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Comportement de formation de gaz dans les liquides biodégradables : influence de la composition chimique

Par

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RÉSUMÉ

La diversité de la nature chimique des liquides isolants biodégradables, associée à des architectures moléculaires et à des polarités spécifiques selon les familles de fluides, conditionne de manière déterminante leur comportement en service. Tout au long du fonctionnement du transformateur, le fluide isolant est soumis à des contraintes thermiques, électriques et oxydatives qui accélèrent les processus de dégradation, entraînant une modification de sa composition chimique initiale par la formation de sous-produits de dégradation, conduisant à une altération progressive de ses propriétés physico-chimiques. Dans ce contexte, la détection et l'analyse, de certains gaz produits dissous, ainsi que et leur répartition constituent non seulement des signaux précoces de défauts, mais aussi de la dégradation du système d'isolation des transformateurs.

Or, cette méthode, pourtant largement utilisée pour le diagnostic des transformateurs de puissance, demeure essentiellement fondée sur des approches statistiques. En pratique, les mêmes outils et critères d'interprétation sont appliqués indépendamment de l'état réel de dégradation de l'huile en conditions d'exploitation. Cette approche limite la prise en compte des mécanismes physico-chimiques gouvernant la formation des gaz. Par ailleurs, bien que les phénomènes de thermo-oxydation des liquides isolants soient bien documentés, le rôle spécifique de l'oxygène dissous dans les mécanismes de génération des gaz lors des défauts de transformateur reste encore insuffisamment exploré.

Cette thèse a pour objectif principal d'approfondir la compréhension de l'impact de l'évolution de la composition chimique sur la tendance à la formation de gaz des liquides isolants biodégradables utilisés dans les transformateurs. Plus précisément, ce travail vise à analyser le degré de corrélation entre le comportement de formation des gaz et les principaux marqueurs de dégradation des liquides diélectriques, à savoir l'indice d'acidité (TAN), le facteur de dissipation diélectrique (tan δ) et la tension interfaciale, ainsi qu'à évaluer l'influence de la teneur en oxygène dissous sur les mécanismes de génération des gaz sous différents types de défauts.

Pour atteindre ces objectifs, une étude expérimentale a été menée en faisant varier la composition chimique de différents liquides isolants biodégradables, incluant un liquide bio hydrocarboné, un ester synthétique (SE) et un ester naturel (NE). Ces variations sont caractérisées par différents états de vieillissement thermique ainsi que par des niveaux contrôlés de concentration d'oxygène dissous. Des défauts électriques et thermiques d'intensité variable sont ensuite appliqués aux fluides afin de générer des gaz, dont les profils sont analysés à l'aide des triangles et pentagones de Duval.

Les résultats de cette recherche démontrent que la formation des gaz dans les liquides isolants biodégradables est avant tout gouvernée par leur structure moléculaire et par l'évolution de leur état chimique en service. Les fortes corrélations établies entre les profils de gaz et les marqueurs de dégradation révèlent que la signature gazeuse reflète principalement l'état du fluide, et non uniquement la nature du défaut. De plus, l'oxygène dissous oriente les voies réactionnelles vers des mécanismes oxydatifs, ce qui réduit certains gaz combustibles et augmente les oxydes de carbone.

Par conséquent, prendre en compte les modifications de l'état chimique du fluide constitue un levier déterminant pour améliorer la fiabilité et la pertinence du diagnostic par analyse des gaz dissous, tant pour les liquides minéraux que pour les liquides non minéraux.

ABSTRACT

The diversity of the chemical nature of biodegradable insulating liquids, associated with distinct molecular architectures and polarities depending on the fluid family, plays a determining role in their in-service behaviour. Throughout transformer operation, the insulating fluid is subjected to thermal, electrical, and oxidative stresses that accelerate degradation processes, leading to changes in its initial chemical composition through the formation of degradation by-products, and resulting in a progressive deterioration of its physicochemical properties. In this context, the detection and analysis of selected dissolved gases and their distribution constitute not only an early indicator of faults but also of the degradation of transformer insulation systems.

However, although this method is widely used for power transformer diagnostics, it remains largely based on statistical approaches. In practice, the same diagnostic tools and interpretation criteria are applied regardless of the actual degradation state of the oil under operating conditions. This limits the consideration of the physicochemical mechanisms governing gas formation. Moreover, while thermo-oxidative aging phenomena of insulating liquids are well documented, the specific role of dissolved oxygen in gas generation mechanisms under transformer fault conditions remains insufficiently explored.

The main objective of this thesis is to deepen the understanding of the impact of chemical composition evolution on the gas formation tendency of biodegradable insulating liquids used in transformers. More specifically, this work aims to analyze the degree of correlation between gas formation behaviour and the main degradation markers of dielectric liquids namely total acid number (TAN), dielectric dissipation factor (tan δ), and interfacial tension (IFT) as well as to assess the influence of dissolved oxygen content on gas generation mechanisms under different types of faults.

To achieve these objectives, an experimental study was conducted by varying the chemical composition of different biodegradable insulating liquids, including a bio-hydrocarbon (Bio-MO), a synthetic ester (SE), and a natural ester (NE). These variations were characterized by different thermal aging states and controlled levels of dissolved oxygen concentration. Electrical and thermal faults of varying intensity were then applied to the fluids to generate gases, whose profiles were analyzed using Duval triangles and pentagons.

The results of this research demonstrate that gas formation in biodegradable insulating liquids is primarily governed by their molecular structure and by the evolution of their chemical state during service. Strong correlations established between gas profiles and TAN, tan δ, and IFT that the gas signature mainly reflects the condition of the fluid rather than solely the nature of the fault. Furthermore, dissolved oxygen directs reaction pathways toward oxidative mechanisms, leading to a reduction in certain combustible gases and an increase in carbon oxides.

Consequently, accounting for changes in the chemical state of the fluid constitutes a key lever for improving the reliability and relevance of dissolved gas analysis diagnostics, for both mineral and non-mineral insulating liquids.

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ΔH	Variation d'enthalpie
AGD	Analyse des gaz dissous
AgM	Marqueur de vieillissement
AH	Antioxydant
ASTM	Société américaine des essais et des matériaux
B0, B1, B2, B3	Séries d'échantillons d'huile minérale bio avec des concentrations oxygène
BDV	Tension de claquage
Bio-MO	Huile minérale bio hydrocarbonée
BTHQ	Butylhydroquinone tertiaire (antioxydant utilisé dans les esters)
C_2H_2	Acétylène
C_2H_4	Éthylène
$\%C_2H_4$	Pourcentage d'augmentation de la concentration Acétylène
C_2H_6	Éthane
CH_4	Méthane
CIGRE	Conseil International des Grands Réseaux Électriques
CO	Oxyde de carbone
CO_2	Dioxyde de carbone
D1	Décharge partielle de faible énergie
D2	Décharge partielle de forte énergie
DDF	Facteur de dissipation électrique
DGA	Dissolved gas analysis
DPv	Degré de polymérisation
DT	Défaut mixte électrique et thermique
H_2	Hydrogène
HS	Défaut de point chaud
IEC	Commission électrotechnique internationale
IEEE C57.155-2014	Guide for Interpretation of Gases Generated in Natural Ester and Synthetic Ester-Immersed Transformers
IFT	Tension interfaciale
ISO	Organisation internationale de normalisation
KOME	Huile de karanja en esters méthyliques
N_2	Azote
NE	Liquide d'Ester naturel
O_2	Oxygène
OECD 301	Tests de biodégradabilité
PD	Décharge partielle
PFAE	Esters d'acides gras de palme
p-value	Valeur de probabilité statistique (test de signification)
r	Coefficient de corrélation
S	Gaz parasite
S0, S1, S2, S3	Séries d'échantillons d'ester synthétique avec des concentrations oxygène
SE	Liquide d'Ester synthétique
T1	Niveaux de température du défaut thermique < 300 °C
T2	Niveaux de température du défaut thermique 300 °C - 700 °C
T3	Niveaux de température du défaut thermique > 700 °C
TAN	Nombre total d'acide
TDCG	Total des gaz combustibles dissous
%TDCG	Pourcentage d'augmentation des gaz combustibles totaux dissous

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CHAPITRE 1

INTRODUCTION GÉNÉRALE

1.1. GÉNÉRALITÉ

L'analyse des gaz dissous (AGD) constitue aujourd'hui l'outil de diagnostic le plus largement utilisé pour la surveillance de l'état interne des transformateurs de puissance. Elle repose sur l'identification et le suivi des gaz générés par la décomposition des matériaux isolants sous l'effet de contraintes électriques et thermiques [1]. La présence et l'évolution de gaz tels que l'hydrogène (H_2), le méthane (CH_4), l'éthane (C_2H_6), l'éthylène (C_2H_4), l'acétylène (C_2H_2), ainsi que le monoxyde et le dioxyde de carbone (CO, CO_2), fournissent des informations essentielles sur la nature, la localisation et la sévérité des défauts internes, qu'il s'agisse de décharges partielles, d'échauffements localisés ou d'arcs électriques [2].

Historiquement développée et validée pour les huiles minérales, AGD repose sur des méthodes d'interprétation fondées sur des seuils de concentration, des rapports de gaz et des outils graphiques empiriques [3]. En pratique, ces mêmes outils et critères d'interprétation sont généralement appliqués indépendamment de l'état réel de dégradation du liquide isolant en conditions d'exploitation. Or, le niveau de dégradation du fluide, induite par le vieillissement et les contraintes subies, impacte les mécanismes de formation des gaz et peut influencer de manière significative les profils de gaz observés [4].

Cette limitation devient particulièrement critique avec l'introduction croissante de liquides isolants biodégradables, tels que les esters naturels, les esters synthétiques et les liquides hydrocarbonés biosourcés. La composition chimique spécifique de ces fluides affecte non seulement les voies réactionnelles de décomposition, mais également les volumes et proportions relatives des gaz générés sous des contraintes électriques et thermiques comparables. Dans le cas des esters, la présence de groupements fonctionnels polaires conduisent fréquemment à des concentrations globalement plus faibles de gaz dissous, ce qui peut compliquer la détection précoce des défauts si les critères conventionnels sont appliqués sans adaptation [5].

Dans un contexte où la fiabilité du réseau électrique dépend étroitement de la performance des transformateurs de puissance, éléments critiques de l'infrastructure, la disponibilité d'outils de diagnostic adaptés est indispensable pour la détection précoce des défaillances naissantes. Le vieillissement progressif du parc de transformateurs impose ainsi une évaluation fine et continue de l'état des équipements afin d'optimiser les décisions de maintenance, de réparation, de remplacement et de priorisation des interventions.

En analysant la dégradation progressive du système d'isolation huile papier des transformateurs de puissance, et plus particulièrement l'évolution de l'état chimique des liquides isolants biodégradables, cette recherche vise à approfondir la compréhension de leur influence sur les mécanismes de génération des gaz dissous sous contraintes électriques et thermiques. Les résultats obtenus contribuent à l'amélioration des stratégies de surveillance conditionnelle, fondées sur l'exploitation conjointe de l'analyse des gaz dissous et d'indicateurs physiques, chimiques et diélectriques mesurables. Cette approche permet une interprétation plus fiable et plus pertinente des diagnostics, ainsi qu'une gestion optimisée de la durée d'exploitation des transformateurs.

1.2. PROBLÉMATIQUE

Au cours des dernières années, de nombreux travaux ont cherché à élucider les mécanismes fondamentaux du gazage en vue d'optimiser les outils de diagnostic des transformateurs en service. Il a été démontré que la formation de gaz dépend de plusieurs paramètres, parmi lesquels l'état réel de l'huile isolante, reflété par ses marqueurs de vieillissement et l'évolution progressive de sa composition chimique, constitue un facteur déterminant influençant le volume de gaz produits [6]. Toutefois, il n'existe à ce jour aucun outil ou méthode intégrant le vieillissement de l'huile dans le diagnostic du gazage, alors même que la relation entre la génération de gaz et les marqueurs de vieillissement pourrait constituer un indicateur essentiel de l'évolution des défauts. Par ailleurs, bien que les mécanismes de thermo-oxydation aient été largement décrits et que la corrélation entre le phénomène de formation de "*stray gassing*" et l'oxydation ait été mise en évidence dans la littérature,

l'influence de la concentration initiale en oxygène sur la tendance au gazage des liquides isolants lors d'un défaut de transformateur demeure encore peu explorée.

1.3. OBJECTIF DE LA RECHERCHE

L'objectif global de cette recherche est de comprendre l'impact de l'évolution de la composition chimique sur la tendance au gazage des liquides isolants biodégradables utilisés dans les transformateurs. L'étude vise à analyser les corrélations entre les marqueurs de vieillissement (acidité, tension interfaciale, facteur de dissipation, degré de polymérisation) et aussi l'influence de l'oxygène dissous sur la génération de gaz sous contraintes électriques et thermiques. L'objectif étant de permettre le développement d'outils diagnostiques mieux adaptés aux fluides alternatifs et aux conditions réelles de service. La présente thèse examine ainsi l'influence des défauts électriques et thermiques sur le liquide biohydrocarboné, les esters synthétiques et les esters naturels, en fonction de différents états de leur composition chimique.

Dans ce contexte, les objectifs spécifiques présentés ci-dessous constituent le cœur de la recherche. Ils ont été définis en fonction de la littérature existante et des défis associés à l'utilisation des fluides diélectriques à base d'esters et des huiles biominérales dans la technologie d'isolation des transformateurs.

Objectif spécifique 1 : Compréhension du degré de corrélation entre le comportement de formation de gaz et les marqueurs de vieillissement des liquides biodégradables.

Dans ce travail, des échantillons de liquides isolants biodégradables présentant des compositions chimiques distinctes à savoir le Nynas BIO 300X [7], liquide biohydrocarboné (Bio-MO), le MIDEL 1215 [8], ester naturel (NE) et le MIDEL 7131[9], ester synthétique (SE) sont soumis à un vieillissement thermo-oxydatif accéléré à 125 °C, pour des durées comprises entre 250 et 2000 heures. Ce protocole expérimental vise à reproduire l'évolution progressive des fluides isolants en conditions de service, sous l'effet de contraintes thermiques prolongées favorisant l'activation de réactions d'oxydation et la formation de sous-produits de dégradation susceptibles d'altérer leurs propriétés chimiques et diélectriques. Afin de caractériser de

manière pertinente les effets du vieillissement, plusieurs marqueurs clés sont suivis à chaque palier de dégradation, notamment l'indice d'acidité (TAN), le facteur de dissipation diélectrique (DDF) et la tension interfaciale (IFT). Les échantillons ainsi caractérisés sont ensuite soumis à des défauts électriques de différentes intensités, correspondant à des essais de claquage électrique comportant entre 30 et 150 répétitions de décharges électriques, afin d'évaluer l'influence de l'état de dégradation du fluide sur la formation des gaz dissous. L'analyse ne se limite pas à une évaluation isolée des marqueurs de vieillissement, mais vise à établir des corrélations directes entre leur évolution et la quantité ainsi que la nature des gaz générés lors des défauts électriques reproduits en conditions expérimentales contrôlées. Les relations entre les marqueurs de vieillissement (TAN, DDF, IFT) et les paramètres de gazage ont été évaluées à l'aide du coefficient de corrélation linéaire de Pearson (r), permettant de quantifier l'intensité et le sens des relations observées. La significativité statistique de ces corrélations a été appréciée à partir du p-value associée, un seuil de $p < 0.05$ indiquant une relation statistiquement significative, tandis que des valeurs supérieures traduisent des tendances à interpréter avec prudence.

Les profils de gaz obtenus par AGD sont ainsi interprétés en lien avec l'état chimique et diélectrique des liquides, permettant de mieux comprendre l'influence conjointe du vieillissement et de l'intensité des contraintes électriques sur les mécanismes de génération des gaz.

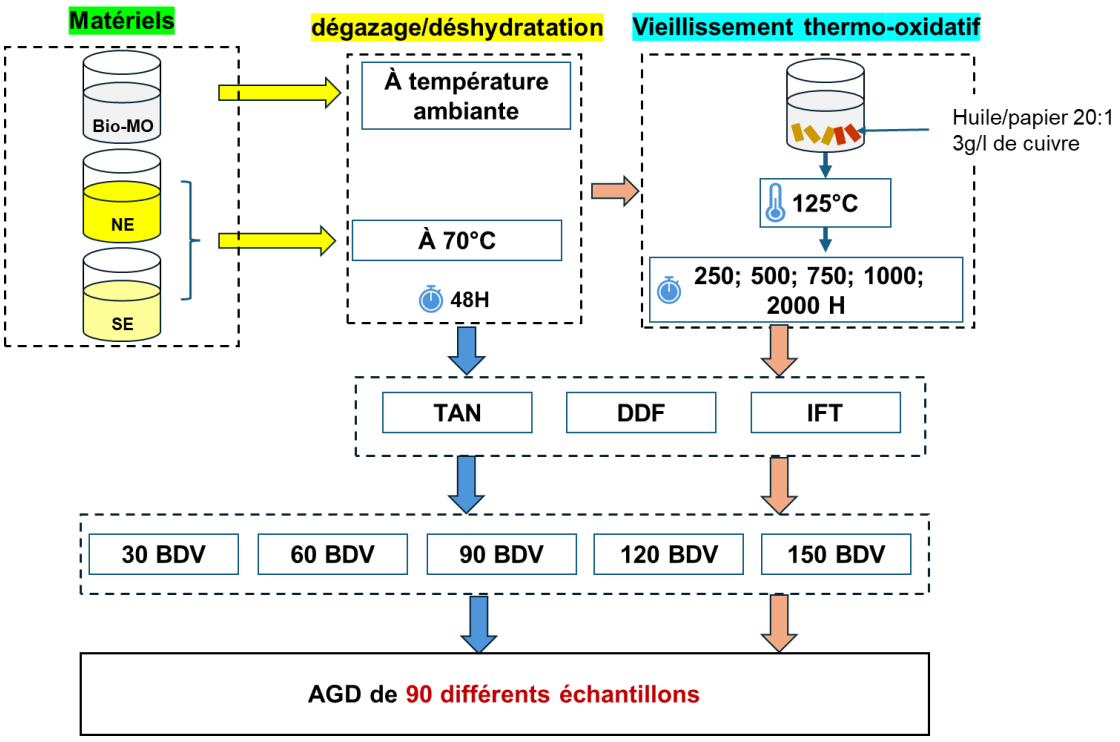

Figure 1.1.Méthodologie expérimentale appliquée à l'étude du vieillissement et du gazage des liquides isolants biodégradables.

Objectif spécifique 2 : Sous défauts, Comprendre l'influence de l'oxygène dissous sur la formation des gaz.

Dans ce contexte, des échantillons de Nynas BIO 300X et de MIDEL 7131 ont été préparés avec des teneurs distinctes en oxygène dissous afin d'évaluer l'influence de ce paramètre sur leur propension à générer des gaz sous différentes sollicitations de défaut. Deux types de contraintes représentatives des conditions réelles en transformateur ont été considérés : les défauts électriques, notamment les décharges d'arc, et les défauts thermiques associés à des points chauds localisés. Cette démarche méthodologique permet de quantifier de manière directe l'impact de la teneur initiale en oxygène dissous sur la nature, la diversité et les proportions relatives des espèces gazeuses formées lors de ces défauts.

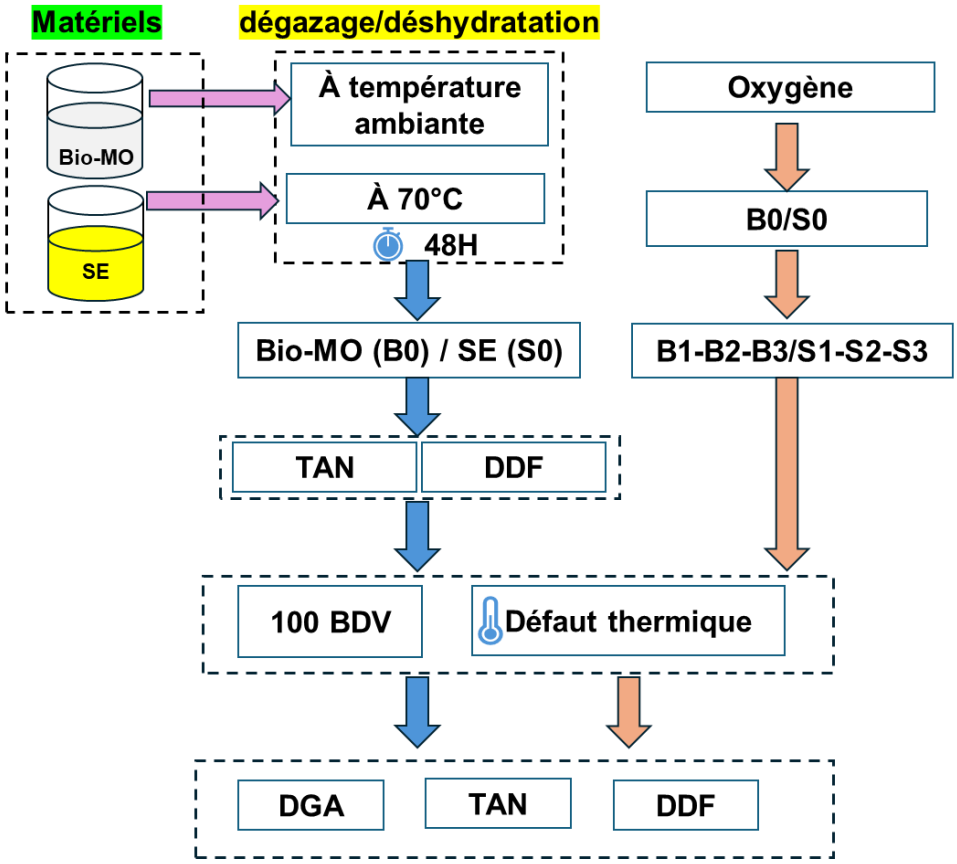

Figure 1.2.Protocole de préparation des échantillons et contrôle de l'oxygène dissous.

1.4. ORIGINALITÉ DE LA RECHERCHE

Cette thèse s'inscrit dans un contexte marqué par l'accélération du vieillissement du système d'isolation des transformateurs de puissance, sous l'effet d'une demande énergétique en constante augmentation, facteurs qui accroissent la probabilité de défaillances imprévues et les conséquences économiques associées. Dans ce contexte, l'amélioration des outils de diagnostic et de surveillance conditionnelle, fondée sur l'évaluation de l'état réel des transformateurs, s'impose comme un enjeu majeur pour la gestion des actifs.

Dans la perspective d'une transition progressive vers des liquides isolants alternatifs à plus faible impact environnemental, cette recherche apporte une contribution originale à la compréhension du comportement des liquides isolants biodégradables en établissant des relations directes entre leur composition chimique, leur état de dégradation et leur tendance à générer des gaz sous contraintes électriques et thermiques. Elle intègre tout d'abord l'évaluation d'une nouvelle génération de liquide hydrocarboné biosourcé, encore peu

déployée en exploitation, et sa comparaison avec des esters naturels et synthétiques dans un cadre expérimental standardisé et représentatif des conditions de service.

L'étude repose ensuite sur une méthodologie expérimentale exhaustive et reproductible, appuyée par une collecte étendue de données couvrant différentes caractérisations de vieillissement et des intensités de défauts variées. Les résultats obtenus mettent en évidence des corrélations cohérentes et quantitatives entre les indicateurs analytiques de dégradation physico-chimique et diélectrique et les observations issues des essais de vieillissement accéléré, renforçant ainsi la validité de l'approche proposée. Enfin, l'analyse met également en évidence l'influence déterminante de l'oxygène dissous sur les mécanismes de formation des gaz et permet d'identifier des signatures de formation de gaz spécifiques en fonction de la structure chimique des esters.

Cette approche vise à fournir aux exploitants des éléments objectifs et directement exploitables pour l'évaluation des performances, de la tendance à la formation des gaz et des implications diagnostiques de ces fluides, afin d'éclairer les choix technologiques et les stratégies de maintenance des transformateurs de puissance.

1.5. ORGANISATION DE LA THÈSE

Cette recherche s'articule autour des objectifs définis précédemment et vise à analyser le comportement de formation de gaz des liquides isolants biodégradables en fonction de leur composition chimique. Dans ce cadre, deux objectifs spécifiques ont été atteints et ont conduit à la publication de deux articles dans des revues de référence du domaine du génie électrique haute tension.

Le premier chapitre propose une introduction générale au projet et situe la problématique étudiée. Il présente l'objectif principal ainsi que les objectifs spécifiques, tout en mettant en évidence les aspects d'originalité qui distinguent les travaux réalisés.

Le deuxième chapitre, publié sous forme d'article, présente une revue de la littérature regroupant les principales études en lien avec ce projet. Cette revue analyse l'influence de la structure moléculaire, de la teneur en oxygène et en humidité, ainsi que des additifs, sur l'évolution des gaz dans le Bio-MO, le NE et le SE.

Les chapitres trois et quatre, également publiés sous forme d'articles, présentent des résultats complémentaires de cette thèse. Ils mettent en évidence que les fluides biodégradables présentent des mécanismes de dégradation et des profils de formation de gaz distincts sous différentes contraintes, et que l'intégration d'analyses statistiques combinées à des outils diagnostiques adaptés permet de prédire l'évolution des défauts et d'améliorer l'évaluation de l'état des transformateurs. Par ailleurs, la présence d'oxygène dissous modifie de manière significative ces profils gazeux, soulignant la nécessité d'adapter les modèles classiques de AGD afin de garantir un diagnostic fiable des transformateurs utilisant des liquides isolants alternatifs.

Enfin, le chapitre cinq synthétise l'ensemble des conclusions obtenues au cours de ce projet et propose des recommandations pour des recherches futures, offrant ainsi de nouvelles perspectives pour approfondir ce domaine d'étude.

CHAPITRE 2

INFLUENCE OF CHEMICAL COMPOSITION ON THE GAS FORMATION TENDENCY OF BIODEGRADABLE DIELECTRIC LIQUIDS: A COMPRÉHENSIVE REVIEW

AVANT PROPOS

Ce chapitre reproduit et étend le contenu de: M. T. Agouassi, U. Mohan Rao, I. Fofana and Y. Hadjadj, " Influence of Chemical Composition on the Gas Formation Behaviour of Biodegradable Dielectric Liquids: A Comprehensive Review."

ÉTAT DE LA PUBLICATION : soumis

REVUE : Electric Power Systems Research

TITRE EN FRANÇAIS : Influence de la composition chimique sur le comportement de formation de gaz des liquides diélectriques biodégradables : Revue.

RÉSUMÉ : La transition vers des liquides diélectriques biodégradables dans les transformateurs de puissance introduit de nouveaux défis pour le diagnostic des défauts. L'analyse des gaz dissous (AGD) demeure la technique de référence ; toutefois, les schémas d'interprétation développés pour les huiles minérales produisent souvent des résultats incohérents lorsqu'ils sont appliqués à des fluides alternatifs. La compréhension du rôle de la composition chimique dans le comportement de formation de gaz est donc essentielle pour améliorer la fiabilité du diagnostic et orienter l'adoption à grande échelle de ces liquides. Cette revue examine l'influence de la structure moléculaire, de la teneur en oxygène et en humidité, ainsi que des additifs, sur l'évolution des gaz dans les huiles biohydrocarbonées (Bio-MO), les esters naturels (NE) et les esters synthétiques (SE). Les Bio-MO se dégradent selon des mécanismes similaires à ceux des huiles minérales, dominés par la rupture des chaînes hydrocarbonées. Tout comme les Bio-MO et les NE présentent généralement un gazage positif, attribuable respectivement aux hydrocarbures insaturés et aux acides gras, tandis que les SE montrent le plus souvent un gazage négatif, reflétant la structure de leur squelette ester à base de polyols.

Le phénomène de *stray gassing*, souvent associé à la rupture des liaisons C–C en conditions normales d'exploitation, ajoute une complexité supplémentaire à l'interprétation diagnostique, en particulier pour les fluides non inhibés. Aux températures plus basses, l'hydrogène et l'éthylène dominent la formation des gaz, tandis que les fluides à base d'esters présentent une plus grande stabilité sous contraintes localisées de type point chaud. Les procédés de régénération et de reconditionnement peuvent également modifier le comportement de gazage, bien que certaines limitations persistent pour les esters naturels. En consolidant les données disponibles, cette revue clarifie le lien entre la composition chimique et l'évolution des gaz, en mettant en évidence leurs implications pour la fiabilité des transformateurs et l'interprétation des défauts. Elle ne se limite pas à rassembler les résultats expérimentaux, mais établit également un lien théorique entre les mécanismes moléculaires de décomposition et le diagnostic des défauts des transformateurs. Elle souligne ainsi comment des réactions chimiques microscopiques gouvernent la fiabilité macroscopique des systèmes électriques, fournissant une base conceptuelle pour une surveillance prédictive de l'isolation des transformateurs utilisant des fluides biodégradables.

2.1. ABSTRACT

The shift toward biodegradable dielectric liquids in power transformers introduces new challenges for fault diagnostics. Dissolved Gas Analysis (DGA) remains the cornerstone technique, yet interpretation schemes developed for mineral oils often yield inconsistent results when applied to alternative fluids. Understanding how chemical composition governs gas formation behaviour is therefore essential for improving diagnostic reliability and guiding the broader adoption of these liquids. This review examines the influence of molecular structure, oxygen and moisture content, and additives on gas evolution in bio-based hydrocarbon oils (Bio-MO), natural esters (NE), and synthetic esters (SE). Bio-MO degrades through pathways like mineral oils, dominated by hydrocarbon chain scission. Like Bio-MO, NE typically displays positive gas formation due to unsaturated hydrocarbons and fatty acids, whereas SE generally show negative gas formation, reflecting their polyol ester backbone. Stray gassing, often linked to C–C bond cleavage under normal operating conditions, adds further complexity to

diagnostics, particularly in non-inhibited fluids. At lower temperatures, hydrogen and ethylene dominate gas formation, while ester-based fluids demonstrate greater stability under localized hot-spot stresses. Regeneration and reclamation can also modify gas formation behaviour, though persistent challenges remain for NE. By consolidating current evidence, this review clarifies the link between chemical composition and gas evolution, highlighting implications for transformer reliability and fault interpretation. This review not only consolidates experimental findings but also establishes a theoretical linkage between molecular decomposition mechanisms and transformer fault diagnostics. It emphasizes how microscopic chemical reactions govern the macroscopic reliability of power systems, thereby providing a conceptual foundation for predictive insulation monitoring in biodegradable transformer fluids.

2.2. INTRODUCTION

In the context of the energy transition and the pursuit of environmentally friendly solutions, biodegradable dielectric liquids are gaining attention as promising alternatives to conventional mineral oils in power transformers. Natural and synthetic esters are particularly valued for their high biodegradability, low flammability, and favorable thermal stability. Similarly, bio-based hydrocarbon liquids, derived from biological residues and by-products mainly of plant origin, represent another sustainable option. Their production involves biomass pyrolysis followed by intensive hydrotreating and isomerization, processes that eliminate impurities and adjust molecular structures. The resulting hydrogenated hydrocarbons are free of toxic aromatics and characterized by low molecular weight, very low viscosity, high biodegradability, and improved oxidative stability, making them suitable substitutes for mineral oils in transformer applications. These advances align with global efforts to promote the use of renewable resources from agriculture, marine biomass, and forestry in the development of bio-based insulating fluids, thereby reducing dependence on petroleum-derived products while ensuring sustainable and reliable transformer operations [1] [2].

Beyond the environmental motivation, understanding these mechanisms is crucial from a system-engineering perspective. The gas formation behaviour of insulating liquids directly affects the accuracy of DGA, which is a cornerstone diagnostic technique for transformer health

assessment. Hence, elucidating the physico-chemical pathways governing gas evolution is not only a chemical challenge but also a key element of insulation coordination and reliability modelling in electric power systems.

These advances in the development of bio-based insulating liquids have naturally shifted the research focus toward understanding their diagnostic behavior under electrical and thermal stresses. DGA, long established as the primary tool for transformers fault detection, has been progressively adapted to account for the specific gas formation patterns and aging mechanisms of biodegradable fluids. Since the early 2000s, research has progressively refined the interpretation of DGA by linking gas generation not only to electrical faults but also to chemical decay products in oils (Sabau, 2002) [3]. With the introduction of biodegradable fluids, studies showed that esters generate the same diagnostic gases as mineral oils but at lower levels, requiring adapted criteria (Imad-U-Khan, 2007), while new Duval Triangles extended diagnostics to non-mineral oils and low-temperature faults (Duval, 2008) [4] [5]. Atanasova-Höhlein et al. (2010) showed that mineral oils, natural esters, and synthetic esters have distinct gas formation fingerprints under thermal oxidation: methane dominates in mineral oils, ethane in natural esters, and ethylene in synthetic esters. Peroxides and viscosity were identified as key oxidation markers, emphasizing the need for fluid-specific DGA interpretation [6].

Comparative investigations confirmed that natural esters exhibit the lowest gas formation, synthetic esters and silicones intermediate levels, and mineral oils have the highest variability depending on refining (N'Cho, 2011) [7]. Standardization followed with IEEE C57.155-2014, which established guidelines for ester fluids, while Duval and Lamarre (2017) introduced the Duval Pentagons to enhance fault differentiation in both mineral and ester oils [8] [9]. Large-scale consolidation came with CIGRE TB 771 (2019), which analyzed over 330,000 DGA cases to refine fault zones, integrate paper involvement indicators, and adapt tools for alternative liquids [10]. In parallel, research also underlined that gas solubility differs across liquids, with mineral oils dissolving more oxygen and nitrogen than esters, a factor that directly affects dissolved gas concentrations and diagnostic reliability [11]. Shortly after, experimental studies highlighted the influence of cellulose paper on gas formation (Betié,

2019), and comparative work confirmed that aging strongly alters gas formation behaviour across mineral oils and esters, affecting diagnostic accuracy (Loiselle, 2020) [12] [13].

In this context, a comprehensive literature review on the influence of chemical composition on the gas formation of biodegradable dielectric liquids is essential. Such an approach will enable a better understanding of fluid-specific degradation mechanisms, a comparison of the associated gas profiles, an assessment of the robustness of current standards, and ultimately, guidance in selecting both fluids and diagnostic methods to ensure reliable and sustainable transformer operation.

2.3. OVERVIEW OF BIODEGRADABLE DIELECTRIC LIQUIDS

2.3.1. NATURAL ESTER LIQUIDS

The chemical structure of vegetable oils, widely studied as biodegradable alternatives to mineral oils in transformers, is primarily based on triglycerides. These molecules consist of a glycerol backbone linked to three fatty acid chains, which vary in chain length and degree of saturation (saturated, mono-, di-, or polyunsaturated), as an illustrative example, the molecular structure of a long-chain fatty ester, shown in Figure 2.1 [14]. The level of unsaturation and chain length directly influences oxidation stability and service life: oils rich in oleic acid (C18:1), such as high-oleic sunflower oil, exhibit superior resistance to oxidation, whereas those dominated by linoleic (C18:2) or linolenic (C18:3) acids are more prone to oxidative degradation [15]. Chemical modifications such as transesterification or epoxidation enhance the oxidative stability of raw vegetable oils like karanja and jatropha. Natural esters, which generally retain the glycerol backbone, exhibit greater resistance to hydrolysis and improved compatibility with cellulose paper due to polar –COO groups. The absence of reactive double bonds increases their stability, while the degree of fatty acid saturation influences low-temperature behaviour, saturated oils crystallize more easily, whereas unsaturated ones remain fluid, offering advantages in cold environments [16-17].

Such structural characteristics directly affect the dielectric, thermal, and aging behaviour of natural esters when used in power transformers. [18] highlighted the technical and economic role of natural esters as insulating fluids in power transformers. This insulating liquid with a

high flash point (>300 °C), enhances the thermal and economic performance of power transformers. They raise the thermal class of impregnated paper up to 140 °C and slow its aging rate by a factor of 5–8 compared with mineral oil, owing to transesterification, which stabilizes cellulose and limits acid formation, and continuous drying, resulting from their high water-absorption capacity. These mechanisms maintain paper dryness and extend the lifespan of solid insulation. A 20 °C increase in winding temperature (85 °C instead of 65 °C) allows the apparent power to double (e.g., 30 → 60 MVA) without compromising reliability. The cooling code changes to KNAN/KNAF, leading to reduced medium-voltage cable and equipment costs, about 20% lower arc energy, and simplified infrastructure requirements. confirming the feasibility of using smaller, more economical, and flexible transformers with reduced short-circuit currents and no-load losses.

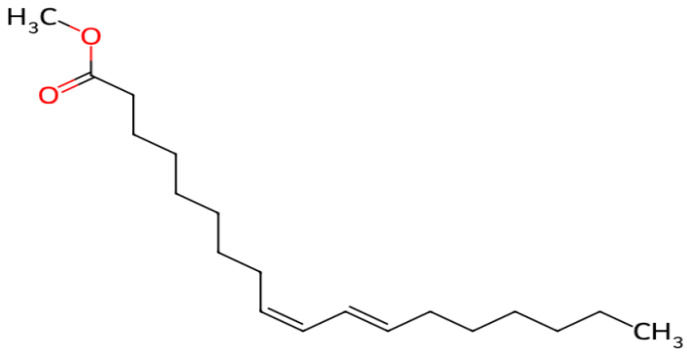

Figure 2.1. Methyl ester (9-cis, 11-trans).

2.3.2. Synthetic Esters

Synthetic esters designed for dielectric applications in high-voltage transformers are characterized by a carefully engineered molecular structure based on polyfunctional alcohols, such as pentaerythritol, trimethylolpropane, or neopentyl glycol, reacting through esterification with short- to medium-chain saturated fatty acids (typically C5–C10), Figure 2.2 illustrates the molecular structure of pentaerythritol trioleate, a polyol ester representative of synthetic ester dielectric fluids, composed of a pentaerythritol backbone esterified with oleic acid chains [19]. The central polyol backbone supports multiple ester groups, up to four in the case of pentaerythritol, creating a symmetrical, branched, and three-dimensional molecule. This configuration maximizes the functional density of ester groups while minimizing steric

hindrance, thereby providing a unique combination of thermal stability, controlled fluidity, and low volatility. From a physicochemical perspective, the complete saturation of side chains, without double bonds or unstable secondary branches, reduces the susceptibility to oxidation and yields high flash points (>250 °C), low pour points (<–50 °C), and stable viscosity across a wide temperature range. Furthermore, ester groups (–COOR) establish moderate polar interactions, enabling efficient solvation of cellulosic materials while maintaining high dielectric strength. Their synthesis relies on well-controlled catalytic processes, including purification and neutralization steps to ensure extremely low residual acidity (TAN < 0.01 mg KOH/g), a critical requirement for long-term insulation durability [20]. Synthetic esters also exhibit significant hygroscopic capacity, allowing them to tolerate moisture absorption without critical deterioration of insulating properties. This ability is directly related to the moderate polarity of ester bonds and their molecular mobility. In service, these fluids demonstrate excellent stability under combined electrical and thermal stresses, with AC breakdown voltages exceeding 70 kV and strong resistance to carbonization after prolonging thermal aging. In addition, their high biodegradability (>85% in 28 days according to OECD 301B), non-toxicity to aquatic organisms, and low bioaccumulation potential make them particularly attractive for use in environmentally sensitive or urban settings [21].

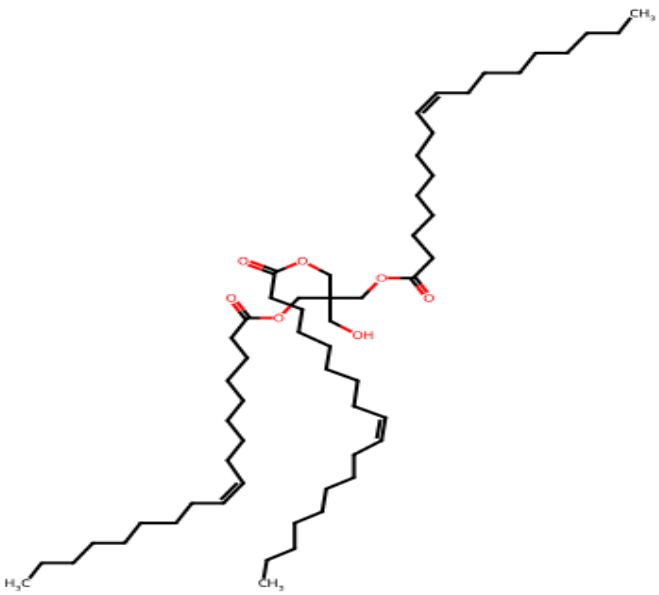

Figure 2.2. Pentaerythritol trioleate.

2.3.3. BIO-BASED HYDROCARBON LIQUIDS

Bio-hydrocarbon dielectric fluids are distinguished by their high bio-based carbon content (>99%), based on the presence of the C-14 isotope, a key indicator of sustainability measured according to ASTM D6866 [22], which reflects a fully renewable origin and an almost zero carbon footprint. This biogenic carbon, derived from biomass, belongs to the natural CO_2 cycle, thereby offsetting emissions through photosynthetic sequestration. Their high biodegradability (OECD 301 tests) results from a process of catalytic hydro-treatment and isomerization, producing saturated, nontoxic, low-molecular-weight molecules [23]. Chemically, [24], showed that bio-based hydrocarbon liquids, such as isoalkanes, present fundamental differences from conventional mineral oils in both composition and structure. They are mainly composed of saturated hydrocarbons with linear or branched chains (e.g., C18, C22), Figure 2.3 illustrates the molecular structure of a linear alkane (n-alkane), consisting solely of C–C and C–H bonds, representative of saturated hydrocarbons found in mineral oils and bio-based hydrocarbon dielectric fluids [25]. Resulting in a uniform molecular profile without aromatic or cyclic components. This homogeneity allows for an ordered molecular arrangement at low temperatures, which enhances cohesive energy density and spatial ductility. In contrast, mineral oils are heterogeneous mixtures containing alkanes, cycloalkanes, aromatics, and polycyclic compounds, with paraffins representing only about 11% of their composition. Mineral oils, due to their cyclic and aromatic components, show higher polarity and dielectric constant but greater susceptibility to oxidation, whereas bio-based isoalkanes, derived from renewable biomass through processes like Fischer–Tropsch synthesis, have minimal cyclic content, offering lower polarity, higher chemical stability, and more uniform structures than petroleum-refined oils.

Their exceptionally low viscosity (3.7 mm²/s at 40 °C) and high specific heat capacity (2.14 kJ/kg·K) enable a marked enhancement of heat transfer under natural convection (ONAN), reducing hot-spot temperatures by 4–6 K in transformers designed for mineral oil and up to 12 K in those using synthetic esters. Two pilot projects were conducted to evaluate the performance of the bio-based hydrocarbon insulating liquid (Bio-MO) in power transformers.

The first, a 420 kV–350 MVA ODAF-cooled unit, exhibited identical thermal and electrical behaviour to mineral oil without requiring any design modifications or deviations from standard factory acceptance tests. The second, a 145 kV–25 MVA ONAN-cooled transformer installed in an environmentally sensitive area in the Dolomites, demonstrated superior heat transfer and lower temperature gradients; for instance, the top-oil temperature rise was 45.2 K compared with 60 K for mineral oil [26].

In addition to these large-scale demonstrations, recent laboratory research has provided deeper insight into the microscopic conduction mechanisms governing the dielectric behaviour of bio-hydrocarbon fluids and their interaction with solid insulation. [27] investigated the influence of moisture on the AC conductivity of pressboard impregnated with Bio-MO, revealing that both conduction and relaxation phenomena are controlled by quantum tunneling and hopping mechanisms between water nanodroplets dispersed within the cellulose–oil matrix. The study identified a single activation energy (~1.03 eV) that remains constant regardless of frequency, temperature, or moisture level, approximately 20% higher than that observed in mineral oil systems, indicating the dominance of electron tunneling as the charge transport process. This invariant activation energy enabled normalization of frequency–temperature response curves, simplifying the application of Frequency Domain Spectroscopy (FDS) for precise moisture estimation. Such findings provide a quantitative and physically grounded diagnostic approach for assessing moisture and aging in transformer insulation impregnated with biodegradable hydrocarbon liquids, complementing large-scale performance validations with fundamental electro-physical understanding.

From an industrial standpoint, tests conducted by [28] confirm the full compatibility of Bio-MO with 110–400 kV instrument transformers, without requiring any design modification. Breakdown, accelerated aging, and internal-arc tests show that units filled with this fluid maintain partial discharges below 10 pC, exhibit thermal stability equal to or greater than mineral oil, and ensure operational safety compliant with IEC 61869-1, Class II. These findings validate the drop-in replacement capability of this bio-hydrocarbon fluid while meeting the growing sustainability demands of modern power networks.

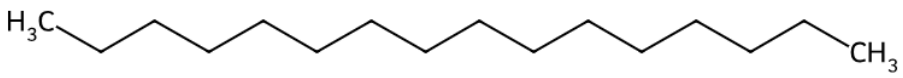

Figure 2.3.Hexadecane.

2.4. INFLUENCE OF MOLECULAR STRUCTURE ON FORMATION AND EVOLUTION FAULT GASES

2.4.1. GAS FORMATION TOWARD ELECTRICAL FAULT

Electrical breakdown in dielectric liquids occurs when the electric field exceeds the medium's dielectric strength, initiating filamentary streamers that induce localized vaporization and ionization. This phenomenon is extremely fast, releasing a large amount of energy within a very short time interval. According to the bubble theory, microbubbles formed near the electrodes enable electron avalanches that dissociate C–H and C–C bonds, producing gases such as H_2, CH_4, C_2H_4, and C_2H_2. Although this framework is widely adopted, it should be noted that the bubble-assisted streamer mechanism is primarily inferred from indirect electrical and gaseous observations, as direct experimental visualization of bond rupture under these transient conditions remains extremely challenging. At temperatures approaching 10^4 K and electron densities around 10^{19} cm^{-3}, intense pyrolysis and radical recombination generate hydrogen and carbonaceous species, linking the transient streamer activity to gas formation. These values are typically estimated from numerical models and post-mortem analyses rather than direct in situ measurements. This correlation establishes DGA as a key diagnostic tool for

identifying and assessing the severity of internal discharges in transformer insulation systems [29 -30].

During electrical fault events, the absorbed energy in the liquid is rapidly redistributed among molecular bonds, and the hierarchy of bond dissociation energies determines which chemical bonds are first to rupture:

$$\mathrm{E_a(C–C)} < \mathrm{E_a(C–H)} < \mathrm{E_a(C \equiv C)} < \mathrm{E_a(C = O)}$$

Based on this energetic hierarchy, degradation pathways are often rationalized; however, the actual sequence of bond cleavage may be influenced by local temperature gradients, electric field enhancement, and transient radical concentrations. Because bio-based hydrocarbon liquids and mineral oils are primarily composed of saturated hydrocarbons containing nonpolar C–C single bonds, their degradation follows comparable fragmentation pathways. Consequently, [31] reported similar gaseous compositions under electrical faults; nevertheless, variations in molecular distribution, branching, and additive packages may introduce deviations that are not always explicitly addressed in the literature. Diagnostic interpretations based on DGA therefore remain broadly consistent across these liquids, although this assumption may not strictly hold under all operating or aging conditions. Hydrocarbon-based oils generally yield higher concentrations of combustible gases because their degradation primarily involves C–C and C–H bond scission ($\Delta H \approx$ 355–414 kJ·mol^{-1}), concentrating gaseous production on H_2, CH_4, C_2H_6, C_2H_4, and ultimately C_2H_2, the principal marker of arcing faults ($\Delta H \approx$ 607 kJ·mol^{-1}). Conversely, ester-based insulating liquids consume part of the available energy through ester bond cleavage ($\Delta H =$ 359.7–417.4 kJ·mol^{-1}) and decarboxylation ($\Delta H =$ 43.9–71.1 kJ·mol^{-1}), thereby enhancing CO_2 and CO production while reducing the fraction of combustible hydrocarbons. It should be emphasized, however, that these reaction pathways are primarily inferred from thermodynamic considerations and gas analysis, rather than directly observed chemical kinetics. The cleavage of these polar ester bonds and subsequent oxidation reactions favor the formation of CO and CO_2 through decarboxylation processes. These reactions divert part of the absorbed energy from

hydrocarbon gas formation, leading to a distinct gaseous signature that includes higher proportions of oxygenated species [32].

Building on this distinction, it is essential to differentiate arcing from other electrical fault types, particularly partial discharges (PDs). [33] showed that the insulating fluid in power transformers is subjected to various electrical stresses, such as transient overvoltage's, lightning impulses, and distorted AC or DC voltages arising from HVDC systems and renewable energy integration that can trigger PDs even at low voltages. These discharges occur at much lower energy levels than arcing events and consequently produce distinctly different gas generation patterns and diagnostic signatures. In hydrocarbon oil, partial discharges do not have enough energy to massively break C–C bonds, but they promote the cleavage of C–H bonds, mainly generating H_2 along with small amounts of CH_4 and C_2H_6. Acetylene (C_2H_2), which is typical of severe arcing, is rarely produced or only appears in trace amounts. In esters, the presence of ester groups leads to preferential reactions on C–O bonds, resulting primarily in light carbonyl gases (CO and CO_2) in addition to some H_2. However, the relative proportions of these gases may vary significantly depending on moisture content, oxygen availability, and aging state of the fluid. Thus, PDs cause moderate gas formation, dominated by H_2 in mineral oils and by CO/CO_2 in esters, which serves as a distinctive marker for diagnosis [34]. Consequently, although natural esters and mineral oils exhibit similar DGA fingerprints, mineral oil generally yields higher proportions of combustible hydrocarbons, whereas esters generate a broader spectrum of gases enriched with oxygenated compounds. This intrinsic difference complicates DGA interpretation in ester-based fluids, prompting the development of refined diagnostic tools, updated Duval Triangles and Pentagons, with adjusted gas thresholds and exclusion of non-diagnostic gases to better distinguish electrical from thermal-oxidative faults.

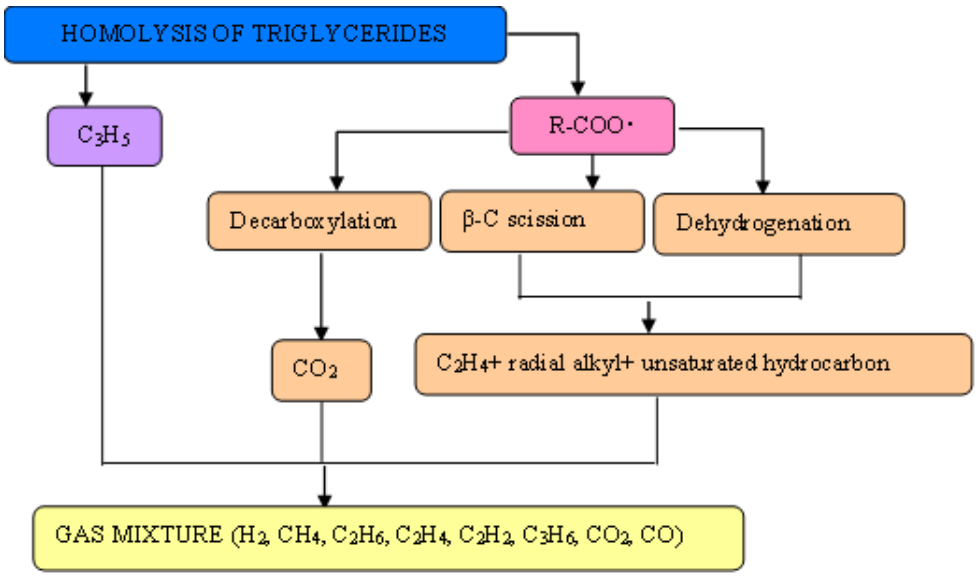

Figure 2.4. The decomposition schemes of triglycerides

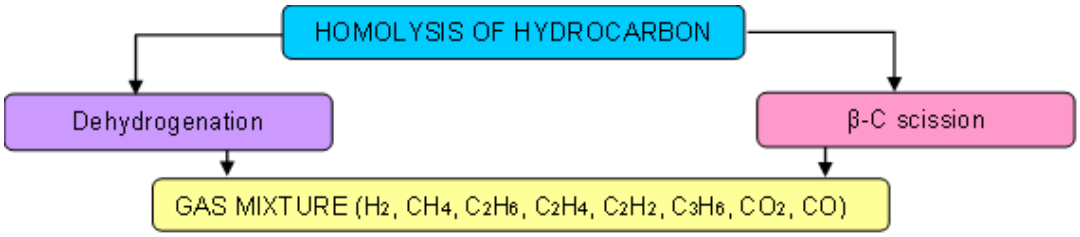

Figure 2.5. The decomposition schemes of hydrocarbon.

2.4.2. GAS FORMATION TOWARD THERMAL FAULT

Electrical arcing faults deposit energy locally in the insulating liquid, whereas thermal faults involve prolonged and more uniformly distributed heating. These thermal stresses, typically caused by overloading, inadequate cooling, or localized hot-spots, lead to slower degradation kinetics and distinct gas generation mechanisms compared to electrical discharges [35].

The thermal decomposition of acyclic saturated hydrocarbons (alkanes) proceeds mainly through a radical chain mechanism involving the cleavage of C–C or C–H bonds. Since the dissociation energy of C–C bonds (83–85 kcal/mol) is lower than that of C–H bonds (96–99 kcal/mol), their rupture is more likely to occur at moderate temperatures, initiating radical formation. These radicals recombine to form light hydrocarbons such as H_2, CH_4, C_2H_6, and C_2H_4. Hydrocarbon oil is composed of hydrocarbons such as aliphatic, alicyclic, and aromatic

hydrocarbons, which introduces variability in degradation behaviour that is often simplified in mechanistic interpretations. The most vulnerable point where the hydrocarbon would be cut is at the end of the carbon chain in the oil molecule. Then, CH_4 is produced by combining with H_2 after cleavage at the end of the chain. For long-chain alkanes (n > 20), as in the case of polyolefins, pyrolysis generates smaller fragments (C_1–C_5 hydrocarbons) and radicals, with the product distribution depending on temperature and experimental conditions [36].

The thermal decomposition of natural esters and synthetic esters follows distinct pathways due to their molecular structures but shares common radical-driven mechanisms. In natural esters, composed of triglycerides with varying fatty acid chains, pyrolysis occurs typically between 350–450 °C, with scission of C–H and C–C bonds at allylic positions leading to CH_4, C_2H_6, C_2H_4, and C_2H_2, while the ester groups promote CO and CO_2 formation via decarboxylation It should be noted that these temperature ranges and pathways are largely derived from laboratory simulations and may not fully capture the complexity of in-service thermal gradients. In contrast, synthetic esters such as pentaerythritol ester ($C_{41}H_{76}O_8$) undergo initial ester bond cleavage followed by decarboxylation and β-C–C scission at higher simulated temperatures (1600–2200 K), generating mainly CO_2 and C_2H_4 as stable products, with additional gases (C_3H_4, C_3H_6, H_2, CH_4, C_2H_6, C_3H_8) appearing above 2000 K. This highlights the need for caution when extrapolating high-temperature experimental results to practical transformer diagnostics. Thus, while natural esters decompose at lower temperatures and yield a broad mix of hydrocarbons and carbon oxides, synthetic esters exhibit a higher thermal stability and produce a gas profile dominated by CO_2 and ethylene under severe overheating [37-38].

Under low thermal stress (200–300°C), gas generation strongly depends on liquid composition. Rajab et al. (2015–2019) showed that mineral oil mainly produces CH_4 (≈ 45 %) and H_2 (≈ 10 %), while monoesters yield larger amounts of CO (≈ 60 %) and C_2H_6 (≈ 20 %) from ester bond cleavage. Unsaturated monoesters exhibit the highest generation rates due to C=C bond reactivity, whereas saturated ones remain more stable. CO_2 formation is moderate, confirming oxidative rather than pyrolytic reactions, and no C_2H_4 or C_2H_2 appears below 300°C.

Nevertheless, these results are obtained under controlled laboratory conditions and may be influenced by oxygen availability, moisture content, and aging state, factors that are not always systematically addressed. The overall gas generation rate decreases in the order unsaturated monoester > saturated monoester > natural ester > mineral oil, highlighting the dominant influence of molecular structure on degradation kinetics [39-40-41]. Figure 2.6 Profiles of dissolved gases formed in various insulating liquids under thermal faults as a function of temperature, based on laboratory experiments according to [39-49].

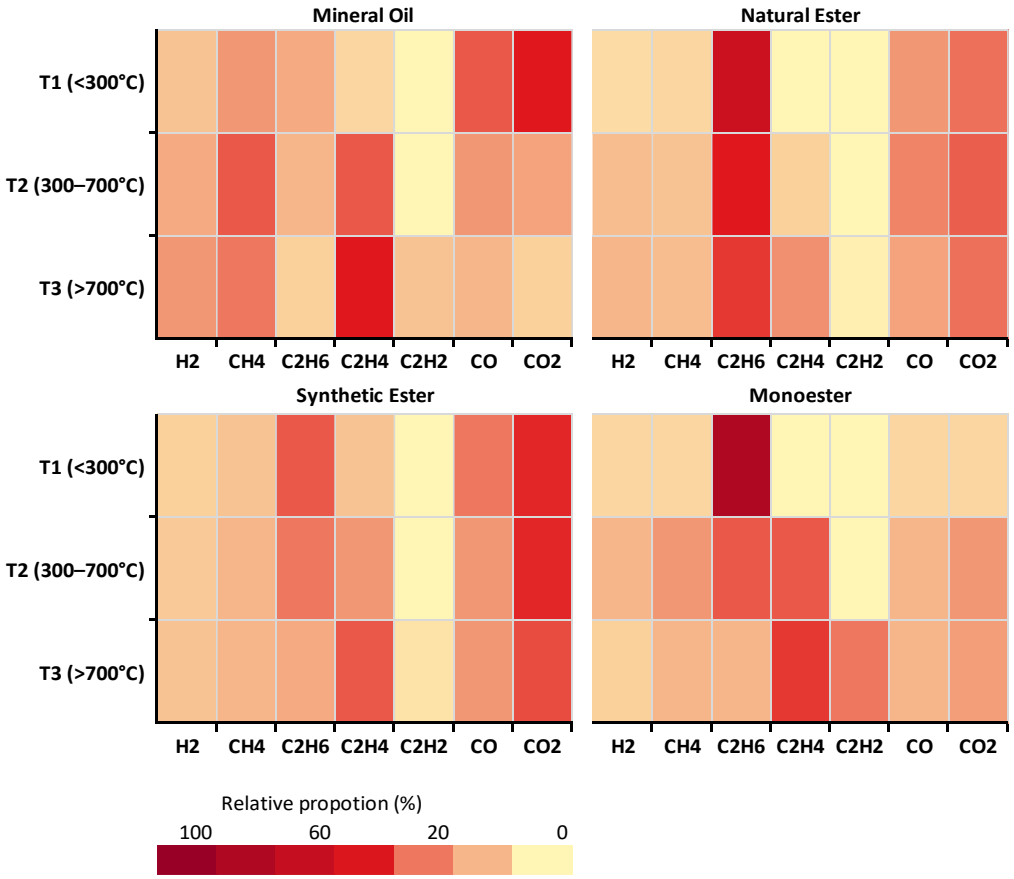

Figure 2.6 : The Profiles of dissolved gases generated in different type of insulating liquids under thermal faults as a function of fault temperature.

2.4.3. GAS FORMATION TOWARD COUPLED ELECTRICAL-THERMAL FAULT

Oil-immersed transformers are subject to three main types of internal faults: thermal, electrical, and electro-thermal. In practice, thermal and electrical faults often occur together, giving rise to an electro-thermal fault. Such faults result from the combined influence of temperature and voltage stress [50]. This coupling introduces additional complexity in fault

diagnosis, as gas generation reflects the superposition and interaction of multiple stress mechanisms.

A winding inter-turn fault in an oil-immersed transformer is a typical case of an electro-thermal fault. This defect originates from the progressive deterioration of insulation between adjacent turns, leading to a local short circuit that drives abnormally high circulating currents in the affected coil. From an electrical perspective, this increases local fault currents and alters electromagnetic fields, while from a thermal perspective, it produces rapid and localized overheating that often exceeds the insulation's thermal limit. Numerical simulations indicate that even limited fault extents can result in severe operating conditions: a fault involving only 1.4% of the turns can raise the short-circuit current above 6500 A and push the winding temperature beyond 394 K within a few seconds, causing irreversible damage to the coil [51]. Although such simulations provide valuable insight, their extrapolation to in-service conditions remains dependent on assumptions regarding cooling efficiency, material condition, and fault duration.

In [52-53], formation in transformers insulating liquids under thermal, electrical, and electro-thermal stresses reveal distinct fault signatures and important differences between vegetable oil and mineral oil. In vegetable oil, methane (CH_4) and acetylene (C_2H_2) are the characteristic gases of electrical faults, with acetylene prevailing under high-energy discharges, whereas ethane (C_2H_6) is the dominant product of thermal faults across 200–700°C, its generation accelerating with temperature rise. Under combined electro-thermal faults, the gas profile varies with both thermal and electrical intensity: at low temperatures (120–200 °C), partial discharges enhance acetylene formation, while at medium to high temperatures (500–700°C), ethane predominates, although strong discharges still promote acetylene. At extreme conditions (800 °C), sharp increases of ethane and methane are observed, with a simultaneous decrease of breakdown voltage, indicating that heat lowers the threshold for electrical discharges. These observations suggest a strong coupling between thermal softening of the liquid and discharge-driven chemical decomposition.

In contrast, in [54] mineral oil shows greater production of acetylene (C_2H_2) and ethylene (C_2H_4), reflecting the decomposition of unsaturated hydrocarbons during arcing and overheating; acetylene levels are typically 5–10 times higher than in vegetable oils. More generally, fault severity governs gas profiles: CH_4 and H_2 dominate under low-intensity electro-thermal conditions, while C_2H_2 and C_2H_4 prevail at higher intensities. Carbon oxides (CO, CO_2) mainly originate from solid insulation degradation, limiting their value as markers of liquid-phase electro-thermal faults [48-49-50]. Overall, the results indicate that electro-thermal faults in transformer oils generate mixed gas patterns, with CH_4 and H_2 prevailing under low intensity combined stresses, whereas C_2H_2 and C_2H_4 become dominant under severe discharge conditions coupled with thermal loading. The overlap between thermal and electrical gas markers complicates fault discrimination, particularly when applying diagnostic criteria originally developed for mineral oils. These outcomes emphasize the necessity of developing fluid-specific diagnostic criteria to ensure reliable fault interpretation.

2.4.4. THERMO-OXIDATIVE GAS EVOLUTION OF INSULATING LIQUIDS

It is widely recognized that oxidation is one of the dominant processes responsible for the deterioration of insulating oils. Dissolved oxygen, reaching about 20,000 ppm at equilibrium in free-breathing transformers, acts as a highly aggressive species, providing the chemical energy that drives the decomposition of hydrocarbon molecules, this reaction is strongly temperature-dependent, with higher temperatures significantly accelerating the degradation process [55]. The overall oxidation rate obeys the Arrhenius relation:

$$k = A \cdot e^{\left(\frac{-E_a}{RT}\right)}$$

where A is the pre-exponential factor, Ea the activation energy, R the gas constant, and T the absolute temperature. Natural esters, containing unsaturated fatty chains, exhibit lower Ea (~300 $kJ \cdot mol^{-1}$) and thus higher oxidation rates. Synthetic esters, being fully saturated, are more stable, while bio-hydrocarbon liquids exhibit slower oxidation but greater radical recombination, yielding higher combustible gas content.

According to [56], Stray gassing, or thermo-oxidative gas evolution, refers to the generation of dissolved gases in the absence of faults, typically at 90–200°C. Observed in both new and aged oils, it is often misdiagnosed as a T1 fault (IEC 60599) and is particularly prevalent in free-breathing transformers with uninhibited mineral oils. This behaviour is now recognized as strongly influenced by dissolved oxygen and catalyzed by copper. The oxidation mechanism of insulating liquids, whether natural esters, synthetic esters, or hydrocarbon-based liquids, follows the same fundamental principles and is well documented in the literature. In all cases, degradation proceeds through hydrogen abstraction: from the carbon backbone in hydrocarbon liquids; from the bis-allylic hydrogens of polyunsaturated fatty acids, notably linoleic and linolenic acids, in natural esters; and from the α-methylene groups adjacent to the ester linkage in synthetic esters [57].

Although the oxidation mechanism is fundamentally common to all classes of dielectric liquids, the specific reaction pathways and resulting gas profiles vary according to the chemical structure of each fluid. [58-59] showed that the main difference from the oxidation of mineral oil is the decomposition of the hydroperoxy and ketoperoxy species. In hydrocarbon liquids, the presence of carbon monoxide is not always a direct indicator of cellulose degradation, as it can also originate from the insulating fluid itself. Under moderate yet sustained heating, peroxides formed during oxidation may decompose and release CO, a process strongly intensified by copper catalysis and the depletion of passivators in aged oils. This phenomenon typically generates methane (CH_4), ethane (C_2H_6), hydrogen (H_2), carbon monoxide (CO), and carbon dioxide (CO_2), while ethylene (C_2H_4) appears only at higher temperatures. Copper further accelerates oxidation, enhancing the production of CO_2, CH_4, and C_2H_6, whereas uninhibited oils exhibit significantly higher gas concentrations than inhibited oils when exposed to comparable oxygen conditions.

In [60], Synthetic esters subjected to thermal aging predominantly form CH_4, C_2H_4, and CO_2, with CH_4 peaking early from alkyl group cleavage, C_2H_4 rising steadily with ester chain breakdown, and CO_2 dominating through oxidation, while acetylene (C_2H_2) is absent at such moderate energy levels. Natural esters exhibit distinctive gas formation patterns, where H_2 and

C_2H_6 typically prevail, while CH_4 and C_2H_4 remain minor and C_2H_2 is absent, indicating a benign oxidative origin. [61] demonstrated that, the behaviour is largely dictated by fatty acid composition: rapeseed esters, rich in polyunsaturated acids, generate higher CO and CO_2, whereas high-oleic esters (e.g., HOSUN) yield minimal gases. In contrast, soybean and rice bran esters produce notable ethane through peroxidation of C=C bonds, especially omega-3 fatty acids, while modified esters without double bonds show no ethane evolution. These findings emphasize that gas formation is governed by molecular structure, oxygen availability, and catalytic effects, underscoring the need for diagnostic models beyond conventional mineral-oil criteria.

2.4.5. CASE STUDIES OF STRAY GASSING AND IMPLICATIONS FOR TRANSFORMER CONDITION ASSESSMENT

The study in [62] highlighted several real cases of power and distribution transformers exhibiting abnormal dissolved gas generation without any detectable internal fault, a phenomenon known as stray gassing. This behaviour, observed at moderate temperatures (100–120°C), results primarily from catalytic reactions between the insulating oil and metallic components such as grain-oriented steel, zinc coatings, or protective varnishes. The investigated cases include large power units rated up to 300 MVA–420 kV and smaller distribution transformers around 400 kVA–12 kV, all showing hydrogen production highly dependent on oil temperature and the nature of metallic surfaces. In contrast, other transformers exhibited generations of saturated hydrocarbons (methane, ethane, propane) attributed to slow oxidation processes in non-inhibited oils, particularly during the first years of operation. These reactions generally reach a stable plateau after an initial growth phase and have no impact on the electrical integrity of the equipment.

Expanding on these insights, [63] examined the role of stray gassing within preventive maintenance frameworks and transformer health index computation, focusing on a 2000 kVA uninhibited mineral oil-immersed transformer used in solar photovoltaic (PV) plants. Through comparative DGA analysis based on IEEE C57.104-2019, IEC 60599:2015, and CSUS guidelines, the authors observed that elevated H_2, CH_4, and C_2H_6 concentrations, commonly

interpreted as corona or partial discharges were in fact the result of temperature-induced catalytic reactions linked to harmonic distortions typical of PV systems. The study proposed localized stray gassing thresholds, suggesting that hydrogen concentrations between 250–1000 μL/L correspond to normal aging behaviour in PV transformers, while recommending a sampling interval of 4–6 months for optimal condition assessment. Following oil replacement, the observed gas concentrations stabilized, confirming the non-critical and reversible nature of stray gassing.

In [64], the study comparing 400 kV–250 MVA transformers over four years of operation found that natural esters exhibit higher DDF and acidity from polar groups but offer superior dielectric strength (75–80 kV vs. 65–70 kV) and greater water solubility, helping maintain cellulose insulation dryness. The DGA results revealed elevated C_2H_6 concentrations in NE-filled units from the early stages of service. This gas is produced by spontaneous low-temperature decomposition rather than thermal faults, confirming the occurrence of stray gassing. Consequently, ethane in ester-based transformers cannot be interpreted solely as a symptom of overheating, and diagnostic practices must be adapted to prevent false fault identification.

Overall, this studied highlights that catalytic stray gassing can mislead DGA interpretation by resembling thermal faults, stressing the importance of evaluating gas generation trends and operating conditions. It recommends adapting diagnostic thresholds for esters and integrating stray gassing into Health Index models to enhance reliability and avoid unnecessary maintenance actions.

2.5. MODIFACTION OF CHEMICAL COMPOSITION AND ITS IMPACTS ON GAS FORMATION

2.5.1. MOISTURE CONTENT

[65] defined moisture or water content in oil-paper insulation as critical factor that accelerates aging of the insulation system and increases the risk of dielectric failures. Its distribution depends on temperature, the type of liquid, and the properties of the paper: mineral and silicone oils, being non-polar, have low water solubility compared to esters, which are more

polar, yet most of the moisture remains trapped in the cellulose. Thermal variations drive a dynamic migration process: at higher temperatures, water is released from the paper into the oil, while cooling causes it to be reabsorbed by the cellulose. Governed by the solubility limits of the oil and the adsorption capacity of the paper, this process involves sorption (adsorption/absorption) and desorption mechanisms, making moisture monitoring and control essential to ensure transformer reliability. Although these processes are well established, the transient nature of moisture redistribution complicates its quantification under real operating conditions, making moisture monitoring and control essential for ensuring transformer reliability.

Results of [66] showed that moisture levels have a notable impact on gas generation in both soy seed-based oil and mineral oil, but their effects differ between the two. In mineral oil, increased moisture content generally leads to higher production of fault gases such as methane, ethylene, and acetylene, with gas quantities increasing proportionally as moisture levels rise, especially when pressboard is present. This results in higher gas ratios that are indicative of faults. Conversely, in soy seed-based oil, gas generation patterns are distinct; during partial discharge faults, only hydrogen is predominantly produced, and its amount tends to increase with moisture when no pressboard is present, whereas the trend reverses when pressboard is included, with hydrogen production decreasing as moisture increases. Additionally, for arcing and overheating faults, gases tend to be produced more in drier soy seed-based oil, contrasting with mineral oil, where gas quantities increase with moisture. Interestingly, soy seed-based oil can absorb additional moisture beyond the initial added amount, causing its moisture content to surpass the levels introduced during testing, which influences the types and quantities of gases generated during fault conditions. Overall, while increased moisture generally enhances fault gas production in mineral oil, in soy seed-based oil the relationship is more complex and can be influenced by factors such as the presence of pressboard and the specific fault type.

In [67], although water content is shown to influence gas generation in transformer oils, its role is complex and closely linked to oxygen and temperature. Under high oxygen

conditions, increasing the water content of paper and oil generally suppressed hydrocarbon gas formation, with ethylene, methane, ethane, and hydrogen generation rates decreasing significantly at 120 °C and 140 °C. By contrast, at lower temperatures around 100 °C, no clear correlation between water content and gas formation was observed. These results suggest that moisture does not act as an isolated controlling parameter but rather modulates gas formation indirectly through its interaction with oxygen availability and thermo-oxidative aging mechanisms. Overall, the study indicates that higher water content may mitigate stray gassing when combined with elevated oxygen levels and thermal stress; however, it remains difficult to establish whether water acts as a direct causal factor or primarily influences gas generation through secondary effects on oxidation kinetics and insulation degradation.

2.5.2. ANTIOXIDANTS AND METAL PASSIVATOR

In [68], the oxidation of insulating liquids initiates (I) with the dissociation of hydrocarbon molecules (RH) into radicals (R•) and hydrogen (H•). These radicals rapidly react with oxygen to form peroxy radicals (ROO•), driving the propagation phase (P). Oxidation then proceeds via two competing pathways: autooxidation, where ROO• generates hydroperoxides (ROOH) that decompose into alkoxy and hydroxyl radicals, sustaining a self-propagating cycle; and termination (T), where radicals combine to yield stable products such as oxygenated compounds (aldehydes, alcohols, acids) and hydrocarbon residues, This process is significantly intensified by metal catalysts, particularly dissolved copper, and is closely associated with stray gassing. Antioxidants (AH), such as butylated hydroxytoluene (BHT), also known as 2,6-di-tert-butyl-p-cresol (DBPC), delay oxidation by scavenging free radicals and limiting peroxide formation, thereby enhancing the oxidation stability of insulating oils. They act as hydrogen donors, neutralizing alkyl (R·), alkoxy (RO·), and peroxy (ROO·) radicals to form stable products (RH, ROH, ROOH) while generating antioxidant radicals (A·). These antioxidant radicals further react with free radicals to yield non-radical products (RA, ROA, ROOA). Ultimately, antioxidant efficiency decreases over time as these compounds are progressively consumed and transformed into oxidized derivatives [68]. Figure 2.7 illustrates the oxidation mechanism reactions of insulating liquids as well as the antioxydant process. In

addition, metal deactivating agents, including passivators like benzotriazole (BTA) and Irgamet 39, or chelating agents such as Irgamet 30 are employed to suppress copper's catalytic activity and thereby reduce by-product formation [69-70].

Antioxidants act by stabilizing free radicals generated during the thermo-oxidative degradation of hydrocarbon oils. In uninhibited oils, there is no protection against radical chain reactions, so once a C–C or C–H bond is cleaved, the resulting radicals (H·, CH_3·, etc.) propagate rapidly, leading to high levels of H_2, CH_4, and C_2H_6. When antioxidants are added, they interrupt these radical chain reactions by reacting preferentially with peroxy (ROO·) and alkyl (R·) radicals, forming stable, non-propagating products. This prevents further oxidative breakdown of hydrocarbons and sharply reduces stray gas generation. In inhibited-passivated oils, metal passivators suppress catalytic reactions at copper surfaces that normally accelerate oxidation. However, some passivators can also promote secondary reactions that release small amounts of H_2, which explains why these oils show intermediate gas levels [71]. However, some passivators may also promote secondary reactions that release limited amounts of H_2, which may explain why such oils often exhibit intermediate gas generation levels rather than complete suppression of gas formation. For natural esters, the addition of antioxidants primarily enhances oxidative stability, with relatively little influence on breakdown voltage. Among the inhibitors investigated, tert-butylhydroquinone (TBHQ) and citric acid were reported to be the most effective, whereas propyl gallate exhibited limited efficiency [72]. These results underline the importance of carefully selecting antioxidant systems tailored to ester chemistry, as additive performance cannot be directly extrapolated from mineral oil formulations.

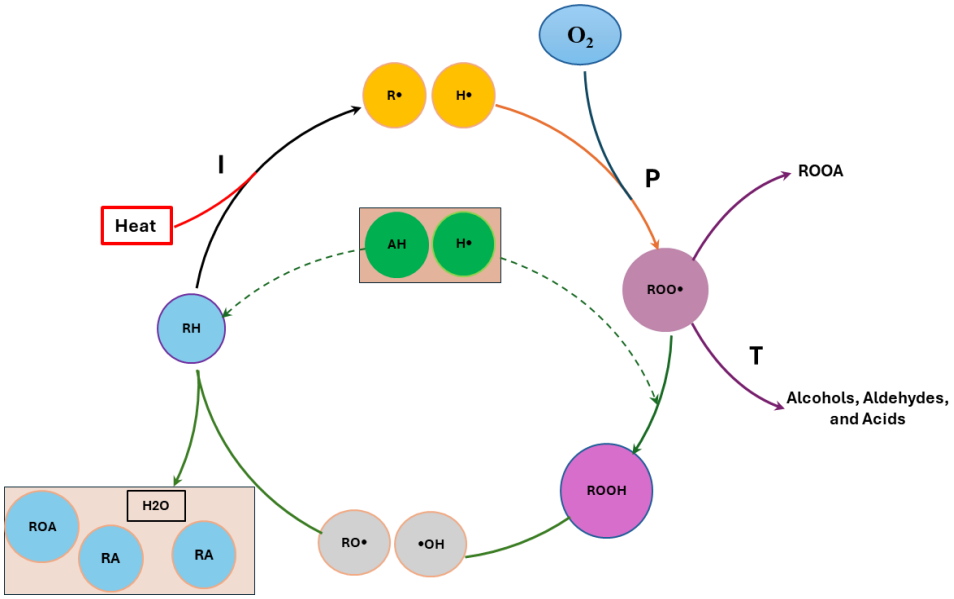

Figure 2.7 : Oxidation mechanism of insulating liquids and antioxidant action.

2.5.3. NANOPARTICLES

As explained in [73–74], nanofluids, obtained by dispersing nanoparticles into insulating liquids, have been proposed as advanced dielectric materials offering improved thermal, electrical, and insulation performance for transformer applications. Recent studies on nano-ester liquids indicate that incorporating nanoparticles into natural and synthetic esters may enhance insulation reliability and potentially extend service life. Depending on their electrical properties, nanoparticles are commonly classified as insulating, semiconductive, or conductive. Although these improvements are frequently reported, their effectiveness strongly depends on nanoparticle type, concentration, dispersion stability, and compatibility with the base fluid, factors that are not always systematically addressed across studies.

[75] highlighted that the addition of metal oxide nanoparticles, such as SiO_2, TiO_2, and Al_2O_3, to hydrocarbon oils can alter decomposition behaviour under thermal and electrical stresses. Owing to their high specific surface area and modified thermal conductivity, nanoparticles may promote localized temperature gradients within the liquid. However, the formation of such localized hot spots is generally inferred from thermal and gas evolution data rather than being directly measured. Certain nanoparticles, particularly TiO_2 and Al_2O_3, have also been reported to exhibit catalytic surface activity, which may lower the apparent activation

energy of pyrolysis reactions and enhance the formation of reactive radicals ($H\cdot$, $CH_3\cdot$). It should be noted, however, that distinguishing between purely thermal effects and true catalytic mechanisms remains challenging, as both processes may occur simultaneously. The effect is reported to be more pronounced for SiO_2 and Al_2O_3, which can store and locally redistribute heat, whereas TiO_2 may, under certain conditions, interact with oxygenated radicals and partially mitigate gas formation. Nanoparticle concentration also plays a critical role, as excessive loading promotes agglomeration, reducing the effective surface area and limiting the reproducibility and generalization of reported results.

In [76], the influence of Al_2O_3 and SiO_2 nanoparticles on the gas formation behaviour of mineral oils and vegetable oils under thermal aging was investigated. The authors reported that nanoparticles tended to reduce CO formation, while their effect on hydrocarbon gases varied with the base fluid. In vegetable oils and oil blends, C_2H_6 formation was reduced, whereas hydrocarbon oils exhibited a more limited response. These results indicate that nanoparticle effects on gas evolution are fluid-specific and do not follow a universal trend.

The combined localized thermal and potential catalytic effects of nanoparticles may artificially amplify dissolved gas levels, leading to conservative or misleading DGA diagnoses. This behaviour underscores the limitations of applying conventional DGA criteria to nanofluid-filled transformers and highlights the need for revised diagnostic frameworks.

2.5.4. INSULATING PAPER

Cellulose paper, composed of glucose-linked polymeric chains, is a fundamental component of transformer insulation systems. Its molecular structure governs both mechanical integrity and thermal stability and therefore plays a decisive role in the formation of degradation by-products and dissolved gases under thermal and oxidative aging conditions [77]. Because cellulose degradation involves depolymerization, dehydration, and oxidation reactions, its contribution to gas generation is intrinsically coupled to both temperature and moisture content, complicating the attribution of gas origin in oil–paper systems.

In [78–79], ester-filled transformers, CO and CO_2 can be produced in significant quantities not only from cellulose degradation but also from the thermal decomposition of the

liquid itself. At moderate temperatures, ester fluids typically exhibit high CO_2/CO ratios, which progressively decrease as temperature increases. This overlap in gas signatures makes it difficult to discriminate between fluid-derived and paper-derived carbon oxides. In contrast, in mineral oil–paper systems, carbon oxides are generated predominantly through the thermal aging of cellulose, with CO_2 as the dominant species under normal operating conditions. In such systems, CO and CO_2 concentrations are therefore more directly correlated with the extent of paper degradation. Consequently, while CO and CO_2 serve as reliable indicators of solid insulation aging in mineral oil-filled transformers, their diagnostic relevance in ester-filled systems is reduced due to the strong influence of fluid chemistry on carbon oxide generation

Experimental investigations reported in [11] demonstrated that the presence of cellulose paper significantly amplifies the gas formation of transformer oil under electrical discharge conditions. This effect has been attributed to the introduction of additional reactive interfaces and degradation pathways at the oil–paper boundary. As the proportion of paper increases, gas generation rises almost linearly in new oils and approaches saturation at approximately 20% paper content in aged oils. This saturation behaviour suggests a limiting effect imposed by the availability of reactive sites or by the accumulation of degradation by-products. Hydrogen is the dominant gas produced (up to ~85% of total gas volume), followed by methane, with smaller contributions from ethane and ethylene; CO and CO_2 are also formed through combined radical recombination reactions and cellulose decomposition. Moreover, cellulose alters gas distribution by adsorbing or retaining certain degradation products, which may reduce the apparent concentration of heavier hydrocarbons while simultaneously increasing moisture and polar compounds in the oil. These interactions further distort DGA signatures and complicate fault diagnosis.

The influence of cellulose type on gas formation behaviour in natural ester systems was further highlighted in [80]. The study showed that Grade 3 paper, composed of a wood pulp–cotton mixture, exhibited more severe degradation than thermally upgraded kraft (TUK) or diamond-dotted paper (DDP). This accelerated degradation resulted in a stronger reduction of the degree of polymerization and the release of larger amounts of acidic by-products, which in

turn promoted oil deterioration and intensified gas-forming reactions. Due to the hydrophilic nature of natural esters, water released from degrading paper is readily absorbed by the liquid phase, enhancing hydrolysis reactions and generating additional acids and gases. In this context, the most affected gases are carbon oxides (CO and CO_2), which are characteristic indicators of cellulose decomposition. Papers with lower thermal stability therefore amplify CO and CO_2 formation in ester-filled transformers, whereas more thermally stable papers (TUK and DDP) contribute to limiting gas generation and preserving insulation performance.

Overall, cellulose paper not only accelerates hydrogen-dominated gas production under electrical stress but also modifies the relative proportions of dissolved gases through its interactions with the insulating liquid. These combined effects blur the distinction between liquid-phase and solid-phase gas sources, significantly complicating the diagnostic interpretation of DGA in oil–paper insulation systems, particularly for transformers employing ester-based fluids.

2.5.5. INSULATING LIQUID CONDITIONS (AGING)

DGA is a key diagnostic tool for transformers, but its reliability is strongly influenced by gas solubility, which depends on the type of insulating liquid, its density, viscosity, and aging condition. [81] showed that gas solubility in insulating liquids, expressed by the Ostwald coefficient, strongly depends on the liquid type, density, viscosity, and aging condition. Light gases such as H_2 and CH_4 exhibit low solubility and may volatilize, while C_2-hydrocarbons dissolve more readily; aging further reduces solubility, especially for CO and CO_2, affecting the accuracy of DGA interpretation.

As reported in [82], aging by-products such as free radicals, acids, dissolved gases, and colloidal species alter insulating liquid chemistry and promote gas generation under electrical and thermal stresses. Although reclamation using Fuller’s earth can mitigate gas formation by removing degradation products, its effectiveness is highly dependent on the adsorbent type and often requires multiple treatment passes, thereby limiting reproducibility, process efficiency, and large-scale industrial applicability.

During electrical discharges, these degradation products intensify molecular dissociation, enhancing H_2, CH_4, and C_2H_2 generation in mineral oils, whereas under thermal stress they catalyze oxidation and hydrolysis, reinforcing CO and CO_2 formation in esters. Cellulosic particles can also absorb or recombine gases, altering diagnostic signatures. Overall, the progressive build-up of by-products amplifies both the quantity and diversity of dissolved gases, underscoring the need to integrate aging markers such as acidity, turbidity, and viscosity into DGA for more reliable fault interpretation across mineral and ester-based liquids [13] [83].

Integrating aging markers into DGA is critical for accurate diagnostics of biodegradable insulating liquids. In natural and synthetic esters, strong correlations between rising acidity, declining interfacial tension, and increased gas generation (C_2H_2, TDCG; $r \geq 0.88–0.99$) highlight the roles of hydrolysis and oxidation in shaping gas profiles. Bio-based mineral oils exhibited the steepest gas formation, with acetylene surpassing 2500 ppm after 2000 h and strong links to TAN and DDF ($r \geq 0.95$), indicating acid-driven radical decomposition. Although aging intensified gas concentrations, Duval's triangle and pentagon consistently pointed to low-energy discharges (D1), reflecting ester-specific pathways that generate fewer combustible hydrocarbons. Overall, combining TAN, IFT, and DDF with DGA enhances fault identification and mitigates diagnostic risks across bio-hydrocarbon, natural, and synthetic esters [84--85].

[86] showed that gas solubility in insulating liquids, expressed by the Ostwald coefficient, strongly depends on the liquid type, density, viscosity, and aging condition. Light gases such as H_2 and CH_4 exhibit low solubility and may volatilize, while C_2-hydrocarbons dissolve more readily; aging further reduces solubility, especially for CO and CO_2, affecting the accuracy of DGA interpretation.

2.5.6. MIXED INSULATING LIQUIDS

[87] obtained mixed insulating oils (MIOs) by blending mineral oils with synthetic or natural esters, have been increasingly investigated as alternative insulating fluids for transformer applications. These mixtures aim to combine the cost-effectiveness, availability, and low dielectric losses of mineral oils with the improved biodegradability and enhanced

thermal stability of esters. However, despite these apparent advantages, their behaviour under electrical and thermal stress remains insufficiently understood, particularly with respect to gas generation and diagnostic reliability. Given that DGA is a cornerstone technique for transformer condition monitoring, understanding the influence of ester content on gas formation mechanisms in mixed oils is essential for evaluating their suitability and long-term performance.

Experimental studies in [88] on mixed insulating oils consistently indicate that pure mineral oil generally exhibits the lowest gas formation, whereas the incorporation of esters leads to a marked increase in gas generation. This behaviour has been attributed to differences in molecular structure, polarity, and viscosity between hydrocarbons and esters. Highly refined hydrocarbon oils tend to dissolve hydrogen more effectively and limit its release into the gas phase, while ester components promote the formation of oxygenated gases such as CO and CO_2, particularly under aging conditions. As aging progresses, ester-containing blends may exhibit gas production levels up to three times higher than mineral oil, highlighting the amplifying role of ester chemistry in degradation processes. Blends with higher ester fractions (typically 15–20%) consistently show enhanced gas formation following thermal and electrical stresses, with Duval Triangle and Pentagon interpretations often indicating a transition from low-energy discharges in fresh oils to higher-energy discharge signatures in aged, ester-rich mixtures. This apparent escalation in fault severity underscores the risk of misinterpretation when applying diagnostic criteria developed exclusively for mineral oils.

In [89], thermal fault investigations conducted on mixed oils composed of approximately 76% mineral oil, 19% soybean oil, and 5% palm ester further illustrate the complexity of gas formation behaviour in these systems. Compared with mineral oil, these blends generate significantly higher concentrations of H_2 and C_2H_6, with hydrogen levels approaching three times those measured in mineral oil, as well as elevated CO_2 concentrations associated with ester bond decomposition. Within the temperature range 150–450°C, CO_2 dominates the gas profile (>85%), reflecting ester-driven decarboxylation mechanisms. At temperatures above 600°C, hydrocarbon gas formation increases sharply, with C_2H_4 emerging as a key indicator of severe thermal stress. These results demonstrate that ester components intensify both

hydrogen and oxygenated gas formation, leading to gas signatures that are more pronounced and diagnostic than those of mineral oil alone.

Additional studies examining the gas formation of mixed insulating oils under repetitive electric sparking, in both fresh and oxidatively aged conditions, further highlight the strong dependence of gas formation on oil composition. Under sparking stress, mineral oil produces the highest amounts of hydrogen and combustible gases, whereas ester oils generally exhibit lower gas production, particularly for acetylene, reflecting their higher thermal and chemical stability. Aging significantly intensifies gas evolution, with oxidatively aged MIOs displaying higher apparent discharge intensities than fresh samples, a behaviour closely linked to the accumulation of polar degradation by-products. DGA results indicate that conventional ratio-based diagnostic methods (IEC, Rogers, Dornenburg) provide limited accuracy for MIOs, primarily due to disproportionate hydrogen generation. In contrast, Duval's graphical tools (Triangles and Pentagons) demonstrate improved fault discrimination, distinguishing low-energy discharges in fresh oils from high-energy discharges in aged blends. Nevertheless, even these tools may be challenged by the overlapping gas signatures resulting from combined thermal and electrical stresses. Furthermore, total dissolved combustible gas (TDCG) levels tend to decrease with increasing ester content in fresh oils, whereas aged samples exhibit more complex and non-monotonic trends, reflecting the coupled effects of aging, oxidation, and electrical stress [90–91].

Overall, these studies indicate that mixed insulating oils exhibit gas formation behaviors that are distinct from those of pure mineral oils and ester oils. Their intermediate and evolving gas signatures complicate the direct application of existing DGA interpretation frameworks. These findings emphasize the practical necessity of developing adapted diagnostic models, revised gas ratio thresholds, and adjusted protection relay settings for transformers operating with MIOs. Such adaptations are essential to ensure reliable fault detection while supporting the safe and sustainable deployment of mixed insulating oils as environmentally favorable alternatives in power transformer applications.

2.6. CHALLENGES AND FUTURE DIRECTIONS

Although notable progress has been made in characterizing the gas formation behaviour of biodegradable dielectric liquids, several challenges limit their broader application. Diagnostic reliability remains a major concern, as most dissolved gas analysis (DGA) interpretation schemes were originally developed for mineral oils and often produce inconsistent results when applied to alternative fluids. The phenomenon of stray gassing adds further uncertainty, particularly in non-inhibited esters, where the underlying mechanisms of gas evolution under normal operating conditions are still not fully understood. In addition, the long-term aging and degradation pathways of bio-based hydrocarbon oils, natural esters, and synthetic esters are not yet comprehensively established, partly due to the limited availability of field data under diverse climatic and loading conditions. Regeneration and reclamation processes also pose open questions, since their influence on gas formation and fluid stability especially in natural esters remains insufficiently documented.

Looking forward, future research should prioritize the development of fluid-specific DGA interpretation methods, potentially supported by machine-learning approaches that can capture nonlinear relationships in gas generation. Additive engineering represents another promising strategy to reduce stray gassing and enhance chemical stability. Large-scale, long-term monitoring programs are also needed to validate laboratory findings and provide robust data for model development. Finally, progress will require greater standardization, including internationally recognized protocols for testing and benchmarking gas formation behaviour. Addressing these challenges will be essential to improving diagnostic accuracy, extending fluid lifetime, and accelerating the reliable adoption of biodegradable dielectric liquids in power transformers.

2.7. CONCLUSIONS

Dissolved Gas Analysis (DGA) remains a cornerstone of preventive maintenance in power transformers, enabling early detection and classification of incipient faults. Its strength lies in interpreting complex gas mixtures, with tools such as the Duval pentagon providing a more comprehensive framework than traditional methods. Nevertheless, accuracy is still

constrained by variability in gas extraction, fluid type, and diagnostic methodology, particularly for ester-based liquids where stray gassing can obscure fault signatures.

The gas formation behaviour of insulating liquids is largely governed by chemical composition, oxygen content, and aging. Bio-MO degrade via pathways like conventional mineral oils, dominated by hydrocarbon chain scission. NE generally exhibit positive gas formation due to diverse fatty acids, while SE, with more uniform molecular structures, tend to display negative gas formation. Across all fluids, aging by-products, such as acids, colloids, and cellulose residues, can amplify gas evolution and mask true fault indicators, emphasizing the need for integrated diagnostic approaches.

Looking forward, future research should focus on improving diagnostic reliability, advancing fluid management strategies, and exploring chemical modifications to enhance stability and performance. Addressing these areas will be essential for the safe and widespread adoption of biodegradable dielectric liquids in transformer applications.

CHAPITRE 3

UNDERSTANDING THE RELATIONSHIP BETWEEN INSULATION AGING AND GASSING TENDENCY OF SOME BIODEGRADABLE DIELECTRIC FLUIDS

AVANT PROPOS

Ce chapitre reproduit et étend le contenu de: M. T. Agouassi, U. Mohan Rao, I. Fofana and Y. Hadjadj, "Understanding the Relationship Between Insulation Aging and Gassing Tendency of Some Biodegradable Dielectric Fluids," in *IEEE Transactions on Dielectrics and Electrical Insulation*, doi: 10.1109/TDEI.2025.3596945.

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TITRE EN FRANÇAIS : Compréhension de la relation entre le vieillissement de l'isolation et la tendance au gazage de certains fluides diélectriques biodégradables.

RÉSUMÉ : Cette étude examine les mécanismes de dégradation et les comportements de génération de gaz de trois fluides diélectriques biodégradables, huiles Bio-minérales (Bio-MO), esters naturels (NE) et esters synthétiques (SE), soumis à une contrainte électrique, en mettant l'accent sur leur application dans les transformateurs de puissance. La recherche adopte un protocole expérimental étendu incluant plusieurs durées de vieillissement (250 à 2000 heures) et des essais répétés de tenue en tension (BDV) afin de simuler des conditions de défaut par arc et d'assurer une analyse de tendances reproductibles. Des caractérisations clés telles que le facteur de dissipation (DDF), la tension interfaciale (IFT) et l'indice d'acide (TAN) ont été combinées à l'analyse des gaz dissous (DGA) pour suivre la dégradation des fluides. Une contribution originale de ce travail réside dans le cadre statistique introduit pour quantifier les relations entre l'augmentation des gaz (%C_2H_2, %TDCG) et les marqueurs de vieillissement au moyen de coefficients de corrélation (r, valeur p). Par ailleurs, les outils de diagnostic de Duval (Triangle 1/Pentagone 1 pour le Bio-MO, Triangle 3/Pentagone 3 pour les esters) ont révélé que les types de défauts évoluent avec le vieillissement.

Plus précisément, le Bio-MO est passé de décharges à haute énergie (D2) à des décharges à basse énergie (D1), fortement corrélées à l'augmentation du %DDF et du %TAN. En revanche, les NE et SE ont maintenu des diagnostics D1 stables. Ces résultats offrent une approche prédictive pour l'identification des défauts et l'évaluation de l'état des transformateurs, ouvrant la voie à une mise en œuvre élargie avec des ensembles d'échantillons plus importants et une validation sur le terrain.

3.1. ABSTRACT

This study investigates the degradation mechanisms and gas generation behaviors of three biodegradable dielectric fluids, bio-based mineral oils (Bio-MO), natural esters (NE), and synthetic esters (SE), under electrical stress, focusing on their application in power transformers. The research adopts an extended experimental protocol that includes multiple aging durations (250–2000 hours) and repeated breakdown voltage (BDV) tests to simulate arc fault conditions and ensure reproducible trend analysis. Key characterizations such as Dissipation Factor (DDF), Interfacial Tension (IFT), and Total Acid Number (TAN) were combined with DGA to monitor fluid degradation. A novel contribution of this work is the statistical correlation framework introduced to quantify the relationships between increases in gases (%C_2H_2, %TDCG) and aging markers using correlation coefficients (r, p-value). Furthermore, Duval's diagnostic tools (Triangle 1/Pentagon 1 for Bio-MO, Triangle 3/Pentagon 3 for esters) revealed that fault types evolve with aging. Specifically, Bio-MO transitioned from high-energy (D2) to low-energy (D1) discharges, strongly correlated with rising %DDF and %TAN. In contrast, NE and SE maintained stable D1 diagnostics. These findings offer a predictive approach to fault identification and transformer health assessment, paving the way for broader implementation with larger sample sets and field validation.

Index Terms: Bio-based mineral oils, ester liquids, gassing tendency, electrical fault, power transformers.

3.2. INTRODUCTION

The use of biodegradable dielectric fluids is a major concern for industry and utilities as substitutes for mineral oils traditionally used as insulators in oil-filled transformers. Several new insulation liquids have been introduced to the market in recent years. Among them, bio-based hydrocarbon insulating liquids, derived from renewable bio-residues through hydro-processing and isomerization, stand out for their high-purity hydrocarbon structure, low viscosity, and excellent thermal stability. They are fully compatible with existing transformer technologies and offer a lower carbon footprint compared to both mineral oils and ester-based fluids, thanks to their sustainable feedstock origin [1]. Moreover, these fluids outperform esters in oxidation resistance and heat dissipation, helping to reduce hotspot formation and extend transformer service life. Their biodegradability, combined with safe environmental behaviour in the event of spills, positions them as a compelling alternative aligned with modern sustainability goals [2–3].

Although these biodegradable liquids demonstrate clear environmental and performance advantages, their practical application still requires deeper investigation, particularly regarding their aging behaviour under real-world operating conditions. Aging processes, influenced by thermal, electrical, and environmental stresses, critically affect transformer reliability [4]. Degradation of the oil–paper insulation system leads to acid formation, increased water content, sludge, and dissolved gases, while also degrading the paper's mechanical properties and lowering the degree of polymerization. The accumulation of polar degradation products reduces interfacial tension, and moisture migration accelerates cellulose deterioration. Furthermore, electrical and thermal stresses can break molecular bonds (C–C, C–H, or C–O), generating gases such as H_2, CH_4, C_2H_6, C_2H_4, C_2H_2, CO, and CO_2. The severity of these phenomena depends on the energy input and the chemical nature of the fluid [5].

This study examines the correlation between gas generation and aging markers (AgM) in biodegradable insulating liquids, specifically bio-hydrocarbons, synthetic esters, and natural esters exposed to high-energy electrical arcs, to improve their use in power transformers.

3.3. EXPERIMENTAL

3.3.1. THERMAL AGING

The liquids were thermally aged at 125 ± 2 °C following a modified ASTM D1963 procedure, using a 20:1 oil-to-paper ratio with 0.25 mm-thick kraft paper and 3 g/L of copper as a catalyst, over durations ranging from 250 to 2000 hours. After each breakdown test, 50 ml samples were collected using syringes for gas analysis (ASTM D3612). Aging markers were determined as follows: TAN was measured according to ASTM D974 using colorimetric titration; IFT was measured using method by ASTM D971; and the DDF was evaluated following ASTM D924 using dielectric loss angle measurement at power frequency. Additionally, the DP of the paper insulation was determined according to ASTM D4243, based on intrinsic viscosity measurement. Tables 3.1 and 3.2 present the aging marker codes and corresponding measurements.

Table 3.1 : Aging marker codes and measurements

Aging		Measurements		
Time, Hours	Markers code	DDF	IFT, mN/m	Acidity, mg KOH/g
Bio-MO				
0	Unaged	2.64E-04	51	0.002
250	AgM1	2.89E-04	48	0.004
500	AgM2	3.47E-04	48	0.018
750	AgM3	7.25E-04	47	0.024
1000	AgM4	7.61E-04	47	0.035
2000	AgM5	1.44E-03	43	0.047
NE				
0	Unaged	5.05E-03	22	0.037
250	AgM1	1.47E-02	19	0.105
500	AgM2	2.38E-02	18	0.148
750	AgM3	2.76E-02	17	0.188
1000	AgM4	4.54E-02	15	0.236
2000	AgM5	5.41E-02	14	0.252
SE				
0	Unaged	1.45E-03	25	0.032
250	AgM1	3.04E-03	25	0.064
500	AgM2	4.32E-03	24	0.085
750	AgM3	8.11E-03	24	0.125
1000	AgM4	8.23E-03	23	0.155
2000	AgM5	2.93E-02	19	0.187

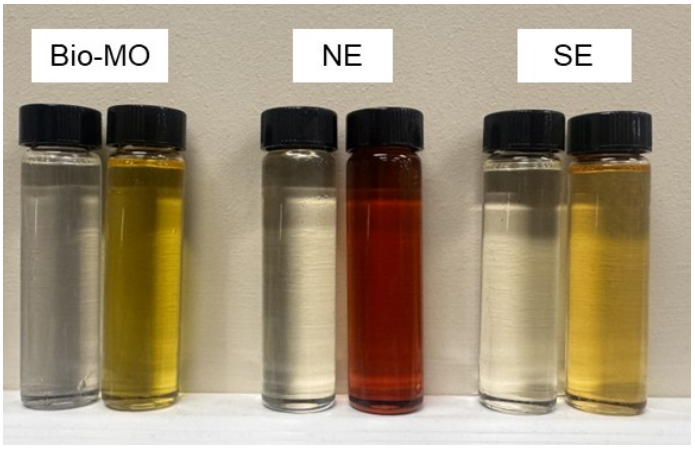


Figure 3.1. Visual Comparison of Bio-MO, NE, and SE After 1000 Hours of Thermal Aging.

Table 3.2 : Measurements of the degree of polymerization (Dp)

	0H	250H	500H	750H	1000H	2000H
Dp	1030	Bio-MO				
		582	509	498	477	418
		NE				
		924	885	882	855	823
		SE				
		904	870	860	825	790

3.3.2. ELECTRICAL FAULT

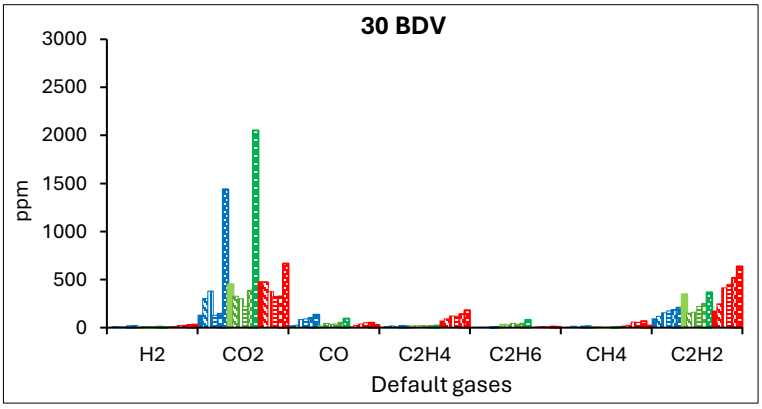
Electric arc discharge faults were conducted using flat electrodes spaced 2.5 mm apart. The test cell was filled with insulating liquid, and 60 Hz AC voltage was applied at a steady rate of 2 kV/s to generate arc intensities between the x-y electrodes. Fault intensities were simulated through 30, 60, 90, 120, and 150 breakdown repetitions, with a 2-minute interval between each, using a setup like that described in [6].

3.4. RESULTS AND DISCUSSIONS

3.4.1. DISSOLVED GASES AFTER AN ARCING FAULT

Figure 3.1 shows the evolution of dissolved gas concentrations in SE, NE, and Bio-MO over aging time. As thermal aging progresses from 0 to 2000 hours, all fluids exhibit a steady increase in gases such as H_2, CO_2, CO, CH_4, C_2H_4, C2H6, and especially C_2H_2 following electrical arc faults. This trend suggests that aging increases the susceptibility of fluids to decomposition under fault energy. Acetylene (C_2H_2) exhibits the most pronounced rise, particularly in aged Bio-MO, confirming its relevance as a key arc fault indicator [7], as shown

in Table 3.3. Bio-MO also exhibits the highest TDCG levels (see Table 3.4), reflecting its greater tendency to fragment under thermal and electrical stress, despite good initial stability. In contrast, NE and SE produce less C_2H_2, even after 2000 hours, likely due to the stabilizing effect of polar ester groups. The observed increases in CO and CO_2, especially in NE and Bio-MO, further suggest that oxidation aging of liquids significantly contributes to gas generation.



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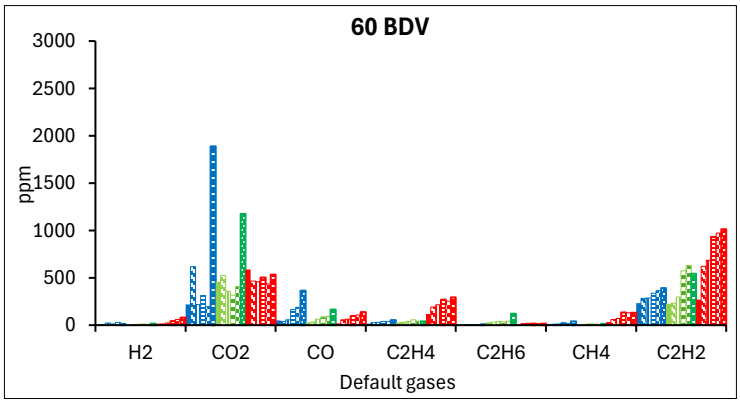

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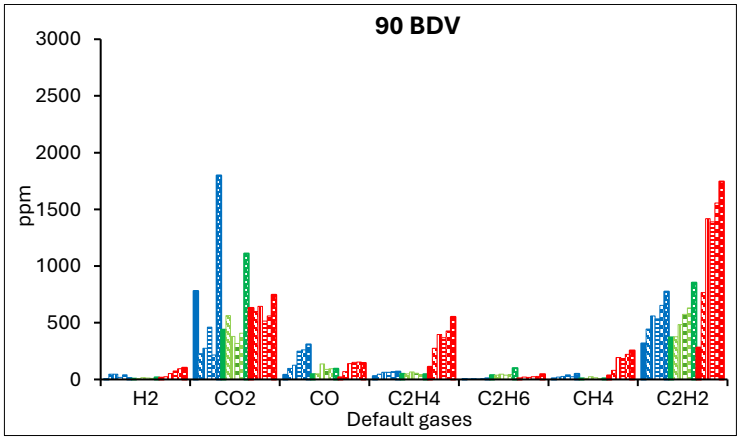

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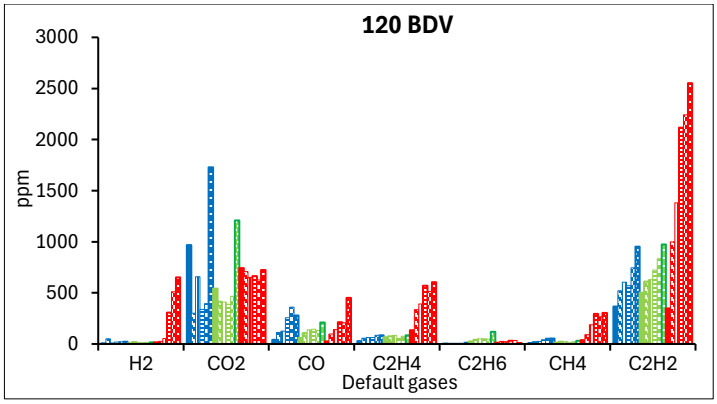

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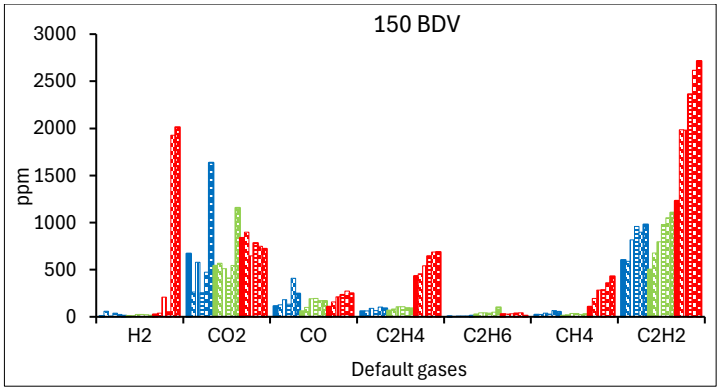

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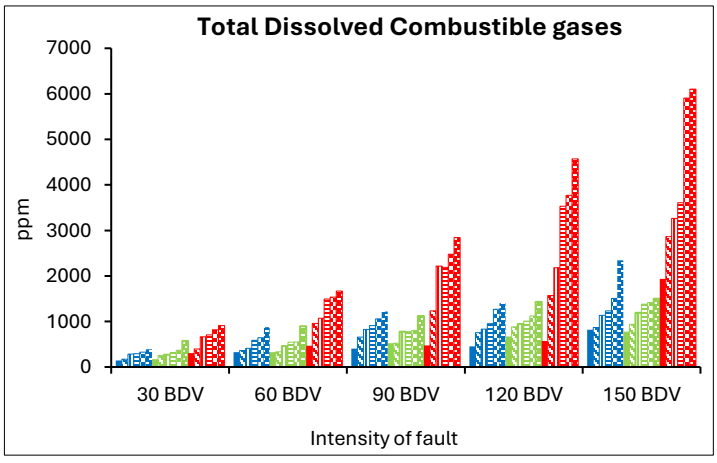

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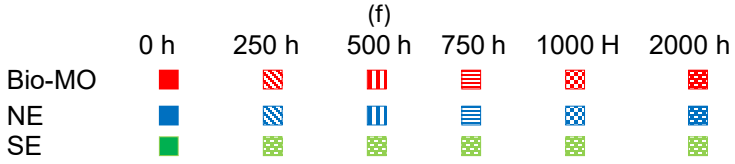


Figure 3.2: Fault Gas Profiles at: a) 30 BDV, b) 60 BDV, c) 90 BDV, d) 120 BDV, e) 150 BDV, and f) Total dissolved combustible gases at different intensities in Bio-Based and Ester Fluids.

Thermal aging enhances gas generation under arc stress, with Bio-MO exhibiting a particularly pronounced increase in acetylene production. To better assess fluid degradation, statistical correlations between %TDCG, %C_2H_2, and aging indicators (%DDF, %TAN, %IFT) under repeated BDV stresses are analyzed using the Pearson correlation coefficient (r) and p-values.

Table 3.3: Values of the concentration of dissolved acetylene
In samples after an arcing fault

Hours	**Repeated Breakdown voltage**				
	30	**60**	**90**	**120**	**150**
Bio-MO					
0	177	269	269	348	1230
250	248	620	766	999	1985
500	413	685	1417	1382	1981
750	451	932	1391	2115	2362
1000	517	973	1556	2240	2240
2000	638	981	1745	2551	2616
NE					
0	348	226	369	502	581
250	150	232	375	611	677
500	159	296	485	630	797
750	221	349	573	724	979
1000	246	369	630	834	1051
2000	365	545	854	975	1104
SE					
0	99	233	316	366	603
250	117	284	444	519	589
500	155	287	560	603	815
750	175	337	535	571	959
1000	183	363	653	744	897
2000	206	391	773	953	981

Table 3.4 : Values of the concentration of total dissolved Combustible gases in samples after arcing.

Hours	Repeated Breakdown voltage				
	30	60	90	120	150
Bio-MO					
0	304	465	437	572	1993
250	396	959	1235	1571	2860
500	660	1074	2214	2178	3261
750	704	1495	2191	3530	3606
1000	815	1538	2479	3767	5908
2000	908	1669	2844	4569	6105
NE					
0	169	327	521	672	774
250	256	335	524	880	937
500	268	461	774	942	1194
750	317	542	779	1005	1381
1000	367	554	804	1124	1414
2000	575	895	1119	1433	1501
SE					
0	144	329	402	453	815
250	171	364	659	757	871
500	282	411	828	829	1138
750	289	584	909	954	1231
1000	328	642	1056	1271	1507
2000	392	873	1221	1401	2345

3.4.2. ACIDITY-C_2H_2/TDCG CORRELATION

The analysis of correlations between acidity or and the concentrations of C_2H_2, Table 3.5, and TDCG, Table 3.6, highlights the impact of fluid chemistry on gas generation during electrical faults. In Bio-MO, strong correlations ($r \geq 0.87$) suggest that the increase in acidity, mainly due to the formation of low molecular weight acids (LMAs) like formic and acetic acid, directly contributes to higher C_2H_2 and TDCG generation. These small acids are highly reactive under arc energy, leading to chain scission and gas release [8]. In contrast, ester liquids exhibit different gas formation behavior. Although they also show high correlations, gas generation is comparatively lower despite higher acidity levels. This is partly due to the formation of high molecular weight acids (HMAs), such as oleic acid, which are less volatile and less prone to fragmentation [9]. Additionally, the cage effect on esters, resulting from their high polarity and viscosity, creates a molecular environment that confines reactive radicals (R•), reduces their mobility, and favors recombination over gas-producing reactions [10]. While repeated electrical

discharge can partially overcome this confinement, chemical stability and low volatility of HMAs still lead to reduced gas generation. In contrast, Bio-MO, composed of non-polar saturated hydrocarbons, exhibits a weaker cage effect, allowing radicals to escape more easily and produce higher levels of gases. Overall, gas generation is not only influenced by acidity but also by molecular structure and radical dynamics.

Table 3.5 : Correlation between dissolved C_2H_2 concentration and TAN value for Bio-MO, NE, and SE.

BDV	30	60	90	120	150
Bio-MO					
r	0.99	0.89	0.92	0.95	0.87
p-value	0.001	0.04	0.02	0.01	0.06
NE					
r	0.89	0.89	0.93	0.94	0.99
p-value	0.04	0.04	0.02	0.02	0.002
SE					
r	0.96	0.99	0.93	0.90	0.85
p-value	0.01	0.001	0.02	0.04	0.07

Table 3.6 : Correlation between TDCG concentration and TAN value for BIO-MO, NE, AND SE.

BDV	30	60	90	120	150
Bio-MO					
r	0.97	0.93	0.95	0.96	0.94
p-value	0.005	0.023	0.015	0.009	0.019
NE					
r	0.83	0.86	0.86	0.88	0.96
p-value	0.08	0.06	0.06	0.05	0.01
SE					
r	0.93	0.98	0.98	0.98	0.92
p-value	0.02	0.003	0.002	0.004	0.03

3.4.3. INTERFACIAL TENSION -C_2H_2/TDCG CORRELATION

The decrease in IFT in insulating liquids reflects their degradation behaviour and is strongly influenced by molecular structure [11]. Ester-based fluids, which contain polar ester groups, are highly susceptible to hydrolysis and oxidation. These reactions produce amphiphilic by-products, such as fatty acids and alcohols, that accumulate at the oil–water interface, disrupt intermolecular cohesion, and significantly reduce IFT. Moisture accelerates this process by promoting hydrolysis, increasing fluid polarity, and advancing degradation [12]. In contrast, Bio-MO, composed of non-polar saturated chains, is less reactive to hydrolysis and

exhibits a more gradual decline in IFT, primarily due to oxidation, which aligns with their limited IFT reduction (~15%). Conversely, NE and SE experience more pronounced degradation, with IFT reductions of 36.6% and 24.5%, respectively. Table 3.7 and 3.8, correlation analysis between IFT and gas formation (C_2H_2, TDCG) under increasing BDV levels reveals distinct degradation patterns. In Bio-MO, moderate to strong negative correlations ($r = –0.831$ to $–0.874$) are observed but are not statistically significant, reflecting the limited formation of polar by-products and minimal IFT variation. In contrast, NE and SE exhibit strong, statistically significant negative correlations ($r < –0.88$, $p < 0.05$), attributed to their polar structures that promote oxidative and hydrolytic degradation. Despite this, esters generate fewer gases, as their degradation tends to produce high-molecular-weight, low-volatility compounds. Bio-MO, however, forms simpler, more volatile fragments, resulting in greater gas generation. Ultimately, IFT alone cannot reliably predict degradation or gas formation across different insulating fluids.

Table 3.7 : Correlation between dissolved C_2H_2 concentration and IFT value for Bio-MO, NE, and SE.

BDV	30	60	90	120	150
Bio-MO					
r	-0.83	-0.62	-0.68	-0.74	-0.87
p-value	0.08	0.3	0.2	0.2	0.05
NE					
r	-0.95	-0.94	-0.96	-0.99	-0.92
p-value	0.02	0.02	0.01	0.002	0.03
SE					
r	-0.83	-0.89	-0.95	-0.99	-0.64
p-value	0.08	0.05	0.01	0.002	0.3

Table 3.8 : Correlation between TDCG concentration and IFT value for Bio-MO, NE, and SE.

BDV	30	60	90	120	150
Bio-MO					
r	-0.74	-0.72	-0.73	-0.79	-0.75
p-value	0.2	0.2	0.2	0.1	0.1
NE					
r	-0.93	-0.91	-0.89	-0.96	-0.87
p-value	0.02	0.03	0.04	0.01	0.06
SE					
r	-0.86	-0.95	-0.92	-0.92	-0.99
p-value	0.06	0.01	0.03	0.03	0.001

3.4.4. DIELECTRIC DISSIPATION FACTOR C_2H_2/TDCG CORRELATION

Based on the correlation data in Tables 3.9 and 3.10 and supported by [13], the Dissipation Factor (DDF), or tan δ, emerges as a critical indicator of dielectric aging, closely linked to dissolved gas formation under electrical stress. In Bio-MO, moderate to strong correlations were observed between DDF and both C2H2 (r = 0.769–0.968) and TDCG (r = 0.807–0.931), particularly at higher BDVs, with statistical significance at BDV 30, 120, and 150. NE showed consistently strong correlations ($r > 0.88$, $p < 0.05$) across all BDVs, while SE exhibited similar trends, especially between BDV 90–150. These results highlight that as esters degrade, polar compounds form, elevating both DDF and gas generation. During arcing faults, intense localized energy causes rapid pyrolysis and partial oxidation of oil molecules, forming fault gases. Additionally, arcs produce ionized species (R^+, OH^-, COO^-), which transiently increase conductivity. In aged oils rich in polar by-products, this ionization is more pronounced and persistent, leading to higher DDF values and irreversible deterioration of dielectric properties.

Table 3.9 : Correlation between C_2H_2 concentration and DDF value for Bio-MO, NE, and SE.

BDV	30	60	90	120	150
Bio-MO					
r	0.91	0.82	0.77	0.90	0.97
p-value	0.03	0.09	0.1	0.04	0.007
NE					
r	0.93	0.92	0.95	0.97	0.93
p-value	0.02	0.03	0.01	0.005	0.02
SE					
r	0.78	0.83	0.88	0.93	0.63
p-value	0.1	0.08	0.05	0.02	0.3

Table 3.10 : Correlation between TDCG concentration and DDF value for Bio-MO, NE, AND SE.

BDV	30	60	90	120	150
Bio-MO					
r	0.84	0.89	0.81	0.93	0.84
p-value	0.07	0.04	0.1	0.02	0.08
NE					
r	0.91	0.90	0.89	0.94	0.88
p-value	0.03	0.04	0.04	0.02	0.05
SE					
r	0.80	0.92	0.86	0.82	0.97
p-value	0.1	0.03	0.06	0.1	0.006

3.4.5. DEGREE OF POLYMERIZATION CO/CO_2 CORRELATION

The generation trends of CO and CO_2 in Bio-MO, NE, and SE after arcing faults show distinct correlations with fault intensity and thermal aging. CO concentrations strongly and inversely correlate with the degree of polymerization (DP), especially under high fault intensity, indicating its origin from cellulose degradation. This aligns with [14] and [15], who identified CO as a key pyrolysis product of aged paper under electrical stress. In contrast, CO_2 shows weaker and statistically insignificant correlations with DP, especially in esters (NE, SE), suggesting it originates mainly from fluid degradation. This is supported by [16], who linked CO_2 formation in esters to thermal oxidation of their oxygen-rich molecules, independent of cellulose. [17] further confirmed this by showing that PPO (Pongamia pinnata oil) produced higher CO_2 but much lower CO levels than mineral oil when aged thermally. Scanning electron microscope (SEM) and X-ray powder diffraction (XRD) analyses also showed less cellulose degradation in PPO-impregnated samples, reflecting its protective effect. Thus, CO is a reliable marker of insulation aging and fault severity, while CO_2 reflects fluid degradation. Lower CO levels in esters at similar CO_2 outputs confirm their enhanced preservation of paper insulation.

Table 3.11 : Values of the concentration of dissolved CO_2 in samples after an arcing fault.

Hours	Repeated Breakdown voltage				
	30	60	90	120	150
Bio-MO					
0	482	588	631	742	838
250	478	467	599	707	897
500	375	458	644	651	646
750	325	501	516	663	784
1000	324	435	560	628	750
2000	665	535	745	722	723
NE					
0	450	458	439	543	552
250	327	527	562	415	568
500	300	357	379	409	510
750	220	303	316	390	413
1000	384	336	407	465	546
2000	2053	1175	1110	1209	1156
SE					
0	134	217	780	969	670
250	305	617	227	301	264
500	380	220	275	656	579
750	129	313	462	337	256
1000	145	196	216	394	473
2000	1438	1889	1798	1729	1636

Table 3.12 : Values of the concentration of dissolved CO in samples after an arcing fault.

Hours	Repeated Breakdown voltage				
	30	60	90	120	150
Bio-MO					
0	12	18	19	27	12
250	24	58	69	97	24
500	39	64	138	142	39
750	51	97	150	214	51
1000	51	107	154	207	51
2000	29	137	145	450	29
NE					
0	15	29	46	59	66
250	43	32	48	107	99
500	36	63	138	139	191
750	37	86	88	145	197
1000	51	80	95	132	172
2000	95	164	93	211	169
SE					
0	24	51	41	41	115
250	25	39	97	112	129
500	85	57	127	125	180
750	92	166	249	257	133
1000	100	188	262	360	410
2000	133	365	309	279	246

Table 3.13 : Correlation between CO_2 concentration and DPv value For Bio-MO, NE, and SE after an arcing fault.

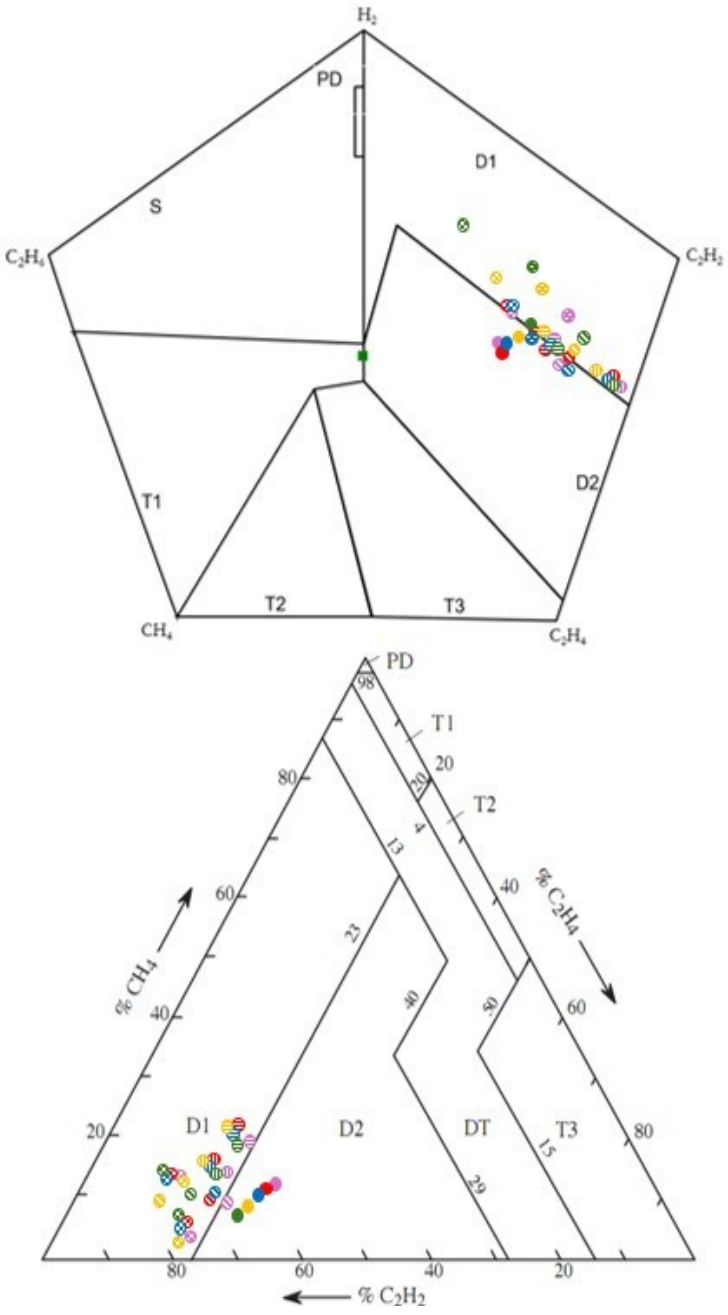
BDV	30 BDV	60 BDV	90 BDV	120BDV	150BDV
Bio-MO					
r	0.06	0.69	–0.03	0.59	0.48
p-value	0.9	0.1	1	0.2	0.3
NE					
r	–0.46	–0.37	–0.42	–0.40	–0.44
p-value	0.4	0.5	0.4	0.4	0.4
SE					
r	-0.52	-0.47	-0.25	-0.18	-0.37
p-value	0.3	0.3	0.6	0.7	0.5

Table 3.14 : Correlation between CO concentration and DPv VALUE FOR Bio-MO, NE, AND SE after an arcing fault

BDV	30	60	90	120	150
Bio-MO					
r	–0.73	–0.85	–0.91	–0.71	–0.88
p-value	0.1	0.03	0.01	0.1	0.02
NE					
r	–0.81	–0.80	–0.64	–0.92	–0.83
p-value	0.05	0.06	0.2	0.01	0.04
SE					
r	-0.92	-0.75	-0.91	-0.85	-0.63
p-value	0.009	0.09	0.01	0.03	0.20

3.5. FAULT GAS ANALYSIS AND DIAGNOSIS

The fault diagnoses obtained using Duval's triangle and pentagon methods (Triangle/Pentagon 1 for Bio-MO, 3 for non-mineral oils), as shown in Figure 3.2, can be interpreted through the lens of statistical correlations between dissolved gases (C_2H_2, TDCG, CO) and aging markers [18] and [19].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D2
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20
T2
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40
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60
% CH4
23
40
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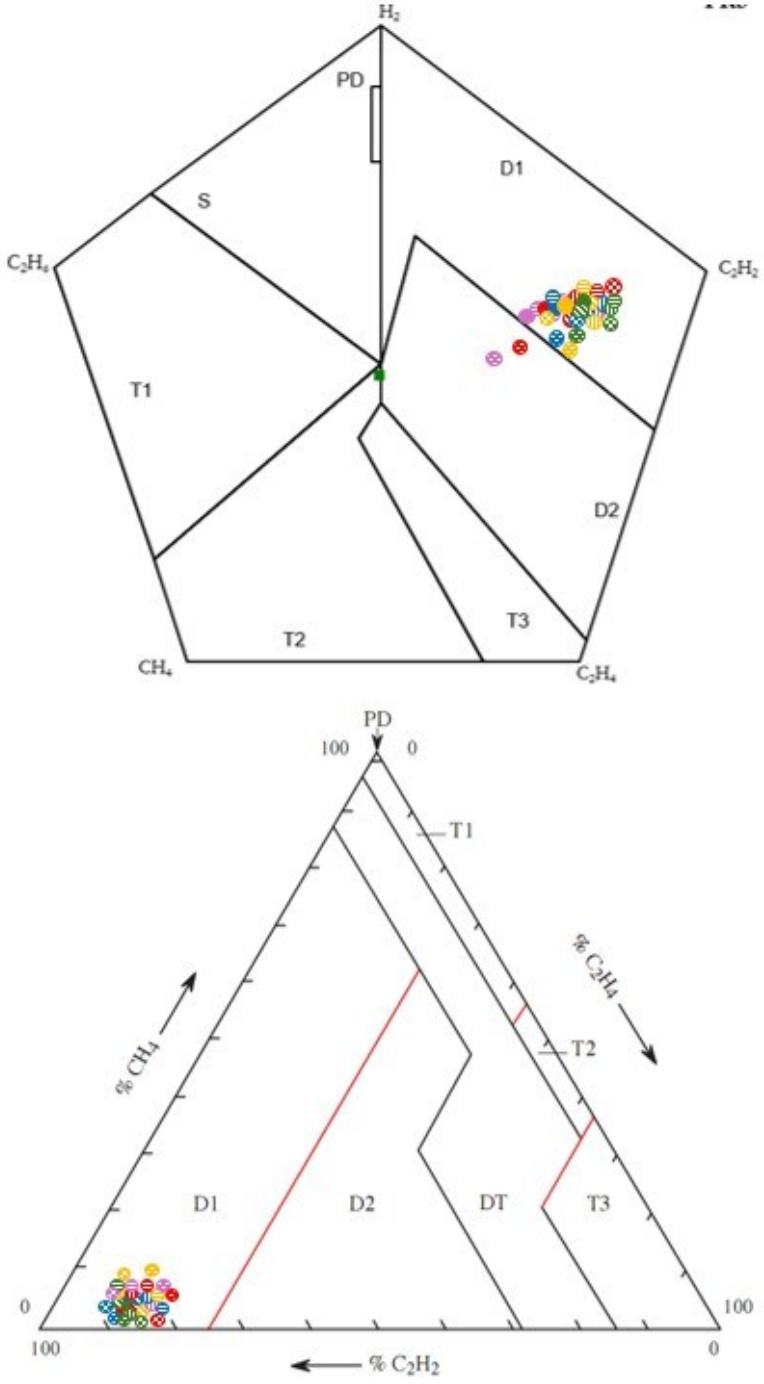
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CH4
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D1
D2
DT
T3
0
100
100
0
% C2H2

(b)

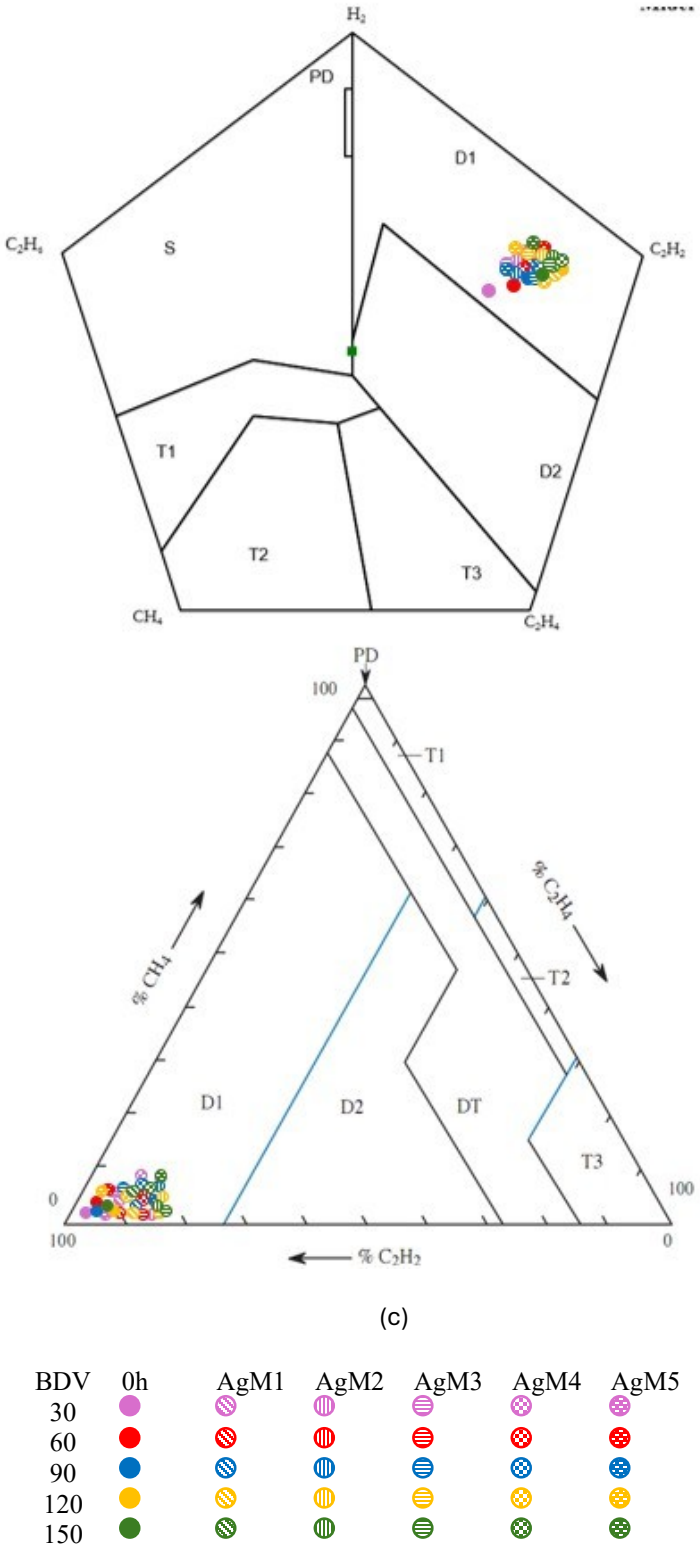

Figure 3.3 : Illustration of fault gas diagnosis using Duval's and Duval's triangle methods:

(a) Bio-MO; (b) NE; (c) SE.

In the case of Bio-MO, powerful correlations between C_2H_2 and acidity ($r > 0.95$, $p < 0.05$), as well as with DDF (up to $r = 0.97$, $p = 0.007$), underscore the fluid's high susceptibility to arc-induced degradation. This explains the frequent D2 diagnoses observed, particularly with Duval's triangle. Partial mismatches often reflect evolving gas ratios caused by increases in fault intensity, which alter the gas profile while maintaining the dominant fault type. For esters (NE and SE), consistently high correlation coefficients (NE: $r = 0.89–0.99$; SE: $r = 0.85–0.99$ between C_2H_2 and acidity) confirm that gas generation increases with aging. However, ester degradation mechanisms, primarily hydrolysis and oxidation, produce high-molecular-weight polar compounds with low volatility, limiting acetylene formation. Similarly, TDCG and DDF also show strong correlations with aging (e.g., NE: $r > 0.88$), yet these gases remain within D1 thresholds, preserving diagnostic stability. Despite a strong negative correlation between CO and Dp ($r \approx –0.9$), reflecting cellulose degradation, CO is excluded from the Duval method, reducing its diagnostic utility and potentially masking advanced aging in liquid-impregnated systems.

Table 3.15 : Fault diagnosis details for Duval's triangle AND Duval's pentagon

Samples	Duval's methods		Fault Matching
	Pentagon	Triangle	
	Code	Code	
Unaged			
Bio-MO**	D2	D2	Matched
NE**	D1	D1	Matched
SE**	D1	D1	Matched
AgM1			
Bio-MO _30	D2	D2	Matched
Bio-MO _60_90_120	D1	D2	Partially matched
Bio-MO _150	D1	D1	Matched
NE**	D1	D1	Matched
SE**	D1	D1	Matched
AgM2			
Bio-MO**	D1	D2	Partially matched
NE**	D1	D1	Matched
SE**	D1	D1	Matched
AgM3			
Bio-MO _30_60	D1	D2	Partially matched
Bio-MO _90_120_150	D1	D1	Matched
NE**	D1	D1	Matched
SE**	D1	D1	Matched
AgM4			
Bio-MO**	D1	D1	Matched
NE**	D1	D1	Matched
SE**	D1	D1	Matched
AgM5			
Bio-MO _30	D2	D1	Partially matched
Bio-MO _60_90_120	D1	D1	Matched
NE_30_60	D1	D2	Partially matched
NE_90_120_150	D1	D1	Matched
SE**	D1	D1	Matched

** Sample at all intensities

3.6. CONTRIBUTION

This study significantly advances previous work on gas formation behaviour in ester-based insulating fluids by introducing and analyzing a bio-based hydrocarbon oil (Bio-MO) under identical arcing fault conditions as those used in earlier studies on synthetic esters and mineral oils. Unlike the work by [6], which focused solely on synthetic esters, and [16], which examined mineral oil and natural esters, the current research provides the first systematic comparison including Bio-MO. This study explores the possible link between gas increases and aging markers as potential predictors of fault evolution.

3.7. CONCLUSION

This study provides a comparative evaluation of the gas formation behaviour and degradation of Bio-MO, SE, and NE under arcing faults and aging. Bio-MO showed the highest gas generation, especially in C2H2, due to the breakdown of volatile light acids. In contrast, NE and SE formed fewer gases thanks to their polar, chemically stable structures. TAN and DDF exhibited strong correlations with gas evolution ($r > 0.9$, $p < 0.05$), confirming their predictive value for fault development. Notably, Duval diagnostics showed a transition from D2 to D1 in Bio-MO, reflecting a shift from high- to low-energy discharges, while SE consistently remained in D1 regardless of aging. The work also introduces a novel statistical framework using correlation coefficients (r, p-value) to link gas formation with aging indicators under repeated breakdown voltages. These insights may offer engineers predictive tools for monitoring fluid degradation and diagnosing fault types. Future studies should involve larger datasets and longer aging durations to reinforce the reliability and scope of the correlations observed.

CHAPITRE 4

INFLUENCE OF DISSOLVED OXYGEN ON THE GASSING TENDENCY OF BIODEGRADABLE INSULATING LIQUIDS UNDER THERMAL AND ELECTRICAL FAULTS

AVANT PROPOS

Ce chapitre reproduit et étend le contenu de: M. T. Agouassi, U. Mohan Rao, I. Fofana and Y. Hadjadj, Fethi Maghnefi " Influence of Dissolved Oxygen on the Gassing Tendency of Biodegradable Insulating Liquids under Thermal and Electrical Faults," in IET.

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TITRE EN FRANÇAIS : Influence de l'oxygène dissous sur la tendance au gazage des liquides isolants biodégradables soumis à des défauts thermiques et électriques.

RÉSUMÉ : La présence d'oxygène constitue un facteur susceptible d'altérer les profils de gaz interprétés par l'AGD, malgré son usage généralisé pour le diagnostic des défauts. Celui-ci accélère non seulement la dégradation des fluides, mais modifie également la nature et la concentration des gaz produits, risquant ainsi de fausser l'interprétation des conditions des transformateurs si les modèles classiques sont appliqués sans précaution. Cette étude examine l'impact de l'oxygène dissous sur le comportement de formation de gaz de deux liquides isolants biodégradables chimiquement distincts, une huile biosourcée (Bio-MO) et un ester synthétique (SE), soumis à des contraintes thermiques et électriques contrôlées.

Les concentrations initiales d'oxygène ont été systématiquement ajustées avant d'exposer les fluides à des défauts simulés en laboratoire (arcs électriques et vieillissement thermique par cycles de chauffage localisés). Les profils de gaz générés ont ensuite été analysés par les méthodes standards de DGA, dont les outils de Duval (Triangle et Pentagone), afin d'évaluer leur pertinence diagnostique. Les résultats mettent en évidence une corrélation étroite entre la teneur en oxygène dissous et la génération de gaz, soulignant la nécessité d'adapter les cadres d'interprétation traditionnels aux spécificités oxydatives des fluides biodégradables. Ces résultats apportent des éléments essentiels pour un diagnostic plus fiable et une meilleure gestion des transformateurs utilisant des liquides isolants alternatifs.

4.1. ABSTRACT

DGA, widely used for fault diagnosis, can be significantly influenced by the presence of oxygen. Oxygen not only accelerates fluid degradation but also alters the type and concentration of fault gases generated, potentially leading to misinterpretation of transformer conditions if conventional DGA models are applied uncritically. This study investigates the impact of dissolved oxygen on the gas formation behaviour of two chemically distinct biodegradable insulating liquids, bio-based hydrocarbons (Bio-MO) and synthetic esters (SE), under controlled thermal and electrical stress conditions. Initial oxygen concentrations were systematically varied before subjecting the fluids to laboratory-simulated faults, including arcing and thermal aging via localized heating cycles. Post-fault gas profiles were analyzed using standard DGA methods, including Duval's Triangle and Pentagon, to assess diagnostic relevance. The results reveal a strong correlation between dissolved oxygen levels and gas generation, emphasizing the need to adapt traditional DGA interpretation frameworks to account for the oxidative sensitivity of biodegradable fluids. These findings provide critical insights for more accurate fault diagnosis and asset management in transformers employing alternative insulating liquids.

4.2. INTRODUCTION

In recent years, the growing emphasis on environmental sustainability and fire safety has driven the power industry to explore alternatives to conventional mineral oils used as

insulating liquids in power transformers. Among these alternatives, biodegradable insulating liquids, particularly synthetic esters, and new bio-based hydrocarbons have emerged as promising candidates due to their renewable origin, lower environmental impact, and favorable dielectric and thermal properties. However, despite their advantages, the long-term performance and degradation behaviour of these fluids under real operating conditions remain less understood, especially concerning their gas formation characteristics under electrical and thermal stresses [1–2].

One of the most critical aspects of transformer monitoring and diagnostics is the analysis of dissolved gases produced during the degradation of insulating liquids. Known as DGA, this technique is widely used to detect and identify electrical faults, such as partial discharges, hot spots, and arcing. Traditional interpretation tools like the Duval Triangle and Pentagon are calibrated for mineral oils and assume specific gas formation patterns. However, due to their distinct chemical structures, biodegradable insulating liquids exhibit unique gas formation behaviors that differ significantly from those of mineral oils. If not thoroughly characterized, these differences can lead to inaccurate fault interpretations [3]. While early studies focused primarily on DGA, research conducted over the past decades has progressively integrated the role of fluid composition and aging by-products in gas generation mechanisms [4].

Dissolved oxygen plays a central role in the degradation of insulating liquids by triggering and sustaining oxidation reactions. When transformer oils or natural esters are exposed to oxygen, hydrocarbon radicals interact with O_2 to form peroxides and reactive species that accelerate aging. This process produces acids, aldehydes, and polymerized products, which increase acidity, viscosity, and turbidity, ultimately impairing heat transfer and electrical performance [5]. In mineral oils, prolonged oxidation leads to sediment and wax formation through polycondensation reactions, while in esters, gelling and film formation hinder fluid circulation. Both effects compromise the cooling and insulation functions, shorten service life, and raise the risk of failures [6].

Additionally, dissolved gas patterns shift depending on fluid type: ethane (C2H6) dominates in soybean-based esters, linked to lipid peroxidation, while methane and ethylene

are more prevalent in mineral and synthetic oils. These findings underline the need to control oxygen ingress in transformers to preserve fluid integrity, slow degradation, and maintain reliable diagnostic interpretations via DGA [7].

This paper aims to evaluate the impact of dissolved oxygen on the gas formation behaviour of bio-based hydrocarbon (Bio-MO) and synthetic ester (SE) insulating liquids under simulated thermal and electrical faults. Gases formed under different O_2 concentrations were analyzed by DGA, with 50 ml samples collected using syringes in accordance with ASTM D3612 and compared to base fluids. Thermal faults were induced using an immersed heating element, while electrical faults were created using a plate-to-plate arc cell. Duval's diagnostic tools were applied to interpret gas patterns, alongside post-fault acidity value and DDF measurements. This comparative approach provides insights into fluid degradation mechanisms and the role of oxygen in fault-induced chemical transformations are expected to improve the interpretation of DGA results for alternative fluids and provide guidance for future standards addressing oxygen-induced degradation in non-mineral insulating liquids.

4.3. OVERVIEW OF OXYGEN'S ROLE IN INSULATION AGING AND DEGRADATION

The oxidation process of insulating liquid is shown in Figure 4.1. This begins with the radical activity of hydrocarbon molecules (RH), some of which dissociate into hydrocarbon radicals (R•) and hydrogen atoms (H•), a process known as initiation (I). These hydrocarbon radicals subsequently react with oxygen (O_2) to form peroxy radicals (ROO•), marking the propagation phase (P). From this point, oxidation progresses through two main reaction pathways: autooxidation (A) and termination (T). In the autooxidation route, peroxy radicals (ROO•) abstract hydrogen atoms from RH to form hydroperoxides (ROOH), which then decompose into alkoxy (RO•) and hydroxyl (OH•) radicals. These new radicals further react with RH, producing alcohol, water, and additional hydrocarbon radicals, thereby sustaining a self-propagating cycle as long as oxygen remains available. In parallel, the termination reaction (T) involves the combination of two peroxy radicals to form non-radical products such as oxygen, aldehydes, alcohols, acids, and hydrocarbon residues. Both autooxidation and

termination contribute to the formation of various degradation by-products and involve radical branching.

The oxidation of insulating materials in transformers results from a complex interaction between internal components and operating conditions. Metallic elements such as copper, steel, and aluminum used in conductors and structural parts play a catalytic role by promoting hydroperoxide decomposition and forming free radicals, especially in the presence of dissolved oxygen. Copper, particularly in its ionic form, accelerates the production of organic acids and oxidative by-products [8].

In ester-based fluids, oxidation is often accompanied by hydrolysis, particularly in the presence of moisture. Esters tend to generate a higher proportion of high molecular weight acids (HMA), less volatile and less soluble in moisture, compared to mineral oils, which produce more low molecular weight acids (LMA). LMAs are more hydrophilic and therefore have a greater influence on the degradation rate of the solid insulation by hydrolysis, whereas HMAs have a limited impact on solid insulation [9].

According to [10], these compounds, accumulating in the paper insulation, initiate cellulose hydrolysis, which is further intensified by absorbed moisture and the formation of hydronium ions (H_3O^+). This dual mechanism of oxidation and hydrolysis leads to a reduction in the DP, degrading the mechanical properties of the paper.

The synergistic interaction between metals, insulating fluid, and oxygen accelerates the chemical aging of the insulation system, leading to the degradation of key physicochemical properties, such as increased DDF, acidity, IFT, and viscosity, while also progressively darkening the color of the insulating liquid [9].

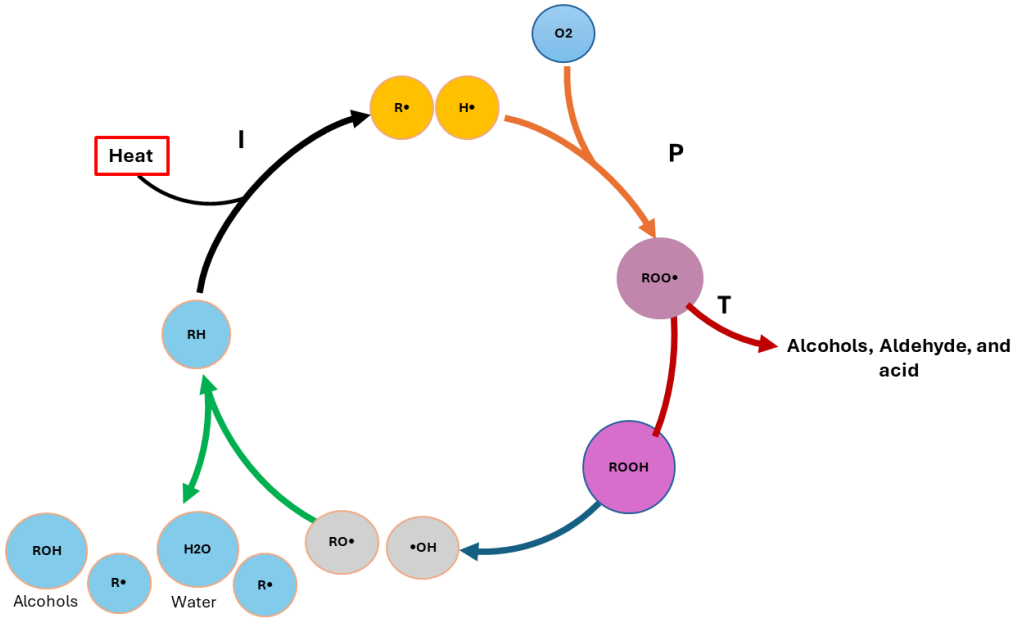


Figure 4.1 : Mechanism of oil oxidation.

4.4. EXPERIMENTAL PREPARATION AND PROCEDURE

4.4.1. MATERIALS

Two liquids chosen for experiments included synthetic ester (SE) and bio-hydrocarbon (Bio-MO) dielectric liquids that are manufactured for HV transformers. Table 4.1 presents the standard methods employed to assess the main properties and characteristics of these oils [1-2].

Table 4.1 : Significant parameters of Bio-MO and SE.

Parameters	**Standard**	**Unit**	**Bio-MO**	**SE**
DDF at 90ºC	IEC 60247	10^{-3}	0.28	8
Water content	ASTM D1533	ppm	10	50
Viscosity at 40ºC	ISO 3104	mm^2/S	3.737	29
Flash point	ISO 2592	ºC	146	260
IFT	ASTM D971	mN/m	50.5	-
Acidity	ASTM D974	mg KOH/g	0.001	<0.03
Inhibitors content	IEC 60666	-	yes	yes

4.5. TEST PROCEDURE

4.5.1. DISSOLVING OXYGEN THE LIQUIDS

In this study, 1300 ml of bio-hydrocarbon and synthetic ester liquids were prepared by degassing and dehydrating at room temperature and 60°C, respectively, for 48 hours to remove dissolved gases and initial moisture (see Table 4.2).

Table 4.2 : Physicochemical characteristics of insulating liquids following degassing and dehydration treatment.

Parameters	Standard	Unit	Bio-MO	SE
DDF at 90ºC	IEC 60247	10^{-3}	0.26	1.45
Water content	ASTM D1533	Ppm	3	31
Acidity	ASTM D974	mgKOH/g	0.002	0.032

The liquids were then transferred to a 2000 ml borosilicate glass container, fully wrapped in aluminum foil to protect them from light. This container was equipped with a hermetically sealed cap connected to a gas supply valve and two additional valves: one for the vacuum pump and pressure sensor, and another for sampling, as shown in Figure 4.2. A magnetic stir bar was placed inside the container to ensure vigorous agitation, promoting a homogeneous distribution of O_2 partial pressure in the liquid phase. Before testing, the entire system was degassed for 24 hours, followed by the introduction of pure oxygen (>99.9%) until a pressure of approximately 5.6 PSI (38.61 kPa) was reached and was stopped.

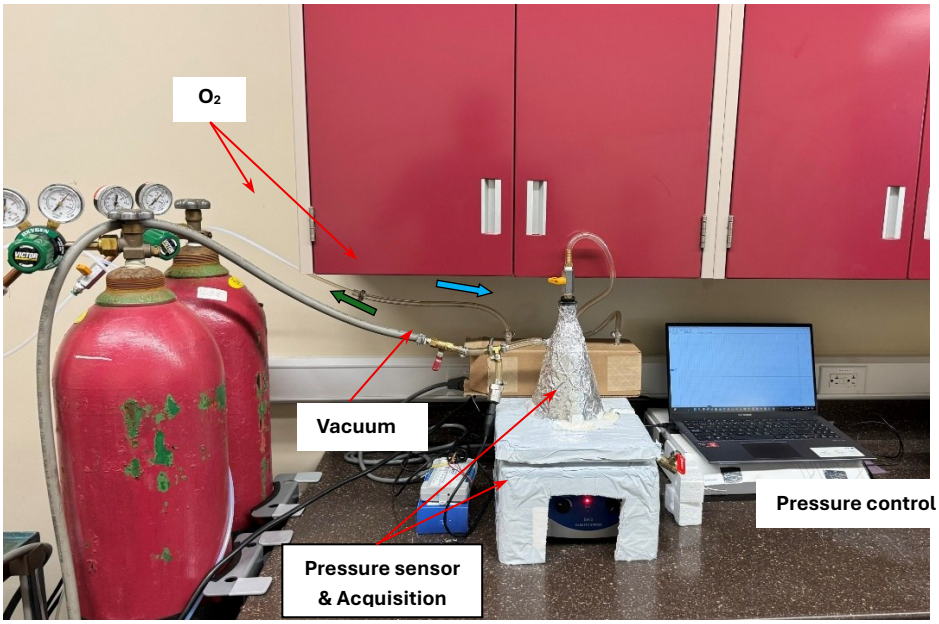


Figure 4.2 : Experimental setup for dissolved oxygen control.

According to [11], the system's progression toward equilibrium may be monitored by continuously measuring the oxygen partial pressure in the gas phase, shown in Figure 4.3. All experiments were conducted at a laboratory ambient temperature of approximately 22°C.

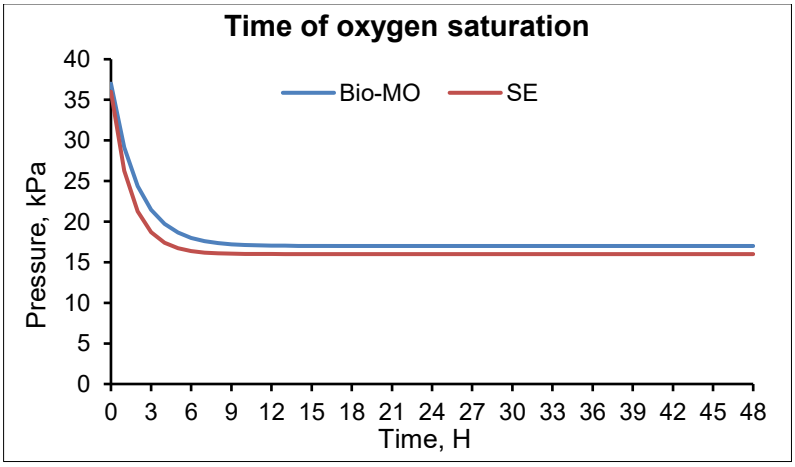


Figure 4.3 : Evolution of O_2 partial pressure in the headspace of a closed flask until equilibrium.

Bio-MO and SE, referred to as B and S samples, respectively, are labeled B0 and S0 after the degassing process. The samples are then categorized into three increasing levels of initial dissolved oxygen concentration, Levels 1 to 3 (saturated state), as detailed in Table 4.3.

Table 4.3: Naming of SE and Bio-MO Samples by Dissolved O_2 Content.

Types of liquids	Abbreviation	Oxygen, ppm
Bio-MO	B0	8186
	B1	13100
	B2	30048
	B3	170000
SE	S0	6780
	S1	20200
	S2	25299
	S3	172000

4.5.2. SIMULATED THERMAL FAULT

According to [12], Thermal faults were simulated by immersing a coil-shaped heating element into the insulating liquid and applying electrical current to produce localized hot spots (HS). At moderate input power (~300 W), the element reached a stable saturation temperature of 320–330 °C, while higher powers (>1200 W) led to non-uniform heating with hot spot temperatures exceeding 1000 °C. This configuration enabled localized heating, thereby facilitating the generation of characteristic fault gases, which were subsequently quantified through DGA to assess the severity of the fault [13].

Consequently, in a hermetically sealed borosilicate glass vessel, fully wrapped in aluminum foil to protect it from light and to prevent gas losses, a constant input of 140 V (delivering 13.84 A) supplied through a variac allowed the reproduction of a controlled thermal fault, as shown in Figure 4.4. To avoid exceeding temperature limits that could compromise the safety of the test cell, the current was switched off after the heating period, which lasted approximately 30 minutes for the Bio-MO. During this period, the liquid temperature reached 130 °C, a value considered critical due to its proximity to the flashpoint (Figure 4.5a). For the SE, the heating period lasted approximately two hours, with the liquid temperature peaking at 230 °C before cooling naturally (Figure 4.5b), corresponding to a T1-type thermal fault. All samples were therefore subjected to a simulated T1-type thermal fault under these controlled conditions. To ensure homogeneous mixing and a uniform temperature throughout the liquid, a magnetic stirrer was used during the entire process. An immersed type-K thermocouple

ensured accurate monitoring of the liquid temperature. For Bio-MO, the abrupt drop after 2.75 h is an artefact caused by a power cut and brief thermocouple handling, not a liquid transition.

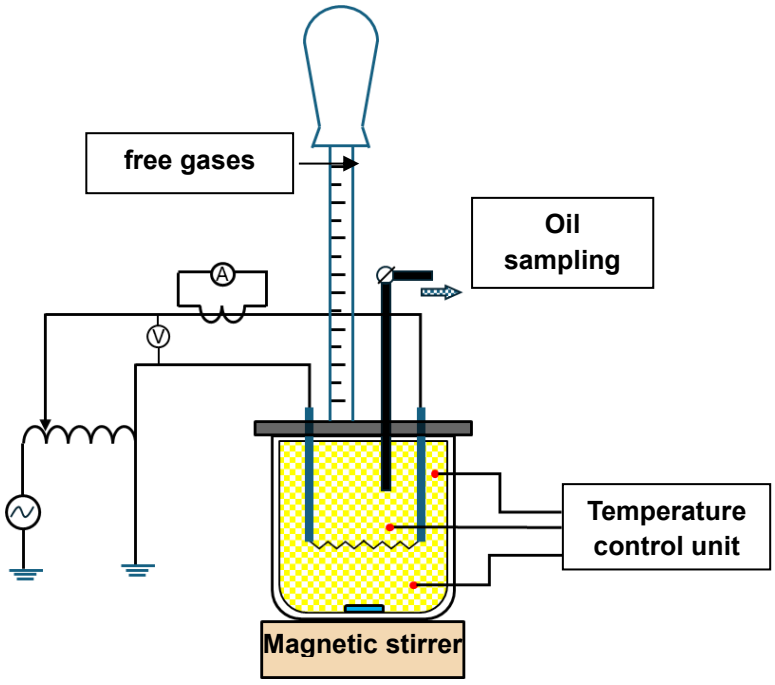
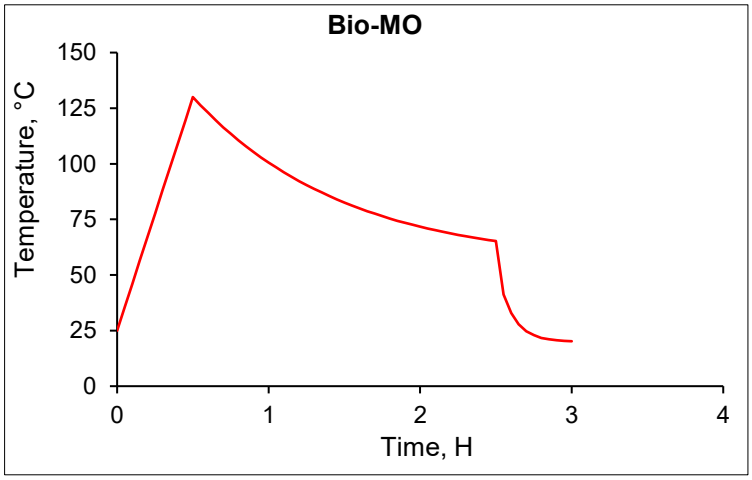
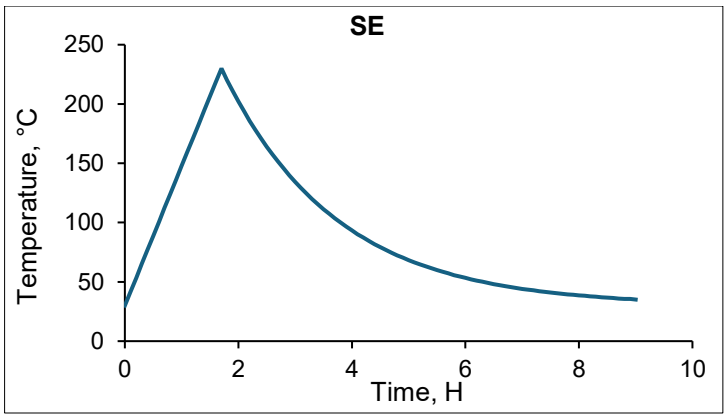


Figure 4.4 : Test cell configuration for thermal fault and electrical circuit connection.



(a)



(b)

Figure 4.5: Heating and cooling period of different liquids: a) Bio-MO, b) SE.

4.5.3. SIMULATED ELECTRICAL FAULT (BDV)

Electric arc discharge faults were generated using flat electrodes spaced 2.5 mm apart. The test cell was filled with an insulating liquid, and a 60 Hz AC voltage was gradually applied at a controlled rate of 2 kV/s to create arc discharges between the electrodes. Fault intensities were simulated through 100 repeated breakdown voltage (BDV) events, with a 2-minute interval between each event, using a setup similar to that described in [14].

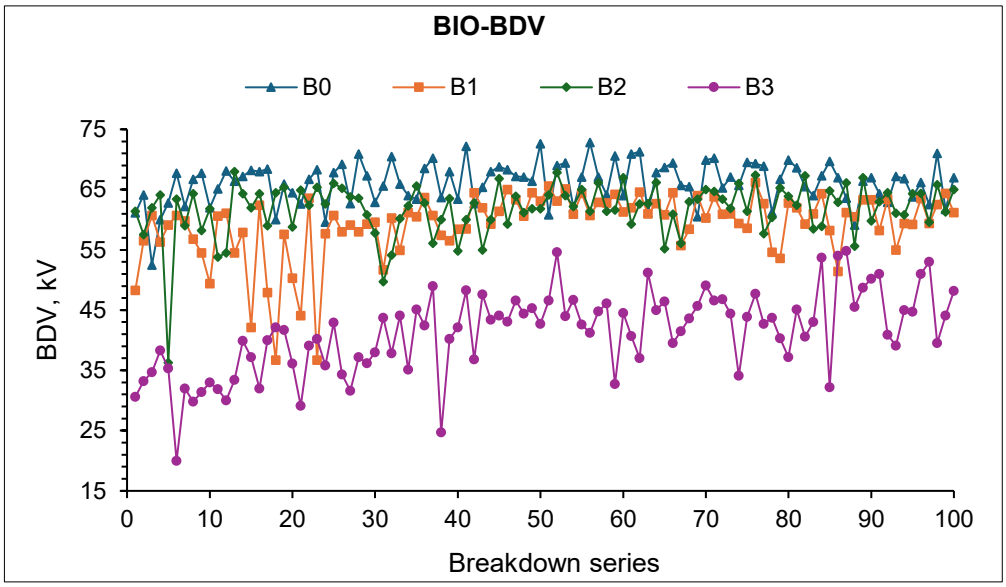


Figure 4.6: Experimental results of arcing faults in various Bio-MO liquid samples.

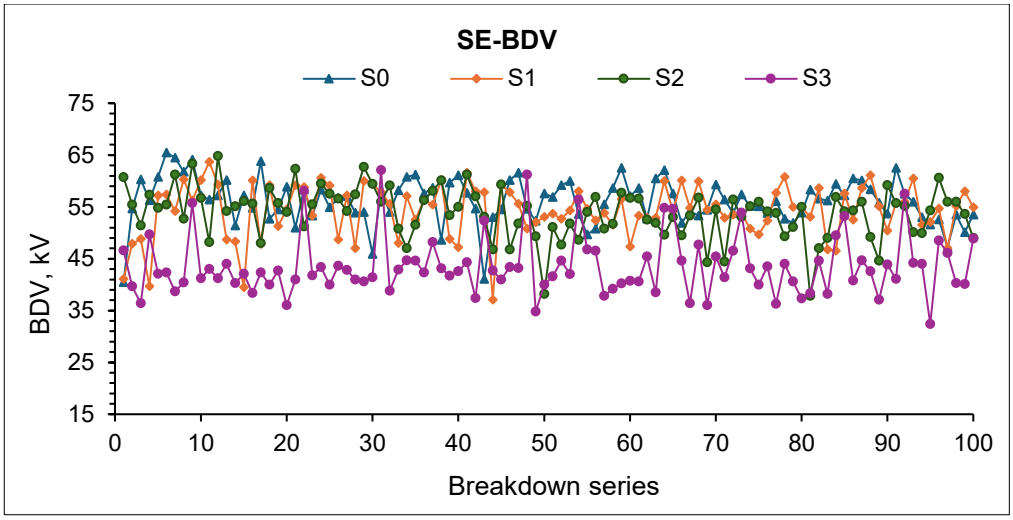


Figure 4.7: Experimental results of arcing faults in various SE liquid samples.

As shown in Figures 4.6 and 4.7, the BDV of dielectric liquids decreases noticeably at high oxygen concentrations (B3 and S3), highlighting the influence of chemical composition on dielectric strength. Higher concentration of O2 levels reduces breakdown voltage by increasing the density of charge carriers through their paramagnetic nature, which facilitates the formation of discharge channels and weakens the liquid's insulating capability [15–16].

4.6. RESULTS AND DISCUSSIONS

4.6.1. ACIDITY

Following exposure to electrical arc and thermal faults, a clear correlation is observed between the rise in acidity after the fault and the initial dissolved oxygen concentration, as shown in Figure 4.8. Bio-MO_BDV and Bio-MO_HS refer to the Bio-MO liquid subjected to breakdown voltage and hotspot faults, respectively. Similarly, SE_BDV and SE_HS refer to the synthetic ester liquid under breakdown voltage and hotspot fault conditions, respectively.

The difference in acidity values between Bio-MO and SE is attributed to the molecular structure of SE, which is primarily composed of polyols bonded to saturated carboxylic acid chains [15].

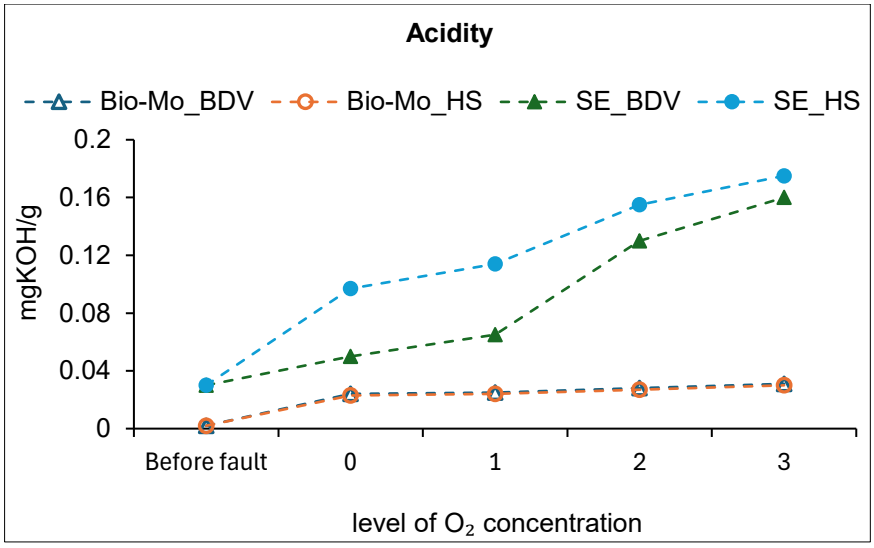


Figure 4.8: Acidity values following fault application under varying O_2 concentrations.

Triplet Oxygen ($^3O_2$), in its stable diradical form, has high activation energy, making its oxidation reactions highly dependent on external energy input. Thus, the thermal energy generated by the heating element, the intense electromagnetic fields generated by electrical arcing faults, which promote the injection of free electrons, constitute a sufficient energy source to break covalent bonds within insulating liquids. This process initiates the formation of free radicals, generally through the abstraction of a hydrogen atom bonded to a carbon atom [17].

According to [18], the SE oxidation proceeds through two main mechanisms. The first involves methyl groups, which exhibit high reactivity toward oxygen due to their proximity to hydroxyl functions, rapidly forming hydroperoxides. The second mechanism involves oxidation through the acyl fragment of the molecule, particularly in the case of pentaerythritol esters. This process is characterized by the decomposition of hydroperoxide and keto-peroxide intermediates, leading to the formation of species such as peroxide acids and peroxide esters. Both pathways occur simultaneously, with the relative contribution of each depending on the molecular structure. Moreover, even a low level of dissolved moisture (measured after treatment at 27.6 ppm) is sufficient to trigger hydrolysis, causing the cleavage of ester bonds and the formation of carboxylic acids and alcohols. The increase in acidity thus results from a synergistic interaction between oxidation and hydrolysis, which is particularly pronounced in

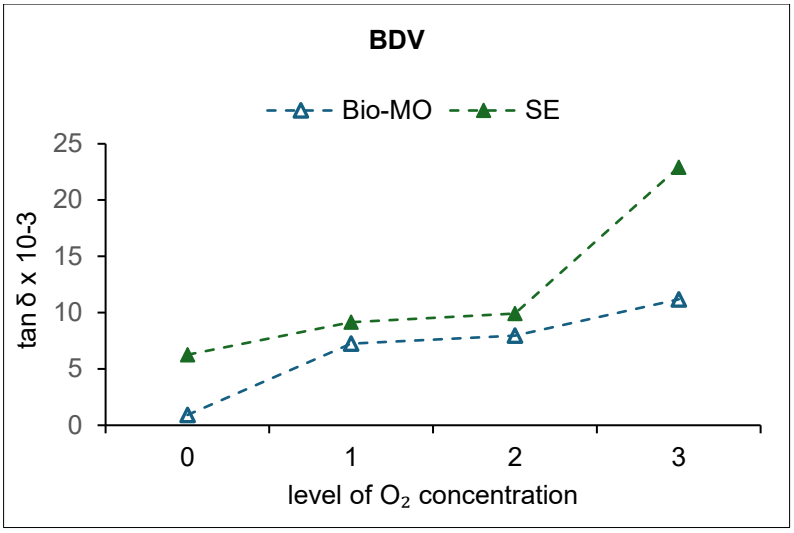
esters due to their polar chemical structure and strong affinity for water. In [19], the authors have shown that the oxidation of synthetic esters is mainly characterized by the formation of high molecular weight acids as oxidation products.

Bio-MO undergoes an oxidation process like that of SE, primarily initiated by the reaction of molecular oxygen with the saturated hydrocarbons present in its structure. Although these compounds are relatively stable, oxygen can interact with activated methylene groups, leading to the formation of hydroperoxides, which decompose into oxidized products such as carboxylic acids, alcohols, and various polar compounds [20]. Bio-MO oxidation produces volatile, hydrophilic, low molecular weight acids that promote hydrolytic degradation of solid insulation [21].

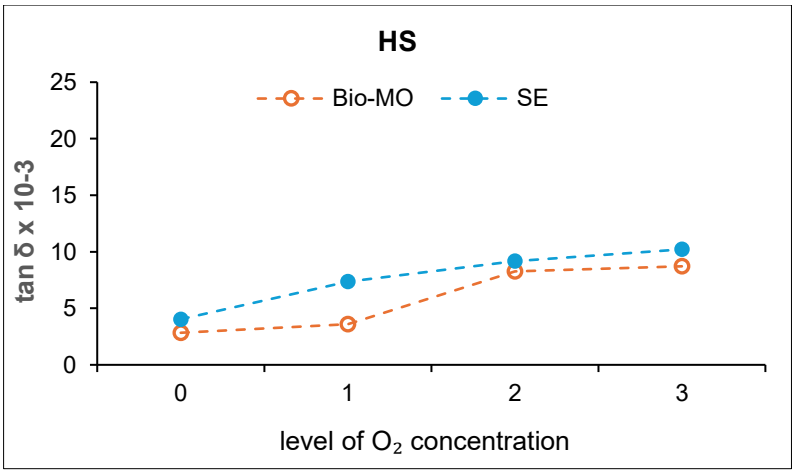
For Bio-MO samples (B0 to B3), the acidity differences between BDV and HS faults remain minimal, at 4.14% to 3.23%, indicating a relatively stable chemical response to different fault stresses. In contrast, a pronounced acidity gap of 94% was observed in the synthetic ester samples between S0_BDV and S0_HS. This disparity can be attributed to the inherently slow reactivity of molecular oxygen, which requires prior formation of radical species to initiate oxidation. Thermal faults promote sustained oxidation by exposing the fluid to uniform heat, enhancing bond degradation and acid formation. Conversely, electrical faults generate highly localized and short-duration heating (~50μs), limiting molecular decomposition. At higher dissolved oxygen levels, acidity differences tend to narrow, suggesting that oxidation reactions intensify under BDV conditions, with oxygen acting as a catalytic agent.

4.6.2. DIELECTRIC DISSIPATION FACTOR

The DDF, or tan δ, is one of the most critical electrical parameters used to monitor the quality of transformer insulating oil. The DDF was measured following the electrical arcing and thermal fault to assess the condition of the oil after the fault. Figure 4.9 presents the DDF of the base Bio-MO and samples with varying oxygen content across a frequency of 60 Hz. The increase in the DDF observed in both synthetic ester (SE) and bio-based mineral oil (Bio-MO) correlates with the degradation processes induced by thermal and electrical faults and is strongly influenced by the initial concentration of dissolved oxygen.



(a)



(b)

Figure 4.9: Dielectric dissipation factor (DDF) at 60 Hz after fault application under different O_2 levels: (a) BDV fault and (b) HS fault.

4.6.3. WATER CONTENT

An increase in the initial dissolved oxygen concentration in the synthetic ester results in a clear rise in water content after both electrical and thermal faults. Prior to fault application, all samples were degassed and dehydrated, with an initial water content of approximately 30 ppm for S0, indicating that the water measured after faults is mainly generated during fault-induced chemical reactions. After electrical arcing, the water content increases from about 70 ppm at S0 to 164.2 ppm at S3. Thermal hot-spot faults lead to significantly higher water contents, ranging from 88.2 ppm at S0 to 371.6 ppm at S3.

The higher water generation under thermal faults is not solely related to the applied energy but is primarily controlled by the effective reaction time. Electrical discharges are short-duration, high-energy events dominated by rapid pyrolysis and radical recombination, which limit oxygen-driven oxidation and hydrolysis processes. In contrast, thermal faults subject the fluid to sustained high temperatures, promoting progressive hydroperoxide decomposition and continuous ester hydrolysis in the presence of dissolved oxygen. This kinetic regime favors cumulative water formation [12-13].

The resulting increase in water content accelerates ester hydrolysis and contributes to the formation of carboxylic acids, as reflected by the rise in TAN. The simultaneous accumulation of water and acidic species enhances the polarity and ionic conductivity of the fluid, leading to increased dielectric losses and a higher DDF. These observations reveal a time-dependent degradation pathway linking O_2 ingress, moisture formation, TAN increase via hydrolysis and oxidation, and elevated dielectric loss (tan δ) in synthetic esters under fault conditions

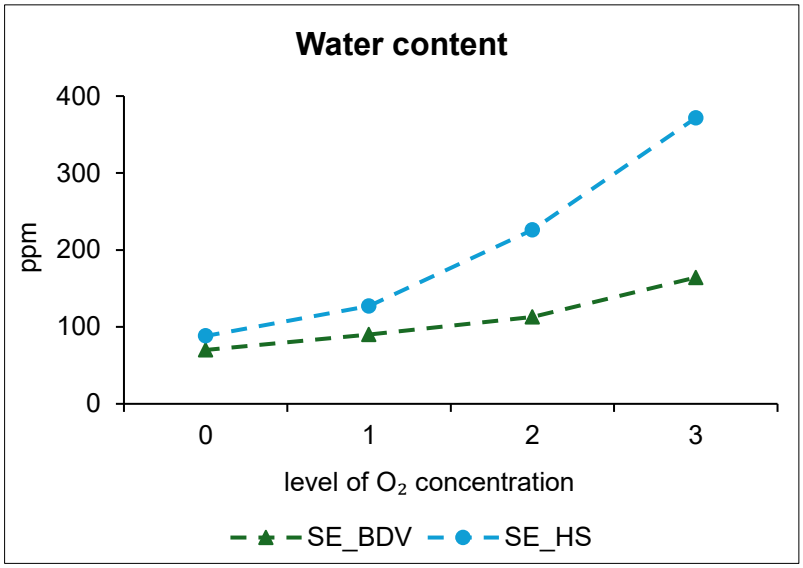


Figure 4.10. Water content evolution in synthetic ester as a function of initial O_2 concentration after faults.

4.7. FAULT GASES

4.7.1. THERMAL FAULT-GENERATED DISSOLVED GASES

Figure 4.11 and 4.12 present the analysis of experimental results, highlighting the effect of dissolved oxygen on the thermal degradation of SE and Bio-MO under a hot-spot type fault. In Bio-MO, the percentage increase in CO_2 across samples B1 to B3, relative to the reference sample, shows a clear upward trend, rising from 10% in B1 to 52% in B2, and reaching a peak of 126% in B3. Thus, CO_2 is identified as the dominant gaseous by-product.

In SE case, a progressive increase in CO is observed relative to the reference sample S0, rising from 2% in S1 to 4% in S2, and peaking at 64% in S3, indicating a significant degradation. As for CO_2, the increase reaches 43% in S1, drops to 6% in S2, then rises again to 54% in S3 (saturated state).

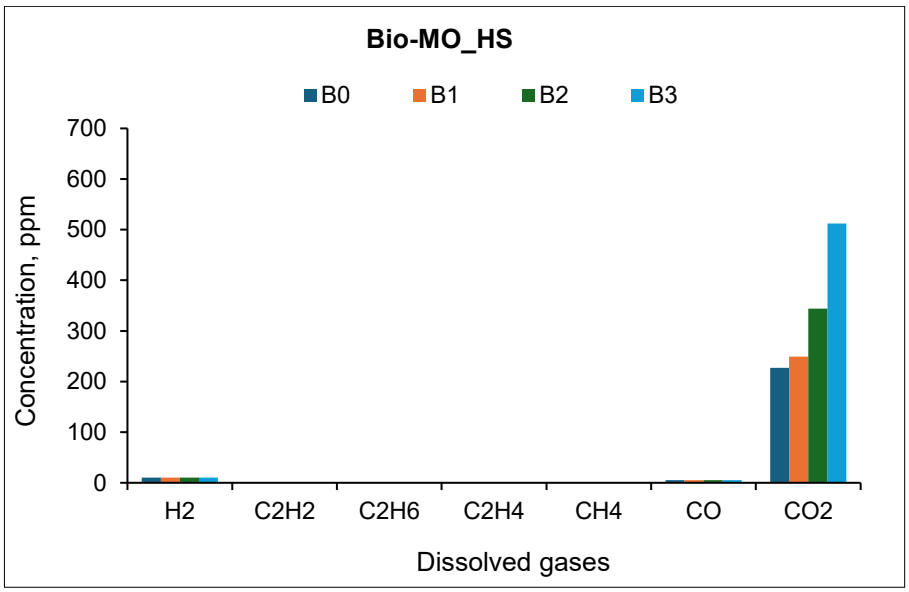
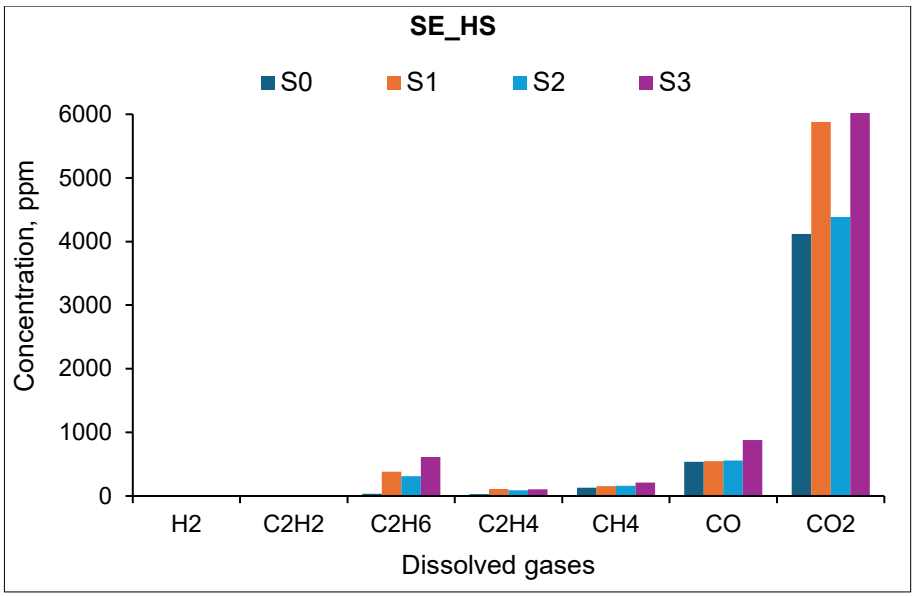
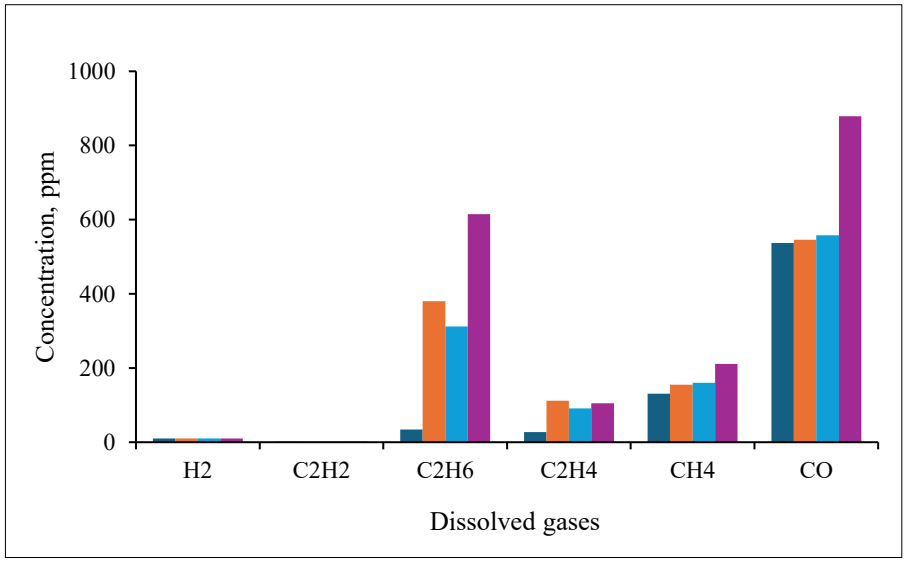


Figure 4.11. Illustration of the results of dissolved gases under the hotspot fault in Bio-MO



a)



(b)

Figure 4.12. Illustration of the results of dissolved gases under the hotspot fault in SE: a) Overall Dissolved Gas Distribution; and b) Enlarged View of Secondary Gas Species.

Based on obtained results, at 230°C, the degradation of synthetic esters, such as those composed of polyols linked to saturated fatty acids, mainly leads to the formation of soluble gases, including carbon monoxide (CO), carbon dioxide (CO_2), and ethane (C_2H_6), through complex mechanisms involving both thermal and oxidative reactions. It is important to clarify

that our experiments were conducted in the absence of cellulose paper, focusing exclusively on the intrinsic gas formation behaviour of the insulating liquids. As reported in [23], hydroperoxide formation, particularly α-acyl hydroperoxides, plays a central role in gas generation during thermos-oxidation. These unstable intermediates can decompose through both radical and non-radical pathways, generating CO_2 via the formation of peroxides. Meanwhile, bimolecular reactions with aldehydes or peroxyesters contribute to the formation of CO and H_2. Even in the early stages of oxidation, the accumulation of hydroperoxides leads to significant gas evolution of CO, CO_2, and H_2 released per mole of decomposed hydroperoxide. Thus, despite the absence of triglycerides, the molecular structure of synthetic esters promotes these complex degradation pathways, complicating the interpretation of DGA results, particularly in identifying the origin of the gases. Moreover, under thermal fault conditions, the gas profile reveals a marked increase in C_2H_6, a gas closely associated with ester oxidation, reaching concentrations up to ten times higher than those measured in the base liquid S0 (34 ppm) [24]. Regarding the influence of dissolved oxygen, its effect on CO_2 production appears relatively moderate, as even the reference sample S0 already exhibits high CO_2 concentrations, indicating that CO_2 formation is largely governed by the intrinsic thermo-oxidative stability of the ester fluid. In contrast, dissolved O_2 exerts a more pronounced influence on the formation of CO and other hydrocarbon gases, whose initially lower concentrations make them more sensitive to variations in oxidative intensity. This suggests that oxygen primarily acts as a reaction pathway modifier, promoting partial oxidation and molecular fragmentation rather than complete oxidation to CO_2.

The pronounced CO_2 peak observed in sample S3 may reflect an optimal range of oxidative activity under elevated dissolved O_2 conditions. However, the slight decline in CO_2 levels in sample S2, despite its relatively high oxygen content, may indicate the onset of oxidative saturation or a shift toward alternative degradation mechanisms. These results confirm that the simulated HS faults correspond to low-temperature conditions. According to IEEE Std C57.155-2014, higher-temperature thermal faults (T2 and T3) would be expected to

generate larger amounts of CO, CO_2, H_2, and unsaturated hydrocarbons, thereby modifying the gas distribution observed here.

In contrast, the gas evolution in Bio-MO shows a different behaviour. Although the total gas production remains lower than in SE, a proportional increase in CO_2 is still observed with rising O_2 concentrations. However, due to the saturated hydrocarbon structure and the absence of ester linkages, the degradation mechanisms are primarily governed by radical-induced pyrolysis and limited oxidation. The increase in acidity with O_2, though less pronounced than in SE, confirms the occurrence of oxidative degradation, yet with a lower tendency to form highly polar or water-soluble by-products. The lower hydrocarbon gas production observed in Bio-MO should not be interpreted as a weakness of DGA but rather as an intrinsic property of this fluid. Owing to its saturated hydrocarbon structure and high oxidative stability, Bio-MO tends to generate lower amounts of combustible gases under thermal stress. Nevertheless, DGA reliably captured the increase in CO_2, which remains a diagnostic marker of thermal activity, confirming that the method is effective even for fluids with reduced gas formation.

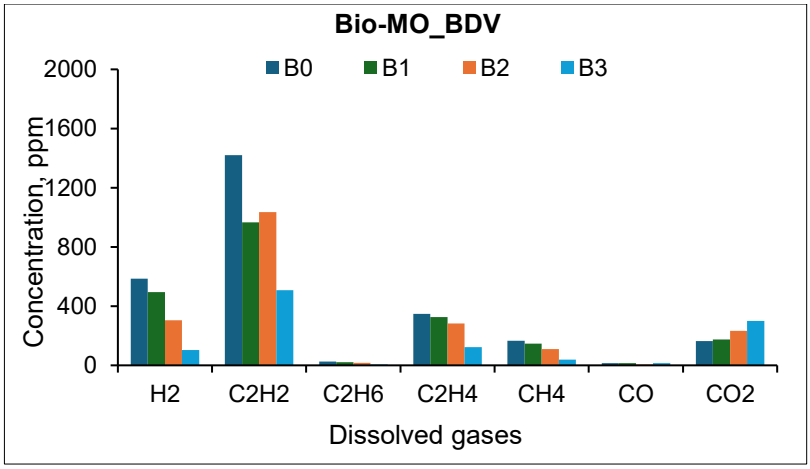
The marked absence of C_2H_2 in all cases suggests that, although the temperatures reached are significant, they remain below the threshold necessary to trigger intense processes such as electrical arcing, which typically generates this gas [25].

4.7.2. ARCING FAULT-GENERATED GASES DISSOLVED IN LIQUIDS

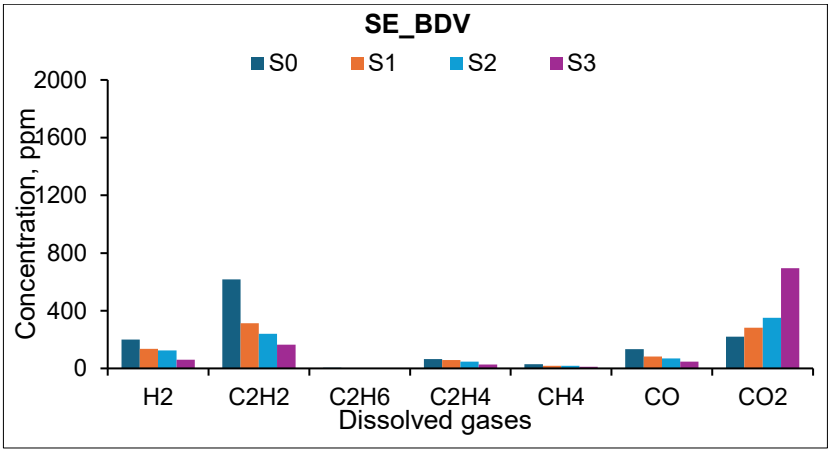
Figure 4.13 comparable gas profiles for both liquids; in all cases, C_2H_2 and H2 exhibit the highest concentration among dissolved hydrocarbon gases. According to [25], this trend is consistent with the energetic conditions of arcing faults, where transient micro-discharges may locally reach very high temperatures, sufficiently intense to promote the formation of C_2H_2. Unlike hydrocarbon-based fluids, synthetic esters produce significant amounts of CO and CO_2 during electrical faults. This is attributed to carbonyl ester groups (–COO–) in their molecular structure, which decompose thermally to release oxygenated gases [26].

In Bio-MO, H_2 decreases from 585 ppm to 497, 304, and 105 ppm, corresponding to 15%, 48%, and 82% reductions, while C_2H_2 drops from 1420 ppm to 966, 1037, and 511 ppm (32%, 27%, and 64%). Conversely, CO_2 increases from 165 ppm to 173, 234, and 300 ppm,

rising by 5%, 42%, and 82%. For SE, H_2 declines from 200 ppm to 135, 124, and 60 ppm (32.5%, 38%, and 70%), and C2H2 from 618 ppm to 315, 241, and 167 ppm (49%, 61%, and 73%). CO_2, however, rises from 219 ppm to 282, 350, and 695 ppm, marking increases of 29%, 60%, and approximately 3 times, respectively. These trends highlight a shift from gas-generating decomposition to oxidation-dominated pathways, as reflected in the pronounced CO_2 increase.



(a)



(b)

Figure 4.13. Illustration of the results of dissolved gases under an arcing fault: a) Bio-MO; and b) SE.

The decrease in absolute concentrations of hydrocarbon gases (H_2, C_2H_2) observed at higher O_2 levels can be attributed to a shift from pyrolytic to oxidative degradation pathways. Dissolved oxygen, acting as a diradical, consumes reactive fragments that would otherwise form combustible gases, leading instead to increased production of CO and CO_2. This explains

the apparent reduction of hydrocarbon gases while confirming that fault activity was still present under oxidative conditions. When a dielectric liquid decomposes under the effect of a high-intensity electrical discharge, it can be assumed that it breaks down into some distinct free radicals, such as C*, H*, CH_3*, CH_2*, and CH*, depending on its molecular structure [27]. This is described as the primary decomposition process of dielectric liquids. The free radicals formed subsequently interact randomly with each other or with surrounding molecules in so-called secondary chemical reactions, forming fault gases [28].

The oxygen molecule, being a diradical species, possesses unique electronic characteristics that make it particularly reactive under certain conditions. Similarly, all broken hydrocarbon chains or “knocked-out” atoms generated during dielectric liquid decomposition are paramagnetic. Under the influence of the strong electric field and high temperatures produced during an electrical arc fault, these paramagnetic species become highly reactive [29]. This environment promotes oxidative decomposition pathways, especially in the presence of abundant dissolved oxygen. The observed increase in CO_2 concentrations, concurrent with the decline of typical hydrocarbon gases such as C_2H_2, H_2, CH_4, C_2H_6, and C_2H_4, supports this hypothesis, indicating a shift from pyrolytic to oxidative mechanisms driven by fault-induced energetic conditions.

4.8. DISSOLVED GASES ANALYSIS AND DIAGNOSIS

To further understand the influence of dissolved O_2 in dielectric liquids on their gas formation under different types of faults, Duval’s Triangle and Pentagon methods for mineral and non-mineral were applied to bio-based mineral oils and synthetic ester fluids, respectively [30–31] (see Figure 4.12 and Figure 4.13).

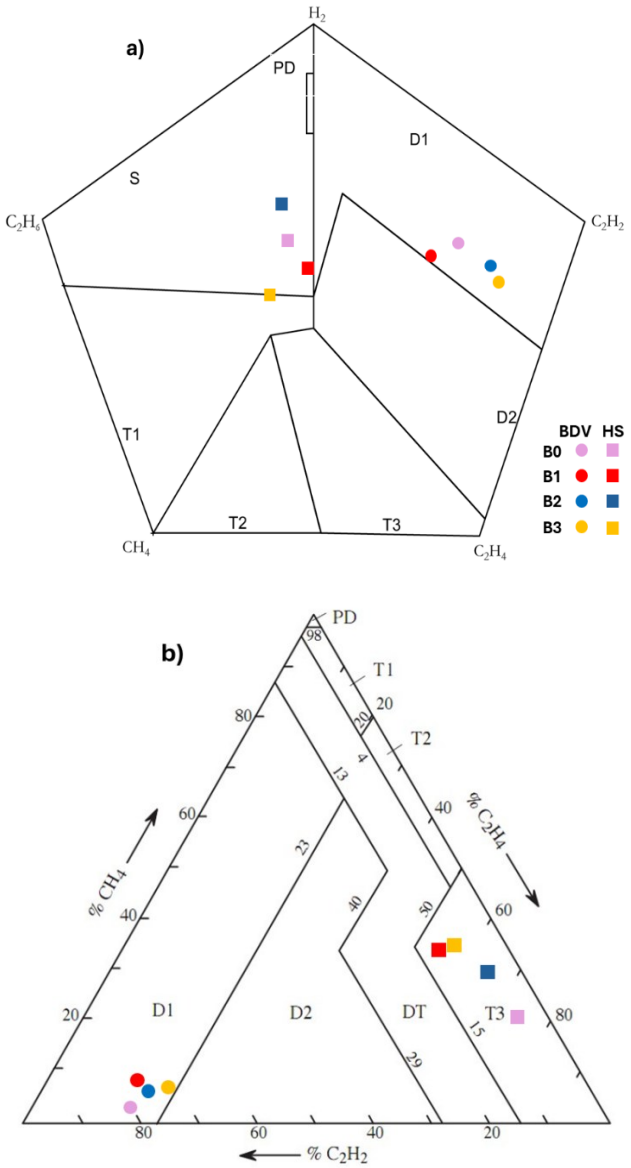
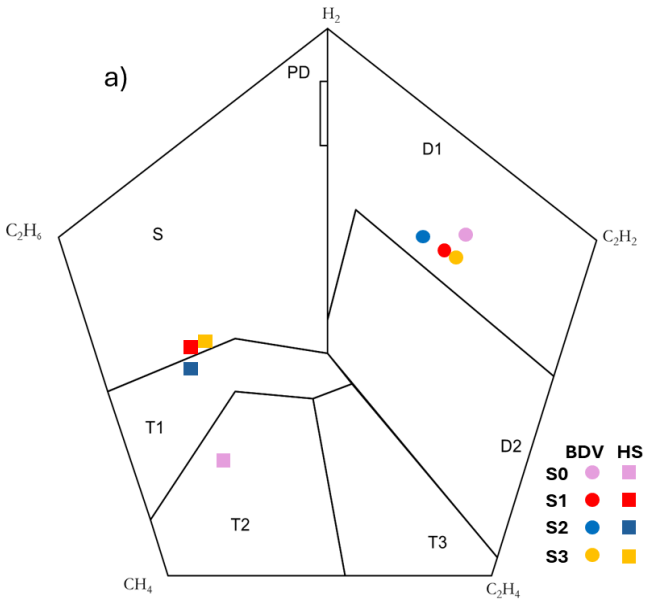


Figure 4.14. Illustration of fault gas diagnosis using a) Duval's pentagon and b) Duval's triangle for Bio-MO.



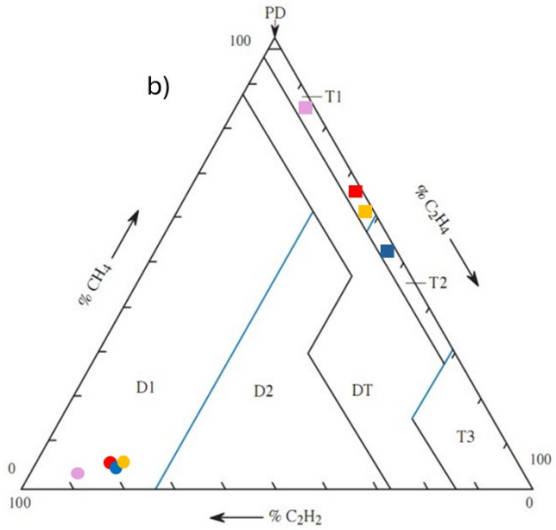


Figure 4.15. Illustration of fault gas diagnosis using a) Duval's pentagon and b) Duval's triangle for SE.

Under arc fault conditions, both diagnostic methods consistently indicated a D1-type (low energy discharge) fault for the base liquids (Bio-MO and SE) as well as for samples with different levels of dissolved oxygen, primarily due to the persistently elevated levels of C_2H_2 and H_2.

A significant mismatch was observed in the diagnostic results HS fault across all analyzed dielectric fluids. For SE, the Duval Pentagon revealed a progressive evolution of fault types: from a zone T2 (Thermal fault of temperature, 300˚C- 700˚C) for the base liquid, to an S zone (stray gassing of oil, T< 200˚C) for samples S1 and S3. This transition reflects a shift in thermal degradation behaviour, strongly influenced by an increase and decrease in C2H6 production promoted by the rising concentration of dissolved oxygen. In parallel, the Duval Triangle shows a similar dynamic, with a diagnostic migration from the T1 zone for the base SE, through a transient shift to T2 for S1, followed by a return to T1 for S2 and S3.

For all Bio-MO samples, the Pentagon method diagnoses in zone S, while the Duval Triangle consistently places the faults within the T3 zone (thermal faults > 700˚C). This divergence for Bio-MO samples is explained by the very low production of hydrocarbon gases under thermal fault, which may be attributed to the high oxidative stability of this liquid.

These findings confirm the catalytic role of dissolved oxygen in liquid decomposition by enhancing gas production through radical mechanisms. Combined diagnostic results and gas composition reveal an increased sensitivity of oxidized esters to thermal degradation.

The results of both diagnostic methods are summarized in Table 4.1 to illustrate the evolution of fault gas patterns.

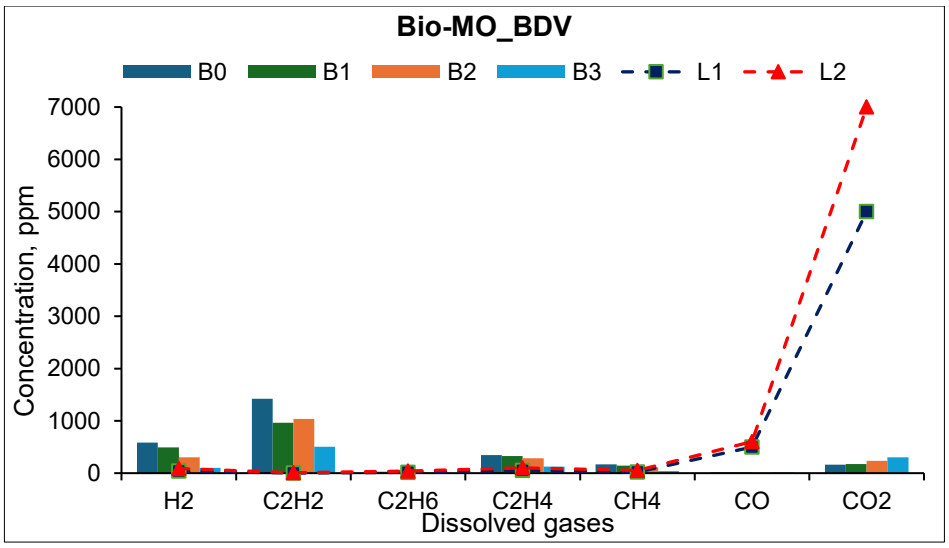
Tableau 4.1. Fault diagnosis details for Duval's triangle and Duval's pentagon

Type of fault	Samples	Results of Duval's diagnostic methods		Fault matching
		Pentagon	**Triangle**	
Arc fault	B0	D1	D1	Matched
	B1	D1	D1	Matched
	B2	D1	D1	Matched
	B3	D1	D1	Matched
	S0	D1	D1	Matched
	S1	D1	D1	Matched
	S2	D1	D1	Matched
	S3	D1	D1	Matched
Hotspot	B0	T3	S	Not matched
	B1	T3	S	Not matched
	B2	T3	S	Not matched
	B3	T3	S	Not matched
	S0	T1	T2	Partially matched (Thermal)
	S1	T2	S	Not matched
	S2	T1	T1	Matched
	S3	T1	S	Not matched

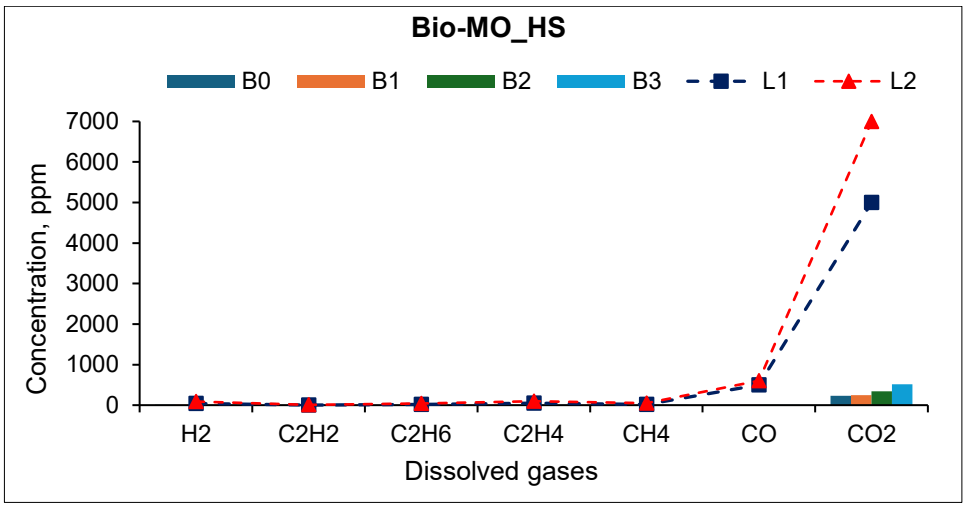
4.9. CRITERIA FOR DGA INTERPRETATION BASED ON OXYGEN EXPOSURE

According to IEEE C57.104-2019, the oxygen to nitrogen (N_2) ratio above 0.2 indicates a free-breathing transformer, while a ratio of 0.2 or less suggests a sealed unit. This helps apply appropriate gas thresholds for DGA interpretation [25].

In this study, the combination of these three parameters, O_2/N_2 ratio, DGA status, and transformer age, will be used to analyze the impact of simulated faults on the evolution of insulating fluids. In this study, an O_2/N_2 ratio greater than 0.2 was selected, as all samples were deliberately exposed to oxygen (see Figure 4.14). It should be noted that, unlike in-service conditions, the O_2/N_2 ratio here does not indicate external leakage but was used as a reference framework to interpret gas evolution under controlled oxygen exposure.

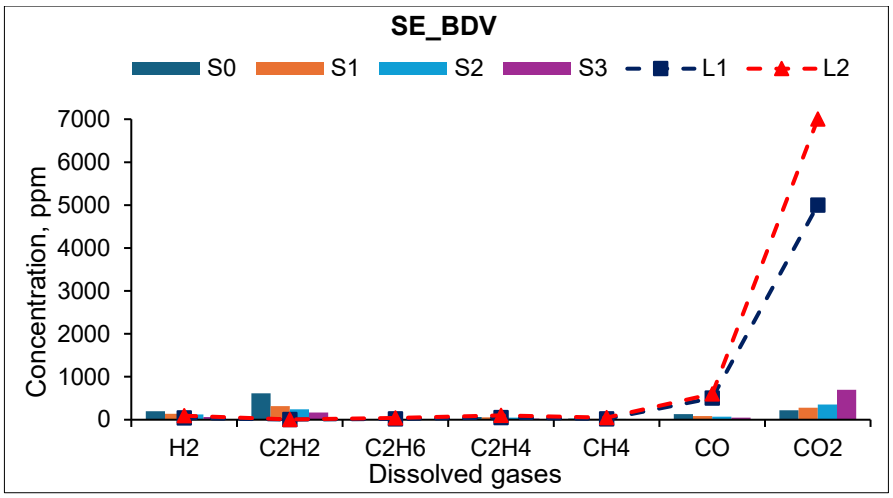


(a)

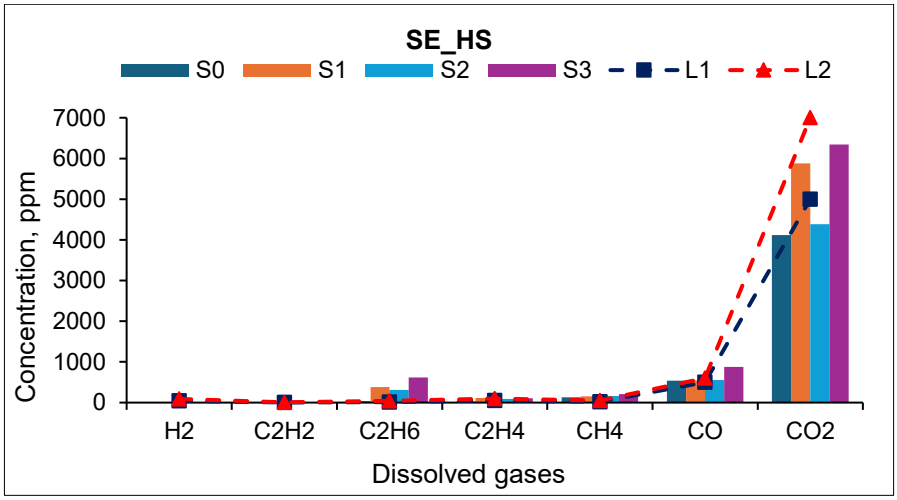


(b)

Figure 4.16. DGA Status Determination According to IEEE C57.104-2019 Thresholds for Bio-MO: a) Arcing and b) Hot spot.



(a)



(b)

Figure 4.17. DGA Status Determination According to IEEE C57.104-2019 Thresholds for SE: a) Arcing and b) Hot spot.

Based on the interpretation method in IEEE C57.104-2019, the analysis reveals that dissolved oxygen has a significant impact on gas generation during faults. In most cases, the gases produced exceeded the limits (L1 and L2) thresholds (90th and 95th percentiles), placing the fluids in DGA status 3, which signals active degradation. An exception was noted for the Bio-MO fluid exposed to a thermal fault, where gas levels stayed below these critical limits, where transformers with DGA Status 1 are considered as probably normal. This suggests that Bio-MO may better resist thermal stress than synthetic esters, even with oxygen present. However, this method alone should not be taken as a definitive diagnosis of transformer condition.

4.10. CONCLUSION

This study highlights the critical influence of dissolved oxygen on the gas formation of biodegradable insulating liquids, specifically synthetic esters (SE) and bio-based hydrocarbons (Bio-MO), under thermal and electrical fault conditions. Experimental results demonstrate that oxygen availability significantly affects the degradation pathways of these fluids, altering both the quantity and nature of dissolved gases produced. Under rich oxygen conditions, oxidative reactions are favored, leading to an increase in polar by-products such as carboxylic acids and water, as well as shifts in gas profiles, typically marked by reduced levels of combustible gases like hydrogen (H_2) and acetylene (C_2H_2), and elevated concentrations of carbon oxides (CO and CO_2).

These oxidative mechanisms are particularly pronounced in ester-based fluids due to their chemical structure, which is more susceptible to radical formation and bond cleavage in the presence of O_2. The presence of oxygen also contributes to a notable rise in TAN and tan δ, indicating deterioration of both physicochemical and electrical performance.

The findings underscore the importance of oxygen management in transformer systems utilizing biodegradable liquids. Moreover, these insights are essential for the accurate interpretation of DGA, as traditional diagnostic tools, calibrated for mineral oils, may misclassify faults if oxygen-related gassing behaviors are not considered. Overall, controlling dissolved oxygen is a key strategy to mitigate premature aging, support safe transformer operation, and optimize the use of environmentally friendly insulating fluids in modern power systems.

CHAPITRE 5

CONCLUSION

5.1. PRINCIPAUX RÉSULTATS

Dans l'ensemble, les travaux de cette recherche apportent des contributions originales en reliant la composition chimique, l'influence de l'oxygène dissous et les mécanismes de vieillissement aux tendances de gazage, et ouvrent la voie au développement d'outils de diagnostic et de surveillance plus fiables.

L'analyse comparative menée sur le Bio-MO, NE et SE met en évidence des comportements de vieillissement et de formation de gaz nettement différenciés, directement liés à leur composition chimique, à leur structure moléculaire et à leur interaction avec l'oxygène dissous. Le Bio-MO, majoritairement composées d'hydrocarbures saturés, présentent une évolution relativement modérée des marqueurs physico-chimiques et diélectriques du vieillissement, mais se distinguent par une production plus marquée de gaz caractéristiques des défauts électriques, notamment C_2H_2, sous contraintes de type arc, traduisant une sensibilité accrue aux mécanismes de pyrolyse et de rupture des liaisons C–C. À l'inverse, les esters naturels, constitués de triglycérides partiellement insaturés, montrent une dégradation chimique plus rapide, dominée par des mécanismes oxydatifs et hydrolytiques, se traduisant par une augmentation prononcée du TAN et du tan δ, ainsi qu'une diminution significative de l'IFT. Cette dégradation ne s'accompagne toutefois pas nécessairement d'une production élevée de gaz combustibles, en raison de la formation préférentielle de sous-produits polaires de faible volatilité. Les esters synthétiques présentent un comportement intermédiaire, avec une meilleure stabilité initiale que les NE, mais une sensibilité croissante aux conditions thermiques, à la durée d'exposition et à la teneur en oxygène dissous, conduisant à des profils gazeux progressivement dominés par les oxydes de carbone lors du vieillissement avancé.

Les résultats ont également mis en évidence le rôle déterminant de l'oxygène dissous dans les mécanismes de vieillissement et de gazage des fluides biodégradables.

L'augmentation de la teneur initiale en O_2 amplifie les réactions oxydatives et hydrolytiques, favorisant la formation de sous-produits polaires, l'augmentation du TAN et du tan δ, ainsi qu'une élévation de la teneur en eau, en particulier sous contraintes thermiques prolongées. Cette influence de l'oxygène modifie de manière significative les signatures gazeuses, en accentuant la production des oxydes de carbone au détriment des gaz hydrocarburés, notamment dans les esters, et souligne l'importance du temps de réaction dans l'évolution des profils de gaz.

L'approche corrélative multiparamètres mise en œuvre a permis d'identifier des relations statistiques fortes entre les marqueurs de vieillissement physico-chimiques et diélectriques, en particulier le TAN, le tan δ et l'IFT, et l'évolution des gaz dissous. Ces relations, évaluées à l'aide du coefficient de corrélation de Pearson (r) et du p-value associée, présentent des coefficients élevés ($r > 0,9$) avec des p-values inférieures à 0,05, indiquant des corrélations statistiquement significatives au seuil de confiance de 95 %. Ces résultats confirment que l'état chimique réel du fluide conditionne fortement la pertinence des diagnostics fondés sur l'AGD et que l'intégration conjointe des marqueurs TAN, tan δ et IFT en renforce significativement la valeur prédictive. Cette analyse statistique vise toutefois à appuyer l'interprétation physico-chimique des tendances observées, sans établir de relation causale stricte, et souligne la nécessité de futures études intégrant des durées de vieillissement plus longues et des ensembles de données élargis afin de consolider la robustesse statistique des corrélations identifiées.

Perspectives industrielles

Les résultats de ce travail présentent une applicabilité directe en milieu industriel, en particulier dans le cadre de la surveillance conditionnelle des transformateurs de puissance reposant sur l'analyse des gaz dissous (AGD). En conditions réelles d'exploitation, le diagnostic par AGD ne repose pas uniquement sur des concentrations instantanées, mais principalement sur le suivi périodique des gaz et l'analyse de leur taux de croissance, paramètre clé pour apprécier la cinétique des phénomènes de dégradation et détecter précocement l'apparition ou l'aggravation de défauts internes.

À la lumière des mécanismes physico-chimiques mis en évidence précédemment, les corrélations établies entre les marqueurs de vieillissement (TAN, tan δ, IFT) et les gaz dissous constituent un cadre opérationnel directement exploitable, ces paramètres faisant déjà partie des programmes de maintenance courante. Les résultats confirment que l'état chimique réel du liquide isolant conditionne non seulement la nature mais également l'intensité des gaz produits en situation de défaut, ce qui implique que l'interprétation de l'AGD doit intégrer explicitement le niveau de dégradation du fluide.

Cette approche globale, combinant indicateurs physico-chimiques, profils gazeux, permettra d'améliorer significativement la fiabilité du diagnostic, en limitant les risques de conclusions erronées sur la nature ou la sévérité des défauts internes, notamment lors de l'utilisation de fluides isolants biodégradables dont le comportement de gazage diffère de celui des huiles minérales conventionnelles.

Enfin, les observations relatives à l'influence de l'oxygène dissous soulignent son rôle déterminant dans l'exploitation des transformateurs, en particulier en fonction de leur conception (libre-respirant ou scellée). Ces résultats suggèrent que l'application des seuils et des rapports diagnostiques classiques de l'AGD doit être adaptée en tenant compte du mode de respiration du transformateur, de la sensibilité intrinsèque du fluide aux phénomènes d'oxydation et des vitesses de formation des gaz, afin d'assurer une interprétation cohérente et représentative des conditions réelles de service.

5.2. PUBLICATIONS

Les articles présentés ci-après, réalisés dans le cadre du développement de cette recherche doctorale, synthétisent les principaux résultats obtenus au cours de ce travail.

1. **M. T. Agouassi,** U. Mohan Rao, I. Fofana and Y. Hadjadj, "Understanding the Relationship Between Insulation Aging and Gas Formation of Some Biodegradable Dielectric Fluids," in IEEE Transactions on Dielectrics and Electrical Insulation, doi: 10.1109/TDEI.2025.3596945. (Publié)

2. **M. T. Agouassi,** U. Mohan Rao, I. Fofana and Y. Hadjadj, Fethi Maghnefi " Influence of Dissolved Oxygen on the Gassing Tendency of Biodegradable Insulating Liquids under Thermal and Electrical Faults," in IET (En cours par l'éditeur)

3. **M. Agouassi**, U. M. Rao, Y. Hadjadj and I. Fofana, "On the Gassing Behaviour of Synthetic Ester Under Arcing Faults," 2023 IEEE Electrical Insulation Conference (EIC), Quebec City, QC, Canada, 2023, pp. 1-4, doi: 10.1109/EIC55835.2023.10177336. (Publié)

4. **M. T. Agouassi,** U. Mohan Rao, I. Fofana and Y. Hadjadj, " Influence of Chemical Composition on the Gassing Behaviour of Biodegradable Dielectric Liquids: A Comprehensive Review," (soumis)

5.3. LIMITATIONS

Bien que cette recherche apporte des contributions significatives, elle comporte certaines limites méthodologiques et expérimentales qu'il convient de préciser afin de situer clairement la portée et le cadre de l'étude :

• **Base statistique réduite :**

Bien qu'un cadre de corrélation statistique ait été introduit (coefficient de corrélation et p-value), de même que différents niveaux de concentration en oxygène, les tailles des échantillons et la diversité des conditions expérimentales demeurent limitées. Des bases de données plus larges et plus variées seraient nécessaires pour renforcer la robustesse et la portée des tendances observées.

• **Paramètres de stress spécifiques et simplifiés :**

Les conditions de défaut appliquées (arcs électriques répétés, cycles de chauffage localisé) ont été distinctement définies de manière contrôlée et simplifiée. Elles ne reflètent pas entièrement la complexité des contraintes électriques et thermiques combinées auxquelles les transformateurs sont exposés en service.

L'influence de l'oxygène dissous a été étudiée uniquement dans des conditions thermiques restreintes (230 °C et 130 °C, correspondant à des défauts de type T1 < 300 °C) et sur un seul cycle de chauffage. De même, la contrainte à haute énergie s'est limitée à 100

répétitions de claquage diélectrique avec des intervalles fixes de 2 minutes, ce qui ne permet pas de couvrir toute la diversité des scénarios possibles.

• **Durées de vieillissement restreintes :**

Le vieillissement simulé, limité à 2000 heures, reste très court au regard de la durée de vie réelle des transformateurs (plusieurs décennies). Les corrélations identifiées pourraient évoluer différemment sur des périodes plus longues et en conditions réelles d'exploitation.

• **Nombre limité de fluides étudiés :**

L'étude s'est concentrée sur trois liquides biodégradables (Bio-MO, NE, SE). Bien que représentatifs, ils ne couvrent pas l'ensemble des formulations disponibles sur le marché, ce qui limite l'extrapolation des résultats à d'autres fluides isolants alternatifs.

5.4. RECOMMENDATIONS

Au regard des limites mises en évidence dans ce travail, plusieurs axes de recherche apparaissent prioritaires afin d'approfondir la compréhension du comportement des liquides isolants biodégradables et de renforcer la transférabilité des résultats vers les applications industrielles. Il est tout d'abord recommandé d'approfondir la modélisation cinétique des réactions de gazage, afin de prédire l'évolution des espèces gazeuses en fonction des paramètres de stress thermique. Cette approche permettrait de relier de manière quantitative l'énergie thermique et électrique effectivement dissipée aux mécanismes de dégradation moléculaire et aux signatures de gaz observées, améliorant ainsi l'interprétation des défauts électriques de type D1 et D2 au-delà d'une lecture fondée uniquement sur la température maximale atteinte. Dans cette optique, l'extension des études aux mélanges esters–huiles minérales apparaît essentielle pour mieux caractériser les interactions chimiques hybrides, notamment dans des scénarios de rétroremplissage (retrofilling) des transformateurs existants, qui constituent un enjeu croissant pour les exploitants.

Il est également recommandé d'élargir l'analyse au suivi des sous-produits liquides de dégradation (acides organiques, alcools, oligomères et polymères), afin de relier plus étroitement les phénomènes de gazage aux mécanismes globaux de vieillissement du fluide et du système huile–papier. Cette approche multiéchelle permettrait d'améliorer la cohérence

entre diagnostics chimiques, diélectriques et gazeux, en particulier dans des situations où la production de gaz ne reflète pas nécessairement l'ampleur réelle de la dégradation chimique.

Dans une perspective d'application industrielle, les futures investigations devraient reproduire plus fidèlement la complexité des contraintes électrothermiques rencontrées en service, en élargissant l'étude de l'oxygène dissous à des plages plus étendues de températures, de cycles thermiques, de durées d'exposition et de scénarios de défauts électriques. L'allongement des durées de vieillissement simulé, combiné à l'exploitation de données issues de transformateurs en exploitation, constituerait un levier majeur pour valider la robustesse et la transférabilité des corrélations établies en laboratoire.

Enfin, Il est recommandé d'explorer des niveaux de rapport O_2/N_2 distincts de ceux actuellement établis pour l'évaluation de l'âge et de l'état des transformateurs. Les seuils usuels, majoritairement dérivés des huiles minérales, pourraient ne pas être pleinement représentatifs du comportement des liquides isolants biodégradables, dont la composition chimique et les mécanismes d'oxydation diffèrent. Une telle démarche permettrait d'affiner l'interprétation des diagnostics fondés sur les gaz dissous et d'améliorer la pertinence des critères d'évaluation en conditions réelles d'exploitation.

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