Application of nanodielectric fluids for the improvement of the insulation system of power transformers

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*Dedicado a
mi abuela Enedina
y mi abuelo Carlos*

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The material from this source included in this thesis is not singled out with typographic means and references.

- Title: **Evaluation of the Stability of Dielectric Nanofluids for Use in Transformers under Real Operating Conditions**

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- Title: **AC Breakdown Voltage of Fe_3O_4 based Nanodielectric Fluids. Part 1: Analysis of Dry Fluids**

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- Title: **AC Breakdown Voltage of Fe_3O_4 based Nanodielectric Fluids. Part 2: Analysis of Fluids with High Moisture Content**

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International conference papers (5)

- Title: **Applicability of Nanodielectric Fluids to the Improvement of Transformer Insulation Properties**

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- Title: **Enhancing transformer liquid insulation with nanodielectric fluids: State of the art and future trends**

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- Title: **Analysing the impact of Moisture on the AC Breakdown Voltage of Fe_3O_4 Based Nanodielectric Fluids**

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- Title: **Analysing the impact of Moisture on the AC Breakdown Voltage on Natural Ester Based Nanodielectric Fluids**

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Other research merits

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- Title: **Streamer simulation in nano-based dielectric fluids at different Fe₃O₄ nanoparticle concentrations**

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Abstract

Power transformers are one of the most important components of electrical systems. The reliability of these elements is vital for the adequate operation of the electrical network; transformer faults can cause power outages and severe accidents which derive in high economic losses.

One of the main elements that allows the safe operation of transformers is the insulating system, which is based in liquid and solid insulation. Transformer solid insulation is composed of different types of cellulose based materials such as Kraft paper and pressboard. The liquid insulation is commonly mineral oil, which is a petroleum derivate, although other fluids are starting to be used such as natural and synthetic esters. The transformer insulating fluid has two basic functions. On the one hand it acts as a cooling agent that dissipates the heat generated in the active part of the transformer during its operation; on the other hand, the liquid accomplishes a role as a dielectric material which provides electrical insulation between elements that operate at different voltage level.

Since the discovery of nanomaterials, a whole field of study has emerged in order to understand the theoretical and practical knowledge of these materials, and to find new applications for their use. In the last years several authors have proposed the use of nanotechnology for the improvement of the dielectric and thermal properties of insulating liquids (mineral oils and natural and synthetic esters) with application in power transformers.

In this thesis an investigation is carried out to analyse how the addition of Fe_3O_4 nanoparticles modifies the properties of mineral oils and natural esters. The thesis put

the main focus on the evaluation of the dielectric properties of the obtained liquids although other aspects such as the manufacturing methods and the stability of the obtained fluids have been also studied.

In the first part of the work a method for the synthesis of nanodielectric fluids is developed, obtaining theoretical and experimental conclusions on how the manufacturing process can be optimized. A detailed study is also carried out to evaluate the stability of the nanofluid dispersion both with mineral oil and with natural ester considering the real operating conditions that those fluids would have in transformers.

Then the dielectric properties of the produced mineral-oil and natural-ester based nanodielectric fluids are experimentally tested in depth. The breakdown voltage of the fluids is evaluated with alternate current and impulse type discharges. The analysis considers the effect of the presence of water in the dielectric fluids, studying the solubility of water in oils with nanoparticles. A statistical analysis is carried out in which the dielectric nanofluids are compared with their base oils, both for mineral oils and for natural esters. Theoretical explanations are proposed to explain the experimental observations obtained in this work. The study is repeated at different concentrations of nanoparticles in order to elucidate how the presence of nanoparticles affects the properties of the different types of fluids.

Resumen

El transformador de potencia es uno de los elementos más importantes de los sistemas eléctricos. Garantizar la fiabilidad de estos equipos es vital para conseguir una adecuada operación de la red eléctrica. Los fallos en los transformadores pueden provocar interrupciones del suministro y derivar en fallos catastróficos que frecuentemente llevan aparejados enormes pérdidas económicas.

Uno de los elementos principales de los transformadores es su sistema de aislamiento compuesto a su vez por el aislamiento sólido y el aislamiento líquido. El aislamiento está constituido por piezas de materiales derivados de la celulosa como son el papel Kraft o el cartón prensado. El aislamiento líquido es habitualmente un aceite mineral, derivado del petróleo, aunque en los últimos años se está extendiendo el uso de fluidos alternativos como son los ésteres naturales y sintéticos. El aislamiento líquido de un transformador tiene dos misiones principales. Por una parte, actúa como refrigerante, disipando las pérdidas caloríficas generadas en la parte activa del transformador durante la operación del equipo. Adicionalmente, el aceite actúa como fluido dieléctrico impregnando el aislamiento celulósico y proporcionando aislamiento eléctrico entre los elementos del transformador que operan a distinto nivel de tensión.

Desde el descubrimiento de los nanomateriales ha surgido un nuevo campo de estudio en el que se trabaja para entender los mecanismos físicos que tienen lugar en estos materiales y se buscan nuevas aplicaciones para los mismos. En los últimos años varios autores han propuesto la aplicación de la nanotecnología a la mejora de las propiedades térmicas y dieléctricas de los fluidos aislantes empleados en los transformadores de potencia.

En esta tesis se lleva a cabo una investigación para analizar cómo la adición de nanopartículas de Fe_3O_4 modifica las propiedades de los aceites minerales y los ésteres naturales. La tesis está centrada en la evaluación de las propiedades dieléctricas de los fluidos obtenidos, aunque también analiza algunos aspectos como los procesos de fabricación y la estabilidad de los nanofluidos dieléctricos.

En la primera parte del trabajo se desarrolla un protocolo experimental para la fabricación de nanofluidos dieléctricos con base aceite mineral y éster natural obteniendo conclusiones experimentales y teóricas que pueden ser aplicadas a la optimización del proceso de fabricación. Además, se lleva a cabo un estudio exhaustivo para evaluar la estabilidad de los nanofluidos en los que se consideran las condiciones de operación reales a las que se estarían sometidos los fluidos al operar en un transformador en servicio.

Después se realiza una evaluación experimental de las propiedades dieléctricas de los nanofluidos con base aceite mineral y éster natural. Se evalúa la tensión de ruptura de los fluidos ante sobretensiones de frecuencia industrial y sobretensiones tipo rayo. Se analiza el efecto de la presencia de agua en las propiedades dieléctricas de los fluidos base y los nanofluidos descubriendo un mecanismo, por el cual la presencia de nanopartículas modifica la solubilidad del agua en el fluido base, que explica las observaciones experimentales. Se lleva a cabo un detallado análisis estadístico de los resultados experimentales para comparar los nanofluidos con los fluidos base empleados, determinando parámetros relevantes para el diseño del transformador como son las tensiones de ruptura para bajas probabilidades de fallo. El estudio se repite para nanofluidos con distintas concentraciones de partículas con el fin de dilucidar cómo afecta la presencia de nanopartículas a las propiedades de los distintos tipos de fluidos y tratar de explicar los mecanismos físicos que ocurren cuando los nanofluidos se somete a sollicitaciones dieléctricas.

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Notation

Abbreviations and acronyms

AC	Alternating Current
AC BV	Alternating Current Breakdown Voltage
ASTM	American Society for Testing and Materials
ANOVA	Analysis of Variance
BV	Breakdown Voltage
DC	Direct Current
DC BV	Direct Current Breakdown Voltage
DLVO	Derjaguin–Landau–Verwey–Overbeek theory
DLS	Dynamic Light Scattering
EDL	Electrical Double Layer
FF1	Ferrofluid manufactured by Magnacol
FF2	Ferrofluid manufactured by MAGRON
FTIR	Fourier Transform Infrared
FWHM	Full Width at Half Maximum of the size distribution
HSD	Honest Significant Difference
HV	High Voltage
ICP	Inductive Coupling Plasma
IEC	International Electrotechnical Commission
IEEE	Institute of Electrical and Electronics Engineers
KF	Karl Fischer
MO	Mineral Oil

NDF	Nanodielectric Fluid
NE	Natural Ester
NP	Nanoparticles
PD	Partial Discharge
PDIV	Partial Discharge Inception Voltage
RS	Relative Saturation
SD	Standar Deviation
SE	Synthetic Ester
St	Standard
UV-Vis	Ultraviolet-Visible

Equations

τ	Charge Relaxation Time
σ	Conductivity
ε	Permittivity
R	Hydrodynamic Radius
k_b	Boltzmann Constant
T	Temperature
η	Solvent Viscosity
D	Diffusion Coefficient of the nanoparticles
μ_m	Viscosity
μ_e	Effective Viscosity
V_p	Particle Packing Volume
a	Scale Parameter in probability Weibull distribution
b	Shape Parameter in probability Weibull distribution
α	Mean value of the AC BV of Normal distribution
β	Standard deviation of Normal distribution
v	Propagation speed of the streamer
d	Distance between electrodes
t	Time to breakdown

Chapter 1

Introduction

Power and distribution transformers are one of the most important and critical equipment in an electrical distribution system. One of the main systems in a transformer is the insulation system, composed by solid and liquid insulation.

The most commonly used solid insulation is the so-called Kraft paper. The paper wraps the copper conductor providing a very good insulation with a low cost. This type of paper offers high resistance to tearing, traction, popping, etc. Another kind of solid insulation are the pressboard pieces of various forms (cylinders, planes, etc), which are made of pressed cellulose.

Regarding the liquid insulation, the most commonly used is the Mineral Oil (MO). MO is obtained from the distillation of petroleum crude oil. It is colorless and consists of cyclic paraffins and cyclic alkanes. Despite of its good electric and thermal properties, in recent years studies have been carried out to find biodegradable alternatives to MO.

One of these biodegradable alternatives are the ester fluids. The esters are classified into two groups: natural and synthetic esters. Natural Esters (NE) are obtained from vegetable seeds such as rapeseed and sunflower, while Synthetic Esters (SE) are manufactured in the laboratory. Esters present certain improvements in their physical properties compared to MO, as a higher flash point and fire point and a greater biodegradability. However, they have some disadvantages, such as their high viscosity

or high economic cost.

During the last 20 years, the search for new applications for nanotechnology has been a great effervescence in science, engineering, and manufacturing. New nanotechnology-based materials with superior properties have been developed and are already used in many everyday products and processes. The application of nanotechnology to high voltage (HV) engineering has been mainly oriented towards the development and characterization of the so-called nanodielectric materials [1]. In 1994, Lewis [2] suggested that “a major field of study in the future development of dielectrics will concern their properties when relatively few molecules are involved. Such smallness arises naturally at interfaces of nanometric thickness and will occur also when dielectrics are employed in the nano-technical devices of the future.” The physical phenomena that govern the behavior of materials at sub-microscopical scale are outlined in [2]. The term “nanodielectric” was introduced by Frechette [3, 4], who defined nanodielectrics as “multicomponent dielectrics possessing nanostructures, the presence of which results in the change of one or several of its dielectric properties.”

During the last decade, the focus has been mainly on nanocomposites manufactured by adding nanoparticles (NP) to solid polymers [1]. It has been widely reported that the dielectric properties of such materials are, in some aspects, superior to those of the matrix polymers, e.g., an increase in partial discharge inception voltage (PDIV), suppression of space charge formation, or enhancement of treeing lifetime have been observed. The physical mechanisms involved in these changes are not yet fully understood, although they seem to be linked to the effect of the interfaces between the particles and the host polymers [4, 5, 6, 7, 8, 9].

Recently, attempts have been made to apply nanotechnology to transformer insulating systems. A few authors have proposed the development of nanotechnology-based alternatives to traditional solid insulation [9, 10]. However, most researchers are working on the development of improved dielectric oils in which NP are incorporated in the base fluid, i.e. mineral oil (MO), natural ester (NE) or synthetic ester (SE). These fluids are usually named nanodielectric fluids (NDF). They are two-phase systems composed of a solid dispersed NP phase and a liquid

dispersion medium (base fluid) [11].

The term nanofluid was originally defined by researchers at Argonne National Laboratory (United States) as a “fluid in which nanometre-sized particles are suspended” [12]. Nanofluids have been mainly applied to improve the heat transfer properties of the cooling liquids utilized in several industrial processes. It has been observed that the addition of NP to refrigerating fluids improves their thermal conductivities and their convective heat transfer performance [12]. Some authors claim that the performance of NDF as insulating or cooling liquids is superior to that of the base refrigerant [13, 14].

Considering that the liquid insulation of transformers acts not only as an electrical insulation but also as a refrigerant, it seems feasible that the application of nanotechnology could lead to liquids with superior thermal and dielectric properties that increase the reliability of the transformer. One of the first authors to suggest the application of nanofluids to transformers was Segal, who analyzed the thermal and dielectric properties of a colloidal fluid containing MO and magnetite NP [15, 16]. As can be seen from the number of scientific works published in international journals and conferences Fig. 1.1, the interest in NDF has risen rapidly over the last 10 years.

It should be noted that NDF are not yet commercially available. Some problems remain unsolved, e.g., stability, interaction with the magnetic fields present in the transformer, and effect on the performance of the solid insulation within the transformer. Production costs must also be considered.

This thesis provides a study about the effect of the addition of Fe_3O_4 NP to MO and NE. Firstly a methodology to manufacture of the nanofluids is established. Then an experimental study to evaluate the stability of the liquids is carried out. Later an experimental study is carried out, in which the dielectric properties (AC Breakdown and Impulse Breakdown) are studied under different concentrations and different moisture degrees. All the results are analyzed using a statistical study and a parametric study.

Fig. 1.1: Numbers of published papers on the subject 'nanofluids for application in transformers' from 2007 to 2018 (based on Google Scholar).

1.1 Scope of thesis

The main objective of the PhD thesis is to study how the addition of NP affects the dielectric properties of insulating fluids and contribute to the theoretical explanation of the experimental observations obtained in this work and in the work of other authors. To achieve this, some specific objectives have been proposed:

- Develop a NDF manufacturing protocol valid for different types of oils and NP.
- Perform a stability study of Fe_3O_4 dispersions in oil at different temperatures and for MO and NE.
- Carry out an AC Breakdown Voltage (AC BV) study for different concentrations of Fe_3O_4 NP in MO and NE.
- Carry out an Impulse Breakdown Voltage (Impulse BV) study for different concentrations of Fe_3O_4 NP in MO and NE.
- Compare the results obtained with their respective dielectric liquids without NP.

1.2 Outline of thesis

The doctoral thesis is structured in seven chapters:

- **Chapter 1:** In this first chapter, a general introduction to the work is presented, the scope of thesis is exposed and the outline of thesis is provided.
- **Chapter 2:** In the second chapter, a review of the state of the art is carried out that include the analysis of the types of materials that have been used by other authors and the results obtained by them.
- **Chapter 3:** In the third chapter, the manufacturing protocol of the nanofluids that will be used during all the thesis experiments is presented. Furthermore, the results of the stability test are shown.
- **Chapter 4:** The fourth chapter describes the MO-based nanodielectric fluids of AC BV test for low moisture contents and different concentrations of NP. The results are compared with those of the base MO and a theoretical explanation is proposed.
- **Chapter 5:** In the fifth chapter, a study of AC BV of MO-based nanodielectric fluids with high moisture contents and different concentrations of NP is carried out. The results are compared with those of the base MO and a theoretical explanation is given.
- **Chapter 6:** The sixth chapter shows the Impulse BV experiments in MO-based nanodielectric fluids with different concentrations of NP. A theoretical explanation is proposed to explain the results.
- **Chapter 7:** In the seventh chapter, presents the AC BV and Impulse BV tests for NE-based nanodielectric fluids with different NP concentrations.
- **Chapter 8:** The eighth chapter presents the main conclusions and contributions obtained from this doctoral thesis and sets outlines the possible future works to be further developed.

Chapter 2

State of the art

In this chapter a report on the state of the art of the electrotechnical use of NDF is provided. The experimental results obtained by different authors, related to the dielectric and thermal properties of NDF, are reviewed and compared. Practical problems, such as the manufacture of the liquids, and basic theoretical aspects are also discussed.

Specifically, this chapter reviews the work of authors in synthesis, dielectric properties and thermal properties of NDF. Finally the conclusions obtained in this chapter are presented.

2.1 NDF synthesis

2.1.1 NDF components

As stated above, NDF fluids are not yet commercially available. The results reported in the literature are mostly for fluids manufactured on a laboratory scale. Different types of NP and base fluids (in which the NP are dispersed) have been tested. Three main groups of NP have been used, namely (1) conductive, such as Fe_3O_4 or ZnO , (2) semi-conductive, such as TiO_2 , Fe_2O_3 , CuO , or CuO_2 , and (3) insulating, such as Al_2O_3 , SiO_2 , or SiO . Typical NP diameters are in the range 10 to 60 nm [17, 18, 19, 20].

Most publications on NDF are concerned with MO-based fluids, but some work

in which NE-based or SE-based oils were investigated has been published [21, 22, 23, 24, 25, 26, 27].

2.1.2 Preparation

The main difficulty involved in the preparation of NDF is the fact that, since NP are non-soluble compounds, stable colloids must be formed in order to suspend them in the base fluid. However, if the NP are directly added to the base fluids, sedimentation or agglomeration of the NP will occur, limiting the desired improvement in the properties of the NDF [24].

In the so called one-step method the NP are simultaneously synthesized by physical vapor deposition or a liquid chemical method, and dispersed within the base fluid. This method results in less NP agglomeration [28], but is not readily implemented except in a specialized laboratory.

To prevent these unwanted effects, in the vast majority of cases the NP to be dispersed in the base fluid are prepared outside it, in a so called two-step manufacturing process. Then, the NP are dispersed in the base fluid using ultrasonic agitation or magnetic stirring. Such processes are popular because of their lower cost and because they do not require the use of specialized equipment.

In most cases a surfactant is added to the base fluid-NP mixture, in order to reduce the repulsive forces between the NP and the base fluid, which in turn facilitates the formation of colloids within the base fluid and makes NP agglomeration less likely.

Several surfactants have been used, e.g., hexadecyl trimethyl ammonium bromide for MO with magnetite (Fe_3O_4) NP [29], silane coupling agent Z6011 for MO with SiO_2 NP [11, 30], and a non-ionic surfactant named Span80 composed of fatty acids for MO with TiO_2 NP. The most widely used surfactant is oleic acid [31, 32, 33, 34, 35].

After the mixing process, the NDF is dried and degassed in order to eliminate bubbles and moisture. Mixing usually involves heating under reduced pressure typically at 60°C and 1 kPa for 24 to 72 hours [13, 36, 37]. Degassing NDF can be

more difficult than degassing conventional MO. In order to remove impurities, the NDF may be passed through a membrane filter that captures particles larger than its pore size [38].

2.1.3 Stability

One of the main problems with NDF is ensuring long-term dispersal of the NP within the base fluid. Dispersal times varying from hours to several months have been reported [24, 31, 32, 39, 40]. The dispersal times depend on the NP concentration, e.g., for MO with SiO_2 NP, NP concentrations of 0.01, 0.02, and 0.1 vol.% lead to dispersal times of 1 month, 2 days, and less than 24 hours, respectively [40]. Atiya et al. [41] showed that, for a MO with TiO_2 -based NF, concentrations of the surfactant cetyltrimethylammonium bromide above 0.3 vol.% increased the NP agglomeration. It has also been reported that the addition of large amounts of surfactant can reduce the dispersal time and degrade the dielectric properties of NDF [42].

2.1.4 Safety

Several agencies have expressed concern about the potential health hazards that nanomaterials can pose for humans [42]. However, taking into account the available toxicological data, the European Commission has suggested that many of them are not dangerous in moderate doses [43]. NP can enter the human body through inhalation, reaching the lungs, other organs, and the central nervous system [44]. NP can also enter the body through the digestive system, due to poor hygiene practices, or through the skin.

The risks are particularly severe when working with NP powder, which is the most widely used form of NP used in NDF manufacturing processes. At present it is recommended that the procedures commonly adopted when working with ultrafine particles in the laboratory should be followed [44], e.g., use of masks, safety glasses, gloves, protective clothing, and security chambers.

2.2 Dielectric properties

Most of the work published on NDF is concerned with their dielectric properties, particularly in comparison with the corresponding properties of the base fluid. Most authors report that dispersion of low NP concentrations in a base fluid improves the performance of the base fluid. However, the reasons for the improvement are not always clear.

Several authors have suggested that, when an NDF is subjected to an electric field, positive ionic charges accumulate on the surface of the NP, attracting negative ionic charges around them [30, 38]. Thus, an electrical double layer (EDL) is formed. The volume of the EDL close to the NP surfaces is called the compact layer, and consists of immobile negative ions strongly attracted to the NP surfaces. The net charge density in the compact layer drops gradually with increasing distance from the NP surfaces, reaching zero in the electrically neutral area of the fluid. The ions in this region, called the diffuse layer of the EDL, are less affected by the electrostatic interaction with the NP and thus have higher mobility [36]. The formation of the EDL in a NDF subjected to an electric field is believed to be the main reason for the improvement in dielectric properties reported by many authors [36, 45].

In order to quantify the improvement in the dielectric properties of the base fluid due to the addition of NP, Hwang [46] defined the charge relaxation time τ of a NDF, which is a measure of the extent to which the times and frequencies of electrodynamic processes in the base fluid are affected by the presence of the NP. τ depends on the DC conductivity (σ) and low frequency permittivity (ϵ) of the NP and the base fluid, and is given by

$$\tau = \frac{2\epsilon_{fluid} + \epsilon_{NP}}{2\sigma_{fluid} + \sigma_{NP}} \quad (2.1)$$

If the relaxation time of the NP is shorter than the time scale of the electrodynamic process being considered, e.g. dielectric breakdown, the effect of the NP on the process will be very noticeable.

On the other hand, if the relaxation time is longer than the time scale of the

process, the NP will have little effect on the breakdown processes. Calculated relaxation times for four types of NP dispersed in MO are shown in Table 2.1 [47]; they differ greatly. Assuming the time scale of dielectric breakdown in MO to be typically 10^{-9} seconds, we would then expect Fe_3O_4 and ZnO to affect the breakdown greatly, but Al_2O_3 and SiO_2 to have little effect. This is inconsistent with some published experimental data, e.g., increases of as much as 30% in the AC BV of MO following the addition of Al_2O_3 and SiO_2 NP (as shown in Table 2.2).

	Magnetite	Zinc Oxide	Alumina	Silica
Electrical Conductivity (S/m)	10^4	10	10^{-12}	1.4×10^{-9}
Relative permittivity	80	7.4	9.9	3.8
Charge Relaxation Time (s)	7.47×10^{-14}	1.05×10^{-11}	42.2	5.18×10^{-2}

Table 2.1: Charge relaxation times for four types of nanoparticles dispersed in MO.

NP / Base Fluid	Conductivity	Average Size NP (nm)	NP Loading	% Increase in AC BV	Ref
Fe_3O_4 / MO	Conductive	10	-	42.8%	[48]
Fe_3O_4 / MO	Conductive	30	-	19.8%	[49]
Fe_3O_4 / MO	Conductive	10	-	44.3%	[17]
ZnO / MO	Conductive	34	0.05 % vol.	8.3%	[48]
TiO_2 / NE	Semi-conductive	20	0.0625% vol.	31%	[22]
TiO_2 / MO	Semi-conductive	<20	0.075% vol.	15%	[50]
TiO_2 / MO	Semi-conductive	10	-	33%	[17]
SiO_2 / MO	Insulating	15	0.02% vol.	26%	[51]
SiO_2 / MO	Insulating	15	0.074% vol.	17%	[52]
Al_2O_3 / MO	Insulating	10	-	35.5%	[17]

Table 2.2: Increase in AC BV of NDF containing various NP in MO or NE.

2.2.1 AC BV

AC BV has been measured by many authors. Most papers present measurements performed in accordance with the IEC 60156 standard [53]. The average AC BV for dry MO is 70.3 ± 16.7 kV [47].

Effect of NP conductivity on AC BV

In Table 2.2, the results reported by various authors for various NDF, obtained by dispersing conductive, semi-conductive, and insulating NP in MO or NE, are compared. Some increase in AC BV was reported in all cases so the conductivity of the NP seems not to have an effect on AC BV.

A possible explanation is that electrons are trapped by the NP, which slows down the propagation of the breakdown streamer and thus increases the breakdown voltage [19].

Effect of NP concentration on AC BV

In Table 2.2, the results reported by various authors for various concentrations of NP in MO or NE oil, are compared. Some authors did not specify the NP concentrations, so they do not appear in the column (NP Loading) of the Table 2.2.

One might expect that the AC BV would increase with increasing NP concentration. However, this is true only up to certain concentration limits, beyond which the AC BV decreases [13]. Table 2.3 shows the results of a study [50] in which increasing concentrations of TiO_2 NP were dispersed in MO. Disregarding the “rogue” result at 0.003 g/L, the AC BV increased with increasing NP concentration up to 0.006 g/L and decreased at higher concentrations, becoming less than the AC BV of MO at 0.05 g/L. The same effect has been reported in [54] and [55], but with different optimal NP concentrations. It was suggested in [56] that the reduction in AC BV at higher NP concentrations might be due to the accumulation of conductive NP chains near the electrodes, facilitating discharges.

The evolution of the AC BV of NDF with NP concentration is similar for

Sample	Mean AC BV (kV)	% Increase in AC BV
Mineral Oil	71.59	0
TiO_2 (0.003 g/L)	67.33	−5.9
TiO_2 (0.006 g/L)	82.483	15.2
TiO_2 (0.01 g/L)	77.82	8.7
TiO_2 (0.03 g/L)	71.76	0.2
TiO_2 (0.05 g/L)	53.25	−25.6

Table 2.3: AC BV of a NDF consisting of various concentrations of TiO_2 nanoparticles dispersed in MO, [50].

conductive, semi-conductive, and insulating NP, but the optimal NP concentrations seem to be dependent on the particle type, the nature of the base fluid, and the manufacturing process [50, 51, 54, 55, 56].

Effect of moisture in the base fluid on AC BV

It is well known that the presence of moisture degrades the dielectric properties of oil. Several authors have suggested that such degradation might be eliminated, or at least significantly reduced, by dispersing NP in the oil [11, 12, 13]. Jin [11] measured the AC BV of MO and a MO-based SiO_2 NDF with moisture levels of 15 and 25 ppm. The SiO_2 NP concentrations were 0.01 and 0.02 vol. %, and the NP sizes were in the range 20 to 30 nm. As shown in Table 2.4, the AC BV increased with increasing NP concentration at a given water concentration, but decreased with increasing water concentration at a given NP concentration. He suggested two phenomena that might lead to these results:

1. Water molecules seem to be attracted to charged conductive NP, and cluster around them. The mobility of the water molecules would therefore decrease, but although the presence of water reduces the AC BV, the reduction would be smaller in the presence of the NP.
2. Some semi-conductive or insulating NP are hydrophilic so that, although they are not conductive, they would bind on their surfaces some of the water molecules dispersed in the oil.

Jin [11] compared the AC BV of two MO-based NDF, one containing hydrophilic silica NP and the other containing silica NP modified with the surfactant silane coupling agent Z6011, which renders them hydrophobic. The AC BV of the latter NDF was similar to that of the base fluid, whereas the AC BV of the NDF containing hydrophilic silica NP was 10 to 25% greater than that of the base fluid (as shown in Table 2.4), presumably because water molecules were bound to the surfaces of the hydrophilic NP.

Weijun Yin [13] reported that, in a MO-based NDF containing Al_2O_3 NP, the AC BV decrease with increasing water content, but a much greater water content was required in samples containing NP to produce a comparable decrease in AC BV, relative to samples without NP (Fig.2.1).

Sample	Moisture (ppm)	Mean AC BV (kV)	% Increase in AC BV
MO	25 ppm	55	-
MO	15 ppm	80	-
MO + 0.01% vol. SiO_2	25 ppm	66	20
MO + 0.01% vol. SiO_2	15 ppm	88	10
MO + 0.02% vol. SiO_2	25 ppm	69	21
MO + 0.02% vol. SiO_2	15 ppm	91	14

Table 2.4: AC BV of MO with two moisture concentrations and two SiO_2 NP concentrations

Effect of NP size on AC BV

In [33], several NE-based NDF were studied. The NE was FR3, and the NDF were manufactured by dispersing Fe_3O_4 NP of sizes 12 nm, 21 nm, and 41 nm, to a concentration of 0.03 vol.% in the FR3, and using oleic acid as surfactant. A range of AC BV was obtained; its mean value increased from 55.1 kV for the FR3 alone to 68.5 kV for the NDF containing the 41 nm NP (Fig. 2.2). The authors suggested that the increase of the AC BV with increasing NP size might be due to the fact that the ability of Fe_3O_4 NP to trap electrical charge carriers increases with increasing NP surface area.

Fig. 2.1: Effect of water on the AC BV of MO and a MO-based NDF containing 2 vol.% of Al_2O_3 NP [13].

Fig. 2.2: Influence of Fe_3O_4 NP size on the mean AC BV of FR3-based NDF [33].

According to Liu et al. [56], space charge density in NDF decreases quickly following application of electrical stress, and thus the internal electric fields appearing within them are lower than those that would appear in the base fluid under the same stress. However, the addition of larger NP would cause field distortion that might

degrade the dielectric properties of the fluids, i.e., a decrease in AC BV at larger NP sizes might be expected.

Effect of thermal aging on AC BV

The effects of thermal aging of NDF on their AC BV have been studied [35, 57, 38, 58]. Karthik et al. [56] synthesized three types of NDF, all based on MO. The dispersed NP were Fe_3O_4 (magnetite) with particle size 10 to 50 nm, SnO (10–50 nm), and insulating SiO_2 (5–20 nm) at a concentration of 0.2 g/L. Oleic acid was added as a surfactant to the Fe_3O_4 NDF, but not to the second and third NDFs. The NDF were poured into hermetically sealed vessels (with an air head) and aged for 675 hours (approximately one month) at a temperature of 120°C. Fig.2.3 (1 = MO; 2 = aged MO; 3 = magnetite NDF; 4 = aged magnetite NDF; 5 = SnO NDF; 6 = aged SnO NDF; 7 = SiO_2 NDF; 8 = aged SiO_2 NDF) shows the average value of the AC BV (extracted from the Weibull distribution fitting) for the MO and for each of the three NDF.

Fig. 2.3: AC BV average values for three MO-based NDF before and after thermal aging at 120°C for 675 hours in air [35].

Addition of each of the three types of NP increased the AC BV of the MO. The increases persisted after the thermal aging. The AC BV reductions after aging in the MO and in the NDF containing Fe_3O_4 were approximately 60% and 50%, respectively. The corresponding reduction in the NDF containing SnO was about 10%, and zero within experimental uncertainty in the NDF containing SiO_2 . The large reduction in

the NDF containing Fe_3O_4 was not explained in detail, although the authors [35] noted that only the NDF was surfactant treated. Similar results were reported in [57] for a MO-based NDF containing TiO_2 NP subjected to thermal aging.

Zhi-Feng et al. [57] suggest that the improved AC BV of aged MO-based NDF compared to aged MO is due to the fact that a fraction of the molecules generated as by-products of the aging reactions can bind to the NP surfaces. Consequently the internal electric field distribution within the aged NDF is more uniform than the corresponding distribution in MO aged in the same manner.

2.2.2 DC BV

Kudelcik et al. [59] reported an increase of the positive DC BV of MO-based NDF containing Fe_3O_4 NP with diameter 10 nm. The DC BV increased with increasing NP concentration up to 1 vol.%, but decreased sharply when the concentration was increased to 2 vol.% (Fig. 2.4). This variation with NP concentration resembles that of the AC BV presented in the section 2.2.1. The authors give two possible reasons for the initial increase in DC BV with increasing NP concentration. Firstly the NP act as electron traps, limiting the concentration of “fast” electrons in the oil and generating “slow” negatively charged NP. The latter slow down the ionization processes which precede breakdown. Secondly the presence of NP can affect the process of bubble formation within the NDF, since the permittivity of the NP is higher than that of the surrounding liquid. Under an applied voltage the charged NP move towards the areas of maximum electrical stress, where most of the bubbles are generated. The authors also suggest that, at higher NP concentrations, local electric field gradients can lead to lower BV.

The same authors [59] subjected the NDF to an external magnetic field of 20 mT, which reduced the DC BV. They suggested that the reason could be the formation of micrometer-sized Fe_3O_4 NP agglomerations in the NDF as a result of magnetic dipole–dipole interactions between NP.

Du [37] investigated the effect of polarity on the DC BV (one grounded electrode) of a MO-based NDF containing 0.075 vol.% of TiO_2 NP. Relative to the unmodified

Fig. 2.4: DC breakdown voltage of MO and MO-based NDF containing three concentrations of Fe_3O_4 NP, as functions of the electrode separation [59].

MO, the DC BV fell by 8% under positive polarity, but increased by 28% under negative polarity. The authors suggest that electron emission is more “violent” under negative polarity than under positive polarity, but do not explain the meaning of “violent” in this context.

2.2.3 Streamer propagation in NDF

A streamer is a transient electrical discharge that may appear when an insulating medium, such as insulating oil, is exposed to a large voltage drop, such as a lightning or switching impulse.

Streamer propagation is generally measured using a standard lighting impulse voltage $1.2/50 \mu s$ in a needle–sphere combination of electrodes with a 25 mm gap. The speed of streamer propagation in dielectric fluids is strongly dependent on the polarity of the applied voltage and its peak amplitude [60]. In the particular case of MO it has been observed that streamers originating from a positive electrode tend to initiate at lower voltages than those originating from a negative electrode, and to propagate faster and further [60].

Several authors have studied streamer propagation in a number of NDF,

comparing their performance with that of the base fluid [17, 19, 21, 39, 49, 61, 62]. They concluded that, under positive polarity (positive streamers), NDF tend to have lower streamer velocities and higher streamer BV than the base fluids, when high densities of high energy electrons are generated.

On the other hand, under negative polarity the ability of NDF to withstand over-voltages does not differ appreciably from that of the base fluid.

The formation mechanisms of streamers in NDF have been studied using finite elements analysis [19, 46, 63, 64]. It is believed that the low mobility of the NP hinders the development of a space charge zone at the streamer tip, thereby suppressing the propagation of the electric field wave that is needed to drive electric-field-dependent molecular ionization, and hence streamer propagation [63]. MO-based NDF exhibit lower space charge densities than pure MO, due perhaps to faster negative charge decay rates in NDF [63]. The trapping of fast electrons by slow NP seems to be the cause of the decrease in positive streamer velocity mentioned above.

A broad theoretical study of streamer propagation in NDF has been published by O'Sullivan [19]. Several models were described and implemented using finite elements analysis. The physical phenomena that take place when a NDF is subjected to an impulse voltage were analyzed. The author concluded that, since streamer propagation in insulating fluids requires ionization of the fluids and, since many of the electrons generated by this ionization are trapped by the NP before they are transported out of the ionization region, the time scales of streamer development in NDF will be significantly longer than those in the unmodified base fluids.

The effect of the NP on the propagation velocity of positive streamers in an MO-based NDF containing Fe_3O_4 NP has been studied in [13] The velocities decreased by as much as 46% compared to MO. A slower propagation velocity implies a greater probability that the impulse voltage will be extinguished before the oil breaks down, so the positive streamer BV will be higher than in unmodified MO. Hwang [61] showed that the higher the NP conductivity, the smaller the reduction in the positive streamer propagation velocity.

The average BV for positive lightning impulses in a NE was found to be 73.9 kV, while for an NE-based NDF containing Fe_3O_4 NP (1 vol.%), it was 101.5 kV [23]. The corresponding BV for negative lightning impulses were 83.8 kV and 93.7 kV, respectively. It has also been reported [49] that the breakdown time measured in a similar NDF (based on a similar NE with Fe_3O_4 NP) was longer for the NDF than for the base fluid (12.0 μs and 9.9 μs , respectively).

Lv et al. [65] investigated an MO-based NDF in which TiO_2 NP (10 nm) had been dispersed (0.075 vol. %). In Table 2.5 the positive and negative Impulse BV are presented. Positive streamers pose a greater risk for MO than negative streamers, since under positive streamers dielectric breakdown occurs at lower voltages values and at shorter breakdown times, e.g., at 97.16 kV for positive streamers and at - 108.46 kV for negative streamers.

Sample	Breakdown Voltage (kV)	Standard Deviation (kV)	Time to Breakdown (μs)	Standard Deviation (μs)
<i>Positive Impulse Breakdown</i>				
Unmodified MO	74.27	5.34	13.18	0.61
NDF	97.16	6.05	25.65	1.70
<i>Negative Impulse Breakdown</i>				
Unmodified MO	-116.42	3.92	49.58	6.43
NDF	-108.46	5.23	11.39	3.77

Table 2.5: Positive and negative Impulse BV and times to breakdown for MO and a MO-based NDF with TiO_2 NP had been dispersed (0.075 vol.%), [65] .

2.2.4 Partial discharge in NDF

Breakdown occurs after discharge initiation and propagation through the oil. The BV measurement alone provides little information on the discharge process. It is of interest to investigate the differences between the discharge mechanisms in the base fluid and the associated NDF, and one approach is to measure the partial discharge (PD) activity in both.

The PDIV, time duration, rise-time, total discharge magnitude, and PD voltage amplitude for MO, and MO-based NDF containing silica and fullerene NP (average particle size 15 nm and 1 nm, respectively), under DC voltage, are compared in [66]. The discharge mechanism in MO depends strongly on the polarity of the applied DC voltage. Under negative polarity the PDIV and the total discharge magnitude were similar for MO and the NDF, but under positive polarity the PDIV increased and the total discharge magnitude decreased relative to the MO values.

The authors suggested that the improved dielectric performance of the NDF could be due to the trapping of electrons, water molecules, acids, or other additives on the surface of the NP, and the subsequent slowing down of the breakdown processes [66]. It was reported [29, 37] that the PDIV of MO increased when TiO_2 NP were added, and the PD magnitudes and pulse rates decreased (Table 2.6). It was also reported that, as expected, increasing the applied voltage from PDIV to 2 x PDIV increased the discharge magnitude and the number of pulses in the MO and the NDF. Fig. 2.5 shows phase-resolved-partial-discharge patterns measured in a 25 mm needle–sphere gap, the needle tip having 50 μm radius of curvature, for applied voltages of (a) PDIV and (b) 2 x PDIV [37].

Sample	PDIV (kV)	SD (kV)	<u>Pulses</u> 10 s	Mean DM (pC)	<u>Pulses</u> 10 s	Mean DM (pC)
MO	30.66	2.66	9	435	245	6.062
MO - TiO_2 NDF	33.13	1.79	6	245	168	5.180

Table 2.6: PDIV, SD magnitudes, number of PD pulses measured and electrical charge in MO and in MO– TiO_2 NDF at 1.0 and 2.0 PDIV, during 10 minutes measurement intervals, [29].

Three MO-based NDF, containing silica ferrofluid, graphene oxide, and SiO_2 NP, were tested under DC and AC voltages and their performances compared with that of MO [67]. The NP concentrations were in the range 0.1 to 0.2 g/L. Under AC voltages all three showed an increase in PDIV compared to MO, but under both positive and negative DC voltages, the measured PDIV were lower than those observed under AC

Fig. 2.5: Phase-resolved-partial-discharge patterns measured in MO and in MO- TiO_2 NDF in a 25 mm needle-sphere gap, the needle tip having a 50 μm radius of curvature, for applied voltages of (a) PDIV and (b) 2 x PDIV, [37].

(Fig. 2.6).

Fig. 2.6: Increase of PDIV for three MO-based NDF under AC and positive and negative DC voltages. The nanoparticles were FF = silica ferrofluid, GO = graphene oxide, and SiO_2 , [66].

Liu et al. [56] observed an increase of 20% in the PDIV of an MO-based NDF containing 0.12 vol.% concentration of aluminum nitride NP, and suggested that the increase could be due to the trapping of electrons on the NP surfaces. They stated that

PD are always caused by a localized increased electric field strength in the volume or on the surface of a defect, e.g., water, bubbles, or particles, the increased field being due to differences in relative permittivity between the defect and the host material.

Although the presence of charged particles in transformer oil generates local electric field distortion within the oil which can lead to the formation of PD, this is not what happens when NP are dispersed in oil [22, 56]. According to the authors of these publications, when NP are dispersed in an insulating fluid, the charge density within the NDF will decrease rapidly with increasing time under an externally applied voltage, and the internal electric field will therefore be lower than that in the base fluid under the same applied voltage. In [22] the authors suggested that the rapid decrease in space charge density could be attributed to a high shallow trap density created by the NP, and hopping transport of charge between those traps. Rapid transfer of charge carriers through the shallow traps implies increased mobility of the charges in the NDF, compared to the base fluid, which in turn reduces the accumulation of space charge [68] and distortion of the electric field distribution. The end result is an increased PDIV and a decreased PD probability.

2.3 Thermal properties

Transformer insulating oil also acts as a cooling agent. In that context, its thermal conductivity is important, as are its viscosity and density. As mentioned in the chapter 1, the addition of NP was initially regarded as a way of improving the thermal properties of cooling liquids used in different industrial processes [12].

Consequently, many publications in this field deal with improvement in the thermal properties of liquids such as water, ethylene glycol, and engine oil when NP are dispersed in them. We consider these first, describing them as nanofluids rather than NDF.

2.3.1 Factors influencing the thermal conductivity of non-MO-based nanofluids

The results obtained by several groups of authors on the thermal properties of various nanofluids were reviewed in an extensive report [12] published in 2007. These authors compared the thermal properties of nanofluids fabricated using different base fluids, e.g., water, ethylene glycol, and engine oil, and several types of NP. Improvement in the thermal properties was observed in most of the nanofluids, relative to the base fluids, but the magnitude of the improvement was dependent on several factors [69, 70, 71, 72, 73, 74, 75, 76]. We consider now the influence of several factors on the thermal conductivity of various nanofluids that have been proposed as coolants with superior performance in a range of applications.

Usually the thermal conductivity of a nanofluid is more sensitive to temperature than its base fluid [72], and in consequence the reported improvements are more noticeable at higher temperatures.

Influence of the choice of base fluid

Xie et al. [76] compared the increases in the thermal conductivity obtained by dispersing aluminum oxide NP in three different base fluids, namely water, ethylene glycol, and pump oil. The highest percentage increase was observed in the base fluid with the lowest thermal conductivity, i.e., pump oil, whereas the lowest percentage increase was observed in water, which has the highest thermal conductivity of the three base fluids.

Ozerinc et al. [69] stated that, according to the “renovated” Maxwell model [77], the thermal conductivity ratio of a nanofluid (thermal conductivity of the nanofluid divided by the thermal conductivity of the base fluid) increases as the thermal conductivity of the base fluid decreases. However, they emphasize that the effect of the NP on other physical properties of the base fluid, e.g., its viscosity, should be considered simultaneously with their effect on the thermal conductivity.

Influence of NP type and concentration

Measurements of the thermal conductivity of nanofluids obtained by dispersing metallic or oxide NP in various cooling agents, mainly water, ethylene alcohol, and engine oil, indicated that:

1. Metallic NP, such as *Cu* or *Fe*, increase the thermal conductivity of the base fluid, even at very low concentrations. Concentrations below 0.5 vol.% may cause increases in the range 10 to 15%, and concentrations of 2.5 vol.% more than 115% [73]. However, metallic NP are not readily available, and tend to oxidize during manufacture or manipulation [12].
2. Low thermal-conductivity NP, e.g., Al_2O_3 , *CuO*, TiO_2 , cause very small thermal conductivity increases at concentrations below 2 vol.%. At concentrations in the range 4 to 10 vol.%, increases in conductivity around 30% were observed in water-based nanofluids with Al_2O_3 and *CuO* NP, and in ethylene glycol-based nanofluids with *CuO* NP [73, 74, 76] (at these concentrations the increase in the viscosity of the NF relative to the base fluid in all cases was less than 30% [12].) Concentrations of *CuO* NP up to 10 to 15 vol. % in ethylene glycol yielded increases of 40 to 50% in the thermal conductivity relative to the base fluid [73, 74, 75, 76]. Nanofluids containing NP concentrations greater than 15 vol.% tend to be unstable, because the NP tend to agglomerate and precipitate. Some authors expect a reduction in thermal conductivity at such NP concentrations [12].

For oxide-type NP, the thermal conductivity of the NP seems to have very little influence on the increase in the thermal conductivity of the nanofluids compared with the base fluids (water, ethylene glycol, and pump oil) [12].

Influence of NP size

The increase in thermal conductivity achieved by the dispersion of NP with diameters in the range 30 to 60 nm in several base fluids, e.g., ethylene glycol, pump oil, and water, has been studied by several research groups [73, 74, 76]. There seems to be

general agreement that the bigger the NP, the bigger the increase. However, the effect of NP agglomeration, which tends to occur more readily with larger NP, was not considered by the authors of these publications.

Influence of NP shape

It seems that cylindrical NP cause larger increases in the thermal conductivity of the base fluid than spherical NP. Xie et al. [76] and Murshed et al. [75] found that the addition of cylindrical NP (SiC and TiO_2) to water and ethylene glycol resulted in an increase in thermal conductivity that was 5 to 10% greater than the corresponding increase following the addition of spherical SiC and TiO_2 NP at similar concentrations to the same base fluids.

2.3.2 Thermal properties of MO- and ester-based NDF

Few publications deal with the thermal properties of transformer- oil-based NDF containing NP [24, 40, 25, 78, 71, 79]; more importance is placed on their dielectric properties.

Two publications have been concerned with the temperature distributions within a transformer when MO-based and ester-based NDF were used as insulation [80]. We consider now the main conclusions presented in the first group of publications.

Thermal conductivity

Nadolny et al.[24] reported on an experimental study in which the thermal conductivities of different MO-based NDF (TiO_2 and fullerene- C_{60} NP) were measured and compared with that of MO. Increases smaller than 1% were obtained for each of the NDF. Similar results were obtained by Jin et al. [77] for MO-based NDF with various concentrations of SiO_2 NP Fig. 2.7a, and by Mansour and Elsaeed [81] for an MO-based NDF with 0.1 vol.% of Al_2O_3 NP. These small increases in thermal conductivity are consistent with the small increases in non-MO based nanofluids containing low NP concentrations (section 2.3.1).

Du et al. [79] carried out an experimental study in which some of the dielectric and thermal properties of two MO-based NDF containing boron nitride and Fe_3O_4 NP were analyzed. Although the increase in the thermal conductivity was below 2% (relative to MO) in all cases (Fig. 2.7b) the NDF showed higher thermal conductivity than the MO. The dielectric properties of both types of NDF were also superior to those of the MO.

We have found only one publication [40] reporting a significant increase (15%) in the thermal conductivity of an NDF (nanodiamond NP at a concentration 0.1 vol.% in MO) compared to that of MO (Fig.2.8). It might be that the hot wire method used in [40] to measure the thermal conductivities yielded unrealistically high values [71].

Fig. 2.7: Temperature dependence of the thermal conductivity of MO-based NDF containing (a) SiO_2 NP (concentrations in vol.%), [76] and (b) boron nitride (BN) and Fe_3O_4 NP (concentrations in weight %), [78].

Viscosity and density

Viscosity and density can influence the thermal performance of cooling liquids. Several authors have studied the effect of NP on the viscosity and density of the base fluids, finding that the effect of NP on the density and viscosity of MO and esters, at typical NP concentrations below 1% vol., was very small [24, 25, 40, 79]. Nadolny et al. [24] made viscosity and density measurements on an MO-based and a SE-based NDF containing fullerene C_{60} NP, and TiO_2 NP coated with the surfactant Span 20 (Table

Fig. 2.8: Increase in thermal conductivity of a MO-based NDF containing various concentrations of nanodiamond NP (concentrations up to 0.16 wt % in the main graph and up to 5% in the rectangular inset), [40].

2.7). Fig. 2.9 shows the viscosity of some of the NDF based on MO, at temperatures between 25 and 80°C. In order to study the influence of the surfactant Span 20, the authors [24] also made measurements on mixtures of MO and surfactant at a concentration 5 g/L. They found that the viscosity increases were in all cases less than 8%.

	Viscosity (mm ² /s)				Density (g/mL)			
	25°C	40°C	60°C	80°C	25°C	40°C	60°C	80°C
MO	17.08	9.39	5.37	3.43	0.867	0.857	0.845	0.832
MO + C60	17.38	9.86	5.46	3.56	0.867	0.856	0.845	0.832
MO + Span	17.61	9.87	5.81	3.61	0.867	0.856	0.846	0.832
MO + Span + <i>TiO</i> ₂	17.99	10.18	6.10	3.69	0.868	0.858	0.846	0.832

Table 2.7: Viscosity and density versus temperature measured on two MO-based NDF, one containing C60 NP and the other *TiO*₂ NP and the surfactant Span, on a mixture of MO and Span, and on the MO, [24].

Raymon et al. [26] measured the viscosity of several NE based NDF containing

four NP (TiO_2 , cadmium sulfite, Al_2O_3 , and Fe_2O_3), each at percentage concentrations of 0.05 g/L, 0.25 g/L, and 0.5 g/L. They found viscosity decreases up to 20% in some of the NDF (relative to the NE) at $90^\circ C$, although the viscosities of most of the NDF were unchanged. As high viscosity is one of the main problems associated with the use of ester based fluids in large transformers, these results are particularly interesting.

Fig. 2.10 shows the kinematic viscosity of MO at $40^\circ C$ as a function of the concentration of functionalized nanodiamonds dispersed within it [40]. The viscosity increased slowly with increasing NP concentration, at concentrations below 1 wt %, but much more rapidly at higher concentrations. This increase with increasing NP concentration is in agreement with [24]. Decreases in viscosity with increasing NP concentration have been reported for other NP/base fluid combinations [82]. However, it should be noted that NDF containing NP concentrations as high as 2.5 wt % would probably not be suitable for transformers, because their dielectric properties would probably be much inferior to those of MO.

Fig. 2.9: Viscosity versus temperature measured on two MO-based NDF containing C60 NP or TiO_2 NP, on a mixture of MO and the surfactant Span, and on the MO [24].

Fig. 2.10: Increase of the viscosity of MO-based NDF with increasing concentration of functionalized nanodiamonds [40].

Chapter 3

Preparation and stability of nanofluids

One of the main problems presented by NDF is the manufacturing method and their long-term stability. This chapter will describes the manufacturing process that was followed in the thesis obtain the NDF that were tested and the stability study that was carried out after the NDF preparation.

3.1 Introduction

Some of the most referenced problems in the field of nanofluids are those related with their stability [22, 83, 32, 84]. The dispersion of the NPs in the base fluid can deteriorate over time, as NP agglomerate to form particles of micrometric or even macro-metric size [30, 85]. The loss of stability of nanofluids is a major problem, since the presence of those aggregates can worsen the properties of nanofluids, giving rise to fluids with poorer properties than those of the base fluid.

A stable nanofluid is one in which the NP remain homogeneously dispersed in the base fluid in the long term. In this case, the attractive Van der Waals forces are compensated with other repulsive forces, mainly of electrostatic, steric, and electro-steric nature [86]. The Derjaguin–Landau–Verwey–Overbeek (DLVO) theory is generally used to describe some of the phenomena involved in the stability of nanofluids [87]; according to it a total “interaction potential” can be calculated as the sum of all the attractive and repulsive forces acting between particles. The

repulsive forces introduce a barrier in the potential that the particles must surpass to agglomerate. If this energy barrier is bigger than the kinetic energy of the particles, the solution remains stable [86].

Some authors have evaluated the stability of NDF for use in transformers reporting dispersal times varying from hours to several months [24, 31, 32, 39, 40]. Most of the works agree in the fact that a low weight fraction of NP implies greater stability than higher weight fractions [88], because as the NP concentration rises the probability of collision between NP increases and in consequence it is more likely that aggregates are formed. It must be highlighted that all authors have used visual inspection as evaluation method to determine the stability of the dispersions. As will be latter discussed in this chapter this evaluation method could be ineffective in all cases.

To improve the stability of NDF it is a common practice to use surfactants, which are products that reduce the surface tension in the fluid, influencing the contact area created between two phases. The surfactant covers the NP, preventing the formation of bonds with other NP through steric interactions.

Although most authors agree in the suitability of using surfactants as stabilizing agents [89], some works report that the addition of large amounts of surfactant can reduce the dispersal time and worsen the dielectric properties of the NDF [90, 41]. In that case, the excess of surfactant would form a double chain around the surface of the NP [91] that could coil up with the surfactant agent that covers the NP forming micelles. With this physics mechanism, the balance between the surfactant effect and the attractive force causes the agglomeration of the NPs.

One of the key factors that should be taken into account when analyzing the stability of NDF for use in transformers, is to consider the conditions these materials will be subjected to during their service life. Transformer's insulating fluids are generally subjected to variable temperature profiles in a typical range 30 – 110°C. Additionally, they coexist with other materials such as the solid insulation that covers the windings, or the metallic elements that constitute the transformer active part or the tank. Although it seems likely that these aspects might have an impact on the

stability of NDF it has not been a common practice within the published works to evaluate the stability of NDF at temperatures different from the ambient one, neither consider the influence of the presence of other materials on the stability. Ghadimi [87] points out that at temperatures above 60°C the bonding between surfactant and NP can be damaged what can jeopardize the stability of nanofluids, but his study was not referred to insulating fluids based materials but to cooling nanofluids. .

This chapter presents the NDF manufacturing process. Also an experimental study is presented that analyzes the stability of several Fe_3O_4 -based NDF manufactured with MO and with a NE as base fluid. Unlike previous published works the study performed in this thesis evaluates the long-term stability of the NDF under real transformer working conditions. The impact of the operating temperature and the interaction with other materials on the stability of the fluids is analyzed. The influence of other aspects, such as the preparation method and the used materials, is discussed as well.

3.2 Manufacturing process

3.2.1 Materials

Base fluid

Two different commercial transformer oils have been used as base fluids: a MO and a NE. The MO was Nytro 4000X, manufactured by Nynas AB (Nynas AB, Stockholm, Sweden), which is composed of 70–90% hydrotreated light naphthenic acid, and 10–30% lubricating oils (C20-50, hydrotreated neutral oil-based) and less than 0.4% 2, 6-di-tert-butyl-p-cresol. This product is commercialized for use in oil-filled electrical equipment, including power and distribution transformers, rectifiers, circuit breakers, and switchgears. The NE was Bioelectra, manufactured by Repsol (Madrid, Spain), which is based on vegetable sunflower oil in a percentage higher than 99% and without the presence of synthetic antioxidants. The physical properties of both insulating liquids are shown in Table 3.1, in the technical sheets of both products are shown in

Annex A

	NE Bioelectra	MO Nytro 4000X
Physics and chemical properties		
Kinematic Viscosity (40°C)	39.2 cSt	9.1 cSt
Flash Point	334°C	146°C
Pour point	-21°C	-54°C
Density (20°C)	0.91 g/cm ³	0.866 g/cm ³
Appearance	Clear and bright	Clear, free from sediment
Water Content	100 mg/kg	<20 mg/kg
Electrical properties		
Breakdown Voltage	65 kV	>70 kV
Disipation Factor	0.03	<0.001
Oxidation Stability		
Total Acidity	0.2 mg KOH/g	<0.01 mg KOH/g
Sludge	0.01%	<0.01%
Dissipation Factor at 90°C, 50 Hz	0.05	<0.01

Table 3.1: Main properties of the base fluids included in the study.

Nanoparticles

Two commercial dispersions of Fe_3O_4 NP were used for manufacturing the NDF under study:

- The first one is composed of Fe_3O_4 NP with an approximate diameter of 10 nm dispersed in a hydrocarbon to a concentration of 50% by weight (i.e., 500 g of NP in 1 kg of dispersion) manufactured by the company Magnacol Ltd (Newtown, UK). From now on this dispersion will be referred to as FF1.
- The second one is a dispersion of Fe_3O_4 NP with a diameter of 10 nm dispersed in a mixture of hydrocarbons, silicon compounds and non-flammable oils manufactured by the company MAGRON (Gyeonggi-Do, Korea), and commercialized by the company Supermagnete (Gottmadingen, Germany)

under the name MFR-DP1. The concentration of this fluid is 60% by weight. From now on this dispersion will be referred to as FF2.

Both dispersions were prepared by the industrial manufacturers using the so-called one-step method in which the NP are simultaneously synthesized and dispersed within the base fluid [28].

The application of the one-step manufacturing method leads to stable fluids at room temperature even with high concentrations of NP (within 50% and 60% by weight). The NP on both fluids are coated with surfactants to inhibit aggregation. Additionally, working with NP dispersions poses less health risk for the workers than using nanopowders [44, 90]. One disadvantage of using NP dispersions is that manufacturers sometimes do not provide enough information about their formulation.

Samples of FF1 and FF2 were subjected to Fourier-Transform Infrared (FTIR) spectroscopy tests to characterize their composition; the FTIR spectra of both dispersions are shown in Fig. 3.1. From these spectra it can be deduced that the carrier liquid is a hydrocarbon in both cases. This is indicated by the sharp peaks around the wavelength 3000 cm^{-1} , belonging to C–H stretching spectral vibrations. In the case of FF1, we can affirm that there is a mixture of hydrocarbons, in which the peak at 1700 cm^{-1} usually refers to a carbonyl of a carboxyl group, an amide, or ester. Also, FF1 has a broad band around 3400 cm^{-1} which is compatible with the presence of a carboxyl group or a mixture of a carboxyl group with hydrocarbons, so we can conclude that the carrier liquid of FF1 is a hydrocarbon and that the surfactant is a carboxylic acid.

In the case of FF2, the carrier liquid is a hydrocarbon as well but the surfactant could not be clearly identified.

Inductive Coupling Plasma (ICP) spectroscopy tests were applied to determine the concentration of Fe and other elements in the NP dispersions obtaining that the concentrations of Fe in FF1 and FF2 were 60 and 50% respectively.

Table 3.2 summarizes the properties of the two applied dispersions deduced from the mentioned tests and from the information provided by the manufacturers.

Physical Property	FF1	FF2
Nanoparticle	Fe_3O_4	Fe_3O_4
Nanoparticle Size	≈ 10 nm	≈ 10 nm
Carrier Liquid	Hydrocarbons	Hydrocarbons
Surfactant	Carboxylic Acid	-
Solid Content	60%	50%
Density (20°C)	1.21 g/cm ³	1.04 g/cm ³
Dynamic Viscosity 27(°C)	87 cP	80 cP
Manufacturer	Magnacol	Magron

Table 3.2: Physical Properties of FF1 and FF2

3.2.2 Syntesis of the NDF

The preparation of a NDF involves the formation of stable colloids, so that the NP remain suspended in the base fluid [87, 92]. The NDFs analyzed in this work were obtained by adding small amounts of FF1 and FF2 to the base fluids up to the desired concentrations, and then subjecting these mixtures to agitation until achieving an homogeneous and stable dispersion.

According to previous works, the method used to disperse the NP in the base fluids plays a very important role in the obtained results, since it seems to affect the NDF final properties and the long-term stability of the dispersion. Petzold et al. [88] compared the stability of the liquids obtained by using several mixing procedures (ultrasound bath, probe-type ultrasonic devices and magnetic stirrers) finding that the probe-type ultrasonic devices achieved the smaller particle diameters with the lower agitation times. Some other references [86, 88], also recommend the use of ultrasound proves instead of ultrasound baths or magnetic stirring. In this work an ultrasonic processor of rated power 750 W and ultrasound wave intensity 670 W/cm², manufactured by the company Sonics & Materials. Inc (Newtown, CT, USA) was applied to disperse the NP into the base fluid (Fig. 3.2).

The sample preparation process applied in this work consists on the following

Fig. 3.1: FTIR spectra of FF1 (top) and FF2 (boton)

Fig. 3.2: Sonicator used to produce the NDF

steps:

- The base fluid (MO or NE) is dried under vacuum (0.1 bar) for 24 h at 70°C.
- To obtain the different desired NP concentrations, the required mass of NP dispersion is weighed in an analytical balance and added to the base fluid. In the case of the MO-based NDF with FF2 the concentrations were 0.05, 0.1, 0.2 and 0.35 g/L (i.e., 0.05 g, 0.1 g, 0.2 g and 0.35 g of Fe_3O_4 NP in 1 L of base fluid). To obtain these concentrations 10, 20, 40, and 70 mg of FF2 were added to 100 mL of MO. In the case of NE-based NDF and FF1, concentrations 0.1 and 0.15 g/L were prepared, as samples with higher concentrations precipitated in a few hours. For the combinations MO + FF1 and NE + FF2 only samples with concentration 0.1 g/L were prepared because of the difficulty to obtain stable samples with higher concentrations.
- The mixture is homogenized with the sonicator, at 40% of the rated power (i.e., power 300 W and ultrasound wave intensity 268 W/cm²), for two hours in intervals of 30 seconds of agitation and 30 s of pause to avoid overheating the oil.
- The obtained NDF are stored at 50°C under vacuum (0.1 bar) to avoid oxidation and to remove the moisture absorbed during the mixing process. All the samples are kept in identical conditions until the beginning of the tests.

Fig. 3.3 shows a photography of some of the obtained MO-based NDF.

3.2.3 Experimental methodology

Unlike previous studies, the stability of the prepared NDF was evaluated under real operating conditions, i.e., considering the temperatures the fluids would be subjected to when operating inside a service-transformer and the effect of the interaction with other materials that coexist with the fluids inside the transformer.

The operation of a transformer involves a continuous generation of heat derived from the flow of current through the conductors that constitute the transformer windings. One of the missions of the insulating fluid is to dissipate these losses

Fig. 3.3: Samples of MO-based NDF with different concentrations of NP. From left to right: MO without NP, MO + FF2 (0.05 g/L), MO + FF2 (0.1 g/L) and MO + FF2 (0.2 g/L).

to the ambient. The service temperature of the elements of a transformer depends on the transformer load, on the room temperature, and on the transformer design. The international standard IEEE C57-91-211 [93] analyzes the typical distribution of temperatures inside a transformer as a function of its loading conditions and establishes that transformer internal temperatures are typically within the range 40 to 110°C. These temperatures are far from the room temperature that has been considered in the stability studies of NDF published to date.

In this work five testing temperatures were considered: 25°C, 50°C, 60°C, 80°C and 110°C. To test the stability of the prepared NDF at those temperatures, samples of NDF were stored in glass sealed vials of 10 mL and kept under controlled temperature conditions for 2 months. In the case of the sample tested at room temperature the evaluation time was extended to one year. All the possible combinations of NP dispersions and base fluid were included in the study; then the stability of four NDF was evaluated: MO + FF1, MO + FF2, NE + FF1 and NE + FF2 all of them with NP's concentration 0.1 g/L. NDF with higher NP concentrations were not included in the study because preliminary tests showed us that the stability of these liquids at temperatures above 25°C was seriously compromised, and also because the samples with concentration 0.1 g/L demonstrated better global physic-chemical properties than the liquids with higher NP concentrations, as will be explained later.

Another objective of the study was to analyze whether the interaction of the

NDF with other materials present inside of the transformer tank has an impact on its stability. The insulating fluid in a transformer coexists with cellulosic materials (i.e., Kraft paper, pressboard, and wood) which act as electrical insulation and support, and with metallic parts (i.e., cooper constituting the windings and iron that constitutes the magnetic core). The present study has analyzed the influence of the cellulosic insulation on the stability of NDF; these materials are in deep contact with the NDF which impregnates them.

Aiming to evaluate this factor, additional testing vials were prepared which include a strip of Kraft paper of mass ≈ 0.5 g. Eight samples were prepared for each testing temperature: four samples for each combination of base fluid and NP dispersion half of them with Kraft paper in the vial and half of them without paper.

The stability of the samples was evaluated both, by means of visual inspection and by means of the measure of the particle size. Traditionally visual inspection has been the most commonly applied technique for the evaluation of the stability of NDF for use in transformers [86]. This method is based on the fact that the loss of stability of the fluids is sometimes noticeable by the apparition of aggregates or precipitates in the fluid. On the other hand, the particle or aggregate size can be used as an indicator of the interactions between particles. In this way, the size of the aggregate decreases the extent to which the chemical barrier increases, and the aggregation process of the particles becomes more difficult.

Particle-size measurements were performed by dynamic light scattering, using a Malvern Panalytical Zetaziser Nano ZS instrument (Malvern, UK). This equipment uses non-invasive back scattering. The Brownian movement of the nanoparticles in suspension induces fluctuations of the scattered intensity which are analyzed by a time-auto-correlation function allowing the obtention of a relaxation time related to the diffusion coefficient D of the nanoparticles. Finally, the hydrodynamic radius is calculated using the Stokes-Einstein equation, $R = k_b T / 6\pi\eta D$, where η is the solvent viscosity and k_b is the Boltzmann constant. The samples were illuminated with a He-Ne laser (632.8 nm) and the scattered light was analyzed at a backscattering angle of 173° . For each sample, at least three measurements were done. The software of the

equipment analyzes the autocorrelation function to obtain the intensity and, using the Mie theory, the volume size distributions. The temperature at the measuring chamber was adjusted to 25°C. Equilibration time was 2 min and at least three measurements were done for each sample.

Attempts were done to apply Zeta potential to the evaluation of the stability of the prepared NDF. The measure of the Zeta potential, which is the electric potential on the surface of the NPs and is proportional to the amount of electrical charge attached to the NP surfaces, has been widely used to evaluate the stability of water-based nanofluids [30]. In the case of the oil-based samples studied in this work, Zeta potential measures were not conclusive, since the applied base fluid are based mainly on hydrocarbons, which are not sufficiently polar, and thus the nanoparticles did not attach enough electrical charge to their surfaces to create a measurable potential.

The possibility of applying the light transmission measurement to the evaluation of the stability was also considered. This technique, based on the fact that NP aggregates have a refractive index greater than that of the medium, was not finally applied because the materials used to prepare the NDF under study absorb in the UV-V what complicates the measurements.

3.3 Results for the stability tests

3.3.1 Visual inspection

During the experiments, a visual inspection of the samples was carried out daily to corroborate that aggregates had not formed in the dispersion. The formation of precipitates was considered as an indication of stability loss. Table 3.3 summarizes the results of the visual inspection analysis. The column “Stability” indicates the time that elapsed without the sample showing any observable precipitate or aggregate.

As explained in section 3.2.3 the testing period for the samples which were subjected to temperatures 50–110°C was two months. After this time if the samples had not precipitated, they were taken out from the oven and the test stopped. The

sample that remained at room temperature was tested for one year.

Base Fluid	NP (0.1 g/L)	Test Temperature	Stability	Final State
Bioelectra (NE)	FF1	25°C	One year	Type 1
		50°C	2 months	Type 1
		60°C	2 months	Type 1
		80°C	2 months	Type 1
		110°C	2 months	Type 1
	FF2	25°C	3 months	Type 2
		50°C	7 weeks	Type 2
		60°C	4 weeks	Type 3
		80°C	2 days	Type 3
Nitro 4000X (MO)	FF1	25°C	Unstable	Type 4
		50°C	Unstable	Type 4
		60°C	Unstable	Type 4
		80°C	Unstable	Type 4
	FF2	25°C	One year	Type 1
		50°C	2 months	Type 1
		60°C	2 months	Type 1
		80°C	12 days	Type 3

Table 3.3: Results of the stability tests according to the visual inspection

The appearance of the solutions at the end of the stability tests was analyzed, distinguishing between five different final appearances:

- **Type 1:** Samples that remain with a good dispersion after the testing period. Examples of this can be seen in Figure 3.4a, which corresponds to a dispersion of NE with NP at concentration 0.1 g/L. and Figure 3.4b, which shows a sample of MO with NP at concentration of 0.1 g/L after 2 months of testing.
- **Type 2:** Samples in which, after some time, the nanoparticles form a precipitate that remains suspended in the solution. An example of this can be seen in Figure 3.4c.

- **Type 3:** Samples in which the nanoparticles form a precipitate at the bottom of the vial. The precipitate is solid and is deposited and adhered at the bottom of the vial. An example of this can be seen in Figure 3.4d.
- **Type 4:** Samples in which the nanoparticles could not be dispersed by ultrasounds during the manufacturing stage. An example of this can be seen in Figure 3.4e.

Fig. 3.4: Appearance of the solutions after the tests (From top left to bottom right): (a) Type 1, NE+FF1 (0.1g/L), (b) Type 1, MO+FF2 (0.1g/L) (c) Type 2, precipitate suspended, (d) Type 3, precipitate at the bottom of the vial, (e) Type 4, NP could not be dispersed.

According to the results obtained with the visual inspection, the following conclusions can be extracted:

- The mixture of the NE and the NP dispersion FF1 (0.1 g/L) was the liquid that presented the best long-term stability, showing a good performance at all tested temperatures. Even the sample that was subjected to 110°C for two months remained stable showing no visible aggregates or deposits at the end of the test.

The same solution remained stable at room temperature for at least one year (after one year the test was discontinued), which is a long time compared with the ones reported in the literature. On the other hand, the mixture of the NE with the NP dispersion FF2 led to a less stable fluid. At room temperature visible NP aggregates appeared after 3 months of testing. The samples that were subjected to higher temperatures also showed visible NP aggregates after 7 weeks of testing, in the case of the sample tested at 50°C, and solid deposits after 4 weeks and 2 days when tested at 60 and 80°C.

- In the case of MO-based samples, the mixture of MO and the NP dispersion FF2 (0.1 g/L) led to a fluid which was highly stable at room temperature. After one year of testing the sample did not show any visible aggregates or deposits. The stability of this mixture was also good when subjected to moderate temperatures (50 and 60°C), for 2 months. However, visible NP aggregates appeared in the fluid after 13 days when the sample was tested at 80°C. The mixture of MO and the dispersion FF1 did not lead to an homogeneous fluid after the ultrasounds stirring and solutions similar to the one shown in Figure 3.4 (e) were formed instead.

As explained before, the magnetic nanoparticles need to be stabilized in the carrier liquid, as a solution to reduce their high surface energy, because otherwise because they tend to form aggregates due to Van der Waals forces. The suppliers of the NP dispersions solve this problem by adding a dispersing agent which usually is a surfactant (for example a fatty acid). When the nanofluid is diluted in the oil the objective is to maintain the dispersion stable. There is a kinetic stabilization against gravitational forces, related with Brownian motion or the viscosity of the medium, and aggregation stabilization through the formation of an adsorption layer. When diluted in the oil, the stability of the dispersion depends on how the aggregation stabilization operates in the system [94, 95].

According to the experimental observations it is clear that the temperature is a variable that has a high impact on the stability of the analyzed NDF. The worsening of stability in the NDF when increasing the temperature may be related with the changes

that occurs in the Brownian Movement of the NP in the NDF. When the temperature increases, the speed of the NP increases as well, what produces a greater number of collisions and these occur with greater energy, as [54] shows. Another effect that might explain the impact of the temperature on the NDF stability is the fact that at higher temperatures the surfactant might suffer some degradation losing its properties and allowing the agglomeration of the NP, as indicated in [91]. Finally, the viscosity of the fluid decreases what favors the formation of aggregates.

Additionally, the results demonstrate that not all the materials combine equally well with the different base fluids. In this sense, the NE, which is a fluid with a certain degree of polarity, seem to form more stable dispersions when a polar surfactant, as the carboxylic acid present in FF1, is added to the mixture. Conversely the surfactant present in FF2 seems to be more suitable to produce MO-based NDF.

As explained before, vials in which samples of Kraft paper coexisted with the NDF were prepared and subjected to the same experimental conditions than the samples listed in Table 3.3. The results of these tests are not shown in Table 3.3, since there were no significant differences (i.e., above 24 h) between the stability times of these samples and those prepared without paper. This appreciation has been confirmed by particle-size measurement which are shown in the next section.

3.3.2 Particle-size measurements

Particle-size measurements were carried out on all the samples that showed certain stability at the end of the two months testing period (one year, room temperature). This includes the fluids obtained from the combinations NE + FF1, NE + FF2 and MO + FF2. The fluid MO + FF1 was not included in the particle-size study since, as was explained before, that combination did not lead to homogeneous dispersions.

Figure 3.5 shows, as an example, three of the measuring registers. It can be observed that the measures show a distribution of particle sizes centered around a central point. Table 3.4 shows the main peak observed in the volume distribution registered for each of the analyzed samples, as well as the full width at half maximum of the size distribution (FWHM). According to the equipment, the main peak is

responsible for more than 98% of the sample scattering. The results have been plotted in Fig. 3.5 as well.

Base Fluid	NP (0.1 g/L)	Test Temperature	Stability	Main Peak (nm)	Peak FWHM (nm)
Bioelectra (NE)	FF1	25°C	One year	116	23
		50°C	2 months	31	33
		60°C	2 months	23	4.6
		80°C	2 months	20	4.8
		110°C	2 months	514	91
	FF2	25°C	3 months	28	6.2
		50°C	7 weeks	17	8.3
		60°C	4 weeks	13	6.2
		80°C	2 days	69	13.4
		25°C	One year	16	12.3
Nytro 4000X (MO)	FF2	50°C	2 months	18	10.5
		60°C	2 months	13	2.3
		80°C	13 days	816	166

Table 3.4: Stability tests according to particle size measurements. FWHM is the full peak width at half maximum.

The increase in the particle size is related with the aggregation of the NP and it is not desirable.

From the obtained results, it can be deduced that in general the formation of aggregates increases with temperature and time, this effect being observed mainly at the highest temperatures tested. As the temperature increases, the surfactant layer increases its capacity for elastic deformation during collisions between particles, reducing its hydrodynamic radius and increasing the mean available volume [96]. This may favor aggregation by allowing a close interaction between particles through Van der Waals interactions.

It should be noted that we have measured the size distribution of the ferrofluids.

Fig. 3.5: Measured particle-size distribution by volume: Red: MO + FF2, Green: NE + FF2, Blue: NE + FF1. Testing temperature 25°C

Mean peak values of around 22 nm (FWHM of 9 nm) for FF1 and 18 nm (FWHM of 10 nm) for FF2 were obtained.

As can be seen, below 60°C for the case of dispersion MO + FF2 (blue curve in Fig. 3.6), all the particle-size measurements are around the 10 nm specified by the supplier, which in practice means that no aggregation has occurred. From 80°C it could be said that the particle size shoots up, making the mixture unstable, what agrees with the conclusions of the visual inspection.

In the case of the measures performed on NE + FF1 samples subjected to stability tests (red curve in Fig. 3.6), an increase on the particle size can be observed as the testing temperature rises. Although the visual inspection seemed to indicate that all the samples of the liquid remained stable for the 2 months period, some of the particle-size measurements showed appreciable changes. In particular, for the samples that were kept at 25°C for one year, the particle-size measurement showed that NP aggregates ten times larger than the original particle size were present in the samples of the fluid, what implies that some degree of aggregation. As can be seen the samples remained stable when subjected to temperatures within 50 and 80°C although significant increases in the particle sizes can be observed on the samples that had been subjected to stability tests at 110°C.

Finally, for the dispersion of NE + FF2 (green curve in Fig. 3.6), it can be observed that although the NP kept a size consistent with the information of the supplier, visible

deposits were present in the samples at the end of the tests. This can be due to the fact that, while there are NP that remain dispersed in the oil, others form aggregates in the system. This would result in a lower concentration of particles in the NDF compared to the calculated ones.

Fig. 3.6: Average particle size of the NDF at the end of the testing period (i.e., 2 months for $T > 30^{\circ}\text{C}$ and one year for $T = 25^{\circ}\text{C}$) and error bar. FWHM is presented as the error bar

Several NDF samples with incorporated Kraft paper were analyzed also by DLS to check if there was any influence over size distribution. Results are not shown as the obtained values are of the same magnitude order than the observed for NDF samples. For example, NE + FF1 with Kraft paper kept at 25°C showed the size distribution main peak at 156 nm (FWHM of 34 nm), but NE + FF2 or MO + FF2 with Kraft paper, also kept at 25°C , showed their main peaks at only 19 nm (FWHM of 7 nm) and 13 nm (FWHM of 5 nm) respectively, in accordance with NDF measurements without Kraft paper. The only difference between samples with paper and without paper is that in the ones without paper the precipitate was deposited at the bottom of the vial, while in the samples with paper the precipitate was deposited on the surface of the paper. This observation seems to indicate that the presence of paper has not a big impact on the

long-term stability of NDF. This is a positive aspect that can facilitate the application of these fluids to service transformers.

According to these results, it seems clear that the long-term stability of NDF depends strongly on the working temperature and that all the analyzed mixtures become less stable when they are subjected to higher temperatures for long periods of time. Although this aspect can be a major problem for the application of NDF to service transformers it had not been pointed out by any other author before [86, 97].

3.4 Physical and chemical evaluation of the NDF

Physical and chemical tests were performed over fresh samples (i.e., not subjected to stability tests) of the mixtures MO + FF2 and NE + FF1, to determine how the addition of different concentrations of Fe_3O_4 NP affects the physical properties of oils. It must be pointed out that the physical-chemical evaluation of the liquids presented in this chapter is not exhaustive and that more work is required to fully understand the behavior of the prepared NDF.

The density and the kinematic viscosity of the prepared NDF were measured finding that the variation of these variables with the increase of the NP concentration was negligible, as can be seen in Fig. 3.7. That lack of change is justified by the very low amounts of NP that were added to the base fluid. The theoretical variation of the density and viscosity was estimated using the mixture rule and Einstein equation 3.1 [12], obtaining that for the higher concentration of NP considered in this work (0.35g/L), the expectable variation of the density would be around 0.01% and the variation of the viscosity would be around 0.1%, what is in agreement with the experimental measurements. Other authors have presented similar results in previous works [24].

$$\mu_e = (1 + 2.5 \cdot V_p) \mu_m \quad (3.1)$$

The resistivity of the liquids was measured using a Baur DTL C tan delta and resistivity tester observing a significant drop on the resistivity values as the NP

Fig. 3.7: (a) Density and (b) viscosity of the prepared NDF

concentration rises as can be seen in Fig. 3.7.

Some dielectric properties of the fluids were also evaluated (i.e., AC BV, tangent delta, and resistivity).

Figure 3.8a shows the evolution of the BV at 50 Hz, measured according to standard IEC 60156 [53]. As can be seen, there is a clear improvement on the dielectric strength of the oil when NP are added to it. This is in agreement with the results shown by many other authors [20, 26, 27, 50, 36, 34] and will be further investigated in chapters 4, 5 and 6.

Fig. 3.8: (a) AC BV (50 Hz) and (b) Tangent delta of the prepared NDF

Regarding the tangent delta and resistivity variation, shown in Figures 3.8b and 3.9a, it can be seen, that the tangent delta increases with the concentration of NP added to the fluids, while the resistivity decreases. These tendencies, which are equally noticeable in NE and MO-based liquids and are negative for the dielectric performance of the fluid, are probably caused by the presence of conductive NP in the oil. Similar variations for these variables have been shown by other authors [98]. The recommendation of IEEE Std C57.106-2006 is that tangent delta of a service oil should be below 0.5; thus, only the NDF with concentration 0.1 g/L would be within admissible limits.

Fig. 3.9: (a) Resistivity and (b) Acidity of the prepared NDF

More research is required to investigate the dependence of the tangent delta with the concentration of NP added to the oil; in particular, it would be important to measure the components of the complex permittivity to evaluate the increase of the dielectric losses of the fluid when conductive NP are added. Rajnak [99] evaluated the complex permittivity of a Fe_3O_4 -based NDF for several concentrations of NP, finding a significant increase of the dielectric losses as higher concentrations of conductive NP are added to the oil. The author demonstrates that the observed increase is mainly due to the polarization and relaxation processes that take place on the NP-counterions system when the NDF is subjected to an electric field, and in much lower extent to the increase of the electric conduction in the fluid.

The fluid's relative permittivity also influences the tangent delta. Miao et al. [100]

investigated the permittivity variation of NDF, finding that the permittivity of NDF rises slightly with the NP concentration; the authors developed a physical model to explain the permittivity change, based on the analysis of the NP inner polarization in presence of an electric field.

Finally, the evolution of the acidity of the oils with the increase of the NP concentrations was measured. As shown in Figure 3.9b, as higher concentrations of NP are dispersed in the base fluid, the acidity of the NDF is higher. This is not a positive factor, because the presence of acids in oil accelerates its ageing rate and can lead to formation of sludges, which are harmful for the solid insulation. However, it should be noted that the measured values are still far from the limit value recommended by IEEE Std C57.106-2006 [93] for a service MO, i.e., 0.2 mg KOH/g, and also from the level of 0.4 mg KOH/g where sludges may start to form. The increase of the acidity might be caused by the presence of the surfactants in the NP dispersions used to prepare the NDF, although more research would be necessary to understand the causes of that increase.

3.5 Conclusions

In this chapter, the stability of several NDF for use in transformers was evaluated. According to the experimental evidence, it can be concluded that although the application of ultrasonic stirring leads to stable NDF with superior dielectric properties compared with the corresponding base fluid, some of these liquids lose stability when subjected to high temperatures for long periods of time. The loss of stability could be related with the loss of the bound between the surfactant and the NP or to some other factors.

Although most published works on transformer NDF evaluate the stability of the liquids at room temperature, the service temperature is a key factor that must be considered in the stability tests, since fluids that perform well at room temperature become non-stable above certain temperature ranges.

The stability of newly developed NDF must be tested at typical transformer

working conditions to guarantee that they can withstand the operating temperatures they will be subjected to. Other aspects, such as the presence of cellulosic insulation do not seem to affect the stability of the samples significantly.

The materials used to produce the NDF also have a major influence on the stability; in this sense, carboxyl functionalized surfactants seem to be more adequate for NE oils, whereas non-carboxylic surfactant of FF2 dissolve better the NDF in low polarity fluids, as MO. Regarding the methodologies that can be applied to the evaluation of the stability of NDF, it has been shown that visual inspection and particle-size measurement can be used as complementary methods to get information about the formation of precipitates in the dispersions and the aggregation phenomena. Although visual inspection has been generally used to analyze the stability of NDF by many authors, that method might fail in detecting moderate aggregation of NP within the fluids. On the other hand, Zeta potential is not a suitable method to characterize the stability of these types of liquids as, given their non-polar nature of the base fluid and the NP concentrations typically used for this application, the NPs do not attach a sufficient amount of charge to their surfaces to enable the measure.

As a general conclusion it can be said that, although the application of NDF to power transformers is promising and the development of these materials will probably lead to more compact and reliable machines in the future, more work is still needed to improve the long-term stability of these liquids under transformer typical operating temperatures.

Chapter 4

AC breakdown voltage of mineral oil based nanodielectric fluids

One of the main factors to determinate the insulating properties of a dielectric oil is the AC BV i.e. the minimum voltage level at 50 Hz that causes the dielectric breakdown of the oil.

As it was seen in the section 2.2.1, one of the most important parameters to know the quality of an insulating oil is the AC BV. Many authors have studied the effect of dispersing NP in the AC BV of the MO as part of the method of characterization of oils, as described by [101, 102, 103]. This method has also been used to see if there is an improvement in the NDF respect to their base oils as reference [104].

One of the main factors that determines the AC BV of an insulating fluid is its moisture. However, as will be explained in chapter 5, the evolution of the BV with moisture has not been studied by many authors up to date maybe because of the difficulty of measuring the moisture content of fluids with presence of NP.

In this chapter the AC BV of several Fe_3O_4 based NDF is tested, investigating the evolution of this parameter with the concentration of NP dissolved in the NDF. In the first part of the chapter the testing procedure is described. Then, the statistical analysis of the results is carried out using parametric and non-parametric analysis. In this chapter, the oils were dried under vacuum conditions before proceeding to the

measurements, this their moisture content was very low and the evaluation carried out in this chapter correspondes to dry fluids.

4.1 Methodology

The experimental study presented in this chapter is based on the evaluation the AC BV of several MO and Fe_3O_4 based NDF. The experimental methodology applied during the study is described next.

4.1.1 Preparation of NDF

The NDF were obtained using the procedure described in chapter 3. This method has proven to be effective to obtain NDFs that remained stable for more than one year.

Therefore, sample preparation was done in the following steps:

1. The MO is dried under vacuum. In this case, the MO used is Nynas Nitro 4000X.
2. The NP is added to the base fluid depending on the desired concentration. In this test, the NP suspension used is FF2 and the considered NP concentrations are 0.05 g/L, 0.1 g/L, 0.2 g/L, 0.3 g/L and 0.4 g/L.
3. The NDF is mixed and homogenized with the sonicator.
4. The obtained NDF is dried at 50°C under vacuum during 48 hours in order to dry the NDF and remove the bubbles.

4.1.2 AC breakdown voltage test

The AC BV measurements of the NDF were carried out according to IEC 60156 standard [53] using a tester Baur DTA 100C (Fig. 4.1). In this part of the thesis, the investigated frequency is power frequency (50 Hz). The testing procedure was as follows:

1. The test cell is filled with 500 mL of the fluid under analysis. In this case, Nynas Nitro 4000X with FF2 at different concentrations.

2. A sample of the fluid under test is taken to obtain its initial moisture content with Karl Fischer method, and then the sample is left in magnetic stirring for five minutes to release any air bubbles that have been formed during the filling of the test cell.
3. Ten measurements of AC BV are carried out with Baur DTA 100C. Between each rupture the fluid is left two minutes under magnetic stirring.
4. A new sample of fluid is taken for moisture determination and ten additional breakdowns are applied.
5. The sequence 1 to 4 is repeated for a fresh sample of fluid.

For each considered condition 40 AC BV values were recorded (i.e. 20 breakdown measurements on two different samples) and the moisture content of the samples was measured four times during the tests.

Fig. 4.1: Baur DTA 100C.

4.2 Results

After the measuring campaign, six groups of 40 measures of AC BV were obtained. A first inspection of the measurements showed that they presented a significant dispersion which did not follow any tendency in relation to the measuring sequence. A statistical analysis of the results was carried out following both a parametric and a non-parametric approach.

Figure 4.2 shows the 40 AC BV values measured on the NDF prepared with NP concentrations 0.05 g/L, 0.1 g/L, 0.2 g/L and the AC BV measured on samples of MO. As explained before, the 20 first points and the next 20 points correspond to different samples of fluid. It is important to note that the maximum voltage that could be applied with the deployed tester was 98 kV, so some of the measurements appear truncated. This happens especially for NDF concentration 0.2 g/L.

Fig. 4.2: AC BV measurements of the fluids with concentrations 0.05, 0.1 and 0.2 g/L.

4.2.1 Non parametric statistical analysis

An analysis of variance ANOVA [105] was performed according to Annex B to compare the AC BV values of the six analyzed fluids. The analysis shown that there are significative statistical differences between the means of the six groups ($p\text{-value}=4.611 \cdot 10^5$, $F= 5.79$). Fig. 4.3 shows box-and-whisker diagrams of the six groups of measurements, including the quartiles and mean values of the AC BV of the six analyzed fluids.

Further comparisons using the Tukey HSD test (Annex B) indicated [106] that the mean value for the AC BV of the MO is significantly different than the AC BV of the

three NFD with NP concentrations 0.05, 0.1 and 0.2 g/L. On the other hand, the AC BV of the NDF with NP concentrations 0.3 and 0.4 g/L did not differ significantly from the AC BV of the MO. Fig. 4.4 shows the multiple comparison of the means, it can be seen there is an overlapping of the confidence bounds obtained for the AC BC of the MO and the NDF with higher concentrations of NP.

Fig. 4.3: Box-and-whisker diagrams of the six groups of AC BV data recorded in the fluid's samples.

It can be concluded that the AC BV of the fluids rises as higher concentrations of NP are added to the MO reaching the highest value for NP concentration 0.2 g/L. For concentrations above 0.2 g/L there is still an improvement with respect to MO but it is not significant enough. According to these results we decided to consider only the results of the AC BV tests on the NDF with NP concentrations within 0.05 and 0.2 g/L for further analysis.

Table 4.1 presents the values of the mean, the standard deviation and the percentiles 2, 50 and 90 of the AC BV values measured for each analysed fluid. Several conclusions can be drawn from these calculations. In the first place the values of both the mean and the median (Percentile 50%) of the AC BV rise as the concentration of NP in the NDF is increased. Improvements of a 10% are observed for the NDF with NP concentration 0.2 g/L. Moreover, the standard deviation of the measurements

Fig. 4.4: Multiple comparison of the means of the AC BV of the five NDF and the AC BV of MO for the six analyzed fluids.

decreases when NP are added to the oil. This can be clearly observed in Fig. 4.5 which shows the histograms of the measurements obtained for all the analysed fluids. As it can be seen, as the concentration of NP rises, the values of the AC BV are more concentrated around 98 kV, which is the maximum voltage that can be applied by the applied tester. This means that most of the samples did not break down at 98 kV, so the real BV of the NDF would be even higher than those displayed in Table 4.1.

The study of the percentiles, shows that the lower BV registered on the NDF increase significantly compared with those recorded in the MO (i.e. percentile 5 is 65.55 kV for MO and 79.24 kV for the NDF with concentration 0.2 g/L). This parameter is important for the transformer design.

Fig. 4.6 shows the cumulative probability of the AC BV values measured on the NDF prepared with NP concentrations 0.05, 0.1 and 0.2 g/L and on samples of MO. As it can be seen, the measurements have a significant dispersion.

4.2.2 Parametric analysis

Table 4.2 presents the p-value and the adhesion to the hypothesis conformity tests for Normal and Weibull distributions of the experimental data for the four analyzed

	MO	NDF 0.05 g/L	NDF 0.1 g/L	NDF 0.2 g/L
Mean (kV)	87.02	93.14	94.12	95.21
Standard Deviation	10.38	7.74	6.92	6.59
Percentile 2 (kV)	63.53	69.25	71.23	71.96
Percentile 50 (kV)	89.00	96.65	98.40	98.20
Percentile 90 (kV)	98.40	98.70	98.60	99.00

Table 4.1: Statistical analysis of the AC BV measurements at dry conditions.

Fig. 4.5: Frequency of ACBV for each fluid at dry condition a) MO, b) MO + 0.05 g/L NP c) MO + 0.1 g/L NP d) MO + 0.2 g/L NP.

fluids. It was performed similarly to that shown by Khaled and Beroual in [107]. The hypothesis is accepted for all the NDF (for a confidence bound 5%) but not for the oils

without NP in both cases of Normal and Weibull distribution.

Fig. 4.6: Cumulative probability of the AC BV measurements performed on the NDF and on MO.

Fluid	Weibull		Normal	
	p-value	Conformity	p-value	Conformity
MO	0.039	Not accepted	0.012	Not accepted
NDF 0.05 g/L	0.335	Accepted	0.176	Accepted
NDF 0.1 g/L	0.499	Accepted	0.469	Accepted
NDF 0.2 g/L	0.099	Accepted	0.051	Accepted

Table 4.2: Hypothesis test of conformity to Normal and Weibull distribution.

The Shapiro-Wilk test was performed and in all cases the null hypothesis was rejected, indicating that the population is not normally distributed.

The values of AC BV obtained for each NDF were fitted to Weibull and Normal distributions. Fig. 4.7 and 4.8 show the cumulative probability of failure vs AC BV according to these distributions for the MO and the NDF.

Fig. 4.7: Fit of the data to a Weibull distribution.

Fig. 4.8: Fit of the data to a Normal distribution.

The correlation coefficients for the Normal distribution fittings are shown in Table 4.3. As can be observed the accuracy of the estimations at low probabilities is not good enough for neither of the two distributions. Other authors report similar discrepancies

on the low-probability zones for several insulating fluids [108, 105].

Fluid	R-square
MO	0.727
NDF 0.05 g/L	0.864
NDF 0.1 g/L	0.875
NDF 0.2 g/L	0.847

Table 4.3: Correlation coefficient for the Normal distribution fitting.

Table 4.4 shows the obtained values for the parameters of Weibull and Normal distribution for each analyzed fluid. For Weibull distribution a is the scale parameter, which predicts the AC BV at a failure probability of 63%, and b is the shape parameter, which is inversely related with the scattering of the measurements. The parameters of the Normal distribution are the mean value of the AC BV (α) and the standard deviation (β).

Fluid	Weibull		Normal	
	a	b	α	β
MO	86.0	19.6	83.3	7.1
NDF 0.05 g/L	90.6	15.9	87.4	7.9
NDF 0.1 g/L	92.8	16.2	89.6	7.8
NDF 0.2 g/L	95.1	16.4	91.8	8.4

Table 4.4: Parameters for the Weibull and Normal adjustments of the AC BV of the different fluids

As it can be seen, the addition of NP leads to an improvement of the dielectric strength, especially for the case of the NDF prepared with concentration of NP 0.2 g/L. Although the values of the parameter b must be inversely connected to the standard deviation no such tendency is observed in this study.

Table 4.5 provides the AC BV estimated with Weibull and Normal distribution for the MO and the NDF for different probabilities of failure. As it can be seen,

both analysis provide similar estimations, showing improvements of up to 15% for the NDF at high probabilities of failure. As aforesaid the accuracy of the estimations corresponding to probabilities below 20% is not good enough.

Fail. Prob.	AC BV (kV)							
	MO		NDF 0.05 g/L		NDF 0.1 g/L		NDF 0.2 g/L	
	W	N	W	N	W	N	W	N
5%	75.5	77.3	75.2	77.6	75.5	78.0	76.5	79.3
10%	78.0	79.0	78.8	80.1	79.5	80.7	80.2	82.3
25%	81.5	81.7	84.3	84.3	85.2	85.3	87.1	87.3
50%	85.0	84.7	89.4	88.9	90.8	90.4	93.4	92.9
75%	87.8	87.8	93.6	93.6	95.6	95.4	98.6	98.5

Table 4.5: Breakdown voltage for different failure probabilities according to Weibull (W) and Normal (N) distributions.

4.3 Discussion

The experimental measurements shown in this chapter demonstrate that the addition of Fe_3O_4 NP in low concentrations achieve significant improvements in the AC BV values, reduces the dispersion of the measurements and increases the breakdown voltages at low probabilities of failure, what is important for transformer insulation design. This statement is valid only from the point of view of the dielectric behavior; as shown in chapter 3, NDF still have serious issues that must be improved, as their long term stability, before they can be applied to transformers.

The improvement of the AC BV might seem surprising if we consider that Fe_3O_4 NP are conductive and that in fact, the resistivity of the resulting NDF fluids is lower than that of the MO, as was shown in chapter 3, (Fig. 3.9).

Other authors have reported enhancements in the AC BV of MO when small amounts of Fe_3O_4 NP are dispersed in them. Table 4.6 summarizes some of the results reported in previous works.

Fluid	Concentration	AC BV (kV)	Increase (%)	Reference
Fe_3O_4 / MO		55.4	44.3	[17]
Fe_3O_4 / MO	100 ppm	54.4	8.4	[29]
NDF 0.2 g/L	50 ppm	49.1	6.1	[109]

Table 4.6: AC BV enhancements reported by other authors in Fe_3O_4 based nanofluids.

Except for [17] in which the concentration of NP is not given, the improvements shown by other authors are similar to the ones found in this chapter.

The theoretical description of the physical processes involved in the dielectric behavior of NDF is a topic that is still under research. Most authors explain the observed behavior in the light of two theories: The electrical double layer (EDL) theory and the electron scavenger (or shallow trap) theory. Although we do not have access to techniques to further investigate the phenomena that occur in the fluid at a microscopic level, the explanations provided by both theories are in agreement with the experimental observations provided in this work.

Fig. 4.9 illustrates the EDL theory. According to it, when a NDF is subjected to an electric field, positive ionic charges accumulate on the surface of the NPs, attracting negative ionic charges around them [107, 27] and forming an EDL. The volume of the EDL close to the NP surfaces is called the compact-layer, and consists of immobile negative ions attracted strongly to the NP surfaces. The net charge density in the compact layer drops gradually with increasing distance from the NP surfaces, reaching zero in the electrically neutral area of the fluid. The ions in this region, called the diffuse layer of the EDL, are less affected by the electrostatic interaction with the NP and thus have higher mobility [110].

The formation of the EDL limits the presence of fast free ions and electrons in the insulating fluid replacing them by slow charged NP. The reduction of the mobility of the electric charges modifies the velocity of propagation of the streamers, which becomes smaller, being thus more likely those streamers are extinguished before a breakdown takes place. Under these conditions a higher electric field will be required

to produce a dielectric breakdown what enhances the AC BV values.

Fig. 4.9: EDL formation in NDF. Adapted from [30,36].

Hwang [46] proposes that the effect of dispersing a certain type of NP in a base fluid on the dielectric breakdown process depends on the NP relaxation time, which is related with the time required for the formation of the EDL and can be calculated from:

$$\tau = \frac{2\varepsilon_{fluid} + \varepsilon_{NP}}{2\sigma_{fluid} + \sigma_{NP}} \quad (4.1)$$

where ε_{fluid} and ε_{NP} are the permittivity of the base fluid and the NP and σ_{fluid} and σ_{BF} are their conductivities.

If the relaxation time of the NP is shorter than the time scale of the electrodynamic process being considered, the effect of the NP on the process will be very noticeable, while if the relaxation time is longer than the time scale of the process the NP will have little effect on the breakdown process.

Considering the conductivity of the MO used in this work ($\sigma_{oil} = 5 \cdot 10^{-14}$ S), the typical value of the relative permittivity of MO ($\varepsilon_{oil} = 2.2$) and the dielectric properties of Fe_3O_4 NP reported in the literature [17] ($\varepsilon_{rFe_3O_4} = 80, \sigma_{Fe_3O_4} = 1 \cdot 10^4$ S), a relaxation time of $7.47 \cdot 10^{-14}$ s was obtained for the NDF under study. Therefore, the calculated relaxation time is much smaller than the time scale of the breakdown processes, and thus the observed improvement would be justified in the light of Hwang's theory.

Du et al [83] propose an alternative explanation for the observed improvement, based in the increase of the shallow trap density of dielectric fluids when NP are

present. Du demonstrates that repeated electron trapping and de-trapping processes is one of the main charge transport processes in NDF; if the fast electrons, generated in presence of an intense electric field are trapped and de-trapped by the shallow traps when moving from high to low field locations, their speed, and so the speed of the streamer propagation, will drop significantly. The described mechanism explains the enhancement of the dielectric properties observed in NDF based in semi-conductive and insulating NP [111] that EDL theory fails to explain, and is valid to explain the results obtained in this work as well.

Clarify the role of the materials present in the NP suspension MFR-DP1 (which was added to the MO to produce the NDF under test) in the obtained results, an additional set of measurements was carried out on NDF containing exclusively MO and NP. Fe_3O_4 NP were dispersed in the MO Nynas Nytro up to a concentration 0.2 g/L. The preparation of this fluid was performed by the company Magnacol U.K. The resulting NDF was less stable in the long term but it did not show any signs of deposits or precipitation during the testing time. 40 AC BV values were recorded in two samples of that fluid following the testing procedure described in section 4.1.

Table 4.7 compares the mean value and the standard deviation of the AC BV values measured on this fluid vs. the parameters obtained on the fluid prepared from the NP suspension MFR-DP1.

Combination of materials	AC BV (kV)	
	Mean	SD
Nynas + MFR-DPI	93.14	7.737
Nynas + NP	94.53	7.740

Table 4.7: Influence of the solvent and surfactant.

As can be seen the behavior of both fluids is very similar what suggest that no significative influence of the solvent and the surfactant is observed in the measurements. The ANOVA analysis confirmed that there are no significant differences between the performance of both fluids (p-value =0.4218, F= 0.65). The result of the test is what could be expected because the concentration of the solvent and

the surfactant in the prepared NDFs prepared with the NP suspension FF2 is below 0.2 g/L in all cases.

4.4 Conclusions

In this chapter, the AC BV of several NDF, prepared by dispersing Fe_3O_4 NP in a commercial MO has been tested.

The analysis of the measurements demonstrates that the AC BV of the MO can be significantly enhanced by adding low concentrations of NP to it. As shown in this chapter, all the analyzed parameters in relation to the breakdown process improved: the mean value of the BV, the BV at low failure probabilities and the standard deviation of the measurements. These improvements are in line with those reported by other authors and can be explained in the light of the proposed theoretical theories.

From the point of view of the dielectric properties the results obtained in this chapter might suggest that NDF present higher AC BV than conventional fluids, what is a positive factor from the reliability point of view. Nevertheless, the application of these fluids is not safe at the present because of other issues, such as the stability problems, the lack of studies about its interaction with paper, etc.

The analysis of the performance of the NDF in dry conditions is relevant, as some of the previously published works do not analyze in deep the moisture contents of the tested samples and then it is not easy to discern if the presented results are due to the interaction of the NP with the ions and electrons or to their effect on the behavior of the water molecules present in the oil. Additionally, it must be noted that NDF is a very recent topic, and then a limited number of experiences have been reported so far in this type of fluids. It is important to carry out more experimental studies of these liquids using either similar combinations of materials and testing conditions or different ones to have enough evidence of the tendencies observed by other authors.

Chapter 5

AC breakdown voltage of mineral oil based nanodielectric fluids in high humidity environments

Water has a negative impact on some of the dielectric properties of insulating fluids. The presence of water and particles are the two main factors that determine the value of the BV of a dielectric oil [93, 112]. Miners [112] reported a reduction of the BV of 25% of MO when the water content increases from 5 to 20 ppm. Water have also an important role in the BV of NE and SE, although absolute moisture contents above 100 ppm are admitted in those fluids without a significant reduction of their BV [93].

The reason for the worsening of the fluids BV is that in presence of an electric field, water molecules tend to migrate towards regions with higher field solicitations, forming conductive paths that facilitate the dielectric breakdown [113, 114].

The present chapter studies the influence of water on the AC BV of several MO based NDF. The fluids under study were prepared with several concentrations of conductive Fe_3O_4 NP and were subjected to different conditioning processes to obtain NDF with a range of moisture contents.

The measurements were analysed from two different perspectives; first the dependence of the AC BV of the different liquids with the absolute moisture was

studied, as was typically done by other authors.

Additionally, a characterization of the solubility curve of the fluids under study suggested us that it was necessary to carry out an additional analysis to determine how the AC BV depends on the relative saturations (RS) of the NDF.

The analysis of the results was carried out using both Weibull and Normal distribution and non-parametric statistical analysis. Finally, a discussion is included in the chapter aimed at explaining the processes and physical mechanisms that can justify the improvement of the dielectric properties of NDF when high amounts of water are dissolved in the fluids.

5.1 Methodology

5.1.1 Preparation and conditioning of NDF

Sample preparation was carried out as described in section 4.1.1. Nynas Nitro 4000X (MO) was used as base fluid and FF2 as NP suspension. In this test, concentrations of 0.05 g/L, 0.1 g/L, 0.2 g/L were used.

Dry samples of NDF with different concentrations of NP were subjected to conditioning processes aimed at obtaining samples with different moisture contents. Additionally fluids with RS 25% and 50% were prepared.

To obtain fluids with RS 25%, samples of MO and NDF with NP concentrations 0.05, 0.1 and 0.2 g/L were kept at room conditions in the laboratory for at least 72 hours. The temperature and relative humidity in the laboratory were stable at values 20°C and 25%, respectively.

Samples with RS 50% were obtained by keeping the samples in an environmental chamber for 72 hours at temperature 30°C and relative humidity 50%. It was ascertained that all the samples had reached steady state condition by the end of the conditioning process.

5.1.2 Moisture measurements

Karl Fischer titration [108] is generally used to determine the absolute moisture content of transformer oils in the lab. The methodology that is commonly applied to characterize the moisture content of a liquid sample cannot be applied when measuring the water content of NDF, because the presence of conductive NP in the titration vessel would affect to the currents measured in the KF equipment currents leading to wrong results.

Alternatively, an oven can be used to heat the sample of the fluid under test, evaporating the water contained in it and driving the water to the titration vessel to be quantified.

In this chapter, the water content was measured using a KF Coulometer (Methrom 831) combined with a Karl-Fischer oven Thermoprep 860. The measuring procedure consisted of filling a 2mL sample of the fluid that is being evaluated in a vial. The vial is fitted in the oven where it is heated up to 110°C. Fig. 5.1 shows a picture of the equipment used.

Fig. 5.1: Karl Fischer coulometric titrator with evaporation oven.

Table 5.1 shows the absolute moisture content of the samples of MO and NDF included in the study measured after the manufacturing and conditioning processes. It must be noted that for each considered NP concentration (0.05, 0.1 and 0.2 g/L), two samples with three different moisture contents were prepared (dry, RS 25% and RS 50%). The values presented in Table 5.1 are the mean values of the moisture content.

	Dry	RS 25%	RS 50%
MO	8.10 ppm	17.62 ppm	41.30 ppm
NDF 0.05 g/L	11.61 ppm	27.40 ppm	50.06 ppm
NDF 0.1 g/L	14.52 ppm	28.72 ppm	55.25 ppm
NDF 0.2 g/L	16.66 ppm	32.47 ppm	63.58 ppm

Table 5.1: Moisture content of the samples after the conditioning process

The moisture contents measured for each fluid at the end of the conditioning processes and the corresponding tendency lines are plotted in Fig. 5.2. Using the solubility curve provided by the manufacturer of the MO it was estimated that the RS for the dry condition was about a 10%. As it can be seen, all the NDF present higher moisture contents than the MO for every conditioned process. Additionally, as the concentration of NP in the fluid increases, the moisture contents obtained for the same conditioning process grow.

Fig. 5.2: Moisture content of the NDF and the MO vs relative saturation of the samples.

The result suggests that the solubility of the NDF under analysis is higher

than that of the base fluid and that the solubility rises as higher masses of NP are dispersed in the base fluid. It must be remarked that the conditions applied during the conditioning process were identical for all fluids under test, and thus the RS of the resulting fluids was the same too. A similar behavior was observed in a previous work on a NE-based NDF [115].

The rise of the solubility may be due to the fact that the NP are able to bound water molecules increasing the amount of water that can be dissolved in the fluids under similar conditions. As will be shown later, this fact has a positive impact on the dielectric properties of the NDF.

5.1.3 AC breakdown voltage test

Authors who have previously worked in the topic of water and NDF, compare the breakdown strength of the base fluids and the NDF under similar absolute moisture contents [13, 11]. Considering that the solubility of NDFs becomes higher as the concentration of NP dispersed in them rises it seems clear that it is also important to compare the AC BV of NDF and MO under similar RS conditions.

In the following subsections the influence of the moisture content of the fluids on their AC BV is analyzed. The dependence of the dielectric strength of the samples with the absolute moisture is analyzed first; then the analysis is repeated considering the evolution of the AC BV with the RS of the fluids.

5.1.4 Measuring procedure

The AC BV of the different samples of MO and NDF was characterized following the experimental procedure described in section 4.1.2. All the NDF under test were analyzed by duplicate, recording 20 breakdowns on two fresh samples. Thereby, at the end of the testing period, 40 breakdown values were available for each NDF at each considered moisture content.

The evolution of the moisture content of the samples was monitored throughout the AC BV testing. Moisture measurements were performed on each fluid sample

before starting the AC BV tests and after the 10th breakdown. Then, four moisture measurements were available for each analyzed fluid and moisture content.

5.2 Results

5.2.1 Evolution of the AC BV with the absolute moisture of the samples

Fig. 5.3 shows the AC BV vs the absolute moisture content of the fluid's samples for all the samples included in the study including a tendency line for each fluid. A Boltzman model was considered to obtain the adjustment curves in agreement with the recommendation of CIGRE WG D1.52 [116].

Fig. 5.3: Measurements of AC BV at 50 Hz vs. moisture content measured on the samples and tendency lines.

Looking at the experimental data in Fig. 5.3, it can be seen that at very low moisture contents all the analyzed fluids show AC BV values within 90 and 100 kV; then, as the moisture content of the fluids rises, the AC BV of all the fluids drops although not all of them worsen their properties at the same rate. In this sense, for

moisture contents around 20 ppm the AC BV of the MO drops to values near 60 kV while the AC BV of the NDF with NP concentration 0.2 g/L is still around 100 kV and remains close to 70 kV when the moisture content rises up to 40 ppm. At very high moisture contents the AC BV of all the fluids drops to values near 25 kV, but while in the MO these values were recorded at moisture contents around 40 ppm, in the NDF these values correspond to moisture contents above 60 ppm.

Table 5.2 shows the AC BV for different moisture contents for the analyzed NDF. These data have been derived from the tendency lines shown in Fig. 5.3. As can be seen all the NDF have higher values of the AC BV than the MO at similar moisture contents. This is especially noticeable for the NDF with NP concentration 0.2 g/L, which present values within a 30 and a 100% higher than those of the MO. These results are in agreement with those shown by other authors [11, 16, 117, 13] in previous works.

Moisture Content	MO	NDF 0.05 g/L	NDF 0.1 g/L	NDF 0.2 g/L
10 ppm	87.8	90.3	91.4	101.5
20 ppm	67.0	74.4	75.5	86.8
30 ppm	47.2	56.6	59.6	71.5
40 ppm	30.6	40.4	44.3	56.4
50 ppm	17.4	27.0	31.1	42.6
60 ppm	5.4	14.1	19.8	30.9

Table 5.2: Statistical analysis of the AC BV measurements vs absolute moisture

5.2.2 Evolution of the AC BV with the relative saturation of the samples

RS 25%

Table 5.3 shows the mean value of the AC BV values of the four analyzed fluids when they were conditioned to RS 25%. As can be seen, the mean and the median (percentile 50%) values are only improved slightly by the presence of NP for the case of the maximum concentration studied (0.2 g/L), while for 0.05 and 0.1 g/L, there is a

worsening of these values.

	MO	NDF 0.05 g/L	NDF 0.1 g/L	NDF 0.2 g/L
Mean (kV)	64.552	60.55	58.46	70.85
Standard Deviation	17.22	6.80	12.95	11.04
Percentile 2 (kV)	27.94	41.04	36.10	41.56
Percentile 50 (kV)	63.05	61.85	59.45	71.20
Percentile 90 (kV)	87.15	67.85	75.00	85.50

Table 5.3: Statistical analysis of the AC BV measurements at RS 25%

An analysis of variance (ANOVA) was performed and it showed that there are significant statistical differences between the means of the four groups (p -value= $9.94 \cdot 10^{-5}$, $F = 7.51$). The Tukey test HSD applied to populations with concentrations of 0.1 and 0.2 g/L shows that those values are significantly different from each other. However, when applying the Tukey test HSD to the three NFD no significant difference is found between them and the MO (Fig. 5.4).

Fig. 5.4: Multiple comparison of the means of the AC BV of the NDF and the AC BV of MO with RS 25%.

On the other hand, a significant reduction of the standard deviation is appreciated for all NP concentrations. There is also a very clear improvement in the lowest AC BV recorded values (characterized by means of percentile 2).

The distribution of AC BV along the tests is shown in Fig. 5.5. As can be shown in Fig. 5.5 the minimum values of the ACBV are higher for NFD than for MO what is an important advantage in transformer design.

Fig. 5.5: Frequency of ACSV for each fluid at 25% RS for MO and NDF with NP concentration 0.2 g/L.

The data of the AC BV measurements on fluid samples conditioned to a RS 25% were fitted to Weibull (Fig. 5.6) and Normal distributions giving similar results.

The Shapiro-Wilk test was performed and in most of the cases the null hypothesis was accepted (significance level 0.05), indicating that the population is normally distributed in all of the cases except for the AC BV of the NDF with concentrations 0.05 g/L.

Table 5.4 shows the BV calculated according to Weibull and Normal distributions for failure probabilities within 5 and 75% for the different fluids included in the study.

As can be seen a certain improvement of the AC BV is observed on most failure probabilities for the samples with NP concentration 0.2 g/L and a very clear improvement is obtained for the lower failure probabilities for all the analyzed fluids.

Fig. 5.6: Fitting of the data to a Weibull distribution - RS 25%.

AC BV (kV)								
Fail. Prob.	MO		NDF 0.05 g/L		NDF 0.1 g/L		NDF 0.2 g/L	
	W	N	W	N	W	N	W	N
5%	36.2	36.5	51.8	53.4	34.5	35.8	52.8	54.8
10%	43.3	43.6	54.4	55.4	40.3	40.6	57.1	58.3
25%	55.5	55.5	58.5	58.5	48.7	48.7	64.1	64.2
50%	68.9	68.6	62.4	62.1	58.0	57.6	71.1	70.6
75%	81.7	81.7	65.6	65.6	66.5	66.5	77.0	77.0

Table 5.4: BV for different failure probabilities according to Weibull (W) and Normal (N) distributions at RS 25%.

RS 50%

The same analysis was repeated for the samples prepared with RS 50%. Table 5.5 shows the statistical analysis of the measurements. As can be seen, the values of the mean of the AC BV were very similar to those of the MO although an improvement is appreciated in the standard deviation of the data. As for the samples conditioned with

RS 25%, again the percentiles study shows that the addition of NP to the MO tends to improve the lower AC BV, although the variation is small in most cases.

	MO	NDF 0.05 g/L	NDF 0.1 g/L	NDF 0.2 g/L
Mean (kV)	29.38	28.16	26.00	28.95
Standard Deviation	7.69	4.00	4.40	4.55
Percentile 2 (kV)	19.21	20.02	17.16	21.14
Percentile 50 (kV)	27.40	28.05	25.50	28.70
Percentile 90 (kV)	37.75	34.40	31.90	36.30

Table 5.5: Statistical analysis of the AC BV measurements at RS 50%

In this case, the ANOVA analysis showed that there are statistical differences between the means of the four groups (p -value=0.0271, F =3.14), and the Tukey HSD test showed that the NDF with NP concentrations 0.1 g/L is the only fluid that behaves differently from MO (Fig. 5.7).

Fig. 5.8 compares the histograms of the AC BV measurements taken on samples of MO and NDF with NP concentration 0.2 g/L conditioned to RS 50%. As can be seen two breakdowns were recorded at values above 40 kV on samples of MO. However, excluding these two breakdowns, the performance of the NDF is better and the measures present less dispersion.

The fitting of the data to a Weibull distribution are shown in Fig. 5.9 and Table 5.6. As can be seen these confirm the tendencies observed in the non-parametric analysis: the lowest values of the AC BV increased very slightly for the NDF with NP concentration 0.2 g/L but the difference is not very noticeable. The Shapiro-Wilk test was performed and in most of the cases the null hypothesis was accepted (significance level 0.05), indicating that the population is normally distributed in all of the cases except for the AC BV of the MO.

Fig. 5.7: Multiple comparison of the means of the AC BV of the NDF and the AC BV of MO with RS 50%.

Fig. 5.8: Frequency of AC BV for MO and NDF with NP concentration 0.2 g/L RS 50%..

5.3 Discussion

The improvement observed in AC BV of NDF vs. MO with similar RS are not very significant. Table 5.7 summarizes the percentage of improvement of the main statistical parameters of the AC BV measurements of the NDF with NP concentration 0.2 g/L and those of the MO for different RS of the fluids. For high failure probabilities (F25, F50

Fig. 5.9: Fitting of the data to a Weibull distribution - RS 50%.

Fail. Prob.	AC BV (kV)							
	MO		NDF 0.05 g/L		NDF 0.1 g/L		NDF 0.2 g/L	
	W	N	W	N	W	N	W	N
5%	19.2	20.1	20.0	20.9	19.2	20.1	21.2	22.2
10%	21.5	22.0	21.9	22.5	21.0	21.5	23.1	23.6
25%	25.1	25.1	25.0	25.0	23.7	23.7	25.9	25.8
50%	28.8	28.6	28.0	27.8	26.5	26.3	28.6	28.3
75%	32.0	32.0	30.6	30.6	28.8	28.8	31.0	30.9

Table 5.6: AC BV (kV) for different failure probabilities according to Weibull and Normal distribution. Fluids conditioned with RS 50%.

and F75 in Table 5.7) data were obtained from the Weibull fitting curve. As the data fitting to the curves in the low region of the curve is poor, for low values of voltage the Percentile 2 of the experimental data is shown.

Fig. 5.10 shows the histograms of the AC BV measurements on those two fluids. As can be seen AC BV shift towards lower values as the RS of the fluids increases.

Increase of the AC BV statistics parameters NDF 0.2 g/L vs. MO (%)

RS	Mean	SD	Perc 2	F 25	F 50	F 75
Dry	9.4	-36.5	13.3	6.9	9.9	12.0
25%	9.8	-35.9	48.0	15.5	3.2	-5.7
50%	-1.4	40.8	10.0	3.2	-0.7	-3.1

Table 5.7: Percentage of improvement of the AC BV parameters of the NDF with NP concentration 0.02 g/L with regard to MO

Fig. 5.10: Histogram of MO and NDF 0.2 g/L for three diferents humidities

Taking into account the higher water solubility in NDF compared with water solubility in MO the AC BV of the NDF increases dramatically if the measures obtained on NDFs and on MO with similar absolute moisture contents (i.e. ppm of water) are compared. Table 5.8 summarizes the improvement in % of the AC BV of the NDF prepared with NP concentration 0.2 g/L with respect to that of the MO. This fluid was the one that achieved the best performance for both low and high humidity levels. As can be seen the improvement of the AC BV is between 30 and 150% depending on the considered moisture content.

This result is in agreement with the data provided by other authors on several NDF prepared with MO as base fluids. In this sense Segal [16] reports an increase of 43% for a Fe_3O_4 based NDF with moisture content above 25 ppm, Zhou an increase

Abs. Moisture	Increase AC BV NDF 0.2 g/L vs. MO
10 ppm	13%
20 ppm	29%
30 ppm	46%
40 ppm	77%
50 ppm	>150%
60 ppm	>150%

Table 5.8: Percentage of improvement of the AC BV of the NDF with NP concentration 0.2 g/L with regard to that of MO vs. absolute moisture

of 190% on a TiO_2 based NDF with moisture content 45 ppm and Jin [11] reports an improvement of 25% on a NDF with SiO_2 NP with a moisture content 25 ppm. Yin [13] reports higher improvements on an Al_2O_3 based NDF, although the NP concentration considered by this author were much higher than the ones considered in this work.

The explanation that has been generally given to the comparatively smaller impact of moisture on the AC BV of NDF is that the water molecules dissolved in the fluids bond to the NP forming clusters around them [117]. The mobility of the water molecules would therefore decrease, and then, although the presence of larger amounts of water would still reduce the AC BV of these fluids, the reduction is smaller in the presence of the NP [11]. The formation of these clusters has been experimentally demonstrated by Du [118] who measured the spatial charge on MO and NDF with growing water contents. A reduction of the space charge and a more homogenous field distribution was observed in the NDF compared with those in the MO with similar moisture contents.

As can be seen when comparing the performance of the NDF with that of the MO for the same RS the improvement is not very sharp. Nevertheless, if the comparison is made for the same ppm the improvement is significant.

The enhancement of the AC BV observed for NDF when compared with the values measured in MO with similar absolute moisture contents is related with the

increase of the solubility of these liquids. In this sense, although the fluids that are compared in Table 5.8 have the same absolute moisture contents, they are not working under the same RS conditions. This finding is similar to that obtained when comparing MO with NE, where the AC BV remains within acceptable limits even with the moisture contents are as high as 400 ppm; however if the evolution of the AC BV with the RS is analyzed the performance is similar to that of MO [27, 22, 21, 24, 119].

In the case of the NDF the increase of the solubility and the enhancement of the AC BV are related with the fact that the water molecules in the fluid bond to the NP preventing them from moving freely acting like charge carriers.

When MO and NDF with similar RS conditions are compared, the observed increases of the AC BV are similar to those observed on dry fluids being these enhancements more related with the effect of the NP on the electron transport processes than with the interaction between the water molecules and the NP.

To complete the work and clarify the role of the materials present in the NP suspension MFR-DP1 (which was added to the MO to produce the NDF under test) in the increase of solubility observed in the analyzed NDF, an additional set of solubility measurements was carried out on NDF containing exclusively MO and NP.

Fe_3O_4 NP were dispersed in the MO Nynas Nytro up to concentrations 0.1 and 0.2 g/L. The preparation of these fluids was performed by the company Magnacol U.K. The resulting NDFs were less stable in the long term but it did not show any signs of deposits or precipitation during the testing time. The fluids were subjected the conditioning process explained in section 5.1.1 and the steady state moisture contents were measured for all the cases. The results of these tests are shown in Table 5.9 together with the results on MO and on the NDF prepared from the NP suspension MFR-DP1.

As can be seen the behavior of both NDF is very similar and the increase in solubility with the concentration of NP can be clearly appreciated in both of them. This suggest that there is no significative influence of the solvent and the surfactant in the measurements and that the reported changes in solubility are related to NP.

Material	Conditioning Process		
	Dry	RS 25%	RS 50%
MO	8.10	17.62	39.30
Nynas + MFR-DP1 0.1g/L	14.50	28.72	55.25
Nynas + NP 0.1 g/L	15.01	26.47	57.32
Nynas + MFR-DP1 0.2g/L	16.66	32.47	63.58
Nynas + NP 0.2 g/L	18.87	37.43	70.51

Table 5.9: Influence of the solvent and surfactant on the moisture solubility

5.4 Conclusions

In this chapter an experimental study has been carried out aimed at analyzing the effect of the water in the AC BV of MO and Fe_3O_4 NDF.

It has been shown that the presence of moisture has a negative impact in the NDF and in the MO, although the extent to what the amount of water affects the AC BV of the NDF is lower.

This is clearly observed when the BV is obtained as a function of the absolute moisture content of the samples. Improvement up to 150% have been found when comparing the AC BV of NDF and MO for similar absolute moisture contents. These results are in agreement with the observations of other authors, although the study presented in this work considers a wider range of scenarios of moisture contents and types of NDF.

In addition, it has been found that the presence of NP increases the solubility of water in the oil and that this increase is clearly related with the enhancement of the AC BV observed in NDF.

The solubility increase of NDF could have positive effects in the oil-cellulose system such as the displacement of the moisture equilibrium towards the oil, allowing the cellulose insulation to operate dryer. More research is necessary to fully understand the interaction between NDF and cellulosic insulation in the future and to make possible the use of these new type of fluids in transformers.

Chapter 6

Impulse breakdown voltage of mineral oil based nanodielectric fluids

In this chapter, an experimental study is presented that evaluates the impulse BV of several MO and Fe_3O_4 based NDF. Liquids with different concentrations of NP were tested to study how the presence of the NP affects the dielectric properties in positive and negative impulse conditions. The results were analyzed with nonparametric statistical analysis and by means of a parametric study through Weibull distribution. Finally, the main physical mechanisms that justify the results obtained are be discussed.

6.1 Introduction

A streamer is a transient electrical discharge which may appear when an insulating medium, such as insulating oil, is exposed to a large voltage drop, such as a lightning or switching impulse. Streamer propagation is generally measured using a standard lighting impulse voltage $1.2/50 \mu s$ in a needle-sphere combination of electrodes with a 25 mm gap. Some studies have maintained this needle-sphere combination of electrodes as [16, 120, 121, 65] although some authors have preferred to use the combination of needle-plane electrodes in their studies as [122] or sphere-sphere as [123].

The speed of streamer propagation in dielectric fluids is strongly dependent on the polarity of the applied voltage and its peak amplitude [120, 124, 125]. In the particular case of MO, streamers originating from a positive electrode tend to initiate at lower voltages than those originating from a negative electrode, and to propagate faster and further and further [60].

According to the survey published by the insurance company Hartford Steam Boiler Inspection & Insurance, which was obtained from a database with thousands of transformers from all over the world investigated during a 20 years period [126], the 17% of the failures originated in transformers are caused by lightning events. In this report lightning is listed as the second cause of transformer failure, only preceded by the failures produced by electrical disturbances (switching surges, voltage spikes, line faults, flashovers) which suppose the 29% of the cases. It seems clear that the use of insulating liquids with a higher dielectric strength under impulse conditions would improve the reliability of transformers greatly.

Several authors have proved that NDF have higher BV than the base fluids when subjected to lighting impulses. Sugumaran [127] studied the impact of adding of two different types of NP (ZrO_2 and TiO_2) to a MO, comparing the impulse BV of the resulting fluids for different NP concentrations obtaining that at lower concentrations (0.005% wt) the improvement was 16% (ZrO_2) and 19% (TiO_2), at medium concentrations (0.01% wt) the improvement was 13% in both cases and at higher concentration (0.05% wt) the improvement was 7% (ZrO_2) and 9% (TiO_2). In [128] Rafiq concludes that the addition of SiO_2 NP leads to an improvement of the dielectric strength under impulse conditions but only for positive impulses, while for negative impulses the author observes a worsening of the properties. In another study by the same author [121], the BV under impulse conditions results are compared using Fe_3O_4 NP of different sizes. Rafiq obtained better results at 20 nm than at 10 or 40 nm, concluding that, “when magnetic nanoparticle’s size is higher than 20nm, the bigger size of NPs may produce chains in close proximity of electrodes that give rise to the internal local electric field causing a breakdown initiation [129]”.

Although some experimental works have been published in the last years on the

topic of impulse properties of Fe_3O_4 based NDF, the topic is still very new and more experiences are necessary to make possible the advance of these materials. One of the challenges is the variety of materials and testing methods used by the different authors what complicates the comparison of results.

In this chapter an exhaustive evaluation of the impulse breakdown voltage of several Fe_3O_4 MO based NDF is carried out studying the differences between the streamer propagation in the MO and in the prepared NDF. Although the thermal properties of dielectric materials are important to describe the behavior of transformer insulation, this paper only handles the dielectric behavior of these materials when subjected to lightning impulse tests. Additional investigation on the thermal aspects would be needed to get a full picture of the system behavior.

The experimental study presented in the chapter extends the previous studies performed by other authors, as the authors evaluate the effect of the NP concentration on the BV and include a detailed statistical analysis based not only in comparing the average values of the BDV of the evaluated liquids but also on the BV for low probabilities of failure. Liquids with three different concentrations of NP were tested to study how the presence of the NP affects the dielectric properties in positive and negative impulse conditions. The results were analyzed with nonparametric statistical analysis and by means of a parametric study through Weibull distribution. The streamer velocity was calculated for all the liquids and the obtained values were used to explain the experimental observations and to describe physical mechanisms to justify the results.

6.2 Materials and method

6.2.1 Preparation of the materials

The NDF used in this chapter were manufactured according to that shown in chapter 3 at concentrations of 0.2, 0.4 and 0.6 g/L. Specifically, Nynas Nitro 4000X and a ferrofluid Nynas based manufactured by Magnacol were used.

6.2.2 Impulse breakdown voltage test

The BV under impulse of the prepared NDF were characterized according to ASTM D 3300–12 standard [130]. The impulses were applied by means of a High Voltage Module Test System, manufactured by HIGH VOLT (Germany) which incorporates a single-phase transformer with rated AC voltage 100 kV (model WGBS 6.6/100-135), and several HV modules that combined as shown in Fig 6.1 constitute an impulse generator. The system is controlled by a High Voltage manual control module (model High Volt SM4). The measurements are recorded with an oscilloscope Lecroy WavePro 950. A diagram of the measuring scheme is shown in Fig 6.1.

Fig. 6.1: Diagram of the measuring scheme.

A normalized lighting impulse wave 1.2/50 μ s was considered in the study. The application of the transient voltages was performed by means of a needle electrode opposing a grounded sphere following the recommendations of ASTM D3300-12 Std [130].

The test cell used in the tests was manufactured according to the recommendations of ASTM D 3300 – 12 Std [130]. It was made in polycarbonate, a material of high dielectric strength, with thickness 15 mm and with the dimensions recommended in the mentioned Std, what guarantees that the electrical breakdown is restricted to the electrode gap. The electrodes consist of a polished brass sphere of 0.5 inches (12.7 mm) diameter and a steel needle with tip ratio 0.35 mm. Fig. 6.2 shows the diagram and a picture of the cell.

Although Std ASTM D 3300-12 recommends setting a distance between electrodes of 25 mm for needle-to-sphere electrodes, the gap spacing used in this work

Fig. 6.2: Diagram of the cell (dimensions are expressed in mm) and picture of the cell.

was modified, as the impulse generator employed does not reach voltages above 110 kV which are not enough to get the electric breakdown of the dielectric fluids evaluated in this work. The distance between electrodes was set at 10 mm for positive impulses and at 3 mm for negative impulses.

For each fluid included in the study a set of ten measures of positive impulse and ten measures of negative impulse was carried out. Therefore, as the experimental work presented in this chapter includes the analysis of four fluids, a MO and three NDF with different concentrations of NPs (0.2 g/L, 0.4 g/L and 0.6 g/L), eighty measures were performed.

Before starting each test, the test cell was filled with 500 ml of the fluid under analysis and the sample was left to rest for ten minutes. Then the impulses were applied allowing the fluid to settle for two minutes after each breakdown. The measuring sequence was as follows:

First, an impulse wave is applied with a crest voltage level which is 5 kV below the expected breakdown level. Three impulse waves are applied with the same voltage. If no breakdown takes place, the crest voltage is increased in steps of 5 kV and successive impulses are applied until the first breakdown takes place. After applying each impulse test without breakdown, a minimum time of 30 s is allowed before applying a new impulse.

When the first breakdown has occurred, the applied voltage is decreased by 5%

and three impulses are applied at the new voltage. If any of the three impulses causes a breakdown, the voltage of the next impulse is decreased by 5%. If no breakdown is recorded after applying three impulses, the crest voltage is increased another 5% and three impulses are applied at the new voltage. The process is repeated until a total of ten breakdowns are recorded, registering for each breakdown, the values of the BV and the time to breakdown. An example of one of the applied impulses is shown in Fig. 6.3 including the main measured parameters (i.e the impulse BV and the time to breakdown).

After each breakdown occurs, the needle is changed and after ten breakdowns, the spherical electrode is replaced too.

After finishing the positive polarity test and before adding a new sample of fluid, the test cell is carefully cleaned with water, ether and detergent, then it is rinsed with distilled water and dried in an oven for 2 h at 110°C. When all the positive polarity tests are finished, the assembly is changed and the procedure is restarted to measure the BV of the four fluids under lightning impulses with negative polarity.

Fig. 6.3: Evolution of voltage during one of the measures.

Some pictures of the work in the laboratory are shown in Fig. 6.4.

Fig. 6.4: Pictures from the laboratory.

6.3 Results

Fig. 6.5 summarizes the results of the positive and negative impulse tests for the four analysed fluids (MO and NDF with NP concentrations 0.2 g/L, 0.4 g/L and 0.6 g/L). In each case, the impulse BV and the time to breakdown of the ten ruptures are plotted.

As can be seen, a clear improvement in the BV of positive impulses is observed when NP are added to the MO. Specifically, the fluid with NP concentration of 0.6 g/L shows the best results of the study for positive impulse. Regarding the negative impulses, only a very slight improvement is appreciated, which is more noticeable for the fluid with NP concentration 0.4 g/L.

It should be noted that the measures of the positive and negative impulses were carried out considering a different gap, so the absolute values of both polarities should not be compared. However, considering that the gap distance in the case of the positive impulse was 3 times larger than that considered for negative impulse tests (10 mm vs. 3mm) it seems clear that the positive impulse supposes a greater risk for the insulating fluids.

6.3.1 Statistic analysis

The mean value of the Impulse BV was calculated for each fluid and each polarity. Fig. 6.6 shows the average values of ten measurements for the fluid at different concentrations of NP, for both positive and negative impulses. As can be seen, the average BV of the fluids improves as the concentration of NP increases for the positive impulses. On the other hand, the results of the average values of the BV for the

Fig. 6.5: BV and time to breakdown recorded for positive and negative impulses on the MO and the NDFs.

negative impulses show that there is hardly any variation of this parameter as NP are added to the oil.

Table 6.1 shows the results of the mean values of the BV measurements and the standard deviation (SD) of the measures. As can be seen, the SD is higher for the fluids prepared with 0.4 g/L and 0.6 g/L concentrations of NP, while for 0.2 g/L, the SD is lower than in the MO. A high presence of NP (0.4 and 0.6 g/L) seems to increase the dispersion of the data obtained.

As shown in Table 6.1, the percentile 10 of the BV enhances greatly when NP are added to the oil. Specifically, for a concentration of 0.6 g/L of NP, the improvement to a percentile 10 is 45%. The improvement of low percentiles can be of great importance

Fig. 6.6: Average value of the BV for the MO and the NDF with different concentrations of NPs. Positive impulses (left) and Negative impulses (right).

when designing a transformer.

	MO	NDF 0.2 g/L	NDF 0.4 g/L	NDF 0.6 g/L
Average (kV)	34.37	35.74	41.31	51.46
SD (kV)	1.39	1.28	2.93	2.44
Percentile 10 (kV)	33.17	34.77	38.39	48.19
Percentile 50 (kV)	34.22	35.44	40.85	51.96
Percentile 90 (kV)	36.62	37.47	45.15	53.75

Table 6.1: Average value, SD and percentiles of the BV under Positive Impulse.

In the case of negative impulses, the results are quite different from what was shown for positive impulses (Table 6.2). First of all, there is no significant improvement in the mean value of the impulse BV for the NDF, although it can be seen that the presence of NP decreases the SD. So, we can conclude that with negative impulses the presence of NPs does not worsen the dielectric properties but neither improves them significantly.

Given that the differences in the mean values of the four liquids are small, an ANOVA [105] was performed to determine if there is significant difference between

	MO	NDF 0.2 g/L	NDF 0.4 g/L	NDF 0.6 g/L
Average (kV)	44.59	46.12	48.52	44.81
SD (kV)	2.49	1.34	1.76	1.10
Percentile 10 (kV)	42.39	44.34	46.53	43.57
Percentile 50 (kV)	44.19	46.61	48.26	44.72
Percentile 90 (kV)	47.26	47.41	50.45	45.95

Table 6.2: Average value, SD and percentiles of the BV under Negative Impulse.

them. The ANOVA analysis shown that there are significative statistical differences between the means of the four groups ($p\text{-value} = 4.0704 \cdot 10^{-5}$, $F = 10.5366$). Further comparisons using the Tukey HSD test [106] indicated that the mean score for the BV of the NDF with NO concentration 0.4 g/L is significantly different than the BV of the three other samples. Fig. 6.7 shows the multiple comparison of the means; as it can be seen there is an overlapping of the confidence bounds obtained for the BV of the MO and the NDF with NP concentrations 0.2 g/L and 0.6 g/L but these do not overlap with the BV of the sample of concentration 0.4 g/L.

Fig. 6.7: Multiple comparison of the means of the BV of the four NDF and the MO.

It can only be pointed out that for lower percentiles the concentration that presents the best performance is the one that was prepared with NP concentration

0.4 g/L. In this case, the percentile 10 is enhanced by 10%.

Additionally, the time to breakdown was analyzed for positive and negative impulses. Table 6.3 shows the average values of the times to breakdown for positive and negative impulses. As can be seen the times calculated for positive impulses are always higher for oils with NP. On the other hand, no significant variations of the times are observed for the negative impulses when NP are added to the MO.

Insulating Fluid	Positive Time (μs)	SD Positive Time (μs)	Negative Time (μs)	SD Negative Time (μs)
MO	7.31	1.07	25.20	8.61
NDF 0.2 g/L	12.42	0.36	26.13	7.68
NDF 0.4 g/L	14.15	1.04	23.66	8.71
NDF 0.6 g/L	11.43	0.52	22.36	6.84

Table 6.3: Times to breakdown for positive and negative impulses for every concentration of NP.

6.3.2 Weibull study

The impulse BV results were adjusted to a Probability Weibull distribution (6.1):

$$P(E) = 1 + e^{-\left(\frac{V}{a}\right)^b} \quad (6.1)$$

where $P(V)$ is the failure rate of the test liquid at an electric field of V , a is the scale parameter (which shows the BV at a failure probability of 63%) and b is the shape parameter (which is related with the dispersion of the BV measurements). The parameters obtained for each fluid are shown in Table 6.4.

Fig. 6.8 shows the positive impulse BV vs the probability of failure for the four analyzed fluids. Additionally, Table 6.5 shows the values of the BV for probability of failure 25, 50 and 50% estimated with the Weibull distribution for the MO and the NDF with NP concentrations 0.2 g/L, 0.4 g/L and 0.6 g/L. As can be seen, the addition of NP leads to a clear improvement of the dielectric strength under impulse conditions.

Fluid	a (kV)	b
MO	35.03	26.01
NDF 0.2 g/L	36.33	31.18
NDF 0.4 g/L	43.68	26.99
NDF 0.6 g/L	52.54	56.65

Table 6.4: Parameters for the Weibull adjustment of the Positive Impulses.

Fig. 6.8: Weibull Probability for Positive Impulse BV.

Failure Probability	MO	NDF 0.2 g/L	NDF 0.4 g/L	NDF 0.6 g/L
25%	33.66	35.04	38.84	49.56
50%	34.28	35.82	42.05	51.72
75%	35.47	36.44	44.71	53.48

Table 6.5: Weibull probability for positive impulse BV (kV) at different concentration of NP.

Fig. 6.9 shows the Negative Impulse BV vs the probability of failure for the different fluids. As can be seen, the presence of NP slightly improves the dielectric

properties under negative impulse conditions. The parameters obtained for each fluid are shown in Table 6.6.

Fig. 6.9: Weibull Probability for Negative Impulse BV.

Fluid	a (kV)	b
MO	45.78	17.49
NDF 0.05 g/L	46.71	43.26
NDF 0.1 g/L	49.35	29.26
NDF 0.2 g/L	45.32	46.69

Table 6.6: Parameters for the Weibull adjustment of the Negative Impulses.

Table 6.7 shows the BV under negative impulse, calculated with the Weibull distribution for failure probabilities 25, 50 and 75%. As can be seen, the presence of NP leads to a minor improvement of the values.

6.3.3 Comparison of the results of positive and negative impulses

As explained before, the electrode distances considered in this chapter for the characterization of positive and negative impulse BV were different; in the case of

Failure Probability	MO	NDF 0.2 g/L	NDF 0.4 g/L	NDF 0.6 g/L
25%	43.78	44.76	47.34	44.33
50%	44.37	45.99	48.57	45.16
75%	46.64	46.94	49.56	45.76

Table 6.7: BV (kV) for different probabilities of failure for negative impulses according to Weibull distribution.

positive impulses a distance 10 mm was set between the electrodes and for the negative impulses it was shortened to 3 mm.

To allow a comparison between the results of the positive and negative impulse tests, an additional set of tests was carried out. The MO used as base fluid was subjected to five new positive impulses tests considering electrode distances 3mm, 5mm, 15mm, 20mm and 25 mm and to an additional negative impulse test with electrode distance 5mm. The testing procedure followed for these measures was the one described in section 6.2.2.

The average values of the 10 BV values recorded for each distance are shown in Table 6.8. The data for the negative impulse values were completed with the specifications provided by the manufacturer for the MO under negative impulse test at normalized distance (i.e. negative BDV at 25mm >300 kV).

The positive and negative impulse BV at different electrode distances are shown in Fig. 6.10. The data of positive and negative impulse were fitted to a quadratic polynomial to make possible the normalization of the results. The obtained relations were Eq. 6.2 and 6.3.

$$BV_{PositiveImpulse}(d) = -1.17 \cdot 10^{-2} \cdot d^2 + 3.32 \cdot d + 5.691 \quad (6.2)$$

$$BV_{NegativeImpulse}(d) = -0.458 \cdot d^2 + 24.42 \cdot d - 24.13 \quad (6.3)$$

Eq. 6.2 and 6.3 were used to normalize the data of the NDF at different electrode distances. Table 6.9 compares the positive and negative BV at 3mm, 10mm and 25mm. These results are a rough estimation, as to calculate them me assumed that Eq. 6.2 and

Electrode distance (mm)	Positive impulse BV (kV)	Negative impulse BDV (kV)
3	16.15	44.59
5	22.06	86.50
10	34.37	-
15	50.78	-
20	68.10	-
25	76.01	300*

Table 6.8: Average value of the positive and negative BDV of MO for different electrode distances. *The value for the negative impulse at 25mm is taken form the specifications of the oil manufacturer

6.3 are valid for the NDF.

Fig. 6.10: Average value of the positive and negative BDV of MO for different electrode distances and tendency line.

6.4 Discussion

To evaluate the impact of the NP in the impulse BV of the MO, the ratios of increase of the average BV, the percentiles and the BV for different failure probabilities have been calculated for positive and negative impulses.

	Gap 3 mm		Gap 10 mm		Gap 25 mm	
	Pos	Neg	Pos	Neg	Pos	Neg
MO	15.49	44.59	34.37	174.27	77.50	300.12
NDF 0.2 g/L	16.86	46.12	35.74	175.80	78.87	301.65
NDF 0.4 g/L	22.43	48.52	41.31	178.20	84.44	304.05
NDF 0.6 g/L	32.58	44.81	51.46	174.49	94.59	300.34

Table 6.9: Comparison of positive and negative impulse BDV for several electrode distances.

Table 6.10 shows the enhancement obtained for positive impulses. As can be seen, the performance of NDF is clearer superior than that of MO under positive impulse. Moreover, as the concentration of NP rises, the percentage of improvement of the BV average value increases, reaching a maximum improvement of 50% at a concentration of NP 0.6 g/L. The percentile values and the BV for different failure probabilities have the same tendency, showing the best results the NDF with higher concentration of NP (0.6 g/L) where the improvement of all the parameters was around 50%.

These results are very similar to the ones presented by other authors. Jariyanurat [131] showed improvements of 45% and 53% with $BaTiO_3$ and ZnO ester based NDF. Rafiq, also reported an improvement of up to 30% in the positive BV Fe_3O_4 [121] and SiO_2 based NDF [128].

The ratios of improvement obtained for the negative impulse measurements are shown in Table 6.10. As can be seen, the improvements in this case are much lower, finding a maximum increase of the average BV of 8% for the NDF with NP concentration 0.4 g/L. For the other two NDF the change is almost null (i.e. in the case of the NDF with NP concentration 0.6 g/L it is below 1%). Regarding the percentiles and the BV for different failure probabilities, similar results are found: the improvements are low, and in some cases a slight worsening is even observed.

These results are also in agreement with those shown by other authors. In, [132] a worsening of the Impulse BV is reported for several NDF prepared with various NP

	NDF 0.2 g/L	NDF 0.4 g/L	NDF 0.6 g/L
Average value	4%	20%	50%
Percentile 10	5%	16%	45%
Percentile 50	4%	19%	52%
Percentile 90	3%	23%	47%
Failure Prob 25%	4%	15%	47%
Failure Prob 50%	4%	24%	51%
Failure Prob 75%	5%	29%	54%

Table 6.10: Ratio of improvement (%) of the BV under positive impulses for the NDF vs. the MO.

	NDF 0.2 g/L	NDF 0.4 g/L	NDF 0.6 g/L
Average value	3%	8%	<1%
Percentile 10	5%	10%	3%
Percentile 50	5%	9%	3%
Percentile 90	<1%	7%	-3%
Failure Prob 25%	2%	8%	1%
Failure Prob 50%	4%	9%	2%
Failure Prob 75%	1%	9%	<1%

Table 6.11: Ratio of improvement (%) of the BV under negative impulses for the NDF vs. the MO.

(ZnO , $BaTiO_3$, TiO_2) at different concentrations (0.01% and 0.03%). A deterioration is also reported by Rafiq et al. in [128] for SiO_2 based NDF. On the other hand, Jariyanurat [131] obtained an improvement of 25% of the BV under negative impulses for a NE and ZnO based NDF.

From all the previous, it can be concluded that there is a significant difference in the variation of the dielectric strength of NDF when they are subjected to positive impulses and to negative impulses. While a major improvement of the BV is obtained for positive impulses at all tested NP concentrations (especially at higher ones), the

impact of NP in the negative impulse BV is small and at high concentrations of NP the properties of the base fluid are even worsened.

Several authors have related the enhancement of the positive-impulse BV of NDF with the fact that part of the fast electrons involved in the streamer are trapped by the NP reducing their mobility [133]. The low mobility of charged NP hinders the formation of a space charge zone at the streamer tip avoiding the propagation of the electric field wave needed to drive electric-field-dependent molecular ionization, and hence streamer propagation [63]. At low concentrations, the distance between NP is very large allowing the movement of most of the electrons, but as the concentration of NP increases, the distance between NP is shorter and electrons are captured to a greater extent, slowing down the propagation of the streamer and giving rise to higher values of BV.

Some theoretical analysis of the streamer propagation phenomena in NDF have been reported [19, 134]. These studies modelled the streamer processes by means of finite elements models and proved that streamer propagation in insulating fluids requires ionization of the fluids and in NDF many of the electrons generated by this ionization are trapped by the NP before they are transported out of the ionization region. For this reason, the time scales of streamer development in NDF are significantly longer than those in the unmodified base fluids.

Lv et al [65] studied the pre-breakdown phenomena in a TiO_2 and MO based NDF using an Intensified Charge Coupled Device camera to capture streamer propagation images. They proved that the shape of the streamer is very different in MO and in NDF. While positive streamers propagate with a tree-like shape in the case of the MO, in the case of NDF the branches are thicker and propagate with a lower speed.

The shape for the negative streamers is very different as well. In this case the streamer presents a bush-like shape in the MO, while in the NDF multi filamentary discharge channels are appreciated that propagate fast towards the ground electrode [65].

The propagation speed of the streamer (v) has been calculated for the

Fig. 6.11: Propagation of the positive streamer for MO (top) and for TiO_2 based NDF. Taken from [65].

Fig. 6.12: Propagation of the negative streamer for MO (top) and for TiO_2 based NDF [65].

experimental data obtained in this work as:

$$v = \frac{d}{t} \quad (6.4)$$

where d is the distance between electrodes and t is the time to breakdown. Table 6.12 shows the calculated speeds for positive and negative impulses.

The average speeds calculated for positive and negative streamer are shown in Table 6.12. As can be seen, there is a decrease of about a 40% in the speed of propagation of positive impulses when NP are added to the MO, while the presence of NP does not seem to affect the speed of propagation of negative streamers. This result is in agreement with the theories and results reported by other authors [65, 13, 135, 136], and confirm that the variation of the streamer propagation speed is

deeply related with the improvements observed of the BV values. If the propagation is slower there is a higher probability of the streamer being extinguished and the rupture does not take place.

It is also interesting to note that the speed of propagation of negative streamers in MO is more than 10 times smaller than the speed of propagation of positive streamers in the same fluid. The difference can be justified by analyzing the electric field distribution across the gap and the subsequent ability of that electric field to produce a molecular ionization that could derive in a dielectric breakdown. The risk associated to positive impulses is much higher than the risk associated to negative ones and in consequence the enhancement of the positive impulse BV is a very advantageous property of the NDF.

Fluid	Positive Speed (km/s)	Negative Speed (km/s)
MO	1.37	0.12
NDF 0.2 g/L	0.80	0.11
NDF 0.4 g/L	0.71	0.13
NDF 0.6 g/L	0.87	0.13

Table 6.12: Streamer propagation speed for positive and negative impulses in MO and in the Fe_3O_4 based NDF.

6.5 Conclusions

In this chapter an experimental evaluation of the impulse BV of Fe_3O_4 based NDF has been carried out showing that the presence of NP improves the dielectric properties significantly under positive impulse conditions. Improvements up to 50% were obtained for fluids with concentrations of NP 0.6 g/L. In the case of negative impulses, the presence of NP hardly modifies the values obtained, but does not worsen the values of Impulse BV either. The experimental measurements were fitted to a Weibull distribution finding similar conclusions: in the case of positive impulses, a considerable improvement of the values of the BV is appreciated. This improvement is

very important at low probabilities of failure raising from 32 kV (aprox.) of BV in MO without NP to a value of 45 kV (aprox.) for a concentration of 0.6 g/L, In the case of negative impulses, this improvement is not significant although the data show a lower dispersion.

The observed results are related with the variation of the streamer propagation speed: In the case of positive streamer, the propagation speed is halved, what hinders the evolution of the discharge and thus increases the BV value.

It is important to note that streamers originating from a positive electrode are the ones that poses a higher risk for the transformer integrity, as they tend to initiate at lower voltages than those originating from a negative electrode, and to propagate faster and further so this differential property of NDF could suppose an important advantage for the design of transformer dielectric insulation.

The results presented in this chapter are in agreement with the results of some other authors that had previously analysed the impulse BV of Fe_3O_4 based NDF, however the present study contributes to a better understanding of the phenomena that take place in NDF since it analyses the performance of these fluids in a wide range of concentrations, provides and exhaustive statistic study and analyses the evolution of the streamer propagation speed with the NP concentration. NDF is a very new topic and although some experiences have been accumulated to date more data is required to evaluate the repeatability of the observations, the lack of dependence on the manufacturing and testing processes and the performance of different combination of materials.

Chapter 7

Dielectric properties of natural ester based nanodielectric fluids

In this chapter a study is presented on the dielectric properties of Fe_3O_4 NDF in a base of sunflower NE. The AC BV and the Impulse BV of NE based NDFs with different concentrations of NP are measured. A nonparametric statistical analysis and a Weibull study of both tests are carried out and the results are discussed, comparing them with those obtained for MO based NDF.

7.1 Introduction

Esters are organic compounds of natural or synthetic origin. NE are obtained from seeds of vegetable origin. There are many types of NE according to their origin, such as sunflower oil, soybean oil, olive oil, palm oil, etc...

The use of NEs in transformers began in the 90s as an alternative to MO. NEs present a number of advantages with respect to MO, such as their higher flash point or their high combustion point (almost twice of those of MO in both cases), as well as their higher biodegradability. However, they have some drawbacks such as a high density (up to four times higher than that of MO) or a greater water solubility in oil (up to fifteen times more, approximately).

The properties of the NFD depends on the type of base-fluid deployed to produce the liquid (MO, NE or SE), the type of NP added to the base fluid (conducting nanoparticles, semiconducting nanoparticles or insulating nanoparticles), the concentration of NP in the NFD and the water content.

Some authors have carried out studies related to dielectric strength of ester-based NFD [137, 107, 138]. While Charalampakos [137] states that conductive NP tend to raise AC BV Ibrahim [20] points that conductive Fe_2NiO_4 added to MO reduces AC BV. By these reasons Makmud [139] affirms that there is noagreement regarding the influence of the different types of NP and its concentrations on the dielectric properties of NE based NDF.

Although researchers have used different types of NP to form the NFD, for the sake of brevity we will focus the discussion on Fe_3O_4 NP that are the ones used in this thesis.

In case of Fe_3O_4 NP AC BV, the results presented by the different authors differ greatly. So, while Li [49] reports 20% increases on the AC BV, the results presented by Peppas [140] are not so clear. This justifies a set of tests to elucidate it. Because of that we carried out studies on NE based NDF with 50 Hz AC voltage and with positive and negative lightning impulses.

7.2 Methodology

7.2.1 Preparation of NDF

Sample preparation was carried out as described in section 3.2.2. Bio Electra (NE) was used as base fluid and FF1 as NP suspension. In the following tests, four fluids were used, pure NE and three NFD with NP concentrations of 0.05 g/L, 0.1 g/L and 0.2 g/L (i.e. 55 ppm, 110 ppm and 220 ppm).

7.2.2 Sample conditioning

Once the samples were prepared with different concentrations of NP, the NDF was conditioned:

- Dry conditions: the four mentioned fluids were introduced in a vacuum oven at 50°C and 0.1 atm during 48 h. The RS of moisture calculated under these conditions is approximately 10%.
- RS 25%: the four fluids were conditioned in an environmental chamber at 30°C and 25% relative humidity conditions. This process lasted for 48 hours.
- RS 50%: the four fluids were conditioned in an environmental chamber at 30°C and 50% relative humidity conditions. This process lasted for 96 hours.
- RS 80%: the samples were conditioned in an environmental chamber at 30°C and 80% relative humidity conditions. This process lasted for 168 hours.

7.2.3 Dielectric tests

The AC BV measurements and the Impulse BV measurements were performed as shown in sections 4.1.2 and 6.2.2 respectively.

7.3 AC breakdown voltage results

7.3.1 Non parametric study of AC BV

In the following, a nonparametric study of the results obtained for AC BV is made. This study is divided by RS of moisture.

Results for RS 10%

Table 7.1 shows the average, median (percentil 50%), SD and some percentiles values of the AC BV for the NE and for the three NDF. As can be seen in the Table 7.1 the average values of AC BV are lower in all cases in which there are NP. The same happens with the different percentiles shown in the table.

	NE	NDF 0.05 g/L	NDF 0.1 g/L	NDF 0.2 g/L
Average (kV)	92.23	74.33	71.34	77.40
Standard Deviation	8.26	7.99	9.47	8.88
Percentile 2 (kV)	76.27	60.21	54.37	59.58
Percentile 50 (kV)	98.10	74.35	73.25	78.55
Percentile 90 (kV)	98.60	86.95	82.47	89.83

Table 7.1: Statistical analysis of the AC BV measurements at RS 10%

Fig. 7.1 shows the histograms for the different NP concentrations at a RS 10%.

Fig. 7.1: Frequency of ACBV for each fluid at 10% RS a) NE, b) NDF 0.05 g/L NP c) NDF 0.1 g/L NP d) NDF 0.2 g/L NP.

As can be seen from the histograms, the measurements made on the NE show the highest values of AC BV. Therefore, the addition of NP to a NE with a RS of 10% has a negative effect on the AC BV. Although the differences on AC BV of the different NFD are slight the one with the best characteristics is that of concentration 0.2 g/L.

However, although AC BV of dry NE diminishes when adding Fe_2O_3 NP it must be noted that the obtained values for AC BV are still valid for transformers. IEC 62770 [141] specifies that new NE must have a AC BV (distance between electrodes 2.5 mm) of 35 kV. All the NFD analyzed exceeds that value. Even mean value of AC BV is higher than 70 kV wich is the required value for new MO in 400 kV transformers.

Results for RS 25%

Table 7.2 shows the nonparametric study centered on the average, SD and percentiles 2, 50 and 90.

Fig. 7.2 shows the histogram in RS 25% conditions.

As can be seen in this case, the fluid that presents better values of mean is the NDF 0.2 g/L, although it is also the one with the greatest dispersion, as can be seen from the standard deviation. In fact the percentile 2% of AC BV is lower than that of the NE without NP added. This is a little handicap since percentile 2% is of great importance for transformer design and operation. Fortunately the difference on percentile 2% of NE and NFD with a NP concentration of 0.2 g/L is only of 4,8%.

	NE	NDF 0.05 g/L	NDF 0.1 g/L	NDF 0.2 g/L
Average (kV)	60.30	47.84	56.15	67.06
Standard Deviation	9.11	7.43	7.37	10.85
Percentile 2 (kV)	45.62	34.78	38.11	43.42
Percentile 50 (kV)	59.65	48.35	57.60	68.35
Percentile 90 (kV)	70.46	55.86	63.36	76.62

Table 7.2: Statistical analysis of the AC BV measurements at RS 25%

Fig. 7.2: Frequency of ACBV for each fluid at 25% RS a) NE, b) NDF 0.05 g/L NP c) NDF 0.1 g/L NP d) NDF 0.2 g/L NP.

Results for RS 50%

Table 7.3 shows the nonparametric study in this case and Fig. 7.3 shows the histogram of the measurements.

RS 50% conditions are rarely found inside a transformer. For this value of RS all the NFD present higher AC BV than pure natural oil. Although all of them presents a higher standard deviation than pure natural oil, their 2% percentile are higher than that of the NE. The fluid with the highest dielectric characteristics (percentiles 2% and 50%) is the NDF 0.05 g/L, whose percentile 50% value presents an improvement of more than 40% compared to the NE.

	NE	NDF 0.05 g/L	NDF 0.1 g/L	NDF 0.2 g/L
Average (kV)	28.61	40.38	36.29	33.17
Standard Deviation	5.59	7.13	8.35	8.18
Percentile 2 (kV)	19.12	29.14	25.08	21.80
Percentile 50 (kV)	29.11	41.90	34.35	31.95
Percentile 90 (kV)	34.47	49.13	46.61	44.11

Table 7.3: Statistical analysis of the AC BV measurements at RS 50%

Fig. 7.3: Frequency of ACBV for each fluid at 50% RS a) NE, b) NDF 0.05 g/L NP c) NDF 0.1 g/L NP d) NDF 0.2 g/L NP.

Results for RS 80%

Table 7.4 shows the nonparametric study in this case and Fig. 7.4 shows the histogram of the measurements.

It can be seen a case very similar to the previous one (RS 50%) with the NDF 0.05 g/L with the highest values in average, and 2% percentile and that these values decrease as the NP concentration increases.

Also in this case, the NDF 0.05 is the one that presents greater dispersion than the others, it can be seen in the SD.

Fig. 7.4: Frequency of ACBV for each fluid at 80% RS a) NE, b) NDF 0.05 g/L NP c) NDF 0.1 g/L NP d) NDF 0.2 g/L NP.

Fig. 7.5 shows the average values of ACBV versus Concentration for every RS.

As can be seen the behavior is quite different for low water contents than for high water contents. While for low water contents the presence of NP worsens the AC BV, for high water contents the presence of NP improves the ACBV.

	NE	NDF 0.05 g/L	NDF 0.1 g/L	NDF 0.2 g/L
Average (kV)	14.93	28.01	26.71	20.90
Standard Deviation	3.68	5.64	3.99	5.10
Percentile 2 (kV)	6.73	18.67	20.24	10.17
Percentile 50 (kV)	15.30	28.51	27.00	22.05
Percentile 90 (kV)	18.27	36.10	31.79	25.73

Table 7.4: Statistical analysis of the AC BV measurements at RS 80%

Fig. 7.5: Average values against concentration for every RS.

The reduction of AC BV with low moisture could be because when the amount of water is low moisture is tightly bonded to ester and the presence of NP does not influence much water mobility. For these contents in water the conductivity of NP prevails and causes the AC BV to lower. However, when the amount of water is high the NPs help to fix the water molecules reducing their mobility and the effect is similar to a lower content of water in ester.

Table 7.5 shows the average humidity values measured at for each NP concentration and each RS. Fig. 7.6 shows the humidity values against your AC BV.

	Dry	RS 25%	RS 50%	RS 80%
NE	117 ppm	284 ppm	455 ppm	1276 ppm
NDF 0.05 g/L	119 ppm	283 ppm	461 ppm	1265 ppm
NDF 0.1 g/L	126 ppm	303 ppm	462 ppm	1284 ppm
NDF 0.2 g/L	139 ppm	322 ppm	401 ppm	1313 ppm

Table 7.5: Moisture Content of the samples after the conditioning process

Fig. 7.6: Fitting of the data to a Weibull distribution - RS 10%.

With respect to the evolution of AC BV with the concentration of NP, some other researchers have reported non monotonous variations of AC BV with the concentration of NP [142, 143] in case of high concentrations of NP, Peppas et al [47] attribute the reduction of AC BV to a decreasing distance among the particles of Fe_3O_4 that can favor the generation of conductive paths between electrodes. More difficult is to explain why the AC BV has a maximum, i.e. the rising on AC BV with concentration for low concentrations, but perhaps it is due to the balance between the mechanisms retarding

the streamer (electron trap) and the mechanism accelerating it (conductivity of the NP).

7.3.2 Weibull analysis

A Weibull study of the AC BV data for each RS was conducted in a similar way that was exposed in chapter 4. Fig. 7.7 to 7.10 shows the cumulative probability of failure of AC BV for the different fluids and its fit to a Weibull curve. Tables 7.6 to 7.9 show the AC BV for different failure probabilities obtained from the Weibull curves.

Fig. 7.7: Fitting of the data to a Weibull distribution - RS 10%.

Failure Probability	AC Breakdown Voltage (kV)			
	NE	NDF 0.05 g/L	NDF 0.1 g/L	NDF 0.2 g/L
5%	72.11	60.95	50.53	61.28
10%	77.45	64.51	55.66	65.59
25%	85.52	69.81	63.84	72.13
50%	93.36	74.81	71.98	78.39
75%	100.2	79.01	79.14	83.68

Table 7.6: Breakdown Voltage for Different Failure Probabilities - RS 10%

Fig. 7.8: Fitting of the data to a Weibull distribution - RS 25%.

Fig. 7.9: Fitting of the data to a Weibull distribution - RS 50%.

Fig. 7.10: Fitting of the data to a Weibull distribution - RS 80%.

Failure Probability	AC Breakdown Voltage (kV)			
	NE	NDF 0.05 g/L	NDF 0.1 g/L	NDF 0.2 g/L
5%	43.21	31.73	48.47	53.76
10%	47.47	35.56	50.77	58.72
25%	54.13	41.43	54.16	63.68
50%	60.72	48.22	57.33	69.41
75%	68.49	53.94	59.95	74.29

Table 7.7: Breakdown Voltage for Different Failure Probabilities - RS 25%

7.3.3 Comparison with the results of other researchers

The first references on NFD manufactured Fe_3O_4 NP and NE were from Chongqing University [144, 139]. The researchers from Chongqing used rapeseed oil with a concentration of NP of 0.004%wt. Water content in the NDF was 288 ppm. They obtained the 50 Hz AC BV from five measurements and found an increment of 20% on AC BV.

They also studied the influence of the water content on AC BV [145] and found

AC Breakdown Voltage (kV)				
Failure Probability	NE	NDF 0.05 g/L	NDF 0.1 g/L	NDF 0.2 g/L
5%	17.89	24.58	20.26	17.29
10%	20.34	28.02	23.50	20.65
25%	24.31	33.93	29.48	25.58
50%	28.45	40.12	36.01	33.17
75%	32.20	45.80	42.12	39.49

Table 7.8: Breakdown Voltage for Different Failure Probabilities - RS 50%

AC Breakdown Voltage (kV)				
Failure Probability	NE	NDF 0.05 g/L	NDF 0.1 g/L	NDF 0.2 g/L
5%	10.42	18.96	17.94	11.78
10%	11.63	21.07	19.92	13.56
25%	13.62	24.41	23.37	17.21
50%	15.52	27.77	27.88	20.90
75%	17.25	31.73	30.01	24.34

Table 7.9: Breakdown Voltage for Different Failure Probabilities - RS 80%

that AC BV is dramatically reduced when the water content exceeds 300 ppm. This test was somewhat different than the previous ones: first the NP concentration was only of 50 ppm and secondly they obtained AC BV as a mean of 45 breakdowns.

In 2015 and 2016 Mohamad [146, 147] presented two papers on AC BV of vegetable oil with Fe_3O_4 NP. In their first study [146] Mohamad used Palm Fatty Acid Ester with three concentrations of Fe_3O_4 : 0.01%, 0.02% and 0.03% by vol. No mention is done for water content. NFD with the lower concentration (0.01% Fe_3O_4) presented less AC BV than NE, but NFD with a higher concentration of NP (0.02% and 0.03%) have an AC BV higher than pure ester. The higher AC BV was obtained for concentrations of 0.02% Fe_3O_4 .

In their second study [147] they compare Palm Fatty Acid Ester with a NFD of this ester with 0.01 g/L of Fe_3O_4 . They apply a nitrogen treatment to the fluids to

maintain the moisture content of the oil below 25 ppm. They prepared four samples of both fluids and for each sample 25 breakdowns were applied to obtain AC BV. The authors obtained an AC BV 42% higher in NFD than in NE. The Standard deviation is more than double for NFD than for NE, but in spite of that even 2% percentile is higher for NFD.

From 2016 to 2017 a research cluster of Greek universities published a set of papers on AC BV of FR3 vegetable oil (soy based) with Fe_3O_4 NP. In [140] Peppas compares two type of NFD, the first one manufactured mixing ester oil with commercial NP of Fe_3O_4 and surfactant and the second one a colloidal NFD manufactured with an in-situ surface coating technique. Water content was maintained low by means of a nitrogen atmosphere. For each type of NFD the concentrations varied from 0,004% w/w (40 ppm) to 0,014% w/w (140 ppm). AC BV of the fluid with commercial NP were higher than that of the pure ester for low concentration of NP and the best results were obtained for a concentration of 80 ppm where AC BV were 20% higher than that of the pure ester. Conversely NFDs with best dielectric characteristics were those with high concentration of Fe_3O_4 NP, in this case the best results were obtained for NP concentrations of 120 ppm (20,5% improvement). In both cases AC BV decreases sharply for high NP concentrations (higher than 140 ppm).

In 2019 Khaled and Beroual published several papers on AC BV of Fe_3O_4 NFD [148, 149]. In [148] Khaled concludes that while Fe_3O_4 NP have a positive effect on SE and MO, no significant influence is found in NFD based on NE. For their tests they used NE MIDEL 1204 with four concentrations, namely 0.05, 0.2, 0.3 and 0.4 g/L. Only the NFD with a concentration 0.4 g/L showed an improvement of the AC BV. The improvement in AC BV is only 7% higher than that of pure NE.

As seen in this section there is no consensus among researches on the effect of Fe_3O_4 NP on NE, while some of them argue that Fe_3O_4 NP increases AC BV others found a non monotonous curve with an maximum value.

As shown in previously in this chapter our results are in line with what is shown by Khaled. In this sense it must be taken into account that the papers from Khaled are of 2019 when we finished our dielectric tests. For this reason, although our results

coincide with those of Khaled, our work can be considered original.

Another important difference between the work from Khaled and our work is that we took into account the water content of NFD, while Khaled does not inform about the water content in the studied NFD. We shown that evolution of AC BV is different for high water contents and for low water contents and we argued an explanation to the phenomena.

As shown in this chapter the results presented by the researchers working with Fe_3O_4 are contradictory. In our opinion this may be due to differences in the NE used (rapeseed, palm fatty acid ester, soybean, sunflower) as the molecules of the various esters are very different and its interaction with NP may be different. In light of Peppas [140] who used the same ester (FR3) and two different manufacturing techniques and the obtained NFD had very different properties, another influencing factor is the surfactant used to prepare the NFD. Also the paper from Khaled [148] show that the size of NP has an important effect.

7.4 Impulse breakdown voltage

The impulse BV of the NE based NDF tested in the first part of the chapter were subjected to lightning impulse tests that were prepared following the procedure described in section 7.2.1 and 7.2.2. Once the values of Impulse 1,2/50 μs BV were obtained in the laboratory, a non-parametric study and a Weibull study of the results were carried out. In turn, each of these studies was divided between the impulses under positive conditions and negative conditions.

Under impulse voltages water molecules do not enough have time to align with the external field. Because of that, water does not have a great importance in impulse breakdown tests. For this reason in the study no differences will be made regarding water content.

7.4.1 Statistic analysis

First, the nonparametric study has been performed where the values of average, standard deviation (SD) and percentile 10, 50 y 90 were obtained.

The values obtained under positive impulse conditions are presented in table 7.10

	NE	NDF 0.05 g/L	NDF 0.1 g/L	NDF 0.2 g/L
Average (kV)	35.41	42.31	42.23	38.05
SD (kV)	1.19	2.17	2.88	1.92
Percentile 10 (kV)	34.40	39.80	41.78	36.92
Percentile 50 (kV)	35.50	41.42	43.26	37.65
Percentile 90 (kV)	35.95	42.94	44.52	38.97

Table 7.10: Average value, SD and percentiles of the BV under Positive Impulse (d = 10 mm).

As can be seen in the table 7.10, the NFD have higher lightning positive BV the NE. The fluids with concentrations of 0.05 g/L and 0.1 g/L are the ones with the highest values. At the same time, these NDF have the higher standard deviation, unlike the fluid without NP and the fluid with concentration 0.2 g/L.

In table 7.11 the values obtained under negative impulse conditions are shown.

	NE	NDF 0.05 g/L	NDF 0.1 g/L	NDF 0.2 g/L
Average (kV)	28.90	31.37	32.10	32.82
SD (kV)	1.66	0.82	0.85	0.69
Percentile 10 (kV)	28.04	31.03	31.74	32.17
Percentile 50 (kV)	29.03	31.41	32.17	32.76
Percentile 90 (kV)	31.08	32.92	32.99	34.04

Table 7.11: Average value, SD and percentiles of the BV under Negative Impulse (d = 3 mm).

As in the case of positive impulse, under negative impulse the BV of all the tested NFD are higher than that of NE. In this case, as the in NP concentration increases the

average value of the BV slightly increases, as can be seen in the table. In addition, the deviation of the data is much lower than that of the NE.

Table 7.12 shows the increase (%) of the Average Impulse BV of the NDF with respect to those of the NE. As can be seen, the Impulse BV improves in all situations in which NP are added. Under positive impulse conditions, the fluid with the highest increase is NDF 0.1 g/L with an increase of 23%. In contrast, under negative impulse conditions, the one with the greatest improvement is the NDF 0.2 g/L with an increase of 11%.

	NDF 0.05 g/L	NDF 0.1 g/L	NDF 0.2 g/L
Positive	19%	19%	7%
Negative	8%	11%	13%

Table 7.12: Increase (%) of the average in positive ($d = 10$ mm) and negative ($d = 3$ mm) Impulses BV.

7.4.2 Weibull study

Fitting the dielectric tests to a statistical distribution is useful in order to calculate the failure probability and for design purposes. The statistical distribution used by most authors is the Weibull distribution.

A Weibull study of the data obtained in Impulse BV was carried out, which was divided into positive and negative impulses.

Table 7.13 shows the estimated values of Impulse BV at different failure probabilities estimated for the different NDF according to Weibull distribution.

Fig. 7.11 shows the probability of failure against the values of Impulse BV under positive impulses.

Fig. 7.12 shows the Weibull probability of Impulse BV under negative impulses.

Table 7.14 shows the estimated failure probabilities obtained from Fig. 7.12.

As can be seen in both cases (positive and negative impulses), the addition of

Failure Probability	NE	NDF 0.05 g/L	NDF 0.1 g/L	NDF 0.2 g/L
25%	34.80	40.69	40.31	37.03
50%	35.61	42.52	42.35	37.76
75%	36.23	44.03	43.96	38.46

Table 7.13: Weibull probability for positive impulse BV (kV) at different concentration of NP.

Fig. 7.11: Weibull Probability for Positive Impulse BV.

Failure Probability	NE	NDF 0.05 g/L	NDF 0.1 g/L	NDF 0.2 g/L
25%	28.12	30.84	31.43	32.26
50%	29.14	31.37	32.25	32.83
75%	29.96	31.81	32.92	33.28

Table 7.14: Weibull probability for negative impulse BV (kV) at different concentration of NP.

Fe_3O_4 NP improves the behavior under impulse type overvoltages.

In the case of positive impulses, below 75% of failure probability, the NFD that

Fig. 7.12: Weibull Probability for Negative Impulse BV.

obtains the best result is the NDF 0.05 g/L. Above 75%, the one that obtains the best values is the NDF 0.1 g/L. In the case of negative impulses, as seen in the Average values, the one that obtains the best response is the NDF 0.2 g/L and that is not exceeded in any stretch of failure probability by the others.

7.4.3 Comparison with the work of other authors

Not many authors document BV tests under lightning impulses in NFD composed by Fe_3O_4 NP in a base of NE.

Zhang [144] obtained that NDF obtained with rapeseed oil and Fe_3O_4 NP have a lightning Impulse BV 14% greater the pure rapeseed oil. No distinction is made between positive and negative lightning impulses in his work.

Li published two works on the topic in 2012 [49, 21]. In the first paper [49] rapeseed oil is used as base fluid with a concentration of 0.004% wt of Fe_3O_4 NP. They applied both positive and negative lightning impulses. They found that the BV of NFD in case of positive lightning impulses was 37% greater than that of the pure ester. In case of negative lightning impulses, the increase on BV was only 12%. The authors

were very surprised to realize that, while in the case of the pure ester the rupture voltage under negative impulses is greater than under positive impulses, when they add Fe_3O_4 the rupture voltage under positive impulses is greater than under negative impulses. They think that the explanation to this is the reduction in viscosity of NFD when compared with vegetable oil. They measured the time to breakdown and proved that the reason for the increase in BV was an increment in the time to rupture.

In their second paper [21] Li works with camellia insulating oil with Fe_3O_4 NP added 1% wt. Li measured the positive and negative lightning impulse breakdown of pure camellia oil and on NDF produced using that NE and Fe_3O_4 NP. He found that in case of positive Impulse BV improves in 37% with respect to pure oil and in case of negative lightning impulse the increment in BV was 12%. As in the previous work of Li [49] it was noted that with pure camellia oil negative BV is greater than positive BV, while when NP are added the positive BV is higher. A great handicap of the work from Li is the reduced number of breakdowns used to extract conclusions (only five breakdowns).

Our tests were done with a lower electrode distance than the tests from Li, because our HV laboratory does not permit to reach very high voltages. For this reason the values of BV are different, nevertheless our results are consistent to those from Li in terms of the increase of BV: in our case the increment under positive impulse is around 22% while Li obtains 37%, and the increment under negative impulse is 11% while Li obtains also 11%.

7.5 Discussion

In this section, a study is made comparing the results of the NE-based NDF vs. the NP content. Furthermore the results obtained on NE-based NFD are compared with those obtained for MO-based NFD in chapters 4,5 and 6.

7.5.1 AC breakdown voltage

First, the increase (%) of the percentile 2 of ACBV in NDF with respect to the NE is shown in Table 7.15. The percentile 2 is of great importance in the design of power transformers because is related with the risk failure of a transformer.

Fluid	10%	25%	50%	80%
NDF 0.05 g/L	-21%	-24%	52%	>150%
NDF 0.1 g/L	-29%	-16%	31%	>150%
NDF 0.2 g/L	-22%	-5%	14%	51%

Table 7.15: Increment (%) of Percentile 2 for NE-based NDF.

For low values of moisture the reduction in 2 percentile is around 25%, nevertheless the absolute value of the 2 percentile of AC BV is still enough to have a confident margin. So if the thermal properties of NDF are good enough, the fluid can be used in transformers.

In Table 7.16 the improvement or worsening of the average values of AC BV respect to the value of the oil without NP are shown. As can be seen in NE, at low humidities (RS 10 and 25%) there is a worsening of AC BV values around 20%. At high humidity (RS 50 and 80%) there is a considerable improvement in all values of AC BV with Nanoparticles. This improvement goes from 15% to 80%.

Fluid	10%	25%	50%	80%
NDF 0.05 g/L	-20%	-21%	41%	88%
NDF 0.1 g/L	-23%	-7%	27%	79%
NDF 0.2 g/L	-16%	11%	16%	40%

Table 7.16: Increase (%) Average in AC BV in NE nanofluids

Table 7.17 show the results obtained in chapter 4 for MO-based NFD. As can be seen, the effect of adding NP opposite in NE with respect to MO:

- At low humidity (RS 10%), the MO with NP presents better average values with respect to MO without NP.

Fluid	10%	25%	50%
NDF 0.05 g/L	7%	-6%	-4%
NDF 0.1 g/L	8%	-9%	-11%
NDF 0.2 g/L	9%	10%	-1%

Table 7.17: Increase (%) Average in AC BV in MO nanofluids.

- At high humidity (RS 25 and 50%), the MO with NP presents lower average values compared to MO without NP.

7.5.2 Breakdown voltage on lightning impulse

Table 7.18 shows the voltage increment (in per cent) in case of positive impulses for different failure probabilities of the NDF for a concentration of 0.2 g/L when compared with the base fluid (MO or NE). It can be seen in the table for all cases of Positive Impulses there is always an improvement: in the case of MO, this improvement goes from 4% to 35% as the probability of failure increases. On the other hand, for the case of NE, this improvement is around 6% in all cases.

Probability of Failure	MO	NE
25%	5%	6%
50%	21%	6%
75%	35%	6%

Table 7.18: Increase (%) Base Fluid vs 0.2 g/L - Positive Impulses.

In the case of negative impulses (Table 7.19), the improvement hardly varies from 3% in the case of MO regardless of its probability of failure, while for NE, the increase is around 12% although this decreases when increasing the Probability of Breakdown.

Probability of Failure	MO	NE
25%	2%	15%
50%	3%	13%
75%	3%	11%

Table 7.19: Increase (%) Base Fluid vs 0.2 g/L - Negative Impulses.

7.6 Conclusions

In this chapter an experimental evaluation of the AC BV of NE-based NDF has been carried out showing that the presence of Fe_3O_4 NP has different effects depending on the concentration of NP and the moisture in the NDF. On the one hand, RS 10%, the presence of nanoparticles worsens AC BV values in all concentrations studied, while for RS 25% only the concentration of 0.2 g/L shows a small improvement. On the other hand, RS 50% shows improvements for all AC BV values in all NP concentrations studied, with the largest improvement at a concentration of 0.05 g/L. This behavior is repeated for RS 80%.

In addition, in this chapter tests have been carried out on Impulse BV under positive and negative impulses. In the case of positive impulses, the presence of a low concentration of NP (0.05 and 0.1 g/L) considerably improves the average Impulse BV values, although for higher concentrations, the improvement decreases. In the case of negative impulses, the improvement with the presence of NP also exists although it is very low and hardly varies with the concentration of NP.

This chapter may have a great impact, given that a very low number of authors have worked on Impulse BV in NDF based on NE and the study is a relevant contribution to the state of the art of the topic.

Chapter 8

Conclusions

In this chapter, the main conclusions obtained throughout the thesis work are presented. Also included in this chapter are the original contributions of the thesis along with future developments that can be obtained as a result of this work.

8.1 General conclusions

The performance of several nanodielectric fluid (NDF) that were prepared by adding Fe_3O_4 NP to a MO and a NE was studied during the thesis. The studies have been mainly focused towards the evaluation of the dielectric properties of the liquids. Some work was also performed in order to evaluate the stability and physic chemical properties of the fluids.

The main conclusions of the work are presented below.

8.1.1 Conclusions in relation to the manufacturing process and the stability of NDF

- The manufacturing process defined in the thesis, based on the use of ultrasonic stirring to disperse small amounts of a NP suspension in a Base Fluid, leads to NDF with good long-term stability at ambient temperatures. Fluids that remained stable for more than one year were obtained in the thesis using MO

and NE as base fluids.

- The stability of NDF is jeopardized when the liquids are subjected to high temperatures for long periods of time. The loss of stability could be related with the loss of the bound between the surfactant and the NP or to some other factors.
- The stability of NDF is jeopardized when the liquids are subjected to high temperatures for long periods of time. The loss of stability could be related with the loss of the bound between the surfactant and the NP. When an increase in temperature occurs, surfactants lose their structure by detaching themselves from the NP. Therefore, a good choice of surfactant is fundamental to reach a good stability.
- The materials used to produce the NDF have a major influence on the stability of NDF. Carboxyl functionalized surfactants are more adequate for NE oils, whereas non-carboxylic surfactants dissolve better the NDF in low polarity fluids, as MO.
- The stability of newly developed NDF must be tested at typical transformer working conditions to guarantee that they can withstand the operating temperatures they will be subjected to. Most published works on transformer NDF evaluate the stability of the liquids at room temperature, but fluids that perform well at room temperature may lose stability above certain temperature ranges.
- The presence of cellulosic insulation does not affect the stability of NDF significantly.
- Visual inspection and particle-size measurement can be used as complementary methods to get information about the formation of precipitates in the dispersions and the aggregation phenomena. Although visual inspection has been generally used to analyse the stability of NDF by many authors, the method might fail in detecting moderate aggregation of NP within the fluids. On the other hand, Zeta potential is not a suitable method to characterize the stability of these types of liquids as, given the non-polar nature of the base fluid and the NP concentrations typically used for this application, the NPs do not attach a sufficient amount of

charge to their surfaces to enable the measure.

8.1.2 Conclusions in relation to the manufacturing process and the stability of NDF

In-depth studies have been done in the thesis to evaluate the dielectric properties of NDF produced with a MO as base fluid and considering several concentrations of Fe_3O_4 NP. The thesis analyses the AV BV and the impulse BV. The conclusions in relation to those parameters are presented next.

AC BV of MO based NDF

Previous authors in the field on NDF had suggested that the improvement of the dielectric properties observed when NP are added to a base fluid could be partially caused by the interaction between the NP and the water molecules present in the fluid. To analyze that topic in depth two set of AC BV tests were carried out in the thesis: tests on dry fluids and tests on fluids with growing moisture content.

The analysis of NDF with low concentration of moisture and different concentrations of NP led to the following conclusions:

- The addition of small concentrations Fe_3O_4 NP to the MO leads to an improvement of its AC BV.
- The statistical analysis of the measures showed an increase of the average value of the AC BV, lower values for the standard deviation of NDF compared with MO and higher BV for low probabilities of failure. All those aspects are important for the transformer insulation design.
- The improvement of the AC BV depends on the concentration of NP added to the base fluid. Although the dielectric strength improves with the NP concentration, there is a maximum concentration above which the AC BV of the NDF drops to similar or even worse values than those of the base fluid. The best results were obtained for fluids prepared with NP concentrations 0.2 g/L in which the AC BV increased by 10%.

- The experimental observations can be justified by the superposition of two opposed effects
 - On the one hand, when NDF are subjected to an electric field, the conductive Fe_3O_4 NP attract fast free ions and electrons in the insulating fluid forming an electrical double layer around them. Then, the presence of fast charges in the fluid is limited and those are replaced by charged NP, which are slower. The reduction of the mobility of the electric charges modifies the velocity of propagation of the streamers, which becomes smaller, being thus more likely those streamers are extinguished before a breakdown takes place. Under these conditions a higher electric field will be required to produce a dielectric breakdown what enhances the AC BV values.
 - On the other hand, Fe_3O_4 NP are conductive and the resistivity of the NDF fluids decreases as the concentration of NP rises.
- For low concentrations of NP the first effect predominates but below certain concentrations the increase of the conductivity cannot be compensated by the formation of the double layer.
- Additionally, the effect of the surfactant on the results of the AC BV of NDF was evaluated concluding that the effect of that material is negligible. The result is logical if we consider the extremely low amounts of surfactant that were present in the NDF tested in this work (approximately 0.1 grams of surfactant for one liter of NDF).

The study of the AC BV on fluids with high moisture contents lead to the following conclusions:

- It has been shown that the presence of moisture has a negative impact on the AC BV of the NDF and of the MO, although for the same content of water the reduction for AC BV is lower for the NDF.
- If the AC BV average value is obtained as a function of the absolute moisture content of the samples, improvements up to 150% are found when comparing the AC BV of NDF and MO for similar absolute moisture contents.

- When MO and NDF with similar RS conditions are compared, the observed increases of the AC BV are similar to those observed on dry fluids. Those enhancements are more related with the effect of the NP on the electron transport processes than with the interaction between the water molecules and the NP.
- The impact of the NP on the solubility on NDF was investigated finding that the presence of NP increases the solubility of water in the oil and that this increase is clearly related with the enhancement of the AC BV observed in NDF.
- In the case of the NDF the increase of the solubility and the enhancement of the AC BV are related with the fact that the water molecules in the fluid bond to the NP preventing them from moving freely acting like charge carriers.
- The solubility increase of NDF could have positive effects in the oil-cellulose system such as the displacement of the moisture equilibrium towards the oil, allowing the cellulose insulation to operate dryer.

Impulse BV of MO based NDF

- The experimental evaluation of the impulse BV of Fe_3O_4 based NDF showed that the presence of NP improves the dielectric properties significantly under positive impulse conditions. Improvements up to 50% were obtained for fluids with concentrations of NP 0.6 g/L. In that case the low probability BV raised from a value of 32 kV measured in MO to 45 kV in the NDF.
- The positive-impulse BV increases with the concentration of NP. Although the maximum concentration of NP analysed in this thesis was 0.6 g/L there is probably a maximum concentration above which the impulse BV starts to drop, as happened with the AC BV.
- In the case of negative impulses, the presence of NP hardly modifies the values obtained, but does not worsen the values of Impulse BV either. The only observed improvement is that the BV measures showed lower dispersion.
- The observed results are related with the variation of the streamer propagation speed: In the case of positive streamer, the propagation speed is halved, what

hinders the evolution of the discharge and thus increases the BV value. On the other hand, the presence of NP does not seem to affect the speed of propagation of negative streamers.

- Streamers originating from a positive electrode are the ones that poses a higher risk for the transformer integrity, as they tend to initiate at lower voltages than those originating from a negative electrode, and to propagate faster and further so the increment of positive impulse BV of NDF could suppose an important advantage for the design of transformer dielectric insulation.

8.1.3 Conclusions in relation to the dielectric properties of NE based NDF

The thesis work was completed with an additional set of tests performed on NE based NDF. The fluids were prepared with a Sunflower oil fluid. AC BV and impulse BV were measured in those fluids obtaining the following conclusions:

AC BV of NE based NDF

- When the moisture content is low, the average AC BV of the NDF is lower than that of the pure NE. The same happens with 2% percentile. For dry NFD the reduction in AC BV is about 20%, however it Should be noted that the value of the AC BV of the NFD is higher than that required by standards for dry oils.
- When the moisture content is high, the average value of AC BV of the NFD is higher than that of the pure NE. So the dielectric behavior of wet NFD is better than pure NE.
- The result obtained are consistent with those obtained by Khaled and Beroual.

Impulse BV of NE based NDF

- Under positive lightning impulse the average value of the BV is higher than that of the pure NE. The increment in impulse BV ranges from 7% for high concentration of NP to 19% for low concentrations of NP.

- Under negative lightning impulse the average value of the BV is again higher than that of the pure NE. The increment in impulse BV ranges from 8.5% to 13.5% but in this case, unlike the previous one, the biggest increase is given for high concentrations of NDF.
- Our results are consistent with those from the Chongqing University.

Taking into account all the dielectric tests performed (AC BV, influence of moisture on AC BV, breakdown voltage for positive and negative impulses), it follows that NDF have advantages over NE, because although AC BV is slightly lower, the behavior of AC BV against humidity is better. In addition the positive and negative impulse breaking voltages improve.

In this sense, of the three nanofluids used, the best results have been obtained with an NP concentration of 0.05 g/L and 0.1 g/L where the reduction on AC BV is about 20%, but the behavior of AC BV in case of moisture is better and the behavior in negative and positive impulse breakdown voltage improves.

8.2 Original contributions

The main contributions derived from this thesis are:

- A NDF manufacturing method, based in the dispersion of Fe_3O_4 NP in a base fluid with an ultrasound probe, has been proposed and evaluated. The application of the established methodology lead to NDF with much higher long-term stability than those reported by other authors.
- The impact of the polarity of the surfactant on the long-term stability of NDF has been analysed proposing criteria that can be used to decide whether a combination of materials is suitable to produce stable liquids.
- It has been demonstrated that the stability of NDF is affected by the temperature. This aspect, which is critical for the application of NDF to in-service transformers, had not been studied by any author before.
- It has been proved that the evaluation of the NDF stability requires a combination

of visual inspection and other characterization techniques from the field of materials engineering (FWHM). It has been found that the visual inspection, which is the technique commonly applied to evaluate the stability of NDF, can lead to erroneous conclusions.

- An experimental analysis of the AC breakdown voltage (AC BV) of mineral oil (MO) based NDF has been carried out showing that the AC BV of NDF increases with the concentration of nano particles (NP) added to the base fluid. It has also been found that there is a concentration above which the dielectric strength of the liquids is worsened. Theoretical explanations have been provided to justify the experimental observations.
- A deep experimental study has been carried out to analyse the dependence of the AC BV of NDF with the moisture content of the liquid. The study is a novelty because of the number of analysed scenarios and the adopted experimental approach. It has been proved that one of the mechanisms that contributes to the improvement of NDF in high moisture environments is the fact that the moisture solubility of the liquids rises as NP are added. As water molecules are bounded to the NP they cannot participate in the breakdown process and then, the AC BV of NDF is higher than that of MO with similar absolute moisture contents. This fact had not been reported by any other author before.
- The impulse BV of the MO based NDF have been analysed finding experimental results that have been justified from the theoretical point of view. It has been shown that an increase in the NP concentration improves the impulse BV but only for positive impulses while in negative impulses that improvement is not significant.
- The dielectric strength of natural ester (NE) based NDF has been tested. The AC BV of NDF in dry and high moisture environments has been studied; the impulse BV has also been determined for NE based NDF with several concentrations of NP. A very low number of authors have reported experiences on NE based NDF and the study is a relevant contribution to the state of the art of the topic.

8.3 Future developments

The development of NDF is still at an early stage. Although some of the results that have been obtained on NDF are promising, the prospect of using them in oil-filled transformers is still remote. In this sense there are many future developments that could be carried out as a continuation of this work.

Some proposals for future work are:

- Development of new manufacturing techniques that provide an adequate long-term stability even when the fluids work at temperatures above 100 °C. This includes the search for new surfactants and materials.
- Perform experimental studies to evaluate de NDF properties with ageing.
- Perform experimental and theoretical analysis on the interaction between NDF and solid insulation. The studies should consider the effect of the NP on the dielectric properties of solid insulation, but also the effect on the degradation processes.
- Testing of NDF on real test transformers to study aspects related with its operation such as an analysis of the temperature distribution and the maximum admissible load.
- Development of theoretical models to analyse the microscopical behaviour of insulating fluids.
- Development of models to analyse the temperature distribution and the electric field distribution in transformers insulated with NDF.
- Study the effect of NP on transformer diagnostic techniques, such as dissolved gas analysis, capacitance, and tan delta measurements.
- Analyse the effect of transformer field treatments, e.g., regeneration of oil and field drying, on the properties of NDF.

Appendix A

Technical sheets

The following pages include the technical sheets of the oils used (Nynas Nytro 4000X and Bio Electra).

SUPER GRADE

Nytro 4000X

Maximum performance insulating oil

An inhibited super grade, Nytro 4000X conforms to IEC 60296 Edition 4.0 – including the fulfilment of specific requirements for special applications. Developed and formulated to deliver maximum resistance to oil degradation, Nytro 4000X provides outstanding oxidation stability for a longer transformer life with less maintenance.

Designed for heavy duty

This product has been specially developed for use in oil-filled electrical equipment – including power and distribution transformers, rectifiers, circuit breakers and switchgears.

Performance and benefits

Extremely good heat transfer. Thanks to low viscosity and viscosity index, this super grade offers extremely good heat transfer characteristics, ensuring heat is efficiently removed from core and windings.

Outstanding oxidation stability. Developed and formulated to deliver maximum resistance to oil degradation, this grade provides outstanding oxidation stability for enhanced transformer life and minimum maintenance.

Very good low temperature properties. Naphthenic characteristics allow the transformer to start at the lowest possible temperature – without using pour point depressants.

High dielectric strength. This insulating oil both meets and exceeds the toughest demands on dielectric strength – when stored and handled correctly.

Product description

Nytro 4000X fulfils the requirements for IEC 60296 Edition 4.0 fully inhibited oil. Nynas classify this product as a super grade.

Nytro 4000X is rigorously analysed and passes the following corrosion tests:

- ASTM D1275 method B
- IEC 62535
- DIN 51353

In accordance with IEC 60296 Edition 4.0, all additives are declared.

There's more to us than this

We're delighted you chose one of our transformer oils. If you have any questions about other products and services, get in touch with your local Nynas contact. Besides top quality oils, we offer a wide range of services, including rapid delivery worldwide, sample analysis, training, seminars and much more. All you have to do is ask. Find out more at www.nynas.com

Nytro 4000X

PROPERTY	UNIT	TEST METHOD	SPECIFICATION LIMITS		TYPICAL DATA
			MIN	MAX	
1 - Function					
Viscosity, 40°C	mm ² /s	ISO 3104		12.0	9.1
Viscosity, -30°C	mm ² /s	ISO 3104		1800	850
Pour point	°C	ISO 3016		-40	-54
Water content	mg/kg	IEC 60814		30	<20
Breakdown voltage					
- Before treatment	kV	IEC 60156	30		40-60
- After treatment	kV	IEC 60296	70		>70
Density, 20°C	kg/dm ³	ISO 12185		0.895	0.866
DDF at 90°C		IEC 60247		0.005	<0.001
2 - Refining/stability					
Appearance		IEC 60296	Clear, free from sediment		complies
Acidity	mg KOH/g	IEC 62021		0.01	<0.01
Interfacial tension	mN/m	EN 14210	40		49
Total sulphur content	%	ISO 14596		0.05	<0.01
Corrosive sulphur		DIN 51353	non-corrosive		non-corrosive
Potentially corrosive sulphur		IEC 62535	non-corrosive		non-corrosive
Corrosive sulphur		ASTM D 1275 B	non-corrosive		non-corrosive
DBDS	mg/kg	IEC 62697-1		not detectable	not detectable
Antioxidant	wt %	IEC 60666	0.34	0.40	0.38
Metal passivator additives	mg/kg	IEC 60666		not detectable	not detectable
2-Furfural and related compounds content	mg/kg	IEC 61198		0.05	<0.05
Aromatic content	%	IEC 60590			4
3 - Performance					
Oxidation stability at 120°C,500 h		IEC 61125 C			
Total acidity	mg KOH/g			0.30	<0.01
Sludge	wt %			0.05	<0.01
DDF at 90°C				0.050	<0.010
4 - Health, safety and environment (HSE)					
Flash point, PM	°C	ISO 2719	135		146
PCA	wt %	IP 346		3	<3
PCB		IEC 61619	not detectable		not detectable

Nytro 4000X is an inhibited insulating oil with extremely good electrical and excellent ageing properties meeting IEC 60296 Ed.4 (2012), special applications.

Severely Hydrotreated Insulating Oil
Issuing date: 30/09/2014

Description

Dielectric oil based on plant-derived esters, rapidly biodegradable and non-toxic for both aquatic and land ecosystems. It is an increased safety fluid thanks to its high ignition point and the lack of risk factors on its safety sheet.

To be used as a dielectric insulator in transformers, reactors, and electrical switches. Can be used in both new electrical equipment as well as to fill equipment that was previously using a different type of dielectric fluid. Especially for those cases that require a fluid with a high flash point or for use in environmentally sensitive areas.

Properties

- Vegetable oil in a percentage greater than 99%.
- No synthetic antioxidants.
- No silicones, halogens, or any other component that could pose a risk to health or the environment.
- Ignition point over 300 °C. Reduces risk of fires and their consequences.
- Classified as a type K fluid according to IEC 61100.

Quality levels

- IEC 62770

Technical specifications

Physical and chemical properties	UNIT	METHOD	GUARANTEED VALUE	TYPICAL VALUE
Fire point	°C	ASTM D92	>300	362
Flash point	°C	ASTM D92	>250	330
Density at 20 °C	g/ml	ASTM D4052	<1	0.91
Kinematic viscosity at 100 °C	cSt	ASTM D455	<15	8.5
Kinematic viscosity at 40 °C	cSt	ASTM D455	<50	39.2
Kinematic viscosity at 0 °C	cSt	ASTM D455	<500	275.9
Pour point	°C	ASTM D97	<-10	-22
Appearance	--	ASTM D1524	Clear and bright	
Thermal expansion coefficient 0-50 °C	°C ⁻¹	ASTM D1903		0.00072
Thermal conductivity at 25 °C	W/K m	ASTM D2717		0.1691
Specific heat at 25 °C	J/kg	ASTM D2766		1.97
Acidity (neutralisation index)	mgKOH/g	ASTM D974	<0.06	0.05

A safety data sheet is available on request.

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Technical data sheet for Lubricants. Revision 1. July 2016.

Lubricants

Water content	mg/kg	IEC 60814	<200	150
Oxidation stability				
Total acidity	mgKOH/g	IEC 61125 C	0.6	0.16
Diel. dissipation factor 90 °C, 50 Hz	--	IEC 60247	0.5	0.065
Viscosity increase	%	ASTM D445	<30	10.4

Electrical properties	UNIT	METHOD	GUARANTEED VALUE	TYPICAL VALUE
Dielectric strength	kV	IEC 60156	>35	65
Diel. dissipation factor 90 °C, 50 Hz		IEC 60247	<0.050	0.03
Diel. dissipation factor 25 °C, 50 Hz		ASTM D924		0.002
Electrical conductivity at 25 °C	pS/m	ASTM D2624		3
Dielectric constant at 25 °C		IEC 60247		3.1
Gassing tendency	µl/min	IEC 60628 A		-31.2

Environmental properties	UNIT	METHOD	GUARANTEED VALUE	TYPICAL VALUE
Biodegradability - 28 days	%	OECD 301B	>60	85
Ecotoxicity in aquatic environment	mg/l	OECD 201	>100	>1000
		OECD 202	>100	>1000
		OECD 203	>100	>1000
Ecotoxicity in land environment	mg/kg	OECD 207	>100	>1000
		OECD 208	>100	>1000

A safety data sheet is available on request.

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Appendix B

Analysis of variance

B.1 ANOVA method

In this thesis the dielectric behavior of several fluids with different concentrations of nanoparticles is compared.

When it is desired to compare whether the mean value of two sets of data (in this case AC breakdown Voltage of fluids with two different content of NP) are equal with a statistical significance, the Student's t-distribution is used. However, if the number of data sets to be compared is high the comparison between pair of sets it is not recommended, as the estimation error would accumulate, leading to high values of error. In these cases the ANOVA method is recommended.

The ANalysis Of VAriance (usually called ANOVA) tests the hypothesis that the means of K populations are equal. Two hypothesis are checked in ANOVA: the so-called zero hipótesis (the means of each data set are equal) versus the alternative hypothesis (at least one mean of the data set is different from the others).

$$H_0 : \alpha_1 = \alpha_2 = \dots = \alpha_k$$

$$H_1 : \text{not all group means are equal.}$$

ANOVA is based on the assumption that all populations are normally distributed. Another assumption is that the variances of every set of data are similar. However,

ANOVA work quite well even when the assumption of normality is violated, unless one or more of the distributions are very asymmetric or when the variances are quite different. Transformations of the original data set can correct these violations.

The procedure works by comparing the variance between the whole data set and the variance within each data set as a way to determine if the data sets are all them part of a larger population or are separate populations with different characteristics.

There are several types of ANOVA although the ones used in this thesis are the one-way ANOVA.

One-way ANOVA is a simple special case of the linear model. The one-way ANOVA form of the model is:

$$\gamma_{ij} = \alpha_j + \varepsilon_{ij} \quad (\text{B.1})$$

where:

- γ_{ij} is an observation, in which i represents the observation number, and j represents the data set (sometimes called as “level” or “treatment”) of the predicted variable γ . All γ_{ij} are independent.
- α_j represents the mean for the j th data set (level or treatment).
- ε_{ij} is the random error, independent and normally distributed, with zero mean and constant variance.

The main quantities for using ANOVA are:

- The Global Mean: $\bar{A} = \frac{\sum_{j=1}^K \sum_{i=1}^{n_j} \gamma_{ij}}{n}$, wehere K is the number of data-sets (treatments), n_j is the number of data in the j -th data-set, and n is the total number of data of all the data sets.
- The Mean of each data-sets: $\bar{A}_j = \frac{\sum_{i=1}^{n_j} \gamma_{ij}}{n_j}$
- Sum of squared differences between the data of all sets and the global mean:

$$SCT = \sum_{j=1}^K \sum_{i=1}^{n_j} (\gamma_{ij} - \bar{A})^2$$
- Sum of squared differences among elements of data sets and the mean of its set:

$$SCD = \sum_{j=1}^K \sum_{i=1}^{n_j} (\gamma_{ij} - \bar{A}_j)^2$$

- Variation among the different data sets (residual): $SCE = \sum_{j=1}^K (\bar{A}_j - \bar{A})^2 \cdot n_j$
- Degrees of freedom: the number of elements minus 1. For the whole data set $n - 1$, for each individual set $n_j - 1$, and for the number of treatments $K - 1$. The degrees of freedom associated to the residual is $n - K$.

If all the data sets are parts of the same population SCE is very small. Nevertheless a better understanding is obtained if the indicator is normalized taking into account the degrees of freedom and the sum of squared differences SCD.

Therefore, to check if the data sets belong to a same proportion the following statistics is used:

$$\frac{\frac{SCE}{K-1}}{\frac{SCD}{n-K}} \quad (B.2)$$

This statistics follows a function called F of Fischer-Snedecor versus the degree of confidence of the null hypothesis. The function F is dependent of the degrees of freedom of the treatments and the degree of freedom residual. Usually a 95% confidence ratio is accepted. Looking up in the table of F Fischer-Snedecor with the accepted error (5% = 100%-95%) and the degrees of freedom we obtain a value a . Then we will accept the H_0 hypothesis if

$$F = \frac{\frac{SCE}{K-1}}{\frac{SCD}{n-K}} < a \quad (B.3)$$

B.2 Tukey HSD

If the null hypothesis is not accepted there is at least one data set with a different mean than the other sets. To find which of the data sets is different from the others several tests can be used. One of the most used test is the HSD Tukey test. The Tukey test requires that all data-sets have the same number of data.

The HSD (Honestly Significant Difference) test of Tukey considers that the differences between the mean of a data set and the media of the population to which this data set belongs follow a normal distribution.

$$(\overline{A_1}, \mu_1), (\overline{A_2}, \mu_2), \dots, (\overline{A_K}, \mu_K), \quad (\text{B.4})$$

The means of every treatment (or data set) are compared each other

$$\overline{A_i} - \overline{\mu_j} \quad (\text{B.5})$$

Then, the largest and the smallest difference are obtained. The difference is normalized with the residual variance (S_R^2)

$$\frac{\max(\overline{A_i} - \overline{\mu_i}) - \min(\overline{A_j} - \overline{\mu_j})}{\sqrt{\frac{S_R^2}{n}}} \quad (\text{B.6})$$

A confident degree, α , is chosen. So the probability

$$P_\gamma \left[\frac{\max(\overline{A_i} - \overline{\mu_i}) - \min(\overline{A_j} - \overline{\mu_j})}{\sqrt{\frac{S_R^2}{n}}} \leq q_{\alpha, K, n-1} \right] = 1 - \alpha \quad (\text{B.7})$$

As

$$(\overline{A_i} - \overline{\mu_i}) - (\overline{A_j} - \overline{\mu_j}) \leq \max(\overline{A_i} - \overline{\mu_i}) - \min(\overline{A_j} - \overline{\mu_j}) \quad (\text{B.8})$$

Then

$$P_\gamma \left[\frac{(\overline{A_i} - \overline{\mu_i}) - (\overline{A_j} - \overline{\mu_j})}{\sqrt{\frac{S_R^2}{n}}} \leq q_{\alpha, K, n-1} \right] = 1 - \alpha \quad (\text{B.9})$$

Where $q_{\alpha, K, n-K}$ is the upper $100 \cdot (1 - \alpha)$ th percentile of the Student's t-distribution with parameter K and n-K degrees of freedom.

We define Honest Significant Difference as

$$HSD = q_{\alpha, K, n-K} \cdot \sqrt{\frac{S_R^2}{n}} \quad (\text{B.10})$$

Then

$$(\overline{A_i} - \overline{A_j}) - HSD \leq \mu_i - \mu_j \leq (\overline{A_i} - \overline{A_j}) + HSD \quad (\text{B.11})$$

If the Interval $\mu_i - \mu_j$ does not includes 0 the means of both data sets are significant different. So if

$$|\overline{A}_i - \overline{A}_j| \leq HSD \quad (B.12)$$

We Will accept H_0 and the means are equal

Otherwise if

$$|\overline{A}_i - \overline{A}_j| > HSD \quad (B.13)$$

We will reject H_0 and the mean of the two data sets are significant different.

Bibliography

- [1] Toshikatsu Tanaka and Takahiro Imai. Advances in Nanodielectric Materials Over the Past 50 Years. *IEEE Electrical Insulation Magazine*, 29:10–23, 2013.
- [2] T J Lewis. Nanometric Dielectrics. *Transactions on Dielectrics and Electrical Insulation*, 1(5):812–825, 1994.
- [3] Michel F Frechette and Michel L Trudeau. Introductory Remarks on Nanodielectrics. *Transactions on Dielectrics and Electrical Insulation*, 11(5):808–818, 2004.
- [4] Michel F Fréchette. What Are Nanodielectrics? *IEEE Electrical Insulation Magazine*, 29(6):8–11, 2013.
- [5] Michel F Fréchette, Ashok Vijh, Michel L Trudeau, Davide Fabiani, Stanislaw Gubanski, Clive Reed, Andrej Krivda, Peter Morshuis, Thomas Andritsch, Roman Kochetov, John Fothergill, and Steven Dodd. A “Universal” Panacea for Solving All Electrical Insulation Problems ? In *2010 International Conference on Solid Dielectrics*, pages 3–5, 2010.
- [6] Toshikatsu Tanaka and Masahiro Kozako. Proposal of a Multi-core Model for Polymer Nanocomposite Dielectrics. *IEEE Transactions on Dielectrics and Electrical Insulation*, 12(4):669–681, 2005.
- [7] T Tanaka. A Novel Concept for Electronic Transport in Nanoscale Spaces Formed by Islandic Multi-cored Nanoparticles. *2016 IEEE International Conference on Dielectrics (ICD)*, 1:23–26.
- [8] T. J. Lewis. International conference on solid dielectrics, icsd. In *International*

Conference on Solid Dielectrics, 2004.

- [9] M.A Harmer, Ann Y. Liauw, B.S. Kang, and Mark A. Scialdone. Insulating material containing nanocellulose, Patent, US20140186576 A1, 2012. (12), 2014.
- [10] G. Chandini and R. Karthik. Investigations on critical parameters of nano solid dielectrics for the optimized function of power transformer. *2014 International Conference on Circuits, Power and Computing Technologies, ICCPCT 2014*, pages 370–376, 2014.
- [11] Huifei Jin. *Dielectric Strength and Thermal Conductivity of Mineral Oil based Nanofluids*. PhD thesis, Delft University of Technology, the Netherlands, 2015.
- [12] W. Yu, D.M. France, S.U.S. Choi, and J.L. Routbort. Review and Assessment of Nanofluid Technology for Transportation and Other Applications. *Energy Systems Division, Argonne National Laboratory work*, 2007.
- [13] Niskayuna Weijun Yin. Patent No; US 2013/0285781, 2013.
- [14] Anwar Ahniyaz, Andrea Fornara, Eric Johansson Salazar, and A Materials. The Effect of Ceria Nanoparticles on the Breakdown Strength of Transformer Oil. In *IEEE 11th International Conference on the Properties and Applications of Dielectric Materials (ICPADM)*, pages 289–292, 2015.
- [15] Vladimir Segal and K. Raj. An investigation of power transformer cooling with magnetic fluids. *Indian Journal of Engineering and Materials Sciences*, 5(6):416–422, 1998.
- [16] V. Segal, A. Hjortsberg, A. Rabinovich, D. Nattrass, and K. Raj. AC (60 Hz) and impulse breakdown strength of a colloidal fluid based on transformer oil and magnetite nanoparticles. In *IEEE International Symposium on Electrical Insulation*, volume 2, pages 619–622, 1998.
- [17] Wenxia Sima, Jian Shi, Qing Yang, Sisi Huang, and Xuefei Cao. Effects of conductivity and permittivity of nanoparticle on transformer oil insulation performance: Experiment and theory. *IEEE Transactions on Dielectrics and Electrical Insulation*, 22(1):380–390, 2015.

- [18] Y. Lv, Y. Zhou, C. Li, Q. Wang, and B. Qi. Recent progress in nanofluids based on transformer oil: Preparation and electrical insulation properties. *IEEE Electrical Insulation Magazine*, 30(5):23–32, 2014.
- [19] Francis M O’Sullivan. *A model for the initiation and propagation of electrical streamers in transformer oil and transformer oil based nanofluids*. PhD thesis, Massachusetts Institute of Technology, Dept. of Electrical Engineering and Computer Science, 2007.
- [20] Mohamed E. Ibrahim, Amr M. Abd-Elhady, and Mohamed A. Izzularab. Effect of nanoparticles on transformer oil breakdown strength: Experiment and theory. *IET Science, Measurement & Technology*, 10(8):839–845, 2016.
- [21] Jian Li, Ruijin Liao, and Lijun Yang. Investigation of natural ester based liquid dielectrics and nanofluids. *ICHVE 2012 - 2012 International Conference on High Voltage Engineering and Application*, 56(2 mm):16–21, 2012.
- [22] Yuxiang Zhong, Yuzhen Lv, Chengrong Li, Yuefan Du, Mutian Chen, Shengnan Zhang, You Zhou, and Long Chen. Insulating properties and charge characteristics of natural ester fluid modified by TiO₂ semiconductive nanoparticles. *IEEE Transactions on Dielectrics and Electrical Insulation*, 20(1):135–140, 2013.
- [23] P. Krishna Kumar, S. Senthil Kumar, and M. Ravindran. Investigation on mixed insulating fluids with nano fluids and antioxidants. *2014 International Conference on Advances in Electrical Engineering, ICAEE 2014*, pages 6–9, 2014.
- [24] G Dombek, Z Nadolny, and P Przybyłek. The Study of Thermal Properties of Mineral Oil and Synthetic Ester Modified by Nanoparticles TiO₂ and C₆₀. *International Conference on High Voltage Engineering and Application (ICHVE)*, pages 1–4, 2014.
- [25] Baimei Wang, Jian Li, Bin Du, and Zhaotao Zhang. Study on the stability and viscosity of Fe₃O₄ nano-particles vegetable insulating oils. *ICHVE 2012 - 2012 International Conference on High Voltage Engineering and Application*, pages 307–310, 2012.

- [26] A. Raymon, S. Sakthibalan, C. Cinthal, R. Subramaniaraja, and M. Yuvaraj. Enhancement and comparison of nano-ester insulating fluids. *IEEE Transactions on Dielectrics and Electrical Insulation*, 23(2):892–900, 2016.
- [27] Michael G. Danikas, Aristides Bakandritsos, Georgios D. Peppas, Vasilios P. mpakos, Eleytheria C. Pyrgioti, and Ioannis F. Gonos. Statistical investigation of AC breakdown voltage of nanofluids compared with mineral and natural ester oil. *IET Science, Measurement & Technology*, 10(6):644–652, 2016.
- [28] Yanjiao Li, Jing'en Zhou, Simon Tung, Eric Schneider, and Shengqi Xi. A review on development of nanofluid preparation and characterization. *Powder Technology*, 196(2):89–101, 2009.
- [29] Bin Du, Jian Li, Bai Mei Wang, and Zhao Tao Zhang. Preparation and breakdown strength of Fe₃O₄ nanofluid based on transformer oil. *ICHVE 2012 - 2012 International Conference on High Voltage Engineering and Application*, pages 311–313, 2012.
- [30] Jin Miao, Ming Dong, and Liang Ping Shen. A modified electrical conductivity model for insulating oil-based nanofluids. In *Proceedings of 2012 IEEE International Conference on Condition Monitoring and Diagnosis, CMD 2012*, number September, pages 1126–1129, 2012.
- [31] M. V. Avdeev, M. Balasoiu, V. L. Aksenov, V. M. Garamus, J. Kohlbrecher, D. Bica, and L. Vekas. On the magnetic structure of magnetite/oleic acid/benzene ferrofluids by small-angle neutron scattering. *Journal of Magnetism and Magnetic Materials*, 270(3):371–379, 2004.
- [32] Lucian Pislaru-Danescu, Alexandru M. Morega, Gabriela Telipan, Mihaela Morega, Jean Bogdan Dumitru, and Virgil Marinescu. Magnetic nanofluid applications in electrical engineering. *IEEE Transactions on Magnetics*, 49(11):5489–5497, 2013.
- [33] Jian Li, Bin Du, Feipeng Wang, Wei Yao, and Shuhan Yao. The effect of nanoparticle surfactant polarization on trapping depth of vegetable insulating oil-based nanofluids. *Physics Letters A*, 380(4):604–608, 2016.

- [34] Andrea Cavallini, R. Karthik, and Fabrizio Negri. The effect of magnetite, graphene oxide and silicone oxide nanoparticles on dielectric withstand characteristics of mineral oil. *IEEE Transactions on Dielectrics and Electrical Insulation*, 22(5):2592–2600, 2015.
- [35] R Karthik, F Negri, and A Cavallini. Influence of Ageing on Dielectric characteristics of silicone di oxide , tin oxide and ferro nanofluids based mineral oil. pages 40–43. IEEE.
- [36] Jianzhuo Dai, Ming Dong, Yang Li, and Jierui Zhou. Influence of Nanoparticle Concentration on the Frequency Domain Spectroscopy Properties of Transformer Oil-based Nanofluids. *IEEE, 2016 Annual Report Conference on Electrical Insulation and Dielectric Phenomena.*, pages 587–590, 2016.
- [37] Yuefan Du, Yuzhen Lv, Chengrong Li, Mutian Chen, Yuxiang Zhong, Jianquan Zhou, Xiaoxin Li, and You Zhou. Effect of semiconductive nanoparticles on insulating performances of transformer oil. *IEEE Transactions on Dielectrics and Electrical Insulation*, 19(3):770–776, 2012.
- [38] D U Yue-fan, L V Yu-zhen, Zhou Jian-quan, Chen Mu-tian, L I Xiao-xin, L I Cheng-rong, and A Nanofluids Preparation. Effect of Ageing on Insulating Property of Mineral Oil-based TiO₂ Nanofluids. In *2011 IEEE International Conference on Dielectric Liquids Effect*, pages 0–3, 2011.
- [39] Rongsheng Liu, Leif A A Pettersson, Tommaso Auletta, and Olof Hjortstam. Fundamental research on the application of nanodielectrics to transformers. *Annual Report - Conference on Electrical Insulation and Dielectric Phenomena, CEIDP*, pages 423–427, 2011.
- [40] Gaurav Shukla and Hemantkumar Aiyer. Thermal conductivity enhancement of transformer oil using functionalized nanodiamonds. *IEEE Transactions on Dielectrics and Electrical Insulation*, 22(4):2185–2190, 2015.
- [41] Eman G. Atiya, Diaa Eldin A. Mansour, Reham M. Khattab, and Ahmed M. Azmy. Dispersion behavior and breakdown strength of transformer oil filled with TiO₂nanoparticles. *IEEE Transactions on Dielectrics and Electrical Insulation*,

22(5):2463–2472, 2015.

- [42] Jean B. Dumitru, Alexandru M. Morega, and Mihaela. Morega. Nanofluid Cored Miniature Electrical Transformer with Planar Spiral Windings. *International Conference on Optimization of Electrical and Electronic Equipment*, pages 11–16, 2014.
- [43] European Commission. *Types and uses of nanomaterials, including safety aspects*. 2012.
- [44] R. Kochetov, P. Morshuis, J. Smit, T. Andritsch, and A. Krivda. Precautionary remarks regarding synthesis of nanocomposites. In *Electrical Insulation Conference*, number June, pages 51–54, 2014.
- [45] Diaa-Eldin A. Mansour, Ahmed M. Elsaeed, and Mohamed A. Izzularab. The role of interfacial zone in dielectric properties of transformer oil-based nanofluids. *IEEE Transactions on Dielectrics and Electrical Insulation*, 23(6):3364–3372, Dec 2016.
- [46] Jae-Won George Hwang. *Elucidating the Mechanisms Behind Pre-Breakdown Phenomena in Transformer Oil Systems*. PhD thesis, Massachusetts Institute of Technology, 2010.
- [47] Georgios D. Peppas, Aristides Bakandritsos, Vasilis P. Charalampakos, Eleftheria C. Pyrgioti, Jiri Tucek, Radek Zboril, and Ioannis F. Gonos. Ultrastable Natural Ester-Based Nanofluids for High Voltage Insulation Applications. *ACS Applied Materials & Interfaces*, 8(38):25202–25209, Sep 2016.
- [48] Masahiro Hanai, Satohiko Hosomi, Hiroki Kojima, Naoki Hayakawa, and Hitoshi Okubo. Dependence of TiO₂ and ZnO nanoparticle concentration on electrical insulation characteristics of insulating oil. *Annual Report Conference on Electrical Insulation and Dielectric Phenomena*, pages 780–783, 2013.
- [49] Jian Li, Zhaotao Zhang, Ping Zou, Stanislaw Grzybowski, and Markus Zahn. Preparation of a vegetable oil-based nanofluid and investigation of its breakdown and dielectric properties. *IEEE Electrical Insulation Magazine*, 28(5):43–50, 2012.

- [50] Du Yue-fan, L V Yu-zhen, Zhou Jian-quan, L I Xiao-xin, and L I Cheng-rong. Breakdown Properties of Transformer Oil-based TiO₂ Nanofluid. In *Annual Report Conference on Electrical Insulation and Dielectric Phenomena*, pages 3–6, 2010.
- [51] H. Jin, T. Andritsch, P. H F Morshuis, and J. J. Smit. AC breakdown voltage and viscosity of mineral oil based SiO₂ nanofluids. In *Annual Report - Conference on Electrical Insulation and Dielectric Phenomena, CEIDP*, pages 902–905, 2012.
- [52] Jun Liu, Lijun Zhou, Yang Luo, Xiaofeng Huang, and Guangning Wu. Dielectric Frequency Response of Oil-paper Composite Insulation with Transient Moisture Distribution. *IEEE Transactions on Dielectrics and Electrical Insulation*, 20:1380–1387, 2013.
- [53] International Electrotechnical Commission. IEC 60156:1995. Insulating liquids - Determination of the breakdown voltage at power frequency - Test method, 2003.
- [54] J Ghasemi, S Jafarmadar, and M Nazari. Effect of magnetic nanoparticles on the lightning impulse breakdown voltage of transformer oil. *Journal of Magnetism and Magnetic Materials*, 389:148–152, 2015.
- [55] M Nazari, M H Rasoulifard, and H Hosseini. Dielectric breakdown strength of magnetic nano fluid based on insulation oil after impulse test. *Journal of Magnetism and Magnetic Materials*, 399:1–4, 2016.
- [56] Donglin Liu, Yuanxiang Zhou, Ying Yang, and Ling Zhang. Characterization of High Performance AlN Nanoparticle-Based Transformer Oil Nanofluids. *IEEE Transactions on Dielectrics and Electrical Insulation*, 23(5):2757–2767, 2016.
- [57] H U Zhi-feng, M a Kai-bo, Wang Wei, Muhammad Rafiq, Zhou You, Wang Qi, D U Yue-fan, a Preparation, and Tio Nanofluids. Thermal Aging Properties of Transformer Oil-Based TiO₂ Nanofluids. *Proceedings - IEEE International Conference on Dielectric Liquids*, pages 1–4, 2014.
- [58] Dariusz Zmarz and Dominik Dobry. Analysis of Properties of Aged Mineral Oil Doped with C₆₀ Fullerenes. *IEEE Transactions on Dielectrics and Electrical Insulation*, 21(3):1119–1126, 2014.

- [59] J Kudelcik, P Bury, P Kopcansky, and M Timko. Dielectric breakdown in mineral oil ITO 100 based magnetic fluid. In *12th International Conference on Magnetic Fluids*, volume 9, pages 78–81, 2010.
- [60] Jouya Jadidian, Student Member, Markus Zahn, Nils Lavesson, Ola Widlund, and Karl Borg. Effects of Impulse Voltage Polarity , Peak Amplitude , and Rise Time on Streamers Initiated From a Needle Electrode in Transformer Oil. *IEEE Transactions on Plasma Science*, 40(2):909–918, 2012.
- [61] J. George Hwang, Markus Zahn, Francis M. O’Sullivan, L. A A Pettersson, Olof Hjortstam, and Rongsheng Liu. Effects of nanoparticle charging on streamer development in transformer oil-based nanofluids. *Journal of Applied Physics*, 107(1):1–17, 2010.
- [62] Ajay Katiyar, Purbarun Dhar, Tandra Nandi, Lakshmi Sirisha Maganti, and Sarit K. Das. Enhanced Breakdown Performance of Anatase and Rutile Titania based Nano-oils. *IEEE Transactions on Dielectrics and Electrical Insulation*, pages 3494–3503, 2016.
- [63] J. George Hwang, Francis O’Sullivan, Markus Zahn, Olof Hjortstam, L. A A Pettersson, and Rongsheng Liu. Modeling of streamer propagation in transformer oil-based nanofluids. *Annual Report - Conference on Electrical Insulation and Dielectric Phenomena, CEIDP*, pages 361–366, 2008.
- [64] Jouya Jadidian. *Charge Transport and Breakdown Physics in Liquid / Solid Insulation Systems*. PhD thesis, Massachusetts Institute of Technology, 2013.
- [65] Yuzhen Lv, Yang Ge, Chengrong Li, Qi Wang, You Zhou, Bo Qi, Kai Yi, Xin Chen, and Jinsha Yuan. Effect of TiO₂ Nanoparticles on Streamer Propagation in Transformer Oil under Lightning Impulse Voltage. *IEEE Transactions on Dielectrics and Electrical Insulation*, Vol. 23, No. 4, (April):2110–2115, 2016.
- [66] Huifei Jin, Peter Morshuis, Armando Rodrigo Mor, Johan J Smit, and Thomas Andritsch. Partial Discharge Behavior of Mineral Oil based Nanofluids. *Transactions on Dielectrics and Electrical Insulation*, 22(5):2747–2753, 2015.
- [67] B. X. Du, X. L. Li, and J Li. Effects of BN nanoparticles on space charge

- characteristics of vegetable oil. *IEEE International Conference on High Voltage Engineering and Application (ICHVE)*, pages 1–4.
- [68] Gian Carlo Montanari. Bringing an Insulation to Failure : the Role of Space Charge. *IEEE Transactions on Dielectrics and Electrical Insulation*, 18(2):339–364, 2011.
- [69] Sezer Özerinç, Sadık Kakaç, and Almıla Güvenç Yazıcıoğlu. Enhanced thermal conductivity of nanofluids: a state-of-the-art review. *Microfluidics and Nanofluidics*, 8(2):145–170, 2010.
- [70] W Yu and S U S Choi. The role of interfacial layers in the enhanced thermal conductivity of nanofluids: A renovated Maxwell model. *Journal of Nanoparticle Research*, 5:167–171, 2003.
- [71] Yulong Ding, Hajar Alias, Dongsheng Wen, and Richard A Williams. Heat transfer of aqueous suspensions of carbon nanotubes (CNT nanofluids). *International Journal of Heat and Mass Transfer*, 49:240–250, 2006.
- [72] Xinwei Wang and Xianfan Xu. Thermal Conductivity of Nanoparticle – Fluid Mixture. *Journal of Thermophysics and Heat Transfer*, 13(4), 1999.
- [73] S Lee. Measuring Thermal Conductivity of Fluids Containing Oxide Nanoparticles. *Journal of Heat Transfer*, 121(May 1999), 2016.
- [74] Sarit Kumar Das, Nandy Putra, and Peter Thiesen Wilfried Roetzel. Temperature Dependence of Thermal Conductivity Enhancement for Nanofluids. *Journal of Heat Transfer*, 125(August 2003):567–574, 2019.
- [75] S M S Murshed, K C Leong, and C Yang. Enhanced thermal conductivity of TiO₂ — water based nanofluids. *International Journal of Thermal Science*, 44:367–373, 2005.
- [76] J. Xi T. Liu Y. Ai F. Xie, H. Wang and Q. Wu. Thermal conductivity enhancement of suspensions containing nanosized alumina particles. *Journal of Applied Physics*, 91:1–6, 2002.
- [77] Huifei Jin, Thomas Andritsch, Ioannis A. Tsekmes, Roman Kochetov, Peter H. F.

- Morshuis, and Johan J. Smit. Properties of mineral oil based silica nanofluids. *IEEE Transactions on Dielectrics and Electrical Insulation*, 21(3):1100–1108, 2014.
- [78] Weimin Guan, Miao Jin, Yong Fan, Jiaqi Chen, Pan Xin, Yonghe Li, Kejie Dai, Hailong Zhang, Tao Huang, and Jiangjun Ruan. Finite element modeling of heat transfer in a nanofluid filled transformer. *IEEE Transactions on Magnetics*, 50(2):2–5, 2014.
- [79] B X Du, X L Li, and J Li. Thermal Conductivity and Dielectric Characteristics of Transformer Oil Filled with BN and Fe₃O₄ Nanoparticles. *IEEE Transactions on Dielectrics and Electrical Insulation Vol. 22, No 5*, pages 2530–2536, 2015.
- [80] Kurt Preis, Oszkar Biro, Gerhard Buchgraber, and Igor Ti. Thermal-Electromagnetic Coupling in the Finite-Element Simulation of Power Transformers. *IEEE Transactions on Magnetics*, 42(4):999–1002, 2006.
- [81] Diaa-eldin A Mansour and Ahmed M Elsaed. Heat Transfer Properties of Transformer Oil-Based Nanofluids Filled with Al₂O₃ Nanoparticles Diaa-Eldin. *2014 IEEE International Conference on Power and Energy (PECon)*, pages 123–127, 2014.
- [82] Kazem Bashirnezhad, Shahab Bazri, Mohammad Reza, Marjan Goodarzi, and Mahidzal Dahari. Viscosity of nanofluids: A review of recent experimental studies. *International Communications in Heat and Mass Transfer*, 73:114–123, 2016.
- [83] Chengrong Li. Effect of electron shallow trap on breakdown performance of transformer oil- based nanofluids. *Journal of Applied Physics*, (December 2014), 2011.
- [84] Jin Huang and Xianju Wang. Influence of pH on the stability characteristics of nanofluids. *AIP Advances*, pages 2–4, 2009.
- [85] You Zhou, Yu Xiang Zhong, Mu Tian Chen, Sheng Nan Zhang, Yue Fan Du, Yu Zhen Lv, Chengrong Li, and Tong Liu. Effect of nanoparticles on electrical characteristics of transformer oil-based nanofluids impregnated pressboard. *Conference Record of IEEE International Symposium on Electrical Insulation*, pages 650–653, 2012.

- [86] Rosa Mondragón, J. Enrique Juliá, Antonio Barba, and Juan Carlos Jarque. Preparación y caracterización de nanofluidos: Influencia de variables sobre su estabilidad, estado de aglomeración y propiedades físicas. *Boletín de la Sociedad Española de Cerámica y Vidrio*, 53(2):101–110, 2014.
- [87] A. Ghadimi, R. Saidur, and H. S C Metselaar. A review of nanofluid stability properties and characterization in stationary conditions. *International Journal of Heat and Mass Transfer*, 54(17-18):4051–4068, 2011.
- [88] Gudrun Petzold, Rosana Rojas-Reyna, Mandy Mende, and Simona Schwarz. Application Relevant Characterization of Aqueous Silica Nanodispersions. *Journal of Dispersion Science and Technology*, 30:1216–1222, 2009.
- [89] S. F. M. Nor, N Azis, J Jasni, M Z A A Kadir, R Yunus, and Z Yaakub. Investigation on the electrical properties of palm oil and coconut oil based TiO₂ nanofluids. *IEEE Transactions on Dielectrics and Electrical Insulation*, 24(6):3432–3442, 2017.
- [90] Pusavec A. Rashid P., Krajnik F. Nanofluids: Properties, Applications and Sustainability Aspects in Materials Processing Technologies. *Advances in Sustainable Manufacturing*, pages 107–113.
- [91] C Choi, H S Yoo, and J M Oh. Preparation and heat transfer properties of nanoparticle-in-transformer oil dispersions as advanced energy-efficient coolants. *Current Applied Physics*, 8:710–712, 2008.
- [92] Xiang Qi Wang and Arun S. Mujumdar. Heat transfer characteristics of nanofluids: a review. *International Journal of Thermal Sciences*, 46(1):1–19, 2007.
- [93] Power IEEE Society Energy. *IEEE Draft Guide for Acceptance and Maintenance of Insulating Mineral Oil in Electrical Equipment*, volume 2015. 2015.
- [94] Alexander Kraynov and Thomas E Müller. Concepts for the Stabilization of Metal Nanoparticles in Ionic Liquids, Applications of Ionic Liquids in Science and technology. *Applications of ionic liquids in science and Technology*, page 516, 2011.
- [95] Yolanda Peña Boris I. Kharisov, H. V. Rasika Dias, Oxana V. Kharissova,

Alejandro Vazquez and Idalia Gomezo. Solubilization, dispersion and stabilization of magnetic nanoparticles in water and non-aqueous solvents: recent trends. *RSC Advances.*, 4(85):45354, 2014.

- [96] Daniela Susan-resiga, V Socoliuc, T Boros, Tunde Borbáth, Oana Marinica, Adelina Han, and L Vékás. The influence of particle clustering on the rheological properties of highly concentrated magnetic nanofluids. *Journal of Colloid And Interface Science*, 373(1):110–115, 2012.
- [97] Yu-zhen Lv, Chao Li, Qian Sun, and Meng Huang. Effect of Dispersion Method on Stability and Dielectric Strength of Transformer Oil-Based TiO₂ Nanofluids. *Nanoscale research letters*, pages 4–9, 2016.
- [98] Vaclav Mentlik and Pavel Trnka. Development of a Biodegradable Electro-Insulating Liquid and Its Subsequent Modification by Nanoparticles. *Energies*, 2018.
- [99] L. Tomco et al M. Rajnak, J. Kurimsky, B. Dolnik, K. Marton. Dielectric response of transformer oil based ferrofluid in low frequency range Dielectric response of transformer oil based ferrofluid in low frequency range. *Journal of Applied Physics*, (Dec):1–8, 2013.
- [100] Jin Miao, Ming Dong, Ming Ren, Xuezhou Wu, Liangping Shen and Hao Wang. Effect of nanoparticle polarization on relative permittivity of transformer oil-based nanofluids. *Journal of Applied Physics*, 204103(March 2013):1–6, 2017.
- [101] Viet-hung Dang and A Beroual. Comparative Study of Statistical Breakdown in Mineral , Synthetic and Natural Ester Oils under AC Voltage. In *IEEE Transactions on Dielectrics and Electrical Insulation*, volume 19, pages 1508–1513, 2012.
- [102] Abderrahmane Beroual, Henry B.H. Sitorus, Rudy Setiabudy, and Setijo Bismo. Comparative study of AC and DC breakdown voltages in Jatropha methyl ester oil, mineral oil, and their mixtures. *IEEE Transactions on Dielectrics and Electrical Insulation*, 25(5):1831–1836, 2018.
- [103] Abderrahim Reffas, Hocine Moulai, and Abderrahmane Beroual. Comparison of dielectric properties of olive oil, mineral oil, and other natural and synthetic ester

- liquids under AC and lightning impulse stresses. *IEEE Transactions on Dielectrics and Electrical Insulation*, 25(5):1822–1830, 2018.
- [104] Dhinesh Kumar and Valan Arasu Amirtham. A review on preparation, characterization , properties and applications of nano fl uids. *Renewable and Sustainable Energy Reviews*, 60:21–40, 2016.
- [105] R. G. Miller. *Beyond ANOVA: Basics of Applied Statistics*. Chapman edition, 1997.
- [106] S. McClave. *Statistics*. 11th edition, 2009.
- [107] Usama Khaled and Abderrahmane Beroual. AC Dielectric Strength of Synthetic Ester-Based Fe₃O₄, Al₂O₃ and SiO₂ Nanofluids – Conformity with Normal and Weibull Distributions. *IEEE Transactions on Dielectrics and Electrical Insulation*, 26(2):625–633, 2019.
- [108] Commission International Electrotechnical. CEI/IEC 60814:1997; Insulating liquids – Oil-impregnated paper and pressboard – Determination of water by automatic coulometric Karl Fischer titration Numéro. Technical report, 1997.
- [109] Bin Du, Jian Li, Lijun Yang, Wei Yao, and Shuhan Yao. Dielectric Properties of Vegetable Oil Modified by Monodisperse Fe₃O₄ Nanoparticles. *International Conference on High Voltage Engineering and Application (ICHVE)*, pages 4–7, 2014.
- [110] Dai Jianzhuo, Dong Ming, Li Wang, and Wang Jianyi. Study on AC Breakdown and Broadband Dielectric Response Properties of Transformer Oil-Based Nanofluids. In *International Conference on Condition Monitoring and Diagnosis*, pages 24–27, 2016.
- [111] Yue Fan Du, Yu Zhen Lv, Fo Chi Wang, Xiao Xin Li, and Cheng Rong Li. Effect of TiO₂ nanoparticles on the breakdown strength of transformer oil. *Conference Record of IEEE International Symposium on Electrical Insulation*, 2:1–3, 2010.
- [112] Kamal Miners. Particles and moisture effect on dielectric strength of transformer oil. *Transactions on Power Apparatus and Systems*, (3):751–756, 1982.
- [113] IEC Standard 60422. Mineral Insulating Oils in Electrical Equipment-Supervision and Maintenance Guidance. 2013.

- [114] Ahmed Abu-Siada. *Power transformer condition monitoring and diagnosis*. Institution of Engineering and Technology, 2018.
- [115] Daniel Pérez, Victor Primo, Belén García, and Juan Carlos Burgos. Analysis of Water Solubility in natural-ester based nanodielectric fluids. In *IEEE International Conference on Dielectrics*, 2019.
- [116] Ivanka Atanasova-höhlein, Maja Kon, Tim Gradnik, Č Biljana, Krzysztof Siodla, Knut Brede Liland, Senja Leivo, and Qiang Liu. Experience with Capacitive On-Line Sensors for Moisture Evaluation in Transformer Insulation. *IEEE Electrical Insulation Magazine*, (1):18–26, 2019.
- [117] Y Zhou, S Y Sui, J Li, Z Y Wang, W Cui, Y Z Lv, and C R Li. Statistical analysis of moisture ' s effect on AC breakdown strength of TiO₂ nano fl uids. *Journal of Mollecular Liquids*, 249:420–428, 2018.
- [118] Yuefan Du, Yuzhen Lv, Chengrong Li, Yuxiang Zhong, Mutian Chen, Shengnan Zhang, You Zhou, and Zhengqi Chen. Effect of water adsorption at nanoparticle – oil interface on charge transport in high humidity transformer oil-based nanofluid. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 415:153–158, 2012.
- [119] E Gockenbach and H Borsi. Natural and Synthetic Ester Liquids as alternative to mineral oil for power transformers. In *Annual Report Conference on Electrical Insulation Dielectric Phenomena*, pages 521–524, 2008.
- [120] Pawel Rozga, Marcin Stanek, and Kevin Rapp. Lightning Properties of Selected Insulating Synthetic Esters and Mineral Oil in Point-to-Sphere Electrode System. *IEEE Transactions on Dielectrics and Electrical Insulation*, 25(5):1699–1705, 2018.
- [121] Muhammad Rafiq, Kai Yi, Chengrong Li, Yuzhen Lv, Muhammad Numan, and Usman Nasir. Effect of Fe₃O₄ Nanoparticle Size on Impulse Breakdown Strength of Mineral Oil-Based Nanofluids. *International Conference for Students on Applied Engineering (ICSAE)*, pages 186–189, 2016.
- [122] A Denat, O Lesaint, F Grenoble, and Ecoulements Géophysiques. Breakdown of Liquids in Long Gaps : Influence of Distance , Impulse Shape , Liquid Nature ,

- and Interpretation of Measurements. *IEEE Transactions on Dielectrics and Electrical Insulation*, 22(5):2581–2591, 2015.
- [123] Q Liu, Z D Wang, and F Perrot. Impulse Breakdown Voltages of Ester-based Transformer Oils Determined by Using Different Test Methods. In *Annual Report Conference on Electrical Insulation and Dielectric Phenomena Impulse*, number 1, pages 608–612, 2009.
- [124] Pawel Rozga and Marcin Stanek. Comparative Analysis of Lightning Breakdown Voltage of Natural Ester Liquids of Different Viscosities Supported by Light Emission Measurement. *IEEE Transactions on Dielectrics and Electrical Insulation*, 24(2):991–999, 2017.
- [125] O Lesaint. Prebreakdown phenomena in liquids : propagation ‘ modes ’ and basic physical properties. 2016.
- [126] William Bartley H. Failure Analysis of Transformers. In *36th Annual Conference International Association of Engineering Insurers*, volume 85, 2003.
- [127] Pugazhendhi Sugumaran C. Experimental Evaluation on Dielectric and Thermal Characteristics of Nano Filler Added Transformer Oil. *2012 International Conference on High Voltage Engineering and Application*, pages 207–210, 2012.
- [128] Muhammad Rafiq, Chengrong Li, Yuzhen Lv, Kai Yi, and Ikram Arif. Breakdown Characteristics of Transformer Oil Based Silica Nanofluids. In *2016 19th International Multi-Topic Conference (INMIC)*, pages 1–4. IEEE, 2016.
- [129] Jong-chul Lee, Hyeon-seok Seo, and Youn-jea Kim. The increased dielectric breakdown voltage of transformer oil-based nano fluids by an external magnetic field. *International Journal of Thermal Sciences*, 62:29–33, 2012.
- [130] ASTM. D3300 - 12: Standard Test Method for Dielectric Breakdown Voltage of Insulating Oils of Petroleum Origin Under Impulse Conditions. Technical report, 2019.
- [131] K Jariyanurat. Dielectric Properties of Natural Ester based Nanofluid. In *19th IEEE International Conference on Dielectric Liquids (ICDL)*, pages 29–32, 2017.

- [132] Pichai Muangpratoom, Norasage Pattanadech, Anantawat Kunakorn, and Wanwilai Vittayakorn. Impulse Breakdown Characteristic of Mineral Oil Based Nanofluid. In *19th IEEE International Conference on Dielectric Liquids (ICDL)*, number Icdl, pages 29–32, 2017.
- [133] Diao Eldin A Mansour, Eman G. Atiya, Reham M. Khattab, and Ahmed M. Azmy. Effect of Titania Nanoparticles on the Dielectric Properties of Transformer Oil - Based Nanofluids. *Conference on Electrical Insulation and Dielectric Phenomena, CEIDP*, pages 295–298, 2012.
- [134] Juan Velasco Ares, Ricardo Frascella, Ricardo Albarracín, and Ming Dong. Comparison of Positive Streamers in Liquid Dielectrics with and without Nanoparticles Simulated with Finite-Element Software. *Energies*, (February), 2018.
- [135] Yuzhen Lv, Muhammad Rafiq, Chengrong Li, and Bingliang Shan. Study of Dielectric Breakdown Performance of Transformer Oil Based Magnetic Nanofluids. *Energies*, 10, 2017.
- [136] Mauricio Aljure. Streamer Inception from Ultra-Sharp Needles in Mineral Oil Based Nanofluids. *Energies*, (1), 2018.
- [137] V P Charalampakos. A Comparative Study of Natural Ester based Nanofluids with Fe₂O₃ and SiO₂ Nanoparticles. *19th IEEE International Conference on Dielectric Liquids (ICDL)*, (ICDL):29–32, 2017.
- [138] C. F. Diego, A. Santisteban, F. O. Fernández, F. Delgado, and A. Ortiz. Effect of TiO₂ nanoparticles on the performance of a natural ester dielectric fluid. *2017 IEEE Electrical Insulation Conference, EIC 2017*, (June):1–4, 2017.
- [139] M. Z. H. Makmud, H. A. Illias, C. Y. Chee, and M. S. Sarjadi. Influence of Conductive and Semi-Conductive Nanoparticles on the Dielectric Response of Natural Ester-Based Nanofluid Insulation. *Energies*, 11(333), 2018.
- [140] Georgios D. Peppas, Aristeidis P. Bakandritsos, Eleftheria C. Pyrgioti, Roula Kriptomou, Apostolos Kyritsis, and Ioannis F. Gonos. Dielectric study of self assembled nanofluids by means of AC breakdown tests and dielectric relaxation

- spectroscopy. *ICHVE 2016 - 2016 IEEE International Conference on High Voltage Engineering and Application*, pages 1–4, 2016.
- [141] IEC Standard 60422. Fluids for electrotechnical applications - Unused natural esters for transformers and similar electrical equipment. 2013.
- [142] Kapila Bandara, Chandima Ekanayake, and Tapan Kumar Saha. Compare the performance of natural ester with synthetic ester as transformer insulating oil. *Proceedings of the IEEE International Conference on Properties and Applications of Dielectric Materials*, 2015-October:975–978, 2015.
- [143] Kapila Bandara, Chandima Ekanayake, and Tapan K. Saha. Comparative study to understand behaviour of natural ester as transformer insulating liquid. *2015 IEEE 10th International Conference on Industrial and Information Systems, ICIIS 2015 - Conference Proceedings*, pages 117–121, 2016.
- [144] Zhaotao Zhang, Jian Li, Pin Zou, and Stanislaw Grzybowski. Electrical properties of nano-modified insulating vegetable oil. *Annual Report - Conference on Electrical Insulation and Dielectric Phenomena, CEIDP*, pages 1–4, 2010.
- [145] Bin Du, Jian Li, Baimei Wang, Junru Xiang, and Zhaotao Zhang. Influence of water content on the electrical properties of insulating vegetable oil-based nanofluids. *IEEE Electrical Insulation Conference, EIC 2013*, (June):49–51, 2013.
- [146] M. S. Mohamad, H. Zainuddin, S. A. Ghani, and I. S. Chairul. AC breakdown voltage of natural ester mixed with Iron Oxide for oil-immersed power transformer application. *2015 IEEE Student Conference on Research and Development, SCORd 2015*, pages 16–20, 2015.
- [147] M. S. Mohamad, H. Zainuddin, S. A. Ghani, and I. S. Chairul. Breakdown and partial discharge performance of Palm Fatty Acid Ester (PFAE) oil-based Fe₃O₄ nanofluids. *PECON 2016 - 2016 IEEE 6th International Conference on Power and Energy, Conference Proceeding*, pages 317–321, 2017.
- [148] Usama Khaled and Abderrahmane Beroual. Statistical Investigation of AC Dielectric Strength of Natural Ester Oil- Based Fe₃O₄, Al₂O₃, and SiO₂ Nano-Fluids. *IEEE Access*, 7:60594–60601, 2019.

- [149] Usama Khaled and Abderrahmane Beroual. Influence of Conductive Nanoparticles on the Breakdown Voltage of Mineral Oil, Synthetic and Natural Ester Oil-based Nanofluids. In *2019 IEEE 20th International Conference on Dielectric Liquids (ICDL)*, number Icdl, pages 1–4. IEEE, 2019.