15,20-tetrakis[4-(diethylmethylammonio)phenyl]porphyrinatocobalt(II) tetraiodide.

These authors determined the rate of phenol consumption by measuring the amount of dioxygen using a gas burette at temperatures of 40 °C. They found the major product of the reaction catalyzed by the cobalt(II) porphyrin complex to be the coupling product, 3,5,3′,5′-tetra-*tert*-butyl-4,4′-diphenoquinone (Structure 2.4*e*) which was formed by dimerization. The oxygen insertion product, 2,6-di-*tert*-butyl-1,4-benzoquinone (Structure 2.4*d*) was also formed through the cobalt(III) complex.



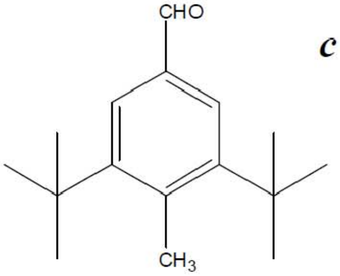
a

4,4′-(ethane-1,2-diylidene)bis(2,6-di-*tert*-butylcyclohexa-2,5-dienone)



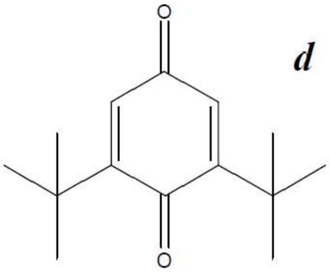
b

4,4′-(ethane-1,2-diyl)bis(2,6-di-*tert*-butylphenol)



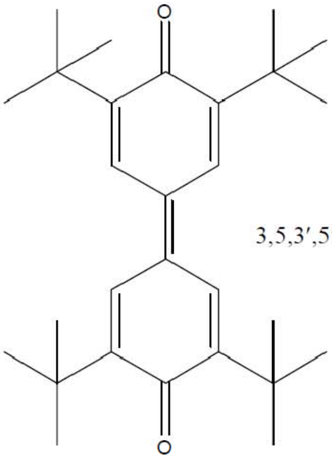
c

3,5-di-*tert*-butyl-4-methylbenzaldehyde



d

2,6-di-*tert*-butylcyclohexa-2,5-diene-1,4-dione



e

3,5,3′,5′-tetra-*tert*-butyl-4,4′-diphenoquinone

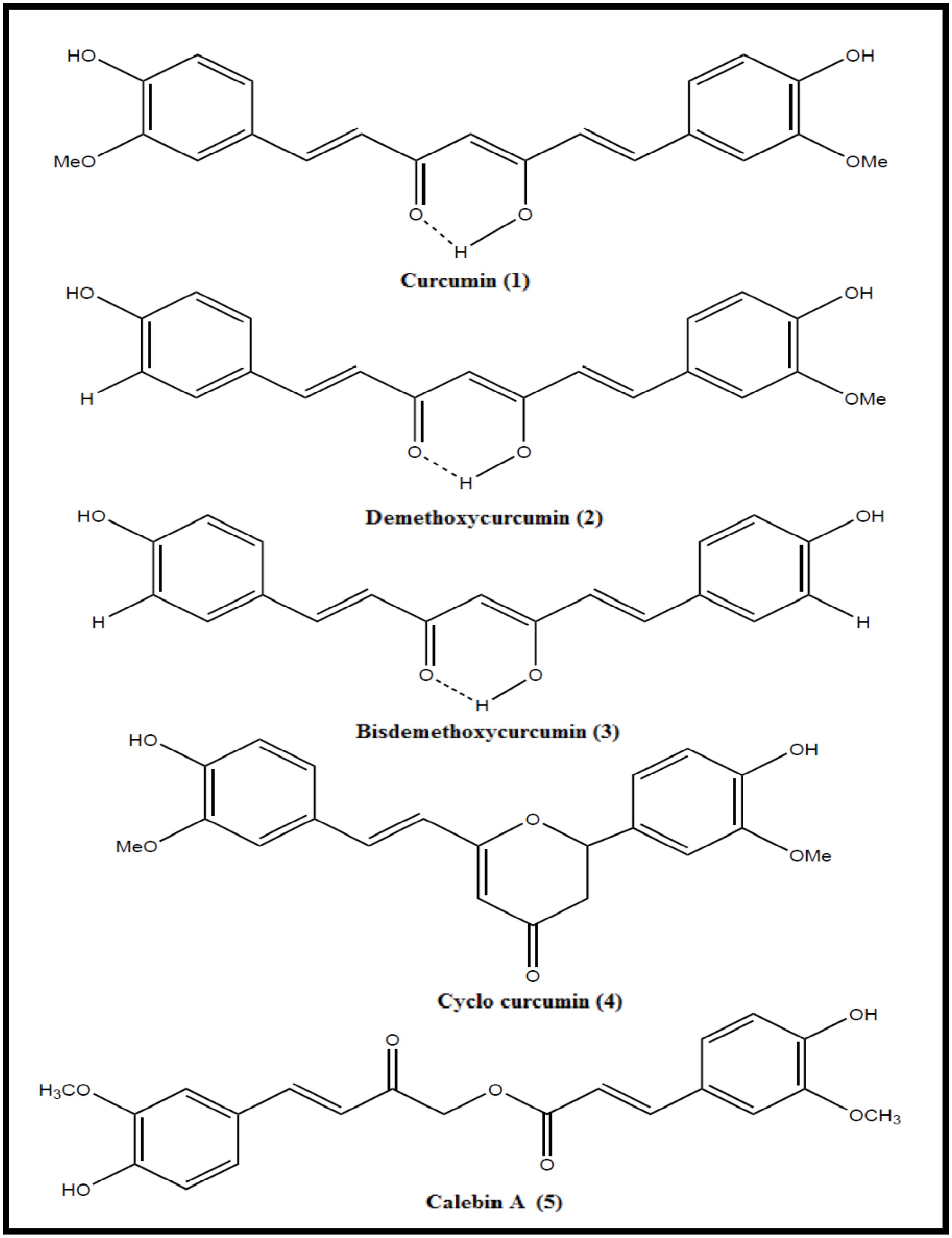
Structure 2.4 Degradation products of AO's, BHT and DBP [24-27].

2.5 TURMERIC EXTRACTS

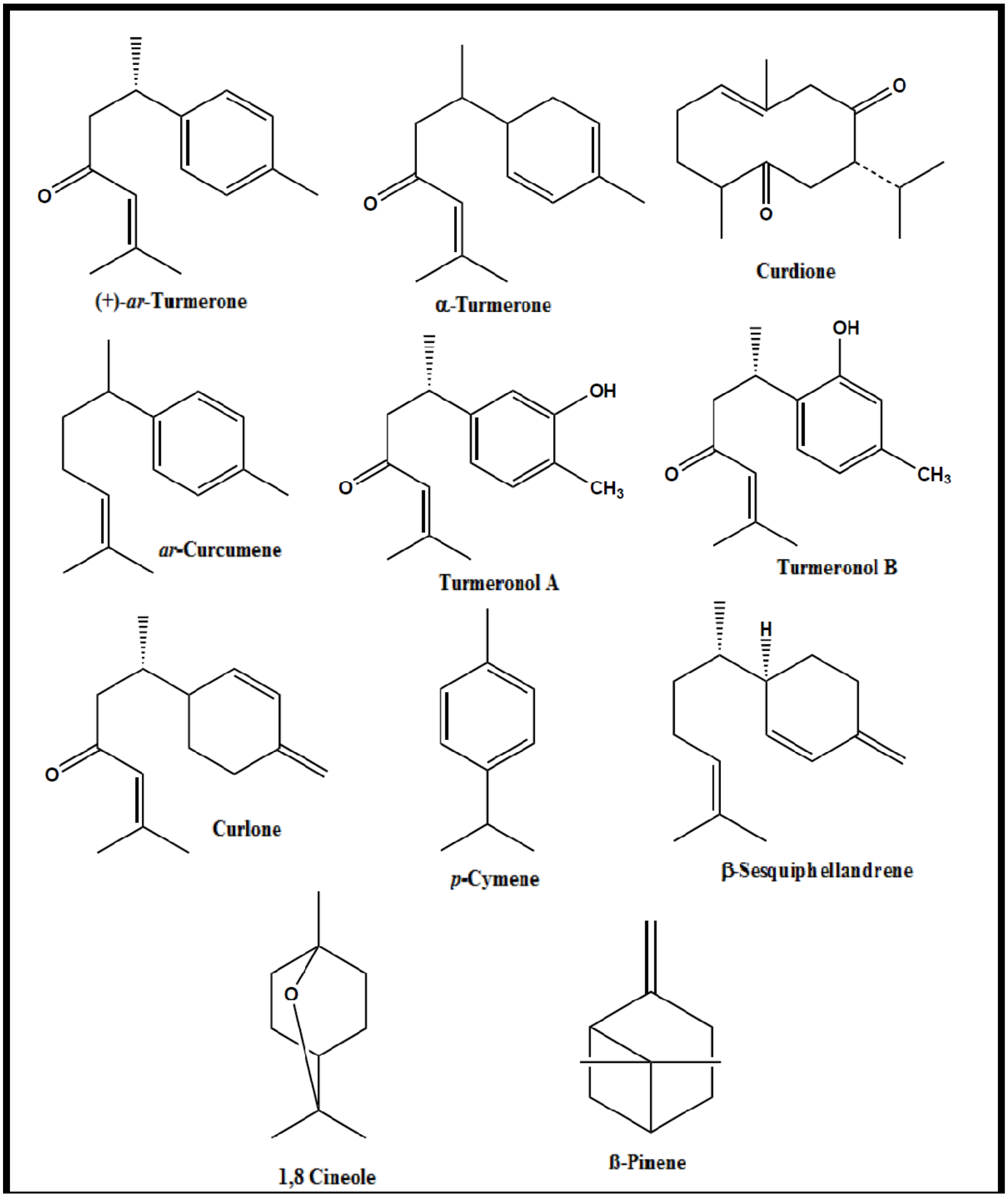
Although antioxidants are currently available for the use in transformer oil, research is focused on the use of cheaper and more natural antioxidants. Turmeric (*Curcuma longa*) belongs to the Zingiberaceae family, which includes spices like ginger and cardamom [28]. It has been used for centuries as a major spice in Asia particularly in India in the form of a dried powdered rhizome for its aroma and flavour [28]. However, turmeric is also well known for its antioxidant properties. In addition, it is known to possess anti-cancer, anti-coagulative and anti-hepatotoxic properties [29]. The aroma of the turmeric powder is attributed to its volatile oils and its bright yellow colour as a result of its phenolic components [28]. The main active components of turmeric are the curcuminoids and essential oils [30]. Structure 2.5 represents the compounds associated with curcuminoids as outlined by Jayaprakasha *et al.* [28].

Jayaprakasha *et al*. [28] summarized that the volatile oil of turmeric is predominantly a mixture of sesquiterpene ketones and alcohols; namely *p*-cymene, β-sesquiphellandrene, α-turmerone, *ar*-turmerone, curlone and other sesquiterpene alcohols. Studies revealed that *ar*-curcumene is generally found in the rhizome oil at a concentration of 12.2% but absent in tuber oil [28]. Structure 2.6 shows the structures of the components present in the volatile oil.

Jayaprakasha *et al.* [31] presented a study on *C. longa*, in which the antioxidant and antimutagenic activity of turmeric oil was characterised. The authors modified the turmeric oleoresin in such a way that the curcumin was removed and only turmeric oil was obtained. The oil was fractioned on a silica gel column. Their findings showed that the turmeric oil contained aromatic turmerone (31.32%), α-turmerone (15.08%) and curlone (9.70%). Fraction III had the highest percentage of α-turmerone and aromatic turmerone and consequently also showed the greatest antioxidant capacity and strongest antimutagenicity activity against sodium azide [31].
Singh *et al.* [32] carried out their study on the comparison of antioxidant activity of the oil and oleoresin fractions of fresh and dried rhizomes of turmeric. The constituents of the fresh and dry rhizomes were determined by GC-MS. Their findings are tabulated in Table 1. The DPPH assay was used to monitor antioxidant activities of the different fractions.



Structure 2.5 Components of the curcuminoid family present in turmeric [28].



Structure 2.6 Structures of compounds present in turmeric oil [28].

Table 1 Summary of the GC-MS results of turmeric fractions [32].

Rhizome Type	Fraction	Composition
fresh	oil	aromatic-turmerone (24.4%), alpha-turmerone (20.5%) and beta-turmerone (11.1%)
	oleoresin	alpha-turmerone (53.4%), beta-turmerone (18.1%) and aromatic-turmerone (6.2%)
dry	oil	alpha-turmerone (21.4%), alpha-santalene (7.2%) and aromatic-curcumene (6.6%)
	oleoresin	aromatic-turmerone (9.6%), alpha-santalene (7.8%) and alpha-turmerone (6.5%)

In summary, their results indicated that the alpha-turmeric content in fresh rhizome was substantial when compared to that of the dry rhizome content.

Of interest from studies by Singh and co workers [32] to our study, is the fact that the free radical scavenging activity of the oleoresin and the oils were comparable to that of the synthetic antioxidant, butylated hydroxyanisole (BHA). They established the order of activity as follows; essential oil (fresh rhizome) > oleoresin (fresh rhizome) > essential oil (dry rhizome) > oleoresin (dry rhizome). They attributed this finding to the fact that alpha- and beta-turmerone content was greater in fresh rhizome.

Nor *et al*. [33] carried out a study on the antioxidant effects of turmeric using accelerated oxidation and deep frying [33]. High temperatures that are used in deep frying, imparts on the loss and quality of the oil as it accelerates oxidation reactions. In order to prolong the life of the oil, antioxidants such as BHA, BHT and tertiary butylated hydroxyquinone (TBHQ) are generally used. Their results showed that the peroxide content was more favourable with 0.2% *C. longa* than 0.02% BHT, after eight hours of frying. Nor and coworkers also found *C. longa* reduced (decreased) the fatty acid value of the oil after 24 hours of frying, which was superior to that of BHT. Their study concluded that *C. longa* as a source of natural antioxidants, can be exploited by the food industry [33].

2.6 INSTRUMENTATION FOR CHARACTERISATION AND ANALYSIS

2.6.1 Nuclear Magnetic Resonance (NMR), Fourier Transform-Infra-Red (FT-IR) and Elemental Analysis

NMR and IR studies on transformer oils have been previously studied [8, 15]. However different transformer oils will have different functional groups depending on the type of transformer oil, nature of the additives added to the oil and progression of oxidation.

FT-IR is generally used for the monitoring of carbonyl and hydroxyl groups in the oil and NMR deciphers structural changes of the oil [8].

IR is a non destructive technique and becomes useful in the determination of chemical functional groups in a sample. Different functional groups are able to absorb characteristic frequencies of IR radiation. Sampling ranges from the conventional nujol, KBr disc and a newer technique: attenuated total reflectance (ATR). This sampling accessory works by measuring the changes that occur in a totally internally reflected infrared beam that comes into contact with the sample. The infrared beam sits on the surface of the crystal which in turn is in contact with the sample [34].

NMR is based on the alignment of atomic nuclei in a sample with or against an external electromagnetic field. A very strong superconducting magnet that is surrounded by liquid helium which in turn is surrounded by liquid nitrogen is used [35]. Through the middle of this magnet there is a small hole that allows for the sample tube [35]. The sample is placed in a static magnetic field, the nuclei are then excited with radio frequency pulse and the frequencies emitted by the sample are then measured [36]. The sample tube contains the sample dissolved in an appropriate deuterated solvent.

CHNS elemental analysers are based on a combustion process. The sample is inserted into a furnace that is maintained at 1000 ºC [37]. In the furnace carbon is converted to carbon dioxide; hydrogen to water; nitrogen to nitrogen gas/oxides of nitrogen and sulfur to sulfur dioxide [37].

The detector system involves non-dispersive infrared absorption detection system and thermal conductivity [38].

2.6.2 Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

The use of ICP-OES is an acceptable instrument for the determination of metals/non-metals in lubricating oils [39]. The principle behind ICP-OES initially involves the sample being transported as a liquid [40]. The liquid is converted into an aerosol in a process known as nebulization. This aerosol is then transported to the plasma, where it is desolvated, vaporized, atomized and ionized by the plasma [40]. The plasma consists of argon gas which is directed through a torch consisting of three concentric tubes made of quartz, on the top of the torch there is a copper coil, radio frequency is applied to the copper coil and a spark induces free electrons in the plasma, this causes further ionization and forms the plasma [40].

2.6.3 Ultra-Violet/Visible (UV/Vis) Spectroscopy

UV-Vis spectroscopy is a technique used to determine the adsorption pattern of a sample. Light is irradiated through a sample placed in a cuvette holder. The absorbance is correlated to the concentration of the sample: $A= \varepsilon cl$, where, ε is the molar coefficient, c is the concentration, l is the length of the cell and A is the absorbance of the sample. This equation is denoted as the Beer-Lambert law [41].

The UV/Vis spectrophotometer is made up of a light source, a monochromator, sample cell holder for the sample cell (quartz or glass), the detector and display unit (computer system) [41].

2.6.4 Gas Chromatography-Flame Ionization/Mass Spectrometry (GC-FID/MS)

GC is a separation technique based on the difference in volatilities of the components in the sample [41]. A typical GC instrument is composed of a stationary phase which the mobile phase (gas) flows through, an injection port, a column in a column oven and a detector [41]. The detector used in this case is the FID detector. This detector is destructive in nature. FID is mass sensitive rather than concentration sensitive [42]. The carrier gas effluent is mixed with hydrogen and then transferred to a stainless steel jet, here the flame at the tip of the jet ionises the analyte molecules [42]. A potential difference is created across the positively charged collector electrode and the grounded jet causes the negative ions to flow to the collector electrode and an analogue signal is produced [42].

The GC can also be coupled to an MS detector; in this case an electron impact detector is used. Once the components have left the column, the sample is transferred to the ion source of the MS. The atom or molecule is bombarded by high energy electrons. Some of the energy is transferred to the molecule. It then ejects an electron to form a positively charged species [43]. This molecular ion then further fragments. The ions are passed through poles of a magnet and are deflected by the magnetic field [43]. The amount of deflection is dependent on the mass to charge ratio [43].

2.6.5 Thermal Analysis (TA)

Thermogravimetric analysis (TGA) is the measurement of weight loss as a function of temperature or time [44]. TGA can be a useful tool to study decomposition of oils and oil blends. Essentially the sample is heated in a furnace and mass changes are recorded by a balance. Differential scanning calorimetry (DSC) is a technique in which the difference in flow rate of the sample and reference is recorded and is measured during a phase change by a thermocouple.

2.7 PHYSICO-CHEMICAL CHARACTERISATION METHODS FOR VIRGIN TRANSFORMER OILS AND TRANSFORMER OIL BLENDS

2.7.1 Acid number, Saponification value and Iodine value

2.7.1.1 Acid number

The acid number is defined as the mass of KOH in mg required to neutralise the acidic components in 1 g of transformer oil [45]. An increase in acid number is generally correlated to a decrease in the dielectric strength [10]. Acid number is sometimes used as the failure criterion to determine whether the oil needs to be removed and then processed.

2.7.1.2 Saponification value

Saponification value is a useful tool in the determination of acid and ester groups that are present in oils. It is defined as the mass of KOH in mg that is required to hydrolyse 1 g of the oil sample [46]. The general equation (Equation 2.4) is given below [46]:

$R\,COOH + KOH\,(excess) \rightarrow R\,COOK + H_2O,\ KOH + HCl \rightarrow KCl + H_2O$ ……………….. (2.4)

2.7.1.3 Iodine value

Iodine value confers the degree of saturation or unsaturation present in oils. It is also known as the number of grams of iodine per 100 grams of oil [47]. The double bonds (if any) in the sample react with iodine monochloride in glacial acetic acid, which is in excess [47]. The un-reacted iodine monochloride that remains behind after the reaction is then decomposed to iodine in the presence of potassium iodide solution. The final step is titration against standardised sodium thiosulphate solution [47].

2.7.2 Metal/Non-metal Analysis

Instruments such as ICP-OES [39] and Atomic absorption spectroscopy (AAS) [48] are generally used for the determination of metals. However the large amount of organics and viscous nature of the oil makes it imperative for the sample to be digested prior to analysis [48]. The metals that are expected to be found are the additive metals rather than wear metals, as the transformer oil analysed was virgin in nature. The presence of wear metals proves to be detrimental to the oil as these metals can serve as catalysts for the ageing process. Table 2 highlights the wear metals and their possible sources as well as additive elements and their functionalities in the transformer oil.

Table 2 Wear metals and additive elements that are generally found in transformer oil samples [39].

Wear metal	**Possible sources**	**Additive element**	**Function**
Al	Engine block, Pistons, Blowers, Oil pump bushings, Oil cooler	B	Corrosion inhibitor, Anti-wear, Anti-oxidant
B	Coolant leak, Grease contamination	Ba	Corrosion inhibitor, Detergent, Rust inhibitor
Ca	Grease contamination	Mg/Ca	Detergent/Dispersive additive
Cr	Cylinders, Piston rings	Mn	Combustion Improvement and smoke dispersion in residual and distillate oil
Cu	Bearings, Oil cooler core	P	Anti-wear, Corrosion inhibitor, Anti-oxidant
Fe	Cylinders, Piston rings, Valve train, Engine block, Oil pump, Rolling elements, Bearings, Spring gears	S	Component of many additives
Pb	Bearings, Gasoline contamination (leaded gasoline)	Si	Defoamant additive
Si	Engine block, Dust from breathers	Zn	Anti-wear, Corrosion inhibitor, Anti-oxidant
Sn	Bearings, Oil cooler core, Connecting rods		

2.7.3 Viscosity, Water and Hydroperoxide content

2.7.3.1 Kinematic viscosity

Kinematic viscosity is defined as the measure of the resistive flow under gravity [49]. Kinematic viscosity is temperature dependent and for a liquid it is found to decrease with increases in temperature. A high viscosity is indicative of a high resistance to flow. The viscosity test is carried out by allowing the oil to flow through a capillary tube and recording the efflux time.

2.7.3.2 Water content

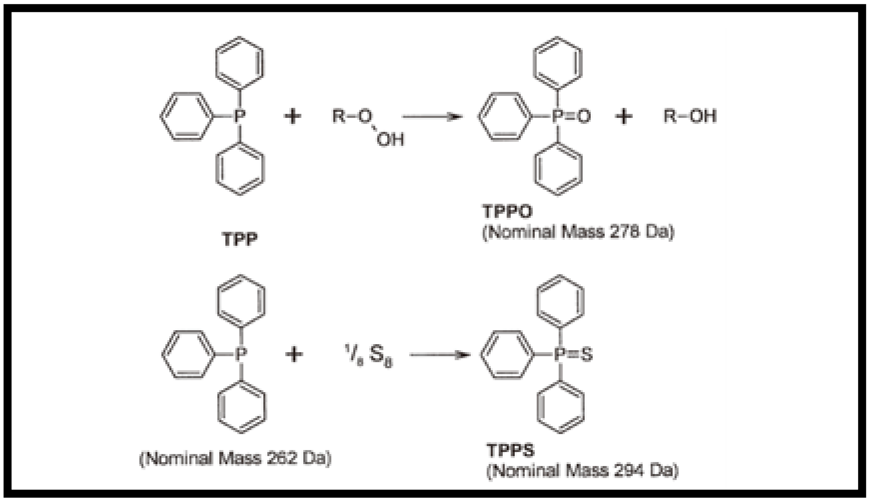
Water content of transformer oil is an important parameter. Increases in the water content subsequently decreases the dielectric strength of the oil, consequently increases in the water content of the oil reduces its insulating properties [10]. The Karl Fischer method is used for the determination of water content in transformer oils. The basis of the reaction is the reduction of iodine by sulfur dioxide in the presence of water [50]. The reaction for the quantification of water in the sample is given by Equation 2.5 below [50]:

$H_2O + I_2 + SO_2 + 3C_5H_5N \rightarrow 2C_5H_5N{\bullet}HI + C_5H_5N{\bullet}SO_3$

$C_5H_5N{\bullet}SO_3 + CH_3OH \rightarrow C_5H_5N{\bullet}HSO_4CH_3$ [50] .... (2.5)

2.7.3.3 Hydroperoxide content

This method has previously been described [51]. The general reaction is described in Scheme 2.5. Essentially triphenylphosphine (TPP) reacts with hydroperoxides found in the oil to form triphenylphosphine oxide (TPPO), to prevent the TPP from reacting with oxygen and conferring inaccurate results, the excess TPP is then reacted with sulfur to form triphenylphosphine sulphide (TPPS) [51]. TPPO is monitored.



Scheme 2.5 Reaction scheme for the determination of hydroperoxide content of transformer oil [51].

2.7.4 Antioxidant assay

The compound, 2,2-diphenyl-1-picrylhydrazyl (DPPH) is a stable free radical that is often used to monitor antioxidant activity. The DPPH free radical (purple colour) absorbs strongly at 517 nm, upon reduction the colour changes to yellow due to the formation of DPPH-H [52]. The DPPH assay is used to compare the effect of doping the oil with AO's or AO extracts in terms of its ability to quench free radicals.

2.7.5 Thermal analysis

Thermogravimetric analysis/differential scanning calomitry serves as a useful tool to monitor the thermal stabilities of the oil. Data obtained from the TGA/DSC results of oils and oil blends can be used in kinetic studies, determination of activation energies [16, 18] and prediction of lifetime [20-21].

2.7.6 Dissipation factor and Dielectric Breakdown Voltage testing

2.7.6.1 Dissipation factor:

The dissipation factor is used to describe the energy loss that occur with the use of dielectric materials. Any two conductors with an insulating material between them is termed a capacitor. If this capacitor is between parallel plates then the capacitance can be calculated by Equation 2.6 [4], where, A is the area of the electrode surface, d the 'gap' between the electrodes, C the capacitance and $\varepsilon = \varepsilon_0 \bullet \varepsilon_r$, where ε_0 and ε_r are the dielectric constant of air and the dielectric material respectively [4].

$$C = \frac{\varepsilon A}{d} \quad \text{..} \ (2.6)$$

Ideally a capacitor should provide no energy loss however this is not the case. The losses that occur in an insulator is termed the leakage current (I_r)/dielectric loss [4]. Dissipation factor (also known as the tangent of the loss angle/tan δ) is thus the ratio of leakage current and capacitance current. Equation 2.7 defines the relationship, where, f = frequency/Hz , R = resistance/Ω , C = capacitance/F [4].

$$\tan\delta = \frac{Ir}{Ic} = \frac{1}{\omega RC}, \ \omega = 2 \prod f \ \text{.......................}(2.7)$$

The dissipation factor testing of virgin transformer oils and antioxidant blends were determined with the use of Tettex 2820 apparatus. A test cell constructed of glass with copper electrodes was used (refer to Figure 6.1). The testing is based on a double vector method [4]. This method compares the current passing through the reference capacitor with the current measured after passing through the test cell. Both capacitors are energized by an external high voltage (HV) alternating current (AC) source and the current is measured by two shunts [4]. Figure 2.3 is a representation of how the Tettex 2820 carries out dissipation factor measurements.

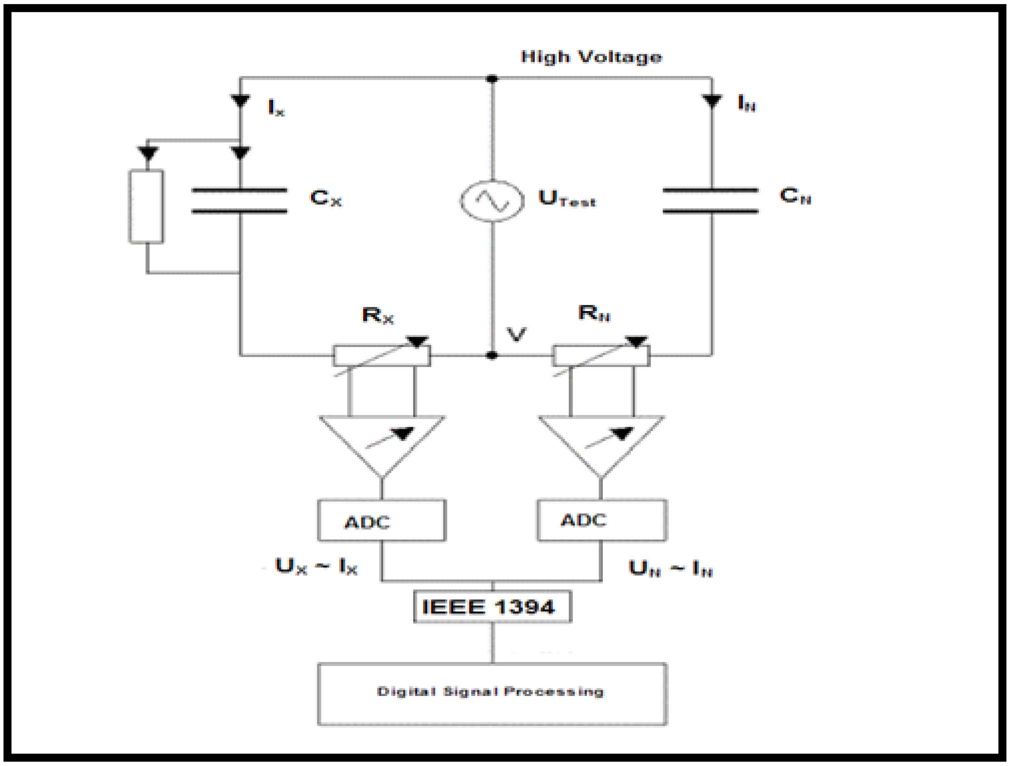


Figure 2.3 Circuit diagram depicting the functioning of the Tettex 2820 apparatus. Adapted from L & tan δ Measuring Bridge Version 1.8 Operating Instructions Haefely Test [4].

In Figure 2.3, C_N represents the standard capacitor, I_N the current flowing through the standard capacitor, C_X the test capacitor (in this case the oil between the parallel copper plates) and I_X the current flowing through the test cell. R_X and R_N are the shunts for the measurement of I_X and I_N respectively. U_{test}, U_x and U_N represents the supply voltage and voltage associated with the test cell and the standard capacitor respectively [4].

Unless otherwise stated the dissipation factor was determined using International Electro-Technical Commission method 247 (IEC 247).

2.6.7.2 Dielectric Breakdown Voltage Testing

Dielectric breakdown voltage (DBV) of a dielectric liquid is defined as a liquid's ability to withstand electrical stress without failure. Essentially it is the maximum voltage that the oil can withstand before allowing a current to pass through it [53]. The current here is defined as 200 mA [53]. It is tested by placing the oil between two electrodes and applying a voltage to it [54]. This test was carried out using IEC 156.

REFERENCES

[1] Heathcote M. J., J & P Transformer Book, Elsevier, **2007**.

[2] U.S. Department of the Interior Bureau of Reclamation, Transformers: Basics, Maintenance, and Diagnostics, Reclaimation: Managing Water in the West, **2005**, www.usbr.gov/pmts/client_service/recent/studytransformers.pdf (accessed 27 July 2011).

[3] Prosr P., Brandt M., Mentlík V. and Michalík J., Condition Assessment of Oil Transformer Insulating System, *International Conference on Renewable Energies and Power Quality (ICREPQ'10)* (Granada (Spain)) **2010**.

[4] Haefely Test AG Operating Instructions, Tettex 2820- Automated C, L & tan δ Measuring Bridge, Version 1.8. **2006**.

[5] Lombard A., Quality assurance of insulating oil for use in new transformers, *Cigre 2009- 6th Southern Africa Regional Conference* (Somerset West, South Africa) **2009**, p. P507.

[6] Coltman J. W., The transformer, *IEEE Industry Application Magazine,* **2002**, *Jan/Feb*:8-15.

[7] Yuliastuti E., Analysis of dielectric properties comparison between mineral oil and synthetic ester oil, Department of Electrical Sustainable Energy, Delft University of Technology **2010**, *Master of Science*.

[8] Verma P., Condition monitoring of transformer oil and paper, Electrical and Instrumentation Engineering, Thapar Institute of Engineering and Technology **2005**, *Doctor of Philosophy*.

[9] Meshkatoddini M. R., Aging study and lifetime estimation of transformer mineral oil, *American Journal of Engineering and Applied Sciences*, **2008**, *4*:384-388.

[10] Robinson N., Transformer oil analysis, **2006**, Wear Check Africa, www.wearcheck.co.za (accessed 7 December 2010).

[11] Barnes M., What is oxidation in lubricating oil?, **2005**, LubeTalk Newsletter, http://www.lubetrak.com/newsletter/Jan24HTML.html (accessed 13 March 2011).

[12] Rudnick L. R., Lubricant Additives: Chemistry and Applications, CRC Press, **2009**.

[13] El-Refaie E. M. M., Salem M. R. and Ahmed W. A., Prediction of the characteristics of transformer oil under different operation conditions, *World Academy of Science, Engineering and Technology*, **2009**, *53*:764-768.

[14] Neto R. C. R., Lima D. O., Pinheiro T. D. S., Almeida R. F., Dantas T. N. C., Dantas M. S. G., Arau´ jo M. A. S., Cavalcante C. L. and Azevedo D. C. S., Thermo-Oxidative Stability of Mineral Naphthenic Insulating Oils: Combined Effect of Antioxidants and Metal Passivator, *Industrial and Engineering Chemistry Research*, **2004**, *43*: 7428-7434.

[15] Georgiev A., Karamancheva I. and Topalova L., Determination of oxidation products in transformer oils using FT-IR spectroscopy, *Journal of Molecular Structure*, **2008**, *872*:18-23.

[16] Mentlík V., Polansky R., Prosr P. and Pihera J., Activation energy of transfomer oils, *Zeszyty Problemowe – Maszyny Elektryczne*, **2008**, *80*:45-49.

[17] Price D. M., Douglas J. H. and Dumont F., Thermogravimetry of Polymers, John Wiley & Sons Ltd, Chichester, **2000**.

[18] Kenar J. A., McElligott J., Hwang H. and Erhan S. Z., A DSC Study of Z2–Z3 Viscosity Blown Soybean Oil, *Journal of American Oil Chemists Society*, **2002**, *79*:1151-1155.

[19] Zelic J., Ugrina L. and Jozic D., Application of thermal methods in the chemisty of cement: Kinetic analysis of Portlandite from non-isothermal thermogravimetric data, *The first international proficiency testing conference* (Sinaia, Romania) **2007**, pp. 420-429.

[20] Nguyen L. H. and Gu M., Decomposition Kinetics, Life Estimation, and Dielectric Study of an Acrylate based Photopolymer for Microfabrication and Photonic Applications, *Macromolecular Chem. Phys.*, **2005**, *206*:1659-1664.

[21] Toop D. J., Theory of Life Testing and Use of Thermogravimetric Analysis to Predict the Thermal Life of Wire Enamels, *IEEE Transactions on electrical insulation*, **1971**, *6*:2-14.

[22] Saha B. and Ghoshal A. K., Thermal degradation kinetics of poly (ethylene terephthalate) from waste soft drinks bottles, *Chemical Engineering Journal* **2005**, *111*:39-43.

[23] Gray I. A. R., Oxidation inhibitors for insulating oils, Transformer Chemistry Services, Durban, www.satcs.co.za/Oxidation_inhibitors_for_insulating_oil-IARGray2008.pdf (accessed 19 July 2010).

[24] Cook C. D., Oxidation of hindered phenols, Contribution from the transformer and allied products laboratory, General Electric Company, **1952**, pubs.acs.org/doi/abs/10.1021/ja01612a019
(accessed 15 September 2010).

[25] Foley L. and Kimmerle F. M., Pulse Voltammetric Determination of Butylated Hydroxy Toluene in Transformer Oils, *Analytical Chemistry*, **1979**, *51*:818-822.

[26] Hassanein M., Gerges S., Abdo M. and EL-Khalafy S., Autoxidation of 2,6-di-tert-butylphenol catalyzed by 5,10,15,20-tetrakis[4-(diethylmethylammonio)phenyl] porphyrinatocobalt(II) tetraiodide in water, *Journal of Molecular Catalysis A: Chemical* **2007**, *268* 24-28.

[27] Hassanein M., Sakaran M. and Shendy S., Oxidation of 2,6-Di-tert-butylphenol by Dioxygen Catalyzed by Tetrasodium Phthalocyaninatocobalt(II) Tetrasulfonate in Aqueous Micellar Media, *Journal of the Iranian Chemical Society*, **2010**, *7*:128-133.

[28] Jayaprakasha G.K., Jagan L., Rao M. and Sakariah K.K., Chemistry and biological activities of *C. longa*, *Trends in Food Science & Technology*, **2005**, *16*:533-548.

[29] Selvam R., Subramanian L., Gayathri R. and Angayarkanni N., The anti-oxidant activity of turmeric (*Curcuma longa*), *Journal of Ethnopharmacology*, **1995**, *47*:59-67.

[30] Asghari G., Mostajeran A. and Shebli M., Curcuminoid and essential oil components of turmeric at different stages of growth cultivated in Iran, *Research in Pharmaceutical Sciences*, **2009**, *1*:55-61.

[31] Jayaprakasha G. K., Jena B. S., Negi P. S. and Sakariah K. K., Evaluation of Antioxidant Activities and Antimutagenicity of Turmeric Oil: A Byproduct from Curcumin Production, *Z. Naturforsch*, **2002**, *57c*:828-835.

[32] Singh G., Kapoor I. P. S., Singh P., de Heluani C. S., de Lampasona M. P. and Catalan C. A. N., Comparative study of chemical composition and antioxidant activity of fresh and dry rhizomes of turmeric (*Curcuma longa Linn.*), *Food and Chemical Toxicology*, **2010**, *48*:1026-1031.

[33] Nor F. M., Mohamed S., Idris N. A. and Ismail R., Antioxidative Properties of *Curcuma longa* Leaf Extract in Accelerated Oxidation and Deep Frying Studies, *Journal of American Oil Chemists Society*, **2009**, *86*:141-147.

[34] Perkin Elmer Life and Analytical Sciences, FT-IR Spectroscopy Attenuated Total Reflectance (ATR), **2005**, www.perkinelmer.com (accessed 16 September 2011).

[35] ARC centre of excellence for free radical chemistry and biochemistry, Teacher Notes on: NMR Spectroscopy, **2006**, http://www.freeradical.org.au/ (accessed 28 Septemeber 2011).

[36] Butler E., Bruker Avance: Beginners Guide **2003**, Germany.

[37] Thompson M., CHNS Elemental Analysers, **2008**, www.rsc.org/amc (accessed 28 September 2011).

[38] H Instruction manual-CHNS-932 C, N, S Leco Corporation

[39] Chausseau M., Lebouil-Arlettaz S. and Thomas G., Wear Metals and Additive Elements Analysis in Used Lubricating Oils Using ICP-OES, **2010**, Horiba Scientific Instruments and systems, Longjume au, www.horiba.com/scientific/ (accessed 21 June 2010).

[40] Boss C. B. and Fredeen K. J., Concepts, Instrumentation and Techniques in Inductively Coupled Plasma Optical Emission Spectrometry, Perkin Elmer Coporation, **2007**.

[41] Skoog D. A, West D. M., Holler F. J and Crouch S. R., Fundamentals of Analytical Chemistry Saunders College Publishing **2003**.

[42] SRI Instruments Documentation, Detectors: Flame Ionization Detector - FID, http://www.srigc.com/documents.htm (accessed 28 September 2011).

[43] Rusay R, Mass Spectrometry, **2010**, http://chemconnections.org/organic/chem227/Ch13-MS-05.pdf (accessed 28 September 2011).

[44] Bilyeu B., Characterization of cure kinetics and physical properties of a high performance, glass fiber-reinforced epoxy prepreg and a novel fluorine-modified, amine-cured commercial epoxy, University of North Texas **2003**, *Doctor of Philosophy*.

[45] ASTM D 974-80, Standard test method for: Neutralization number by color-indicator titration.

[46] KEM: Application note, Saponification value of fat and oil, http://www.kyoto-kem.com/en/pdf/industry/FatVegetableOil/ETIB-99307.pdf (accessed 13 April 2010).

[47] Metrohm- Thermo. Titr. Application Note No. H-076, Determination of Iodine value in fats and oils, http://products.metrohm.com/getAttachment.axd?attaName=47663056-e069-493c-86df-5bc268168a28 (accessed 3 October 2011).

[48] Goncalves I. M., Murillo M. and Gonza´lez A. M., Determination of metals in used lubricating oils by AAS using emulsified samples, *Talanta*, **1998**, *47*:1033-1042.

[49] ASTM D 445-82, Standard Test Method for: Kinematic viscosity of transparent and opaque liquids (and the calculation of dynamic viscosity).

[50] ASTM D 1533-79, Standard test method for: Water in insulating liquids (Karl Fischer method).

[51] Wiklund P., Karlsson C. and Levin M., Determination of Hydroperoxide Content in Complex Hydrocarbon Mixtures by Gas Chromatography/Mass Spectrometry, *Analytical Sciences*, **2009**, *25*:431-436.

[52] Prakash A., Rigelhof F. and Miller E., Antioxidant Activity, Medallion Laboratories, http://www.medlabs.com/Downloads/Antiox_acti_.pdf (accessed 28 September 2011).

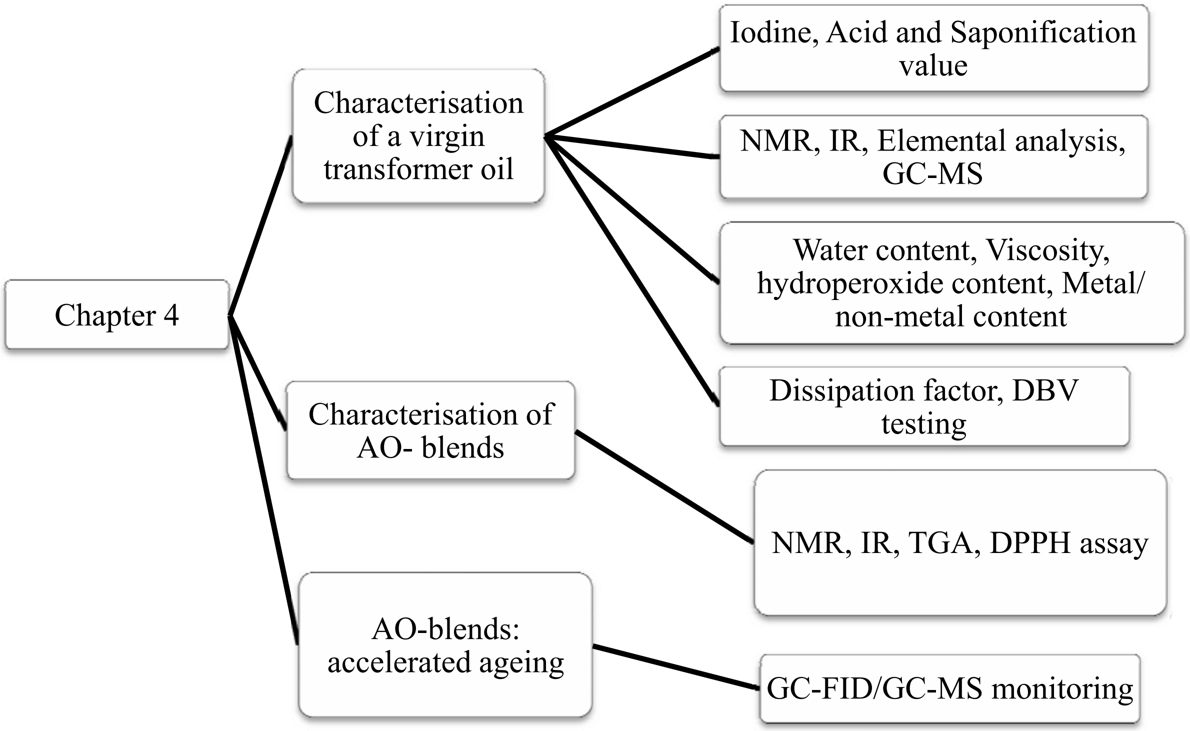
[53] D 877-82, Standard test method for: Dielectric breakdown voltage of insulating liquids using disk electrodes.

[54] Hamrick L., Transformer Oil Sampling, **2009**, ESCO Energy Services Company, www.netaworld.org/files/neta-journals/NWsu09_Hamrick.pdf (accessed 4 January 2011).

CHAPTER 3

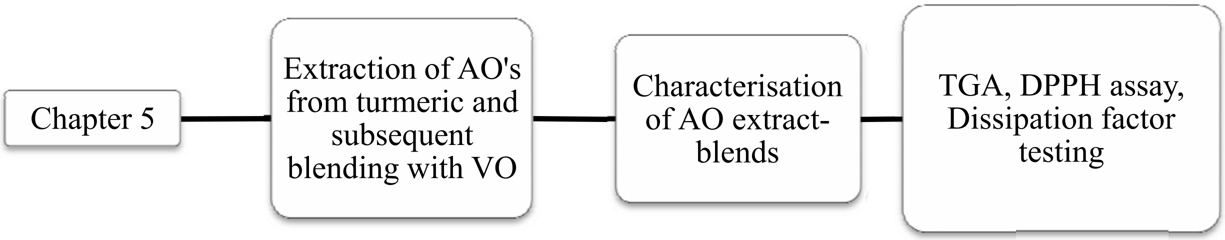
EXPERIMENTAL

This chapter outlines the experimental aspects and different techniques used and their significance in each aspect of research work carried out in this MSc project. Schemes 3.1, 3.2 and 3.3 outlines the general experimental procedures covered in Chapters 4, 5 and 6 respectively. Scheme 3.1 is a flow diagram illustrating the characterisation of virgin transformer oil and its blends with antioxidants (AO’s) and the techniques employed for the characterisation of the oil and its blends. In this study; from previous work, literature review and experimental the evaluation of NMR, IR, DPPH assay and TGA are useful techniques to evaluate the properties of AO blends in comparison to that of virgin oil.



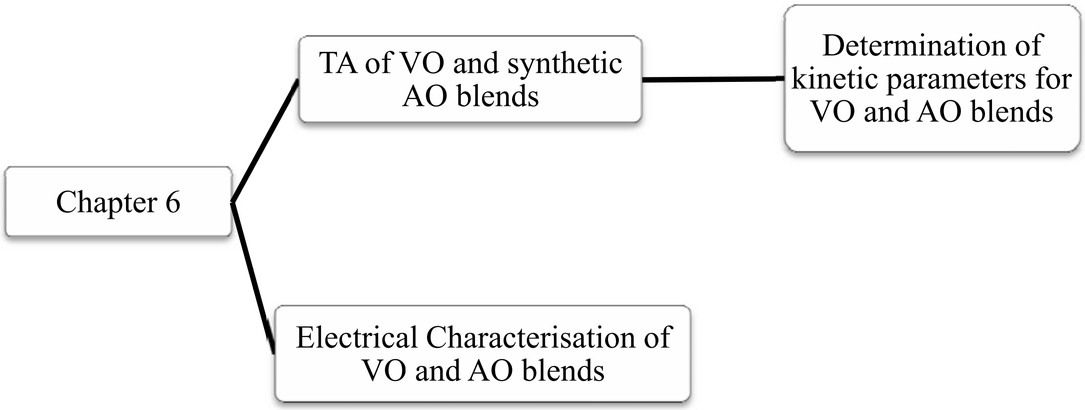
Scheme 3.1 Flow diagram showing an outline of the experimental procedure as per Chapter 4.

Scheme 3.2 outlines the experimental procedure for the extraction of components from turmeric, followed by blending of the extract with virgin oil. The characteristics of the virgin oil and turmeric oil blends were then compared.



Scheme 3.2 Outline of the experimental procedure as per Chapter 5.

Scheme 3.3 outlines the procedure for the determination of kinetic parameters of oil and oil blended with synthetic antioxidants by thermal analysis. Dissipation factor and dielectric breakdown voltage tests were also carried out.



Scheme 3.3 Brief outline of the experimental procedure as elaborated on in chapter 6.

3.1 INSTRUMENTATION

All NMR spectra were obtained using the Bruker AVANCE III 400 MHz instrument, Bruker Corporation, Germany.

The elemental analysis data were obtained using Leco 932 CHNS Elemental Analyser (Leco, USA).

The UV-Vis spectra were obtained using Perkin Elmer Lamda 35 UV Vis Spectrometer/Shimadzu UV 1800 Spectrophotometer.

The FT-IR data were collected using Perkin Elmer Spectrum 100, FT-IR Spectrometer, USA equipped with diamond window Attenuated Total Reflectance (ATR) sampling accessory.

Thermal analysis data was collected using Universal Analysis 2000 by TA Instruments, manufactured in USA.

Metals and non-metals elemental content was determined with Perkin Elmer Optima 5300 DV ICP-OES Spectrophotometer, USA.

GC-MS spectra were obtained using Agilent Technologies 6890 Series GC coupled with Agilent 5973 Mass selective detector and GC-FID using GC-FID Agilent Technologies 6820, USA.

The water content of the oil was determined with Metrohm 870 KF Titrino Plus (Methrohm, Switzerland).

An alternating current source for dissipation factor testing was provided by an AC voltage single step test set manufactured by MWB Limited, India.

3.2 REAGENTS

All chemicals were AR grade unless otherwise stated. Sodium thiosulphate (99%), $CDCl_3$, KIO_3 (99.5%), KI (99.9%), starch, toluene (99.9%), $Ba(OH)_2$ and TLC Silica gel 60 F_{254} plates were purchased from Merck Chemicals. The acids, HCl (32%) and H_2SO_4 (98%) were purchased from Promark Chemicals. Fluorene (98%), TPPO (98%), TPP (99%), BHT (99%), DBP (99%), isopropyl alcohol (99.5%), DPPH and hydranal were purchased from Sigma-Aldrich. Dichloromethane, DCM (99.8%), elemental sulfur (CP grade) and KOH (85%) were purchased from Associated Chemical Enterprise. The oil and density standard (N10) and 0.1 M Wijs solution were purchased from Fluka Analytical.

Nitric acid (69%), methanol (99%), ethanol (99.9%), KHP (99.9%) and salicylic acid were purchased from UniLab, Lab Scan Analytical, Polychem Supplies, Thomas Baker Chemicals and SaarChem respectively. Elemental standards (1000 ppm) of Al, B, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, P, Pb, Si, S, Sn, and Zn were purchased from DLD Scientific.

3.3 EXPERIMENTAL PROCEDURES

3.3.1 Instrumental Analysis: Characterisation techniques

3.3.1.1 ^{13}C NMR and ^{1}H NMR analysis

The ^{13}C, ^{1}H NMR and FT-IR characterisation were carried out to serve as tools for structural identification.

All NMR spectra were recorded on a Bruker AVANCE III 400 MHz instrument. Samples were carried out at room temperature (20-25 °C), the number of scans used was 16 and 2048 for ^{1}H and ^{13}C NMR, respectively. The oils were dissolved in $CDCl_3$. Spectra were analysed using Topspin software.

3.3.1.2 FT-IR analysis

The FT-IR characterisation of the oil samples were done on Perkin Elmer 100 Fourier Transform Infrared Spectrophotometer with a Universal ATR attachment.

3.3.1.3 Elemental Analyzer

In order to determine the C, H and N composition, elemental analysis was carried out on Leco 932 CHNS elemental analyser. The instrument calibration was carried out with micro-analytical standard, acetanilide. Sample sizes of 2 mg were weighed out in triplicate and analysed.

3.3.1.4 Thermal Analysis

Oil samples were analysed with Universal Analysis 2000 by TA Instruments under air conditions using aluminium pans for solid fat index (SFI). The pans were purchased from AMS Laboratory Technologies. Samples were analysed at temperatures ranging from ambient (20-25 °C) to 300 °C at a heating rate of 5 °C min^{-1}.

Determination of apparent activation energies and kinetic parameters for the oil decomposition reaction by non-isothermal analysis [1] employed heating rates of 1, 2, 4, 6, 8 and 10 °C min^{-1}.

3.3.1.5 Elemental Analysis-ICP-OES

The metal/non-metal content of the transformer oil was determined after acid digestion in an open beaker on a hot plate. From the 1000 ppm stock solutions, 50, 20, 10, 5, 2 and 1 ppm standards were prepared. Aqua regia was prepared using HCl and HNO_3. Aqua regia (5 mL) was added to these standards before making them up to the mark using deionised water in 100 mL volumetric flasks. A blank solution was prepared by using the equivalent amount of acid as applied in the standard or sample, prepared in deionised water. The digestion procedures [2] of the oil samples are described in section 4.2.4. The standards and samples were each digested in acid, the solutions filtered through 0.45 μm membrane filters and transferred into ICP-OES vials prior to ICP-OES analysis.

3.3.1.6 GC-FID/GC-MS

a) Composition of virgin transformer oil

Virgin transformer oil was dissolved with DCM and analysed using Agilent Technologies 6890 Series GC coupled with Agilent 5973 Mass selective detector. The instrumental settings have been described in section 4.2.10.

b) Hydroperoxide content

The hydroperoxide content was determined using the procedure outlined by Wiklund *et al*. [3].

Solution A: Fluorene, 0.1443 g and TPP, 2.231 g were dissolved in toluene and the solution was made up to the mark in a 25 mL volumetric flask.

Solution B: Elemental sulfur, 0.4566 g was added to a 50 mL volumetric flask and made to the mark using toluene.

Gas chromatography, glass vials were cleaned using DCM and were oven dried. Three virgin oil samples each weighing 0.5 g were added to three vials. *Solution A*, (250 μL) was added to the oils and the mixture shaken on a mechanical orbital shaker for 15 minutes. The procedure was repeated with *Solution B* (250 μL).

The samples were analysed using GC-FID Agilent Technologies 6820 GC, instrumental settings of which are referred to in section 4.2.8. In order to determine the relative response factor (RRF), 0.1456 g of fluorene and 0.1611 g of TPPO were dissolved in toluene in a 25 mL volumetric flask. The samples and standards were analysed in triplicates by injecting 4 μL volumes.

c) AO degradation monitoring

In order to quantify the presence of AO's in the UV digested oil samples, GC-FID system was utilised (instrumental settings are described in section 4.2.13).

Solution C: Fluorene of mass, 0.1521 g was dissolved in toluene in a 25 mL volumetric flask.

Three samples from the UV digester tubes were collected after every eight hours. Digested oil samples of masses 0.5 g were dissolved in 500 µL *Solution C* in GC auto-sampler vials. In order to determine the RRF, 0.1368 g of fluorene, 0.1266 g BHT and 0.1343 g of DBP were transferred into a 25 mL volumetric flask and the solution made up to the mark using toluene. All standards and samples were analysed in triplicate.

d) AO degradation products identification

To determine the degradation products of the antioxidants that may have formed during exposure of the oils to UV digestion, GC-MS was employed. The oil samples were dissolved in DCM and injection volumes of 0.5 µL was used. Instrumental settings are described in section 4.2.13.

e) Identification of homogenised components of turmeric in virgin oil

Turmeric oil blends were dissolved in DCM. In order to determine the constituents of turmeric that had blended into the oils, 0.5 µL of the solution was injected into the GC-MS. The instrument settings are summarised in Table 8.

3.3.1.7 UV-Vis Spectrophotometric analysis

In all UV-Vis analysis quartz cuvettes were used with path length 1 cm.

The synthetic antioxidant oil blends comprising of 0.3% (w/w) antioxidant in virgin oil (30:70 ratio) were prepared as follows; (i) BHT + VO, and (ii) DBP + VO. The DPPH assay was carried out using a method described by Lee *et al.* (2007) [4] with modifications.

Solution D: A sample of DPPH of mass 0.0036 g was weighed into a 50 mL volumetric flask and made to the mark using DCM.

AO-blend samples of 0.1 g were weighed into poly top vials. An aliquot of 3 mL of *Solution D* was added into the vial and left to react in the dark in the sealed vial for thirty minutes. The DPPH concentration was then measured at 517 nm after thirty minutes using Shimadzu UV 1800 Spectrophotometer.

In the case of antioxidant activity for turmeric oil blends, the following procedure was carried out. DPPH of mass, 0.0388 g was measured into a 50 mL volumetric flask. A 5 mL aliquot was transferred to a 50 mL volumetric flask; both the solutions were made up with DCM. Extract oil blend samples of size 0.2 g, were weighed into poly top vials and 3 mL of the DPPH solution was added to it, the contents was shaken and immediately transferred to a cuvette that had been previously rinsed with DCM. The absorption at 517 nm was monitored over 30 minutes using Perkin Elmer Lamda 35 UV-Vis Spectrometer. Due to the fact that the oil blends themselves showed some absorbance at 517 nm, the reference cuvette contained an oil blend of mass 0.2 g dissolved in 3 mL DCM.

3.3.2 Viscosity and Water Content

The viscosity test for virgin oil was carried out as described in section 4.2.7 [5]. Calibration of the Ostwalds capillary viscometer was achieved using N10 viscosity and density oil standard.
Water content was determined using the Karl Fischer method [6] on the Metrohm 870 KF Titrino Plus. A range of masses (0.1 to 0.5 g) of virgin transformer oil were used for the evaluation of water content. For each sample mass range, three replicate analyses were carried out.

3.3.3 Saponification value

All glassware used was acid washed (10% nitric acid), rinsed with deionised water, rinsed with dichloromethane and dried in the oven. Ethanolic potassium hydroxide (~0.1 M) was prepared in bulk into 2 L plastic bottles using 99.9% ethanol and 85% KOH. Aqueous HCl (0.5 M) was also prepared in bulk. A 10 g sample mass of the virgin oil was added to 25 mL of a 0.1 M alcoholic KOH solution in a 250 mL quick fit conical flask. The solution was refluxed for 30 minutes and titrated while hot with a standard 0.5 M HCl solution, to a phenolphthalein endpoint. A blank was also carried out in which the sample was omitted. KOH solution was standardised using KHP, HCl was standardised using NaOH.

3.3.4 Iodine value

A 2 g sample mass of virgin oil was dissolved in 20 mL of chloroform in a 250 mL conical flask with stopper. To this a 10 mL aliquot of 0.1 M Wijs reagent (ICl), was added. The solution was left to stand in the dark for 1 hour after which 20 mL of a 10% (w/v) KI solution, and 100 mL of deionised water was added.

The liberated iodine was titrated with a standardised sodium thiosulphate solution to a starch endpoint. Sodium thiosulphate was standardised using potassium iodate. Starch indicator was prepared by boiling 1 g of starch in 100 mL of deionised water. The starch was preserved with salicylic acid.

3.3.5 Acid Number

The solvent used for acid number determination (titration solvent) was prepared in a 1 L acid cleaned, DCM rinsed, oven dried glass bottle. The titration solvent comprised of 500 mL toluene, 495 mL isopropyl alcohol and 5 mL deionised water. The ~0.1 M alcoholic KOH was prepared by dissolving 6.8424 g of KOH into 1 L of isopropyl alcohol using a 1 L conical flask. The solution was then heated using a water bath for approximately 5 minutes. After heating the solution, approximately 2 g of $Ba(OH)_2$ was added into the conical flask. The solution was transferred to a volumetric flask and left overnight protected with a guard tube composed of cotton wool and soda lime. The solution was then filtered under vacuum. A 20 g sample mass of transformer oil was dissolved in 100 mL of titration solvent and titrated at room temperature to a phenolphthalein endpoint with a standardised alcoholic KOH solution. Standardisation of alcoholic KOH was achieved using KHP. Blank runs were carried out. Both the blanks and samples were carried out in triplicate.

3.3.6 Dissipation Factor and Dielectric Breakdown testing

The dissipation factor and DBV tests were carried out by Transformer Chemical Services (Durban, 2010) according to the guidelines stipulated in IEC 156 and IEC 247 for dielectric breakdown voltage and dissipation factor respectively.

However if otherwise stated the dissipation factor tests were carried out at the High Voltage Direct Current (HVDC) laboratory at UKZN. All safety precautions as specified for use of the high voltage laboratory were adhered to. The dissipation factor tests were carried out in a glass cell, with copper electrodes as described in Figure 6.1, using the Tettex 2820 apparatus. The cell was cleaned after successive runs using DCM. The cell was filled with the oil sample and connected as per Figure 6.2. A high voltage, alternating current source (100 kV AC supply) was used and the applied voltage was varied. A plastic clamp held the copper plates into place in order to prevent air bubbles from forming in the oil sample. Oil samples were cotton wool plug filtered prior to analysis.

3.3.7 UV digestion

Antioxidant oil blends were digested through exposure to UV light using a Metrohm 705 UV digester, over twenty four hours. The UV digester was fitted with six sample holders (similar to test tubes). The sample tubes were washed with acid, rinsed with DCM and then oven dried.

3.3.8 Extraction of turmeric components

Turmeric (Osmans Taj Mahal®- Extra Special Turmeric Powder) was purchased from local stores in Durban. The samples were cone and quartered. A 20 g sample was weighed and added to a 250 mL quick fit conical flask, to this 50 mL of DCM was added and was allowed to reflux for one hour in a water bath maintained at 50 °C. The solution was then filtered by vacuum filtration. The filtrate was stored for future analysis whilst the solid was discarded. The filtrate was then pre-concentrated by allowing for evaporation of DCM. To the crude extract, 5 mL of 99.9% ethanol was added as per the procedure described by Anderson *et al.* (2000) [7]. This solution was filtered (through gravity) and the filtrate mixed with 1 g of oil in a poly top vial. The mixture was purged with nitrogen and stirred for 3 days using a magnetic stirrer bar on a magnetic plate. The residue that had formed in the oil was discarded and the oil was then filtered using a cotton wool plug. The filtrate was labelled as '*extract oil blend* 1'. Subsequent blending was carried out by repeating the above procedure.

3.3.9 Separation of turmeric extract components using thin layer chromatography (TLC)

Virgin oil and turmeric oil blends were dissolved in DCM, and spotted on TLC silica gel plates. The plates were placed in 50 mL beakers containing the solvent system (99% DCM: 1% methanol (v/v)). The sample plates were examined under UV lamps at λ= 365 nm and λ= 254 nm. The R_f values for each of the spots were calculated.

REFERENCES

[1] Mentlík V., Polansky R., Prosr P. and Pihera J., Activation energy of transfomer oils, *Zeszyty Problemowe – Maszyny Elektryczne*, **2008**, *80*:45-49.

[2] Goncalves I. M., Murillo M. and Gonza´lez A. M., Determination of metals in used lubricating oils by AAS using emulsified samples, *Talanta*, **1998**, *47*:1033-1042.

[3] Wiklund P., Karlsson C. and Levin M., Determination of Hydroperoxide Content in Complex Hydrocarbon Mixtures by Gas Chromatography/Mass Spectrometry, *Analytical Sciences*, **2009**, *25*:431-436.

[4] Lee J. M., Chung S., Chang P. and Lee J. H., Development of a method predicting the oxidative stability of edible oils using 2,2-diphenyl-1-picrylhydrazyl (DPPH), *Food Chemistry*, **2007**, *103*:662–669.

[5] ASTM D 445-82, Standard Test Method for: Kinematic viscosity of transparent and opaque liquids (and the calculation of dynamic viscosity).

[6] ASTM D 1533-79, Standard test method for: Water in insulating liquids (Karl Fischer method).

[7] Anderson A. M., Mitchell M. S. and Mohan R. S., Isolation of Curcumin from Turmeric, *Journal of Chemical Education* **2000**, *77*:359-360.

CHAPTER 4

MANUSCRIPT 1

CHARACTERISATION OF A NAPHTHENIC BASED UNINHIBITED VIRGIN TRANSFORMER OIL AND THE USE OF SYNTHETIC ANTIOXIDANTS.

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ABSTRACT

The bulk of insulation material used in a transformer is comprised of mineral oil. Exposure of these mineral oils to oxidative, thermal and electrical stresses induce ageing [1]. Degeneration of the oil imparts poor quality thus causing it to lose its ability to function optimally. This work focuses on the characterisation of a naphthenic based virgin uninhibited transformer oil (VO) commonly used in South African transformers. While antioxidants (AO's), such as 2,6-di-*tert*-butyl-4-methylphenol (BHT) (Fig. 4.1) and 2,6-di-*tert*-butylphenol (DBP) (Fig. 4.2) have been blended into oils to increase its stability, more work needs to be done to highlight the effects on the oil and efficiency of these AO's. In addition this paper also characterises antioxidant-virgin oil blends as well as the effect of antioxidants on the oil. The common diagnostic chemical characteristics of acid and saponification values showed no detection as expected for virgin transformer oil. The proton and carbon nuclear magnetic resonances (^{1}H NMR and ^{13}C NMR respectively) as well as Fourier transform infra-red (FT-IR) data showed no presence of acids, alcohols or esters, which are common by-products of transformer oil ageing. The ^{1}H-NMR spectra, however indicated the presence of aromatic groups, which later was identified as tetralin by gas chromatography-mass spectrometry (GC-MS). The blending of antioxidants into virgin transformer oil proved to be successful based on evidence sourced from ^{1}H NMR, ^{13}C NMR and IR data. The 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay, served to confirm that blending of BHT and DBP into transformer oils increased the free radical scavenging ability of the oil.

Thermal gravimetric analysis (TGA) data revealed that blending of AO's into transformer oil improved thermal stabilities of the oil. An attempt to identify degradation products of the AO's by subjecting the oil blends to UV irradiation over a period of 24 hours was successfully carried out using GC-MS. Evidently blending of antioxidants has potential to enhance the performance and increase the life-span of transformer oil.

4.1 INTRODUCTION

South Africa is currently facing a major energy crisis with respect to a shortage in power supply. As a result of urban growth and development, increased pressure has been placed on power service providers for more efficient production and delivery. In addition, the increasing demand for electricity coupled with a limited number of power stations has placed huge emphasis on power conservation and generation. Transformers form an integral part of power-stations and play a key role in the transference of power. For efficient transference from power-stations to end-users, the performance of a transformer has to be considered.

Transformer oil functions both as an insulator and coolant [2]. However the oil suffers a drawback in which it is susceptible to ageing, whereby the main mechanism entails oxidation. During ageing, oxidation reactions lead to the formation of carboxylic acids as well as oil sludge resulting in poor functioning of the transformer oil and the transformer unit as a whole [3]. There are two classes of transformer oils: a) uninhibited oils (containing no antioxidants) and b) inhibited oils (containing antioxidants at specified concentrations) [4]. This study has focused on naphthenic-based virgin transformer oil with synthetic antioxidants added. Note that these oils are a key component of transformer insulation and for maintaining optimum functioning of the transformer unit.

In the methodology, naphthenic based virgin transformer oil was chemically characterised in order to relate its chemical properties to its functioning. The oils are characterised using both conventional and international standard routine oil analysis techniques as well as other analytical techniques such as gas chromatography with mass spectrometry. The procedure used involved the blending of antioxidants (free radical scavengers) with virgin uninhibited oil to enhance oil stability.

Currently 2,6-di-*tert*-butyl-4-methylphenol (BHT) (Fig. 4.1) and 2,6-di-*tert*-butylphenol (DBP) (Fig. 4.2) are used as antioxidants (AO's) however owing to their carcinogenic and toxic behavior, the International Electro-technical Commission (IEC) governs that these AO's be used at concentrations not exceeding 0.3% (w/w) [4].

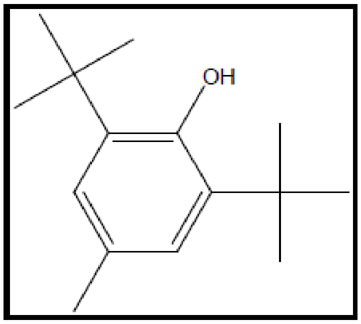

Figure 4.1 Structure of AO, 2,6-di-*tert*-butyl-4-methylphenol (BHT).

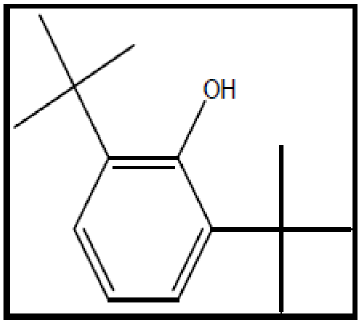

Figure 4.2 Structure of AO, 2,6-di-*tert*-butylphenol (DBP).

Despite the protective role which AO's display, they themselves are susceptible to oxidation reactions over time. Hence the analysis of degradation products is crucial to understanding the intensity of AO protection.

In this study, an accelerated ageing study on inhibited oil by UV-digestion was carried out to monitor the impact of AO blending and thus relate this to transformer oil stability.

4.2 METHODS AND MATERIALS

All analytical grade reagents (AR) were used unless otherwise stated.

4.2.1 Saponification value

A 10 g sample mass of the naphthenic oil was added to 25 mL of a 0.1 M alcoholic KOH solution in a 250 mL conical flask. The solution was refluxed for 30 minutes and titrated while hot with a standard 0.5 M HCl solution to a phenolphthalein endpoint. A blank was also carried out.

4.2.2 Iodine number

A 2 g sample mass of naphthenic oil was dissolved in 20 mL of chloroform to which a 10 mL aliquot of 0.1 M Wijs reagent (ICl) was added. The solution was left to stand in the dark for 1 hour after which 20 mL of a 10% (w/v) KI solution and 100 mL of deionised water was added. The liberated iodine was titrated with a standard 0.0166 M sodium thiosulphate solution to a starch endpoint.

A blank was performed under the same conditions. Replicate titrations were carried out until three iodine values to within 0.1 g I_2/g oil was obtained.

4.2.3 Total acid number (TAN)

A 20 g sample mass of transformer oil was dissolved in 100 mL of the titration solvent (toluene : isopropyl alcohol : deionised water; ratio: 100:99:1) and titrated at room temperature to a phenolphthalein endpoint with a standard 0.1067 M alcoholic KOH solution.

4.2.4 Metal/non-metal content

Sample preparation: In triplicate, 2 g of the naphthenic oil sample was digested in 20 mL of aqua regia [5] using open beaker digestion. The sample solution was pre-concentrated to approx. 10 mL and the resulting solution was filtered.

A 5 mL aliquot of the pre-concentrate was added to a 100 mL volumetric and diluted to the mark with deionised water.

Preparation of standards:

Multi-element standards of Al, B, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, P, Pb, S, Si, Sn, and Zn in the range of 1, 2, 5, 10, 20, 50 ppm were prepared by serial dilution of 1000 ppm standard stock solutions in 5% aqua regia. A blank containing 5% aqua regia was prepared using deionised water.

Instrument: Analysis by inductively coupled plasma-optical emission (ICP-OES) was carried out using the Perkin Elmer Optima 5300 DV ICP-OES Spectrophotometer.

4.2.5 Thermal Gravimetric Analysis

All virgin transformer oils and blends thereof were analysed using the Universal Analysis 2000 by TA Instruments. A temperature ramp rate of 5 ºC min^{-1} from room temperature to 300 ºC was applied in all cases.

4.2.6 Water content

The moisture content was determined by the Karl Fischer (KF) method using the Metrohm 870 KF Titrino Plus Analyser.

4.2.7 Viscosity

The viscosity of transformer oils was determined using Ostwalds capillary viscometer (bore size 2 mm) at a constant temperature of 25 °C using a water bath. Calibration of the viscometer was carried out using a N10 oil standard purchased from Fluka Analytical. Replicate efflux times were recorded to within 0.1 s.

4.2.8 Hydroperoxide content

The hydroperoxide content was analysed according to a method used by Wikland *et al.*[6]. Solution A was prepared by dissolving 2 g of triphenyl phosphine (TPP) and 0.15 g fluorene (internal standard (IS)) in toluene made up to 25 mL. Solution B was prepared by dissolving 0.45 g elemental S dissolved in toluene made up to 50 mL. A sample mass of 0.5 g was weighed into a vial and reacted with 250 µL of solution A for 15 minutes. This was followed by the addition of 250 µL of solution B and reacted for 15 minutes. The amount of triphenyl phosphine oxide (TPPO), produced as a result of the oxidation of TPP, served as an indicator of the hydroperoxide level in the oil. TPPO was analysed by GC-FID (Agilent Technologies 6820 GC system) using a DB-1 column.

Injection Temp: 280 °C , Detector Temp: 280 °C

Column temp: 70 °C for 1 minute

Column ramp temp:

Ramp 1: 20 °C min^{-1}: to 100 °C	Holding time: 1min
Ramp 2: 15 °C min^{-1}: to 150 °C	Holding time: 1min
Ramp 3: 15 °C min^{-1}: to 300 °C	Holding time: 4 min

The relative response factor (RRF) of TPPO to fluorene was used to quantify TPPO.

4.2.9 ^{13}C and ^{1}H NMR, Infrared Spectroscopy and Elemental analysis

All ^{1}H and ^{13}C NMR spectra of virgin transformer oils dissolved in deuterated chloroform (Merck) were recorded on a Bruker AVANCE III 400 MHz instrument at room temperature. Chemical shifts were expressed in ppm relative to TMS. FT-IR spectra were recorded using the - Perkin Elmer 100 Fourier transform infrared (FT-IR) spectrophotometer. The virgin oil was analysed on the Leco 932 CHNS elemental analyser.

4.2.10 GC-MS analysis (virgin oil)

This analysis was performed using the Agilent 6890 GC system, column type: DB5-MS. Injector temp: 250 °C. Column temp: 60 °C for 2 minute. Column ramp temp: 10 °C min^{-1} from 60 to 300 °C.

4.2.11 Dissipation factor and Dielectric Breakdown Voltage (DBV)

The above tests were carried out by Transformer Chemical Services (Durban, 2010) according to the guidelines stipulated in IEC 156 and IEC 247 for dielectric breakdown voltage and dissipation factor respectively.

4.2.12 DPPH assay [7]

Oil blends comprising of 0.3% (w/w) of (i) BHT + VO and (ii) DBP + VO were prepared. A 0.1 g sample mass of the oil blend was added to 3 mL of 1.8 x 10^{-3} M DPPH in dichloromethane (DCM). Samples were left to react in the dark for 30 minutes. The absorbance (at 517 nm) was recorded on a Shimadzu UV 1800 Spectrophotometer. All runs were performed in triplicate and a sample blank was used to eliminate background interferences.

4.2.13 Antioxidant (AO) monitoring

A VO blend containing AO's was exposed to UV light using a UV digester (Metrohm 705 UV digester) over a period of time. A sample mass of 0.5 g of UV irradiated oil was dissolved in 500 μL of 3.66×10^{-2} M fluorene (IS) in toluene and analysed by GC using flame ionisation detection (FID). The RRF of fluorene to DBP and BHT was used to quantify the antioxidant. In addition to monitoring antioxidant depletion, degradation products of the antioxidants were also investigated. This was achieved through dissolution of UV irradiated samples in DCM and analysis by GC-MS using Agilent Technologies 6890 Series GC coupled with Agilent 5973 Mass selective detector. The instrument settings are given below.

Column type: DB5-MS Injector temp: 250 ° C

Column temp: 80 °C for 1 minute Column ramp temp: 10 °C min^{-1} to 260 °C

Holding time: 15 minutes.

4.3 RESULTS AND DISCUSSION

The properties of naphthenic based uninhibited virgin transformer oil are given in Table 3.

Table 3 Properties of naphthenic based uninhibited virgin transformer oil (n.d.[#] = not detected).

Property evaluated	
Acid Number/ (mg KOH/ g oil)	n.d. [#]
Saponification number/ (mg KOH/ g oil)	n.d. [#]
Iodine value/ (g I_2/ 100 g oil)	0.6313 ± 0.0127
Water content/ ppm	129.2 ± 39.2
Kinematic viscosity/ mm^2 s^{-1}	15.64 ± 0.03
Dissipation factor	0.01214 ± 0.00437
Dielectric Breakdown Voltage/ kV	50.4 ± 3.3
Hydroperoxide content/ (g TPPO/ g oil)	0.07734 ± 0.00613
%C	86.00 ± 0.60
%H	13.51 ± 0.23
%N	0.38 ± 0.07

In the evaluation of total acid number and saponification values, none were detected, which seemingly is an expected result for virgin transformer oil.

Ideally no acidic or saponifiable constituents must be present in the unused original oil. Generally, the acid number of new unused transformer oils does not exceed a value of 0.05 mg KOH per gram [8]. Although some forms of transformer oils are classified as naphthenic based, additives present may be aromatic in nature. The iodine value, an indication of saturation, suggests the presence of unsaturated components in the oil. A moisture content of 129.20 ± 39.21 ppm obtained for the virgin oil was significantly higher than the max. moisture content value of 35 ppm prescribed for most oils [8]. According to Dong *et al.* [9] in new and used oils, additives, and contaminants containing OH group make determination of moisture content at low levels (< 2%) difficult. Moisture determination using the KF method for oils with low water content (< 20 ppm) and additives have been very problematic. An alternate method has been proposed by Dong *et al.*[9]. Consequently, a low water content in transformer oil is a desirable property as an increase in moisture content reduces the insulating properties of the oil [10]. In addition an increase in water content may accelerate ageing of other components of the insulating material [8]. The dissipation factor, which essentially is the leakage current through the oil [11], is expected to be less than 0.1 for oils used in Category A transformers (i.e. transformers exceeding 170 kV but less than 400 kV) [11]. A dissipation factor of 0.0121 and DBV of 70 kV was recorded for this naphthenic based oil. These values are deemed to be acceptable. The two classes of metals/non-metals that may be present in transformer oils, are classified as wear elements and additive elements [12]. Wear metals are known to accelerate the degradation process and these metals include Fe, Cu, Sn, etc. [12]. In the case of wear metals they may accumulate in oils as a direct result of contamination arising out of the transformer itself. Additive elements exhibiting antioxidant, anti-wear and anti corrosion activity may be blended into the oil in order to protect the oil as well as the transformer.

Table 4 Metal/non metal content of a naphthenic virgin transformer oil.

Metal	**Concentration/ (μg/g)**
Al	3.877 ± 0.021
B	16.23 ± 5.51
Ca	91.478 ± 9.423
Mg	27.03 ± 2.68
P	0.5244 ± 0.2112
Si	226.1 ± 5.9

In this study a host of metals/ non-metals that included Al, B, Ba, Ca, Cd, Cu, Cr, Fe, Mg, Mn, P, Pb, S, Si, Sn and Zn were investigated and quantified. The absence of wear metals (Table 4) was largely attributed to non-contact of the oil with a transformer (metallic). The presence of Si in highest concentration is due to the use of Si derivatised compounds as defoaming agents [12]. The presence of B, Ca, Mg and P or derivative compounds thereof, as additives, may act as potential anti-wear agents or antioxidants [12].

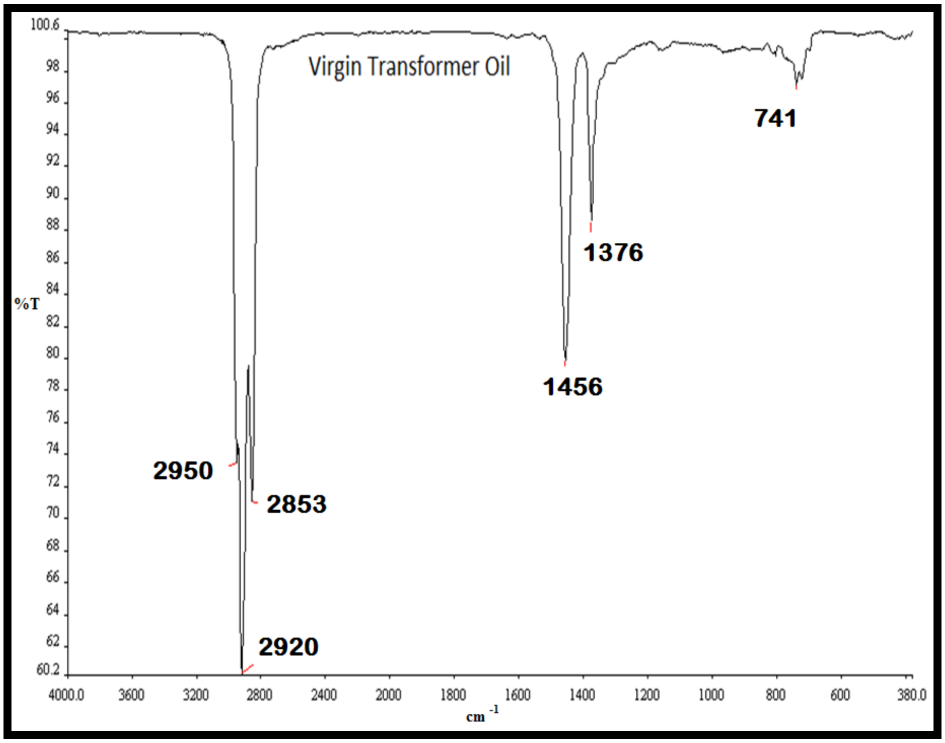

Figure 4.3 FT-IR spectra of naphthenic based virgin transformer oil.

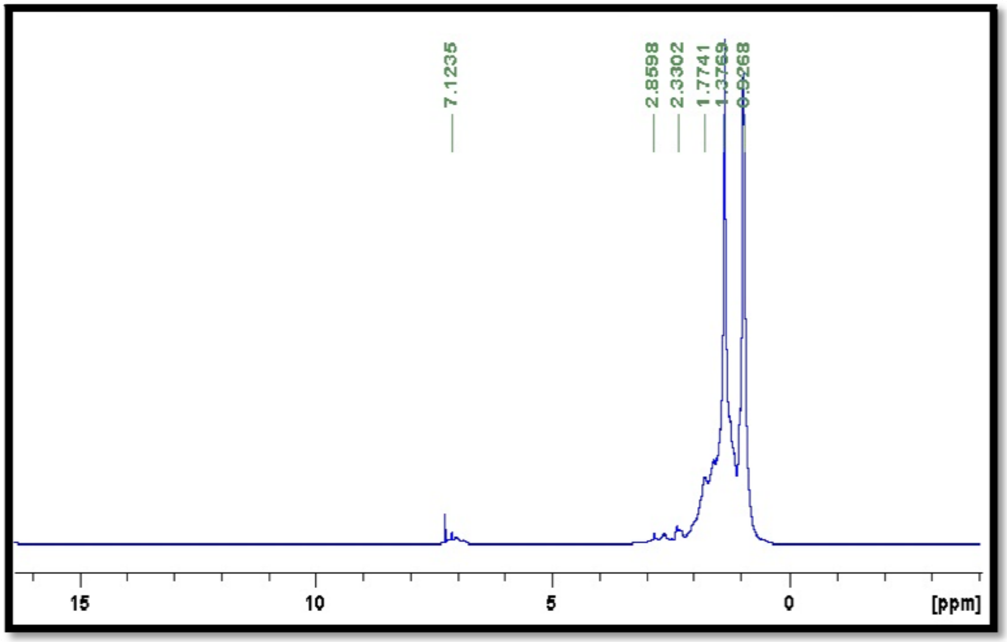

Figure 4.4 ^{1}H NMR of virgin transformer oil.

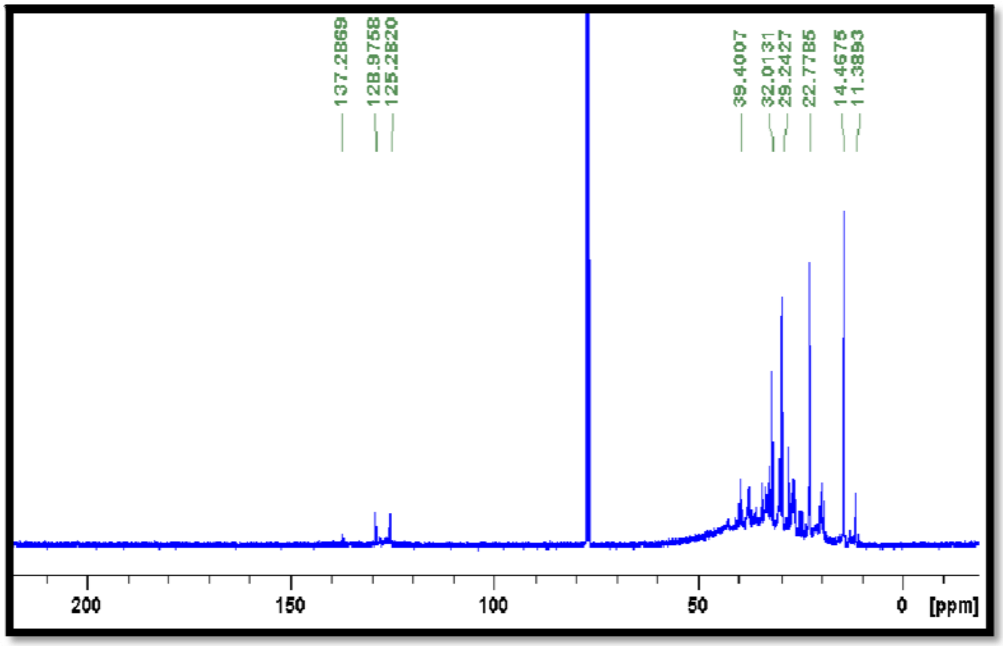

Figure 4.5 ^{13}C NMR of virgin transformer oil.

Characteristic FT-IR data of a naphthenic based virgin transformer oil shown in Figure 4.3, illustrates the C-H stretching of methyl groups at 2950 and 1376 cm^{-1}, C-H stretching in methylene bonds at 2920 and 2853 cm^{-1}, C=C stretching of aromatic groups at 1456 cm^{-1} and C-H out of plane bending vibrations of aromatic groups (Ar-H) at 741 cm^{-1}, the accompanying =C-H stretch is not observed. Data obtained from FT-IR spectra was reinforced by ^{1}H and ^{13}C NMR analysis (Fig. 4.4 and 4.5 respectively). Peaks obtained in ^{1}H and ^{13}C NMR at 7.1-7.2 ppm and 125-137 ppm regions respectively are characteristic of aromatic groups. Other peaks identified in ^{1}H and ^{13}C NMR in the 0.2-2.9 ppm and 11-39 ppm regions respectively are indicative of -CH_3, -CH_2 and -CH groups.

The identification of characteristic components in a naphthenic based virgin transformer oil by GC-MS (Figure 4.6, Table 5) was achieved through comparison of data from a NIST library.

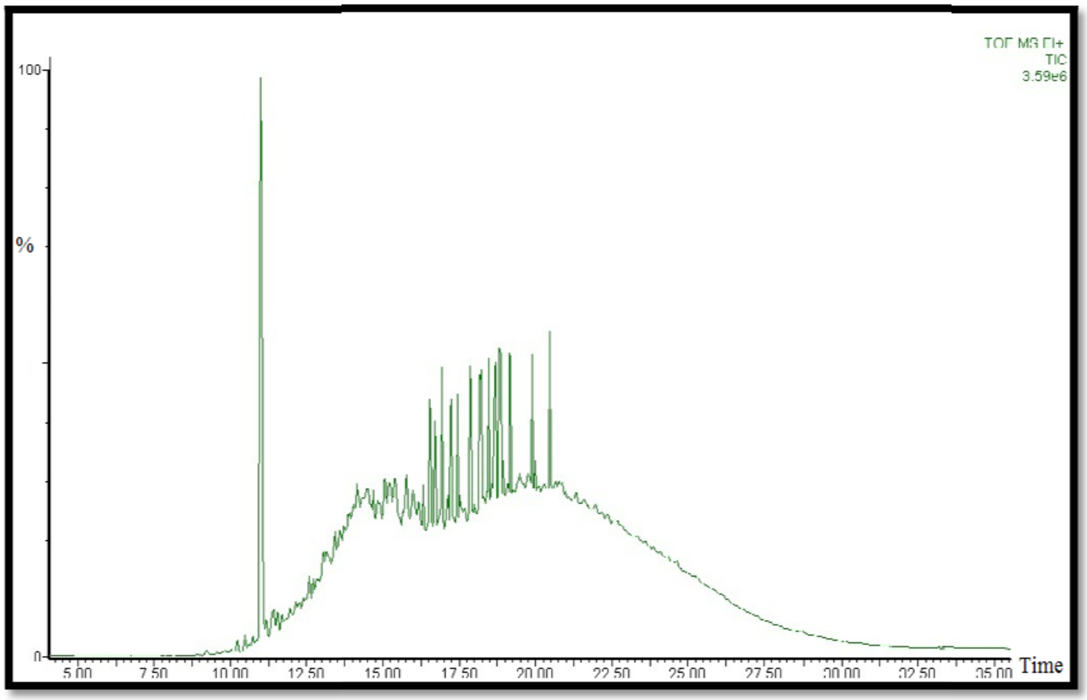

Figure 4.6 GC spectra of a naphthenic based virgin transformer oil.

Components shown in Table 5 were identified using mass spectral data that was based on a minimum certainty factor of 80%. A characteristic base line drift (oil hump) is observed in GC spectra for naphthenic based oil (Fig. 4.6).

Of interest to note from data obtained in Figure 4.6 and Table 5 is the presence of components such as tetralin and derivatives thereof. Tetralin is an additive that reduces the gassing tendency of transformer oils. Other components are six carbon cyclo rings that are generally found in naphthenic based oils [13].

Table 5 Components of a naphthenic based uninhibited virgin transformer oil and their retention times identified by GC-MS.

Component	**Retention time/ min**
butylcyclohexane	8.63
trans-bicyclodecane	9.22
undecane	9.73
Cis- bicyclodecane	10.02
trans-2-methyldecalin	10.21
2,3-Dihydro-5-methyl-1H-indene	10.59
cis-2-methyldecalin	10.62
2,4-Dimethylstyrene	10.74
Tetralin	10.97
Dodecane	11.43
Cyclopentylcyclohexane	11.54
Hexylidencyclohexane	11.55
6-methyldodecane	11.65
6-methyltetralin	12.72
n. id	13.41
1-methyl-4-(4-methylcyclohexyl)cyclohexane	14.90
Decahydro-4,4,8,9,10-pentamethylnaphthalene	15.79
2-Dodecen-1-yl(-)succinic anhydride	18.17
Z,E-2,13-Octadecadien-1-ol	18.46
1-Heptatriacontanol	19.89
Z,Z-3,15-Octadecadien-1-ol acetate	20.46
n. id	24.33

Successful blending of antioxidants with the virgin transformer oil has been verified by the functional groups as identified from FT-IR data (Table 6), ^{1}H and ^{13}C NMR (Table 7).

Table 6 Functional groups of compounds in blended virgin transformer oils from FT-IR spectra.

Blends	**Wavenumber/ cm^{-1}**	**Functional Group**	**Explanation**
0.3% BHT-Virgin Transformer Oil	3649	-OH	Hydroxyl group possibly attached to a benzene ring
	1231	C-OH	C-O stretch on the benzene ring possibly attached to OH group
	859	CH	CH on the benzene ring that is meta di substituted
0.3% DBP-Virgin Transformer Oil	3650	OH	Hydroxyl group attached to a benzene ring
	1230	C-OH	C on the benzene ring attached to OH group

Table 7 Identification of functional groups of compounds in blended virgin transformer oils from ^{1}H and ^{13}C NMR spectra.

Blend	**NMR**	**Chemical Shift/ ppm**	**Explanation**
0.3% BHT-Virgin Transformer Oil.	**^{1}H**	5.08	OH
		2.4	CH_3 (aromatic methyl group)
		1.57	CH_3 (tert. butyl groups)
	^{13}C	34.26	C (quaternary carbon)
		32.1	CH_3 (aromatic methyl group)
		30.39	CH_3 (tert. butyl groups)
0.3% DBP-Virgin Transformer Oil.	**^{1}H**	5.08	OH
		1.57	CH_3 (tert. butyl groups)
	^{13}C	30.39	CH_3 (tert. butyl groups)
		34.4	C (quaternary carbon)

The antioxidants, BHT and DBP, which are free radical scavengers are used as additives to terminate, reduce or significantly slow down free radical process [4]. The antioxidant activity was monitored by a change in the concentration of DPPH, a stable free radical [7].

An electron transfer to DPPH leads to a decrease in absorbance observed at 515-517 nm [7]. Figure 4.7 represents the DPPH concentrations of oil and oil blends.

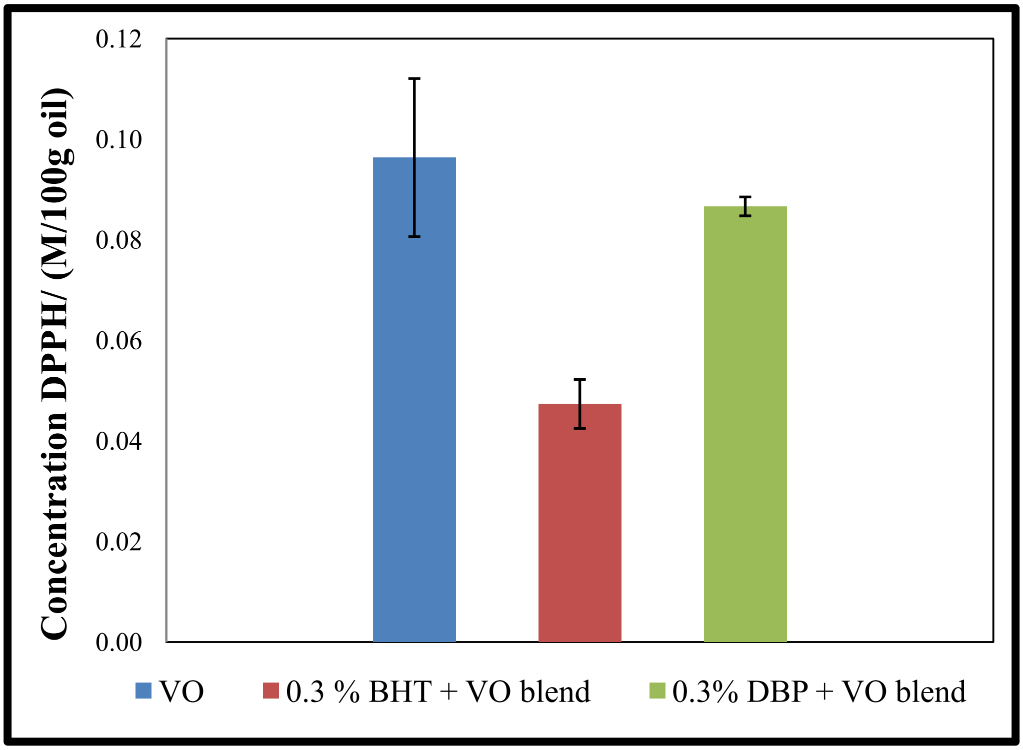

Figure 4.7 Change in concentration of DPPH (per 100 g of virgin transformer oil/blended transformer oil) monitored over a 30 minute period.

A decrease in the concentration of DPPH when comparing uninhibited oil (VO) to inhibited oil (doped with antioxidants) is clearly evident. Thus an addition of the specified antioxidants has increased free radical scavenging ability of the oil. The BHT-oil blend is shown to have a higher DPPH scavenging ability than the DBP-oil blend.

TGA data shown in Fig. 4.8 reflects the thermal stability and weight loss of the virgin oil and oil blends upon accelerated degradation. The onset of degradation for virgin oil, a BHT-oil blend and a DBP-oil blend was found to be 137.72, 139.64 and 144.63 °C respectively. This indicates that the onset of degradation of the oil shifts to a higher temperature upon blending with AO.

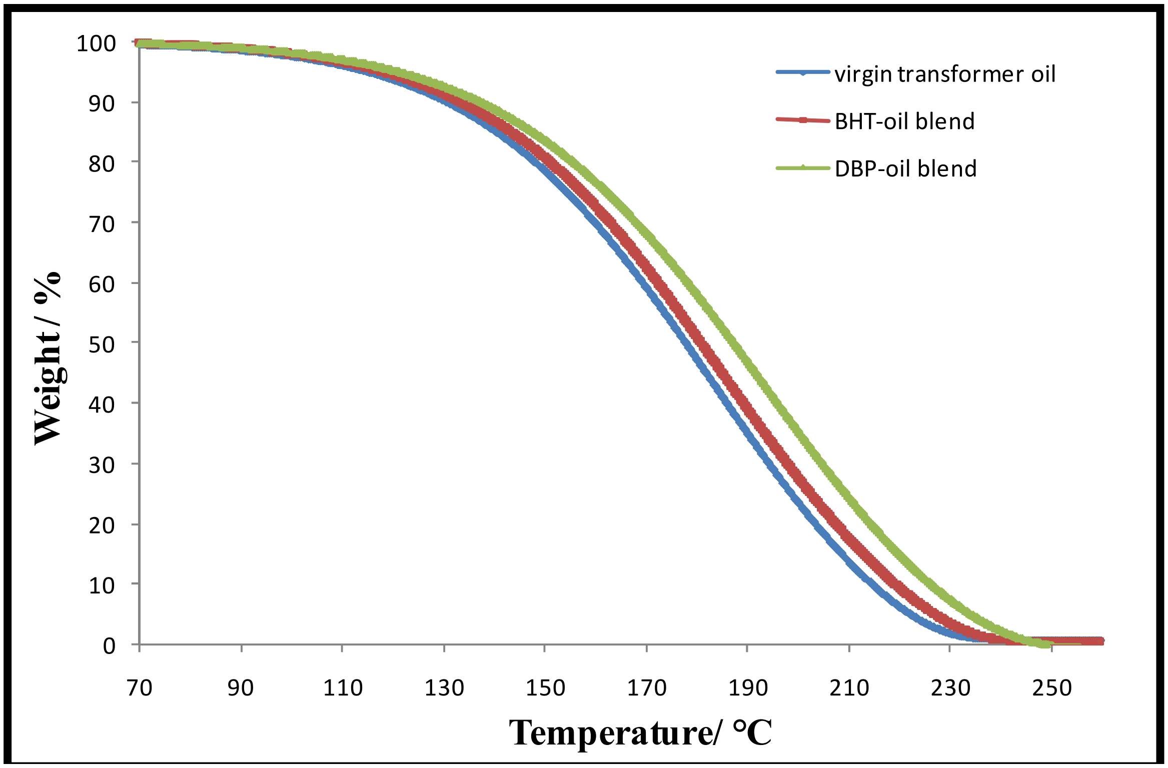

Figure 4.8 TGA of virgin transformer oil and AO-oil blends.

The accelerated ageing study was carried out in a UV digester that initiated rapid ageing over a limited period of time. In this study the concentration of BHT and DBP was monitored over 24 hours with exposure to UV radiation. The results are shown in Figure 4.9.

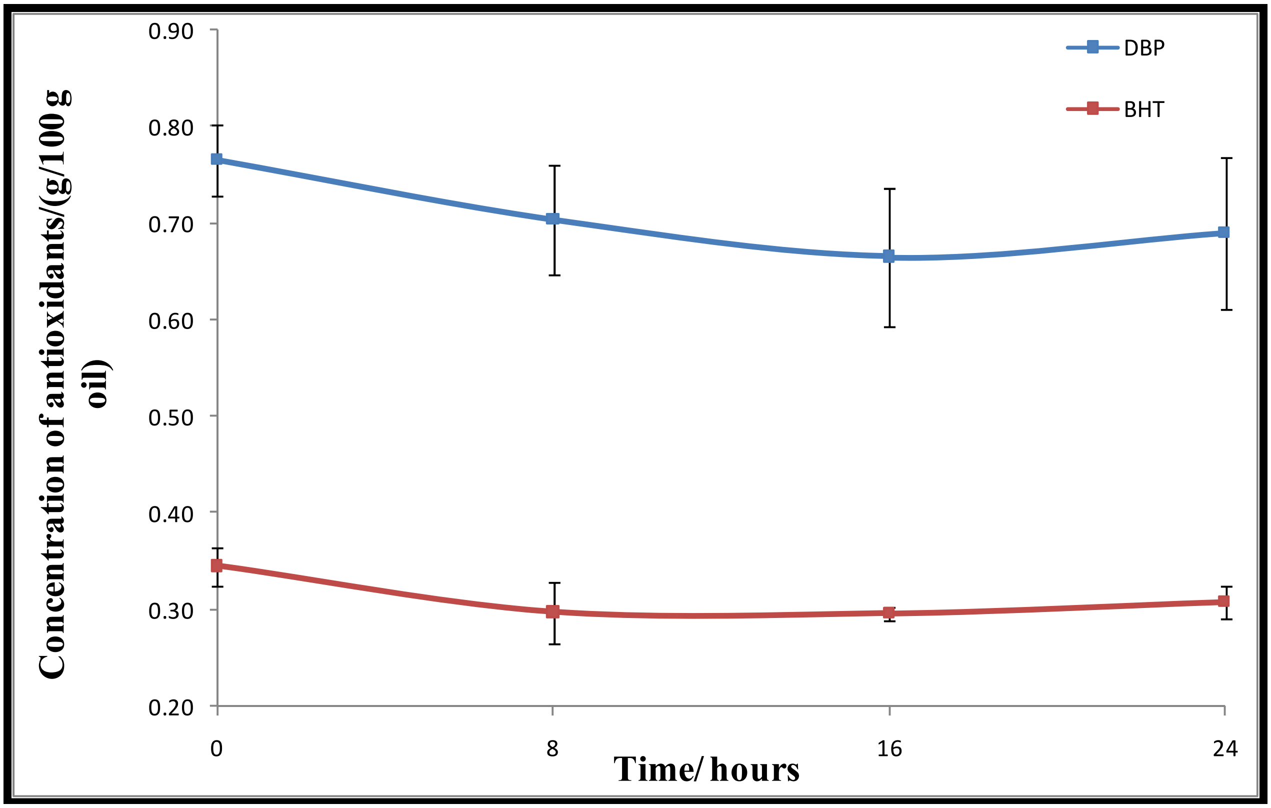

Figure 4.9 Concentration of BHT and DBP over a 24 hour UV exposure period.

A decrease in concentrations of DBP and BHT was observed (Figure 4.9) over the 24 hour time period relative to their initial concentrations. This may be attributed to the oxidation of antioxidants themselves as predicted by the analysis of oxidation products following UV digestion by GC-MS. Identification of products resulting from BHT oxidation included: 2,4-di-*tert*-butyl-6-methylphenol [*m/z* = 220, 205, 191, 55] (a tautermization product), 4,4'-(ethane-1,2-diylidene)bis(2,6-di-*tert*-butylcyclohexa-2,5-dienone) [*m/z* = 433, 218 and 207] and 4,4'-(ethene-1,2-diyl)bis(2,6-di-*tert*-butylphenol) [*m/z* = 435, 234, 123, 57]. The formation of dimerised products in dry media has been reported by Foley and Kimmerle (1979) [14]; however in media with trace amounts of water present it is possible that degradation of BHT follows a radical and ionic pathway [14]. In the oxidation of DBP, the isomeric product 2,5-di-*tert*-butylphenol was successfully identified.

4.4 CONCLUSION

Naphthenic based uninhibited virgin transformer oil has been successfully blended with AO's and their indicative characteristic chemical properties identified. Aromatic additives, such as tetralin, that is used to reduce the gassing tendency of oil [15] is prevalent in virgin oil.

The presence of metals and non metals such as Mg, Ca or P can be attributed to the fact that they possess antiwear or antioxidant properties. However virgin oil was found to be void of wear metals that catalyse oxidation reactions. Blending of virgin transformer oils with DBP and BHT was found to be successful as shown by NMR and FT-IR data. DPPH assay showed an increase in the free radical scavenging ability of blended oils compared to that of virgin oil; TGA confirmed an increase in thermal stabilities of AO-oil blends. Small changes in the concentration of BHT and DBP over 24 hour exposure to UV digestion were observed.

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REFERENCES

[1] Verma P., Condition monitoring of transformer oil and paper, Electrical and Instrumentation Engineering, Thapar Institute of Engineering and Technology **2005**, *Doctor of Philosophy*.

[2] Heathcote M. J., J & P Transformer Book, Elsevier, **2007**.

[3] Meshkatoddini M. R., Aging study and lifetime estimation of transformer mineral oil, *American Journal of Engineering and Applied Sciences*, **2008**, *4*:384-388.

[4] Gray I. A. R., Oxidation inhibitors for insulating oils, Transformer Chemistry Services, Durban, www.satcs.co.za/Oxidation_inhibitors_for_insulating_oil-IARGray2008.pdf (accessed 19 July 2010).

[5] Goncalves I. M., Murillo M. and Gonza´lez A. M., Determination of metals in used lubricating oils by AAS using emulsified samples, *Talanta*, **1998**, *47*:1033-1042.

[6] Wiklund P., Karlsson C. and Levin M., Determination of Hydroperoxide Content in Complex Hydrocarbon Mixtures by Gas Chromatography/Mass Spectrometry, *Analytical Sciences*, **2009**, *25*:431-436.

[7] Lee J. M., Chung S., Chang P. and Lee J. H., Development of a method predicting the oxidative stability of edible oils using 2,2-diphenyl-1-picrylhydrazyl (DPPH), *Food Chemistry*, **2007**, *103*:662–669.

[8] Hamrick L., Transformer Oil Sampling, **2009**, ESCO Energy Services Company, www.netaworld.org/files/neta-journals/NWsu09_Hamrick.pdf (accessed 4 January 2011).

[9] Dong J., Van de Voort F., Yaylayan V. and Ismail A., A new approach to the determination of moisture in hydrocarbon lubricating oils by mid-FTIR spectroscopy, **2009**, Thermal-lube Inc, www.thermal-lube.com (accessed 29 April 2011).

[10] Robinson N., Transformer oil analysis, **2006**, Wear Check Africa, www.wearcheck.co.za (accessed 7 December 2010).

[11] Gray I. A. R., Dissipation factor, power factor and relative permittivity (dielectric constant), Transformer Chemistry Services, Durban www.satcs.co.za/TanD-Res-info.pdf (accessed 19 July 2010).

[12] Chausseau M., Lebouil-Arlettaz S. and Thomas G., Wear Metals and Additive Elements Analysis in Used Lubricating Oils Using ICP-OES, **2010**, Horiba Scientific Instruments and systems, Longjume au, www.horiba.com/scientific/ (accessed 21 June 2010).

[13] Rouse T. O, Mineral Insulating Oils in Transformers, *IEEE Electrical Insulation Magazine*, **1998**, *14*:6-16.

[14] Foley L. and Kimmerle F. M., Pulse Voltammetric Determination of Butylated Hydroxy Toluene in Transformer Oils, *Analytical Chemistry*, **1979**, *51*:818-822.

[15] Lombard A., Transformer oil chemistry affecting the South African market, **2010**, Energize, www.eepublishers.co.za/images/.../01_TT04_Transformer%20Oil.pdf (accessed 18 January 2011).

CHAPTER 5

MANUSCRIPT II

PHYSICO-CHEMICAL PROPERTIES OF TRANSFORMER OIL BLENDS WITH ANTIOXIDANTS EXTRACTED FROM TURMERIC POWDER

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ABSTRACT

The blending of transformer oil with appropriate synthetic antioxidants, such as 2,6-di-*tert*-butyl-4-methylphenol (butylated hydroxyl toluene-BHT) and 2,6-di-*tert*-butylphenol (DBP) has been previously reported. This paper is focused on the use of antioxidant extracts from turmeric (*Curcuma longa)*, a natural source. Turmeric is well known for its antimicrobial, antioxidant and anticarcinogenic properties owing to the active nature of its components. Extracts from powdered turmeric were subsequently blended into naphthenic based uninhibited virgin transformer oil, herein-after referred to as extract-oil blends (E-OB). Analysis of the oil blends by thin layer chromatography (TLC) revealed that five components extracted from turmeric powder blended successfully into the oil. Identification of the components by gas chromatography-mass spectrometry (GC-MS) confirmed the presence of the compounds: curcumene, sesquiphellandrene, *ar*-turmerone, α-turmerone and curlone. Thermogravimetric analysis (TGA) of the extract-oil blends, containing various levels of extracts, revealed an average temperature shift of approximately 8.21°C in the initial onset of degradation in comparison to virgin non-blended oil.

The 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay showed that increasing the fraction (composition) of turmeric extracts in the transformer oil increased the free radical scavenging activity of the oil. Electrical properties of the oil investigated showed that the dissipation factor in the blended oil was found to be lower than that of virgin transformer oil. Evidently, a lower dissipation value renders the oil blend as a superior insulator over normal virgin non-blended oil. The study showed overall improved physico-chemical properties of transformer oil blended with turmeric antioxidant extracts.

5.1 INTRODUCTION

In order to increase the stability of a transformer oil, blending of antioxidants (AO's) into the oils has been reported [1]. AO's that are currently used include BHT and DBP. This paper reports the use of antioxidants extracted from natural sources and subsequent blending of these antioxidants into transformer oil. Turmeric has been widely used in traditional medicine for the treatment of various ailments [2]. The powder is produced by boiling fresh rhizomes in water with subsequent drying in sunlight for approximately 10 days [3]. It is in this form that turmeric is known for its use in Asian cuisines to impart aroma and colour [4]. Turmeric is composed of different active components such as curcuminoids, viz. curcumin, demethoxycurcumin and bisdemethoxycurcumin. Components contained in the volatile oil include *ar*-turmerone, α-turmerone, *ar*-curcumene, curlone and other sesquiterpenes [5]. Curcumin is found to be the most active of the curcuminoids [6]. The focus of this study is to extract components of turmeric powder and ensue blending of this extract with virgin transformer oil, in an effort to effectively impart stability. Consequently, increasing the oxidation stability of the oil through blending is envisaged not to impede the electrical properties of the oil and its properties as a suitable dielectric fluid.

Studies on the effect of turmeric carried out on vegetable oils showed increased AO activity.

For example, in a study on groundnut oil (a vegetable oil) turmeric was found not only to reduce the formation of peroxides but showed an increase in shelf life [7]. In addition, alcoholic extracts of turmeric functioned as effectively as the commercial AO, butylated hydroxyanisole [7]. In this study, the effects of blending turmeric extracts with virgin transformer oil were investigated in terms of the oil's oxidative stability and other physico-chemical properties.

In order to monitor the free radical scavenging activity of the extract-oil blends, the DPPH assay was carried out. Finally, TGA was used to determine if the extract-oil blends improved the thermal stability of the oil.

5.2 METHODS AND MATERIALS

All chemicals used were of analytical grade.

5.2.1 AO Extraction from Turmeric Powder with suitable solvents

Turmeric powder (Osmans Taj Mahal®- Extra Special Turmeric Powder) was coned and quartered in order to obtain a representative sample. A 20 g sample of turmeric was added to 50 mL of dichloromethane (DCM) and refluxed for one hour. The mixture was vacuum filtered, the solid discarded and the filtrate concentrated by solvent evaporation. The filtrate residue was triturated with 99.9% ethanol [8].

The ethanol aliquot was subsequently blended with 1 g of naphthenic based virgin transformer oil. The undissolved resin in the oil was discarded and the blend filtered with a cotton wool plug. The blend was set aside and labeled as "*extract-oil blend1 (E-OB1)*". The experiment was repeated with 40 g of turmeric refluxed in 50 mL of DCM. This extract was labeled as *extract-oil blend2 (E-OB2).* The experiment was repeated with 60 g, and 100 g to obtain *E-OB3 and E-OB5* extracts.

5.2.2 Thin Layer Chromatography (TLC)

The homogenisation of AO turmeric extracts and transformer oils was investigated by TLC. Development of TLC plates was carried out using a 99% DCM: 1% methanol (v/v) solvent system. The R_f values for each of the components were calculated.

5.2.3 GC-MS Analysis

Identification of extracted AO turmeric components was carried out using GC-MS (Agilent 6890 GC system, column type: DB5-MS). Samples were dissolved in DCM and injected into the GC-MS.

Injector temperature: 280 °C. The column parameters are given in Table 8 (temperature ramping).

Table 8 GC column conditions for the separation of extract-oil blends.

T_i/ ºC	Ramp rate/ ºC min^{-1}	T_f/ ºC	Hold time/ min
70	20	100	1
70	20	150	1
150	15	280	4

5.2.4 DPPH Assay

Oil blends of mass 0.2 g were reacted with 3 mL of a 1.97×10^{-1} mmol L^{-1} DPPH solution made up with DCM. The absorbance of DPPH radicals were monitored over a period of 30 minutes at 517 nm using a Perkin Elmer Lamda 35 UV VIS Spectrometer. All samples were analysed in triplicate. A blank was prepared dissolving 0.2 g of the oil blend in 3 mL of DCM.

5.2.5 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis of oils and extract-oil blends were run in duplicate using TGA (Universal Analysis 2000 by TA Instruments).

Samples were run in air at a temperature ramp rate of 5 ºC min^{-1} starting at room temperature (20-25 ºC) to 300 ºC.

5.2.6 Dissipation Factor Test

The dissipation factor was obtained on the Tettex 2820 at a frequency of 50 Hz and voltage values of 2, 4, 6, 8, 10, 12, 14 kV using a glass test cell with copper electrodes (diameter 2 cm) having a gap of 3 cm. The tests were conducted at room temperature.

5.3 RESULTS AND DISCUSSION

Analysis of the extract-oil blends by thin layer chromatography indicated the appearance of five additional components in addition to transformer oil (the uppermost band which moved with the solvent front). Of the five incorporated components, the three coloured components corresponded to R_f values of 0.06, 0.13 and 0.35 respectively (λ= 365 nm) while the remaining two bands identified at λ= 254 nm corresponded to R_f values of 0.78 and 0.89 respectively.

Confirmation of blending was also achieved through gas chromatographic separation where all 5 peaks identified, by mass spectrometry, corresponded to the components of turmeric (Figure 5.1).

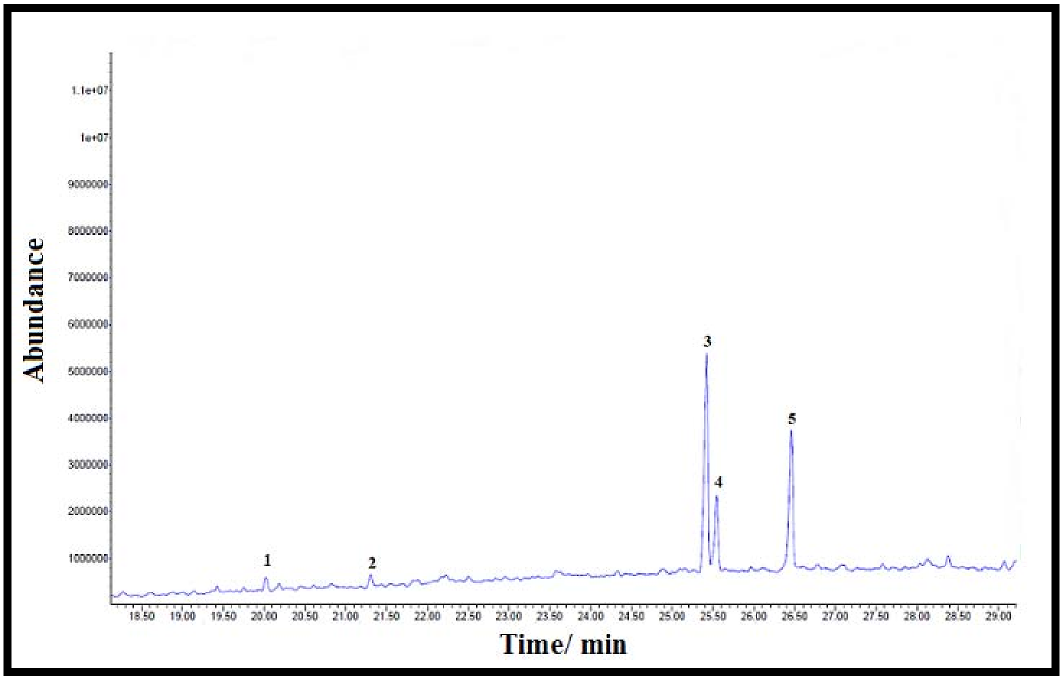

Figure 5.1 A gas chromatogram of an extract-oil blend. The labeled peaks show the constituents of turmeric extract which blended with the virgin transformer oil.

Recorded mass spectrometric data of each component from turmeric in the extract-oil blend are presented in Table 9. Identification of turmeric extracts was carried out using, collectively, the NIST97 and NIST08 databases.

The turmeric extract components were positively identified as curcumene (**1**), sesquiphellandrene (**2**), *ar*-turmerone (**3**), turmerone (**4**) and curlone (**5**).

Table 9 Mass spectrometric data of extract-oil blends showing the different components.

Peak.	**Retention time/ min**	**Mass spectrometric data**	**Compound Id**
1	20.025	119 (100), 132 (85), 105 (56), 202 (34)	curcumene
2	21.318	69 (100), 41 (66), 93 (53), 149 (41), 161 (34), 204 (17)	sesquiphellandrene
3	25.407	83 (100), 119 (68), 201 (20), 216 (29)	*ar*-turmerone
4	25.543	83 (100), 105 (94), 120 (50), 200 (5), 218 (5)	turmerone
5	26.453	83 (30), 105 (16), 120 (100), 218 (2)	curlone

The DPPH assay was carried out to study the effect that an increase in the amounts of extracts, in oil blends, has on its free radical scavenging ability (Figure 5.2). The scavenging reaction for O-BE3 and O-BE5 was completed in less than 5 minutes, while that for O-BE1 and O-BE2 took a longer time to reach completion (8 and 6 minutes respectively).

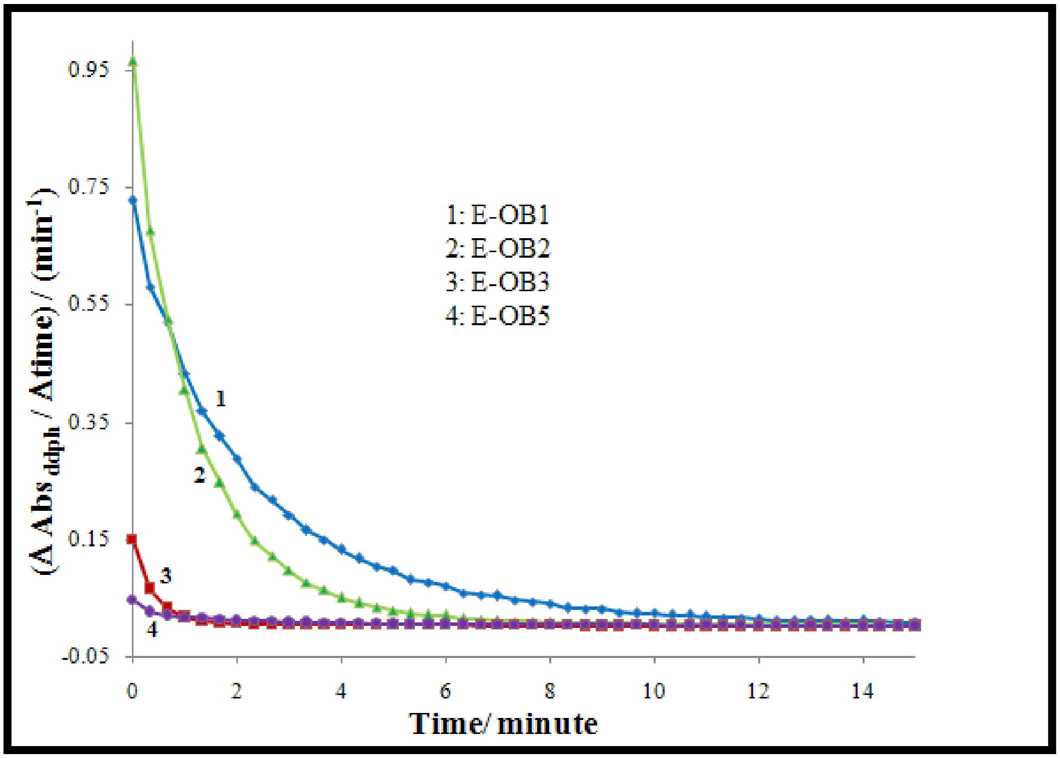

Figure 5.2 UV-Vis absorbance of DPPH at 517 nm.

It is therefore evident that the free radical scavenging activity increased with an increase in turmeric extract. This was expected as a result of an enhanced antioxidant activity of the components in the extract-oil blend. A comparative study between fresh and dry rhizomes of turmeric showed that antioxidant activity of fresh rhizomes was superior to that of dry rhizomes [9]. This could possibly be attributed to a larger amount of alpha- and beta-turmerone present in fresh rhizomes [9]. This implies that antioxidant activity of alpha- and beta-turmerone has the potential to contribute significantly toward enhancing the antioxidant properties of transformer oils into which it is blended.

TGA results have shown that blended oils (including the E-OB1) compared to virgin oil shifted to a higher initial onset of thermal degradation. On average the various extract oil blends shifted from a temperature of 137.72 °C, the initial onset of thermal degradation for the virgin transformer oil (reported in our previous studies under similar conditions [10]), to 145.93 °C.

Our results are in close agreement (in fact superior) with previous studies on antioxidants such as DBP and BHT oil blends, that displayed initial onset degradation temperatures of 144.63 and 139.64 °C respectively [10].

Increase in the levels of extracts in the E-OB's, according to TGA results (Figure 5.3), showed marked increases in the initial onset degradation temperature. However it was observed that as the level of the extract in the blend increased, the residual mass of the E-OB also increased, whereas virgin oil was completely degraded as shown by TGA in Figure 5.3.

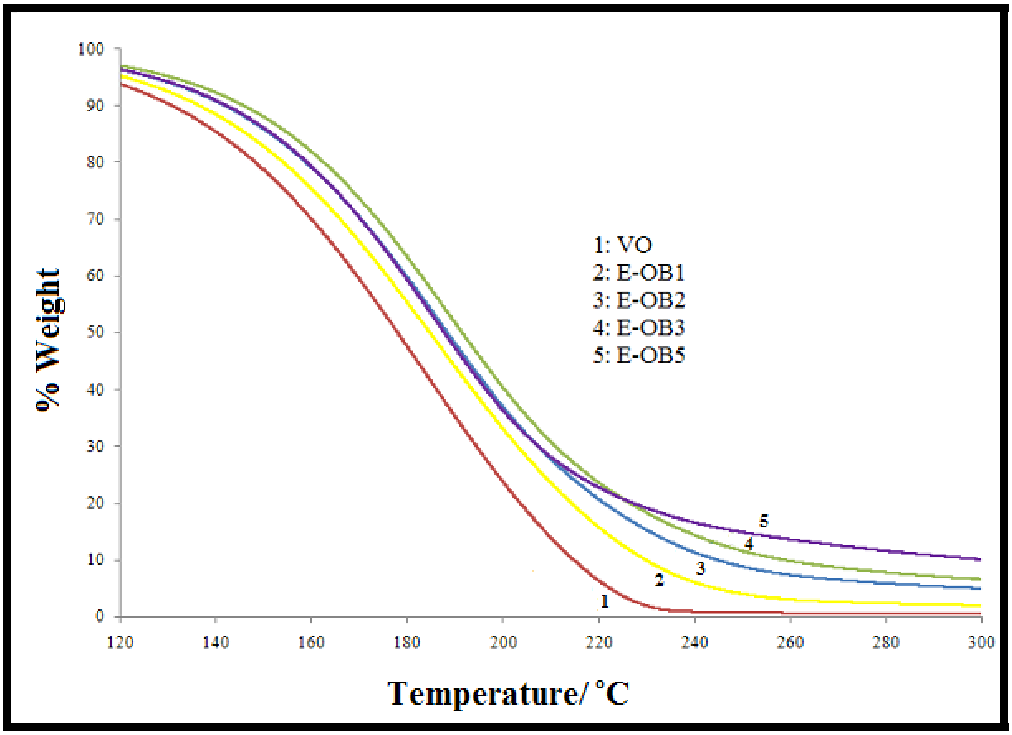

Figure 5.3 TGA of virgin transformer oil and extract-oil blends at a ramp rate of 5 °C min^{-1}.

Despite obtaining favourable results from the antioxidant and thermal stability tests, further evaluations are deemed necessary to confirm the efficacy and functioning of extract-oil blends as effective insulators and /or coolants.

Figure 5.4 shows a decrease in the dissipation factor of the extract-oil blends when compared to that of virgin transformer oil.

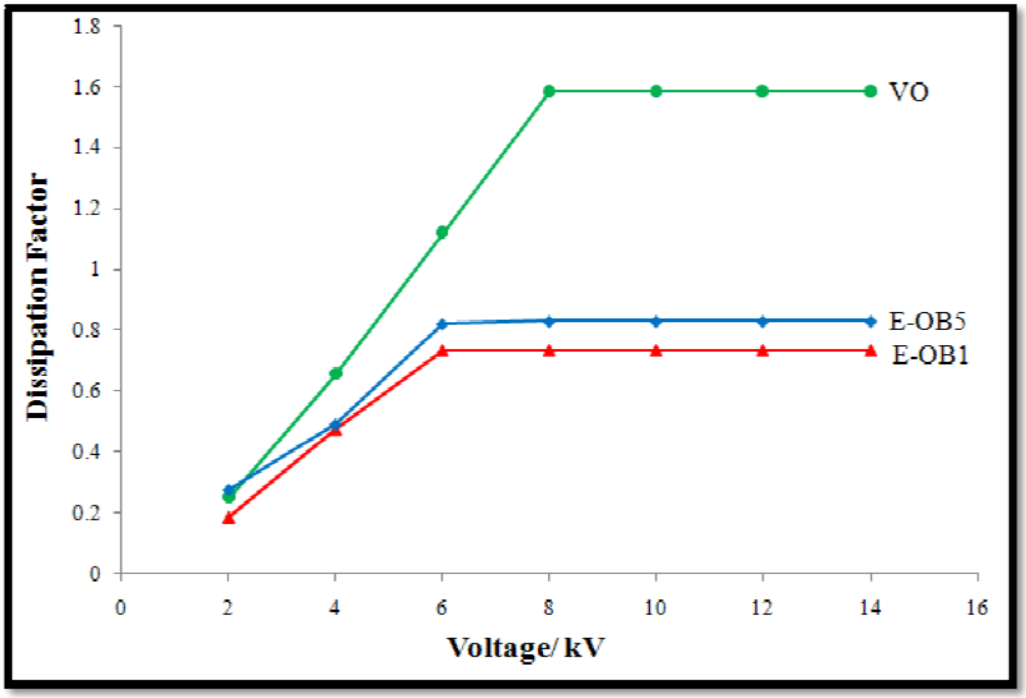

Figure 5.4 Dissipation factor of virgin oils and extract-oil blends at different voltages carried out at a frequency of 50 Hz, at a temperature range of 20-25 ºC.

Generally, a low dissipation factor facilitates efficient functioning of transformer oil as an effective dielectric. Figure 5.5 highlights the acquisition of higher electrical resistance by E-OB1 and E-OB5, over virgin transformer oil, thus rendering it a more efficient and suitable dielectric fluid.

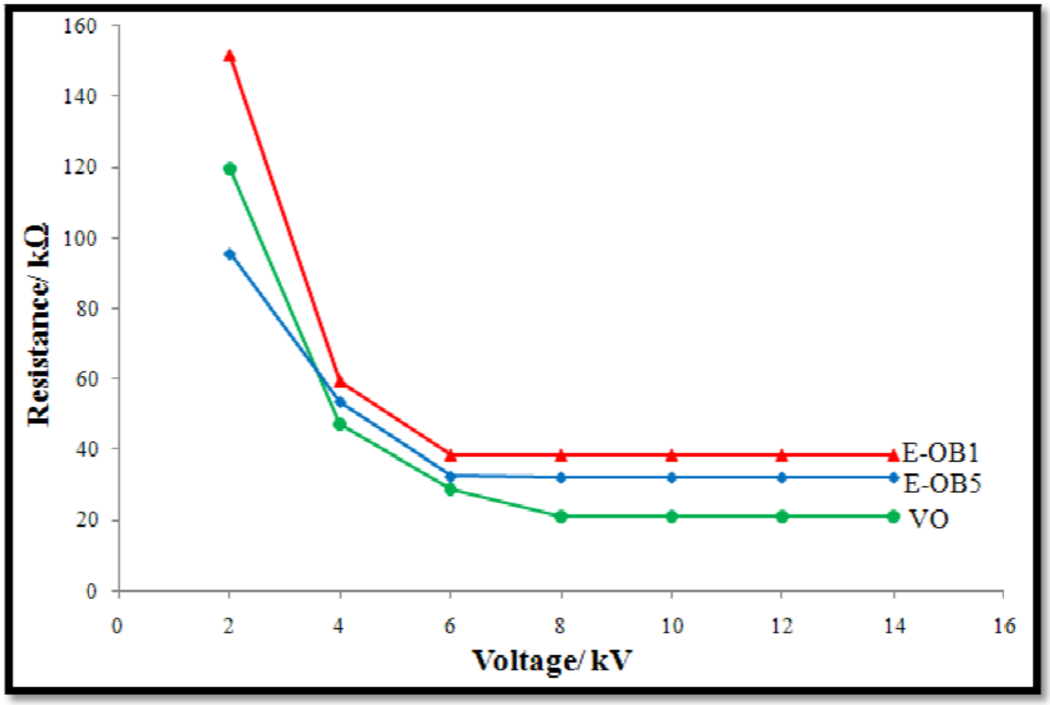

Figure 5.5 Electrical resistance of oils and extract-oil blends at different voltages, frequency of 50 Hz carried out at a temperature range of 20-25 ºC.

5.4 CONCLUSION

The extract-oil blends showed improved thermal stabilities when compared to virgin transformer oil as deduced from the TGA results. This was possibly attributed to an increase in the antioxidant content obtained from the turmeric powder (DPPH assay). Dissipation factor results also showed admirable properties making it suitable to use extract-oil blends as an insulator in transformers. Notwithstanding these encouraging results, further investigations to optimize the use of extract-oil blends as possible dielectric fluids are in progress.

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REFERENCES

[1] Neto R. C. R., Lima D. O., Pinheiro T. D. S., Almeida R. F., Dantas T. N. C., Dantas M. S. G., Arau´ jo M. A. S., Cavalcante C. L. and Azevedo D. C. S., Thermo-Oxidative Stability of Mineral Naphthenic Insulating Oils: Combined Effect of Antioxidants and Metal Passivator, *Industrial and Engineering Chemistry Research*, **2004**, *43*: 7428-7434.

[2] Jayaprakasha G.K., Jagan L., Rao M. and Sakariah K.K., Chemistry and biological activities of *C. longa*, *Trends in Food Science & Technology*, **2005**, *16*:533-548.

[3] Hiserodt R., Hartman T. G., Ho C. and Rosen R. T., Characterization of powdered turmeric by liquid chromatography-mass spectrometry and gas chromatography-mass spectrometry, *Journal of Chromatography A*, **1996**, *740*:51-63.

[4] Sharma R.A., Gescher A.J. and Steward W.P., Curcumin: The story so far, *European Journal of Cancer* **2005**, *41*:1955-1968.

[5] Surwase V.S., Laddha K.S., Kale R.V., Hashmi S. I. and Lokhande S.M., Extraction and Isolation of Turmerone from Turmeric, *Electronic Journal of Environmental, Agricultural and Food Chemistry*, **2011**, *5*:2173-2179.

[6] Asghari G., Mostajeran A. and Shebli M., Curcuminoid and essential oil components of turmeric at different stages of growth cultivated in Iran, *Research in Pharmaceutical Sciences*, **2009**, *1*:55-61.

[7] Selvam R., Subramanian L., Gayathri R. and Angayarkanni N., The anti-oxidant activity of turmeric (*Curcuma longa*), *Journal of Ethnopharmacology*, **1995**, *47*:59-67.

[8] Anderson A. M., Mitchell M. S. and Mohan R. S., Isolation of Curcumin from Turmeric, *Journal of Chemical Education* **2000**, *77*:359-360.

[9] Singh G., Kapoor I. P. S., Singh P., de Heluani C. S., de Lampasona M. P. and Catalan C. A. N., Comparative study of chemical composition and antioxidant

activity of fresh and dry rhizomes of turmeric (*Curcuma longa Linn.*), *Food and Chemical Toxicology*, **2010**, *48*:1026-1031.

[10] Dukhi V., Bissessur A., Ngila J. C. and Ijumba N., Characterisation of a naphthenic based uninhibited virgin transformer oil and the use of synthetic antioxidants., *XVII International Symposium on High Voltage Engineering* (Hannover, Germany) **2011**.

CHAPTER 6

MANUSCRIPT III

THE DETERMINATION OF KINETIC PARAMNETERS OF TRANSFORMER OIL AND ITS BLENDS BY THERMAL ANALYSIS

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ABSTRACT

The insulation of transformer oil comprises of two practices: paper and dielectric fluid (such as mineral transformer oil). Ageing of these oils are induced mainly by thermal, electrical and oxidative stresses. This paper describes the determination of kinetic parameters of a naphthenic based transformer oil and its blends based on the Ozawa, Flynn and Wall (OFW) and Kissinger models using data obtained from thermogravimetric analysis and differential scanning calorimetric, curves. Virgin oil and its blends were analysed from an initial temperature range of 20-25 °C to 300 ºC at temperature ramps of 1, 2, 4, 6, 8, and 10 ºC min^{-1}. The OFW method in conjunction with TGA data was used to calculate the apparent activation energies at each of the selected weight loss (% conversion) values. The activation energies at 10% weight loss were found to be 57.0, 63.7 and 69.3 kJ mol^{-1} for BHT-B, DBP-B and VO, respectively. However, using this method the Ea of the oils showed no significant difference between the virgin oil and its blends. The DSC curves revealed that the decomposition reaction was exothermic in nature. From the DSC data the activation energy was determined using two separate models: OFW and Kissinger methods. Activation energy results from the DSC data showed no significant difference when compared between these two models.

Dissipation factor tests showed superior results for the blends when compared to those of virgin transformer oil. However, the blends showed substantial reductions in their dielectric breakdown voltage. The implication of the reduced breakdown voltage is that the blends show poorer dielectric strength in comparison to virgin transformer oil.

6.1 INTRODUCTION

The efficiency of a transformer is dependent largely on the reliability of its insulation [1]. The bulk of the insulation material is transformer oil itself which is used as a coolant and insulator. Transformer oil is however unfortunately susceptible to ageing, a process where the oil is subjected to a series of oxidation reactions [2]. Ageing leads to the formation of oxidation products that are not only detrimental to the oil but also to the solid paper insulation. It has been established that transformer fouling and subsequent failure is a direct consequence of the ageing of its insulation [2].

Currently many transformer oils have additives blended into them; where the additives serve to retard the oxidation process. In this study 2,6-di-*tert*-butyl-4-methylphenol (BHT) and 2,6-di-*tert*-butylphenol (DBP) have been used as antioxidant additives [3].

Much research has focused on temperature dependence on the rate of reaction as per Arrhenius Law [4]. The Arrhenius Law together with other models have been used to successfully predict the lifetimes of many polymers, including that of transformer oils. A previous study by Meshkatoddini *et al.* (2008) [5] has shown that accelerated ageing of transformer oil and application of the Arrhenius Law can be used to predict the remaining lifetime of mineral oil. Conversely, accelerated ageing studies are rather time consuming and these could possibly take weeks of ageing before one can obtain kinetic parameters. A more favourable approach involves thermo-analytical techniques. These include both TGA and DSC. TGA is a technique that involves the monitoring of mass changes in a sample as a function of temperature under temperature controlled programming, whereas DSC is a comparison of the energy difference between the sample and a reference standard, for a set of programmed temperatures [6]. From this data the activation energy, the minimum amount of energy that is required for the decomposition of the oil can be obtained [4].

Activation energy provides adequate information for the determination of lifetime using some form of failure criterion [7] and can be used to denote the applicability of materials that are used as dielectrics [4]. This parameter can furthermore be employed to determine the suitability of different antioxidants and their optimum concentrations [8]. Increases in activation energies are correlated to greater resistance of the oil to decomposition [4].

In this study, two models are used to determine the activation energies of the decomposition reaction. Equation 6.1 [4] and Equation 6.2 [9] represents the relationship between β (heating rates), temperature (T) and activation energy (Ea), OFW and Kissinger models, respectively.

$$E = \frac{-R}{0.457}\left[\frac{\partial \log \beta}{\partial \frac{1}{T}}\right] \text{.......} \quad (6.1)$$

$$\ln\frac{\beta}{T^2} = \ln\frac{AR}{Ea} - \frac{Ea}{RT} \text{.......} \quad (6.2)$$

An understanding of the activation energy serves only as one of the controlling factors when oils are used as electrical insulators while electrical testing may also be an important aspect to consider. Electrical parameters that were investigated in this paper include: dissipation factor and dielectric breakdown voltage (DBV) testing. These factors were investigated for both the oil and its blends. The results from this study will add to an important database on innovative modification of transformer oils to improve the oil's performance.

6.2 METHODS AND MATERIALS

Virgin transformer oil (VO), virgin oil-BHT blends (BHT-B) and virgin oil-DBP blends (DBP-B) samples were analysed in duplicate with Universal Analysis 2000, TA Instruments. Thermal measurements of the samples were carried out under ambient air conditions ranging from room temperature (20-25 °C) to 300 ºC, at the following ramp rates: 1, 2, 4, 6, 8 and 10 ºC min^{-1}. The corresponding DSC and TGA data were recorded and analysed.

Dissipation factor tests were carried out using a glass test cell with copper electrodes (plate diameter 2 cm and plate gap of 3 cm) as shown in Figure 6.1 and set up in conjunction with the Tettex 2820 apparatus (Figure 6.2) [10]. Testing was carried out at room temperature (24 °C), frequency of 50 Hz and voltages of 2-14 kV in increments of 2 kV using an alternating current source were applied.

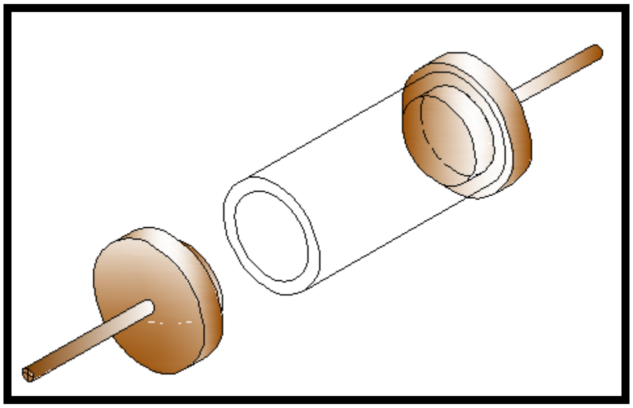

Figure 6.1 Glass test cell with copper plates.

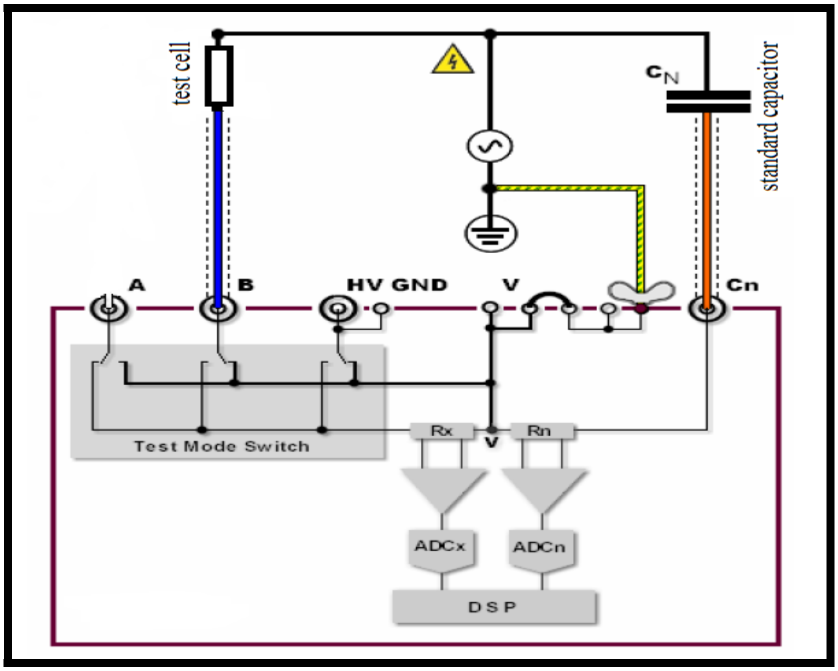

Figure 6.2 Circuit showing incorporation of the test cell using Tettex 2820 adapted from L & tan δ Measuring Bridge Version 1.8 Operating Instructions Haefely Test [10].

DBV testing was carried out in accordance with International Electro Technical Commission 156 (IEC 156) for samples VO, BHT-B and DBP-B.

6.3 RESULTS AND DISCUSSION

6.3.1 Determination of the decomposition activation energy

Due to the time consuming nature of isothermal methods, non-isothermal methods are preferred. The principle of non-isothermal methods is based on repetitive measurements of weight loss and heat flow at different heating-rates. Whilst there are different models/techniques that are used in the determination of activation energy, results in this study uses the OFW model to transform data obtained from TGA. The DSC data was also transformed based on the OFW and Kissinger methods.

6.3.1.1 Thermogravimetric Analysis

From derived TGA data, conversion values of 2.5, 5, 10, 25 and 50% were used to calculate activation energy. Figure 6.3 presents TGA curves of virgin transformer oil (VO) at different heating rates (**a-f**). It is evident that as the rate of heating increases a shift in thermograms to the right relative to its original position has been observed. In figure 6.3 it is also clearly evident that the decomposition reaction is a one step process and total thermal decomposition is achieved at the completion of the analysis. Figure 6.3 also shows how the data from TGA curves are used with respect to the OFW model to obtain temperatures for specified weight loss. For example, at a weight loss of 25%; the temperatures are determined for each β value (i.e. the heating rate). The temperatures for other conversion values are obtained in the same way.

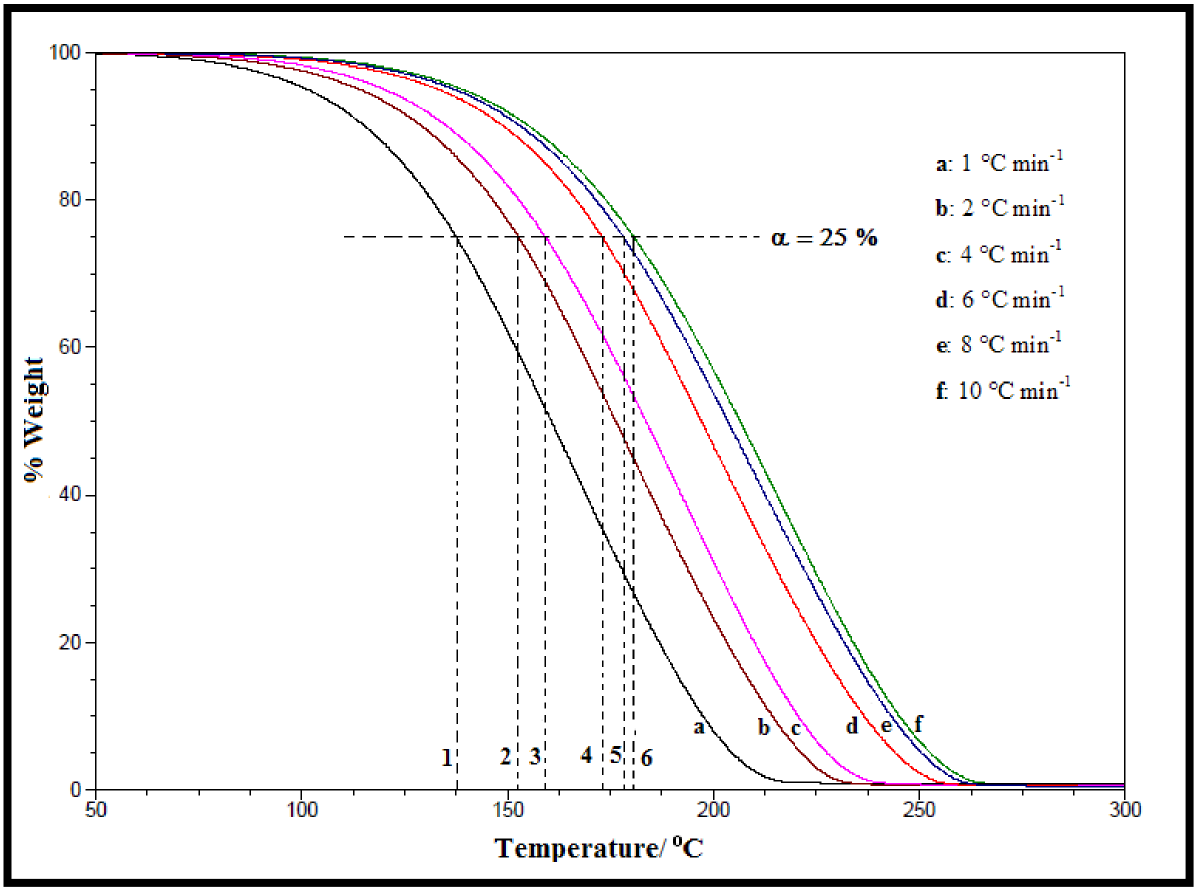

Figure 6.3 Thermograms of VO at different heating rates (**a-f**); **1-6** represents the temperatures obtained for different β values at 25% conversion.

The OFW plot is represented in Figure 6.4 and Table 10, summaries the activation energy of the oils at different α values.

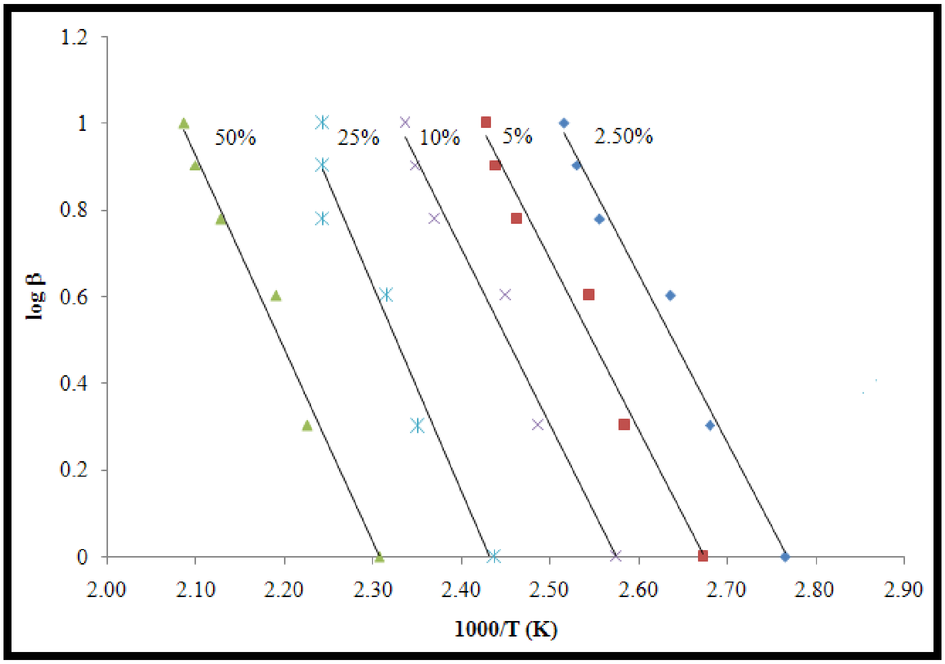

Figure 6.4 Plot of the log β verses 1000/T using the OFW model for virgin oil.

Table 10 Activation energies calculated for oil and oil blends at different conversion values using the OFW model.*

	Activation Energy/ kJ mol^{-1} *		
%α	**VO**	**BHT-B**	**DBP-B**
2.5	68.1 ± 1.5 $^{a\ b}$	60.9 ± 1.0 ^{a}	62.1 ± 0.5 ^{b}
5	68.7 ± 1.8 $^{c\ d}$	57.9 ± 0.9 ^{c}	62.7 ± 0.6 ^{d}
10	69.6 ± 2.3 $^{e\ f}$	57.0 ± 1.8 ^{e}	63.7 ± 0.5 ^{f}
25	76.8 ± 6.0 $^{g\ h}$	57.5 ± 2.7 ^{g}	65.8 ± 0.1 ^{h}
50	76.0 ± 3.4 $^{i\ j}$	59.2 ± 3.4 ^{i}	70.7 ± 1.3 ^{j}

***P ≤ 0.05. Means represented by the same letter across a row are not significantly different using the Student *t*-test. (95% confidence level).**

Activation energies that remain somewhat constant as a function of conversion have the same reaction mechanism for the entire decomposition reaction [4].

Generally at a 1% weight loss of oils during TGA, decomposition is attributed mainly to its water content thus evaluating data at 1% conversion is invalid [4]. The decomposition reaction showed activation energy values between 57 and 77 kJ mol^{-1} for the oil and oil blends. In order to compare the changes in activation energy between VO and BHT-B and VO and DBP-B, the statistical *t* test was carried out. The null hypothesis was accepted at 95% confidence level; therefore no significant difference between activation energies of VO and BHT-B and DBP-B was observed.

6.3.1.2 DSC Analysis

The DSC curves obtained for VO and blends show that there is a positive deviation from the baseline which is indicative of an exothermic reaction.

The initial calculated onset of degradation temperature (T_1) and the maximum heat flow temperature (T_p) from DSC measurements is instrumental in determining the activation energies of the decomposition reaction [11]. The activation energy, Arrhenius factor and rate constant at 90 °C [11-12] are recorded in Table 11.

Table 11 Activation energy, Arrhenius factor (Z) and rate constant (*K*) for oil and oil blends calculated using the OFW method and DSC data.*

		VO	**BHT-B**	**DBP-B**
T_i	**Ea/ kJ mol^{-1}**	66.3 ± 3.5	56.8 ± 3.8	58.7 ± 0.4
	Z/ s^{-1}	1.4×10^{8}	1.7×10^{7}	4.0×10^{6}
	$K_{90°C}$/ s^{-1}	4.1×10^{-2}	1.1×10^{-1}	1.5×10^{-2}
T_p	**Ea/ kJ mol^{-1}**	63.3 ± 3.0	53.0 ± 3.4	85.5 ± 3.0
	Z/ s^{-1}	4.1×10^{6}	1.7×10^{5}	1.2×10^{9}
	$K_{90°C}$/ s^{-1}	3.2×10^{-3}	4.1×10^{-3}	6.2×10^{-4}

$^*P \leq 0.05$.

The DSC data can also be evaluated with the Kissinger method [9]. This model utilises the maximum peak temperature of the DSC curve (T_p). The slope of the Kissinger plot [ln

(β/T^2) verses (1/T)] is used to determine the activation energy. The results of the activation energy from the Kissinger and OFW models are compared as shown in Figure 6.5.

The values obtained by the OFW and Kissinger models were statistically analysed by paired data *t*-test at 95% confidence. On the basis of the paired *t*-test, the two models for determination of activation energies showed no significant difference.

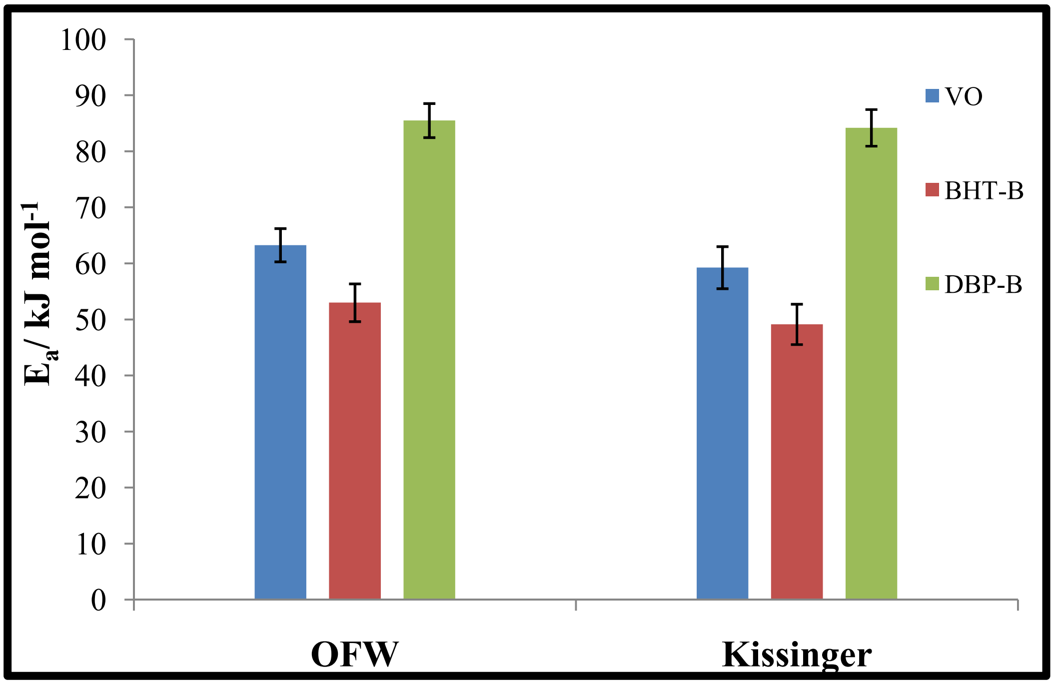

Figure 6.5 Results obtained from DSC data using the Kissinger and OFW model.

It has been previously reported that the presence of wear metals, oxygen and moisture are factors that accelerate the kinetics of the decomposition reaction [5]. Increases in the aromatic content of the oil was thought to bring about poorer resistance to oxidation, however this is not always the case [13]. Although results in this study show no significant differences in the activation energies for VO, BHT-B and DBP-B, addition of aromatics in oils, show functional activity in environments deficient in nitrogen and sulfur impurities [13]. Hindered phenols are also found to show profound activity under conditions in which oxygen is depleted [14].

It should also be noted that keeping the samples under nitrogen conditions in this work represents artificial conditions as in the real world, the transformer oils operate under air (oxygen) conditions. However, in order to study the conditions affecting the degradation of transformer oils, we had to control the oxygen environment. DSC results using both OFW and Kissinger models did however show improved thermal stabilities for DBP-B, as the mean activation energy was found to be higher than that of VO.

6.3.2 Electrical properties of the oils

Results of electrical properties for transformer oil and its blends are shown in Figure 6.6 and 6.7 illustrating the dissipation factor and electrical resistance of the oils, represented at 20 ºC, respectively.

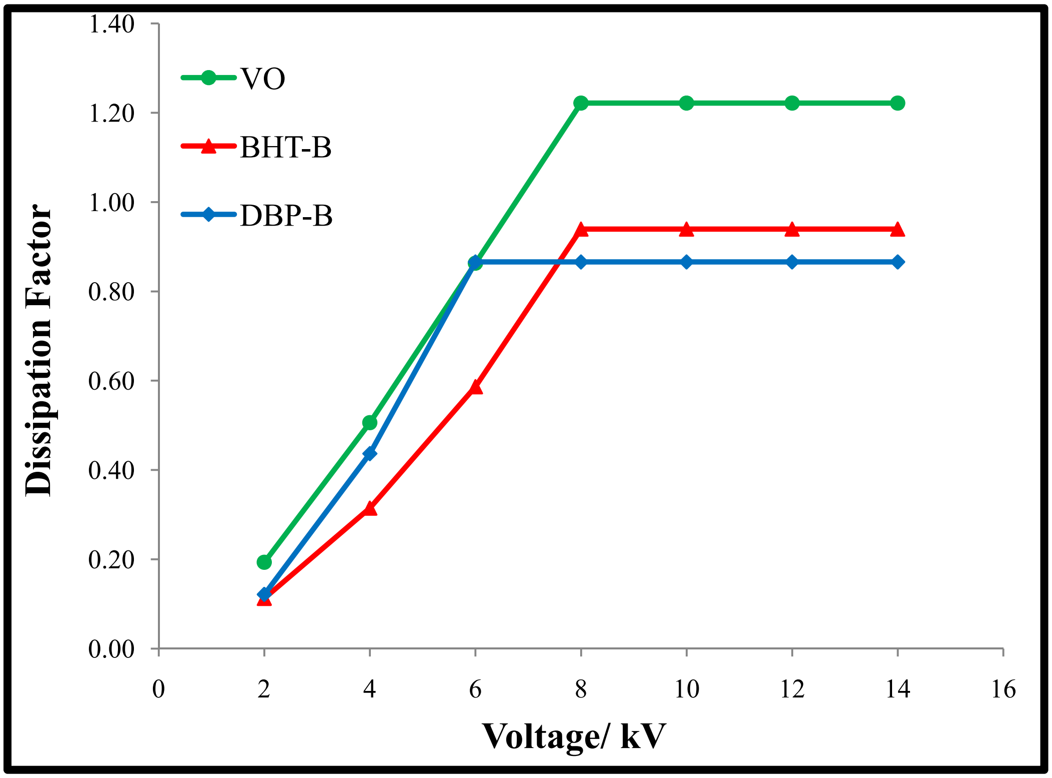

Figure 6.6 Dissipation factor of oils represented at 20 ºC.

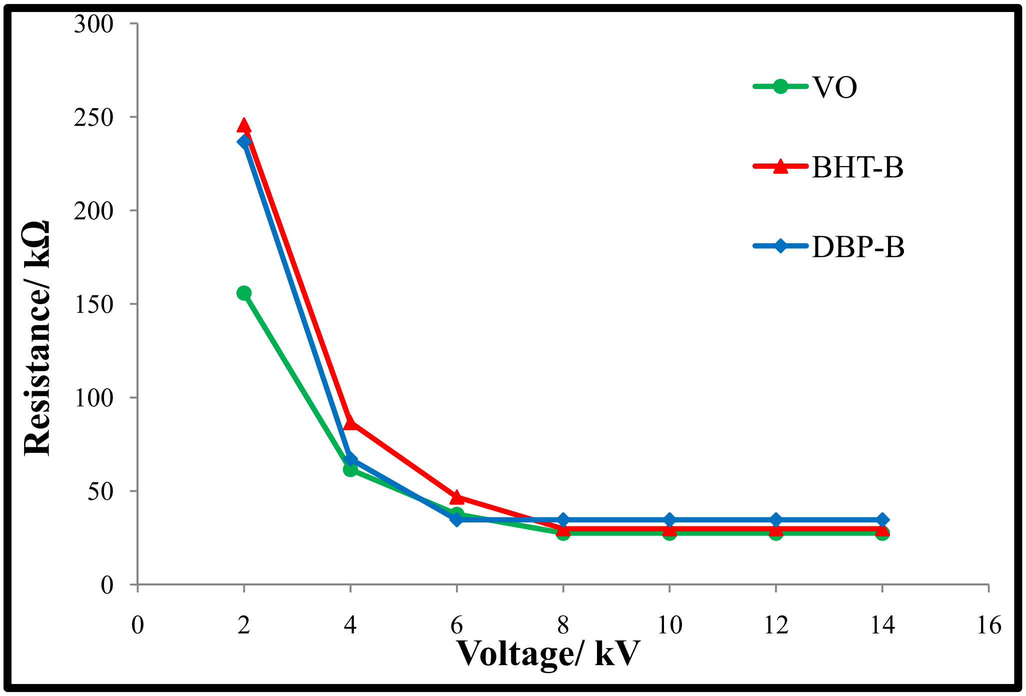

Figure 6.7 Electrical resistance of oils represented at 20 ºC.

Figure 6.6 illustrates that with an increase in applied voltage; an increase in dissipation factor occurs and reaches a constant value. Consequently, a decrease in electrical resistance to a constant value is reached, with an increase in the applied voltage (Figure 6.7). The results also show that the dissipation factors were found to be superior in the case of BHT-B and DBP-B in comparison to virgin oil. Lower values of dissipation factor for BHT-B and DBP-B imply that the blends show smaller dielectric losses. Breakdown in dielectric voltage for BHT-B, DBP-B and VO yielded the following results: 16, 26, and 50 kV, respectively.

Addition of organic additives (aromatics) can affect the breakdown voltage of the oils [13]. The mechanism of breakdown is governed by 'gaseous discharge inside gas bubbles formed in the liquid' [15]. Due to gaseous bubbles having a lower dielectric strength than the liquid, more gaseous bubbles in the oil, the more likely for breakdown to occur [16]. A study carried out by Zaky *et al.* (1976) [15] reported the positive effect that aromatic additives have on the oils breakdown strength.

However the additives that Zaky and co. works (1979) [15] focused on were those aromatics with degassing tendencies (e.g tetralin) [17] and those that can affect the gassing tendencies of the oil [15]. The additives used in this study are aromatic hindered phenols that serve as antioxidants. The negative correlations found in this study are possibly due to the fact that BHT and DBP don't substantially reduce the gassing tendency of the oil. Thus reduction in the DBV values of the blends in our study indicate impediment in the dielectric strength of the oil blends.

6.4 CONCLUSION

Data from TGA shows activation energies in the range of 57 and 77 kJ mol^{-1} for both oil and oil blends, respectively, using the OFW method. Statistical analysis based on Student *t*-test revealed that there were no significant differences between the decomposition activation energy for virgin oil and its blends. In addition, a statistical comparison of the activation energies obtained by the OFW and Kissinger models using DSC data showed that there were no significant differences between these two models. However, DSC results showed a favourable increase in activation energy for DBP-B using both the Kissinger and OFW methods. A lower dissipation factor was obtained for the blends when compared to virgin oil hence the blends showed smaller dielectric losses. In contrast the blends showed more than a 50% reduction in their breakdown voltage, indicating that the blends can only withstand lower electrical stresses when compared to virgin transformer oils.

We note that other factors such as the presence of wear metals influence the decomposition activation energy and these factors need to be considered. Therefore further work should include modelling the activation energy of oils that are currently used in field transformers.

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REFERENCES

[1] Verma P., Condition monitoring of transformer oil and paper, Electrical and Instrumentation Engineering, Thapar Institute of Engineering and Technology **2005**, *Doctor of Philosophy*.

[2] Heathcote M. J., J & P Transformer Book, Elsevier, **2007**.

[3] Gray I. A. R., Oxidation inhibitors for insulating oils, Transformer Chemistry Services, Durban, www.satcs.co.za/Oxidation_inhibitors_for_insulating_oil-IARGray2008.pdf (accessed 19 July 2010).

[4] Mentlík V., Polansky R., Prosr P. and Pihera J., Activation energy of transfomer oils, *Zeszyty Problemowe – Maszyny Elektryczne*, **2008**, *80*:45-49.

[5] Meshkatoddini M. R., Aging study and lifetime estimation of transformer mineral oil, *American Journal of Engineering and Applied Sciences*, **2008**, *4*:384-388.

[6] Brown M. E., Introduction to Thermal Analysis: Techniques and Applications, Chapman and Hall Ltd, **1998**.

[7] Toop D. J., Theory of Life Testing and Use of Thermogravimetric Analysis to Predict the Thermal Life of Wire Enamels, *IEEE Transactions on electrical insulation*, **1971**, *6*:2-14.

[8] Jain S. and Sharma M. P., Oxidation and thermal behavior of Jatropha curcas biodiesel influenced by antioxidants and metal contaminants, *International Journal of Engineering, Science and Technology*, **2011**, *3*:65-75.

[9] Saha B. and Ghoshal A. K., Thermal degradation kinetics of poly (ethylene terephthalate) from waste soft drinks bottles, *Chemical Engineering Journal* **2005**, *111*:39-43.

[10] Haefely Test AG Operating Instructions, Tettex 2820- Automated C, L & tan δ Measuring Bridge, Version 1.8. **2006**.

[11] Kenar J. A., McElligott J., Hwang H. and Erhan S. Z., A DSC Study of Z2–Z3 Viscosity Blown Soybean Oil, *Journal of American Oil Chemists Society*, **2002**, *79*:1151-1155.

[12] Ulkowski M., Musialik M. and Litwinienko G., Use of Differential Scanning Calorimetry To Study Lipid Oxidation. 1. Oxidative Stability of Lecithin and Linolenic Acid, *J. Agric. Food Chem.*, **2005**, *53*:9073-9077.

[13] Evangelou C., Zaky A. A. and Megahed I. Y., The effect of organic additives on the breakdown strength of transformer oils, *Letters to the editor: Journal of Physics D: Appl. Phys.*, **1973**, *6*:L60-L62.

[14] Rudnick L. R., Lubricant Additives: Chemistry and Applications, CRC Press, **2009**.

[15] Zaky A. A., Megahed I. Y. and Evangelou C., The effect of organic additives on the breakdown and gassing properties of mineral oils, *Journal of Physics D: Appl. Phys.*, **1976**, *9*:841-850.

[16] Wadhwa C. L., High Voltage Engineering, New Age International, **2007**.

[17] Lombard A., Transformer oil chemistry affecting the South African market, **2010**, Energize, www.eepublishers.co.za/images/.../01_TT04_Transformer%20Oil.pdf (accessed 18 January 2011).

CHAPTER 7

CONCLUSIONS AND FUTURE WORK

7.1 CONCLUSIONS

The physico-chemical analysis of virgin transformer oil revealed that although this oil was naphthenic in nature, aromatic constituents were present. These additives have some de-gassing tendency. The absence of acidic and saponifiable matter, which are typical oxidation products of oil ageing is favourable. Blending of oils with BHT and DBP appeared to show improved thermal and oxidative stabilities at 5 °C min^{-1} ramp rate. However, BHT and DBP blends were found to have no significant difference from virgin transformer oil when the activation energies were calculated using data obtained from TGA by the OFW method. The small changes in the concentration of these antioxidants in accelerated ageing of the oil blends using UV radiation showed that the antioxidants were stable under exposure to vigorous UV radiation and thermal ageing. However, even with these promising results the blends were found to have unsatisfactory dielectric breakdown voltages when compared to that of virgin transformer oil.

The turmeric components which dissolved in the oil included: curcumene, sesquiphellandrene, *ar*-turmerone, α-turmerone and curlone. These components were found to increase the thermal and oxidation stabilities of the transformer oil. The dissipation factor results were also impressive when compared to unblended virgin oil. This indicates that the oil blends provided smaller dielectric losses when compared to virgin transformer oil by increasing the electrical resistance of the oil. Furthermore, the addition of these components into the oil imparted a yellow colour; therefore this oil lacks the ability to be evaluated by the colour indicator test. Overall, the oil blends with natural antioxidants have the potential to serve as possible dielectrics for use in transformers, exhibiting more favourable outcomes when compared to that of virgin transformer oil.

7.2 FUTURE WORK

An interesting approach for future work would be to monitor uninhibited and inhibited oils from on site transformers. The effect that oils and oil blends have on corrosivity and paper degradation can also be determined.

Future tests can be extended to different types of dielectric fluids such as silicone oils, paraffinic oils, etc. Wear metals, presence of moisture and oxygen are also contributing factors that influence ageing, whose parameters can be investigated by determining activation energy for oils when exposed to these factors.

In terms of turmeric extract oil blends, the results obtained in this study are favourable. Nonetheless, the components in the oils need to be monitored over time in accelerated ageing studies. The turmeric oil blends require additional tests such as DBV measurements and other electrical testing. If the oil blends are to be used in on-site transformers, optimum extract concentration needs to be determined.

APPENDICES

Due to the information overload of the Appendices Section containing the raw data from various physico-chemical characterisation results, this data is contained in a CD included with this dissertation copy.