

UNIVERSITÉ D'ORLÉANS

ÉCOLE DOCTORALE *Energie, Matériaux, Sciences de la Terre et de l'Univers 552*

PRISME — Laboratoire Pluridisciplinaire de Recherche en Ingénierie des
Systèmes, Mécanique, Energétique

THÈSE présentée par :

Carole DONCOEUR

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pour obtenir le grade de : **Docteur de l'Université d'Orléans**

Discipline/ Spécialité : **Énergétique**

**Lubricant degradation mechanisms in
ammonia/hydrogen internal combustion engines**

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Mécanismes de dégradation des lubrifiants dans les moteurs à combustion interne à ammoniac/hydrogène

L'ammoniac suscite un intérêt croissant en tant que potentiel carburant intrinsèquement sans carbone pour des moteurs thermiques destinés au transport longue distance ou non routier. Cependant, ce carburant a une chimie différente de celle des carburants carbonés traditionnels, et donc une réactivité, des caractéristiques de combustion et des compositions de gaz d'échappement différents, modifiant les contraintes auxquelles les lubrifiants sont soumis. Lors de la combustion d'ammoniac ou de mélanges ammoniac/hydrogène, les lubrifiants peuvent être exposés à des oxydes d'azote, de l'ammoniac imbrûlé et de l'eau, autant de composés susceptibles d'altérer leurs propriétés et de se combiner à la dégradation liée à l'oxydation en phase liquide. L'objectif principal de cette thèse est d'identifier les défis spécifiques de la combustion de l'ammoniac et des mélanges ammoniac/hydrogène vis-à-vis du lubrifiant, et d'étudier comment le vieillissement de ce dernier affecte en retour l'efficacité du moteur et les émissions de polluants. Pour cela, une approche expérimentale multiéchelle et multitechnique a été développée. Le comportement à l'oxydation d'huiles de base sans additifs a d'abord été caractérisé, servant de référence pour l'étude des effets d'une exposition aux oxydes d'azote et à l'ammoniac gazeux dans des conditions contrôlées de vieillissement accéléré. La spectroscopie infrarouge, la viscosité et l'analyse élémentaire ont notamment été utilisées pour caractériser l'évolution des huiles. Ces expériences ont permis de mettre en évidence de nouveaux mécanismes de dégradation impliquant l'ammoniac, l'oxygène et les huiles. Pour compléter cette étude, l'évolution de trois différentes huiles moteurs, dont une huile minérale pré-vieillie en laboratoire, a ensuite été explorée directement sur un moteur expérimental alimenté alternativement avec de l'ammoniac et du méthane. L'analyse a permis de démontrer l'incorporation d'azote dans les huiles, sous forme d'ammoniac dissous, corrélé avec la présence de métaux de corrosion, mais aussi sous forme de produits de dégradation. Par ailleurs, l'huile minérale pré-vieillie a conduit à une diminution de l'efficacité du moteur dans les conditions choisies. Les émissions gazeuses et de particules ont été caractérisées au moyen d'un suivi en ligne en temps réel et d'observations microscopiques de particules collectées à l'échappement. Un panorama des morphologies de particules observées avec l'ammoniac et le méthane, en lien avec les différentes huiles, a également été dressé. Ce travail contribue à une meilleure compréhension des mécanismes de dégradation des lubrifiants lors de la combustion de l'ammoniac, ainsi qu'à l'évaluation des conséquences sur le fonctionnement du moteur et les émissions polluantes. Il met en évidence la nécessité d'adapter les formulations de lubrifiants aux spécificités de ce carburant.

Mots clés : lubrifiant, huile moteur, oxydation, ammoniac, particules

Lubricant degradation mechanisms in ammonia/hydrogen internal combustion engines

The use of ammonia, an intrinsically carbon-free molecule, as alternative fuel in internal combustion engines for specific applications such as long-distance or off-road transportation, is attracting growing interest. However, this fuel exhibits different chemistry compared to conventional carbon-based fuels, leading to different reactivity, combustion characteristics, and exhaust gas compositions, modifying the conditions endured by lubricants. In the case of ammonia or ammonia/hydrogen combustion, lubricants can be exposed to nitrogen oxides, unburned ammonia, and water, compounds that may further impair their properties, combined to liquid phase oxidation. The main objective of this thesis is to identify the specific challenges posed by ammonia and ammonia/hydrogen combustion for lubricants, and to investigate how lubricant aging, in turn, affects engine efficiency and pollutant emissions. To this end, a multiscale and multitechnique experimental approach was developed. The oxidation behavior of additive-free base oils was first characterized, and provided the basis for investigating the effects of an exposure to nitrogen oxides and gaseous ammonia under controlled accelerated-aging conditions. Several techniques were used to characterize the evolution of the oils, including infrared spectroscopy, viscosity, and elemental analysis. These experiments revealed new degradation mechanisms involving ammonia, oxygen, and the base oils. To complement this work, the evolution of three different engine oils, including one pre-aged mineral oil with accelerated aging, was investigated directly in a test engine operated with ammonia and methane alternatively. Nitrogen incorporation into the oils was demonstrated, both as dissolved ammonia in all three samples, correlated with the detection of corrosion metals, and as heavier degradation products. Furthermore, the pre-aged mineral oil was associated with reduced engine efficiency under the chosen experimental conditions. Gaseous and particulate emissions were characterized through real-time in-line monitoring combined with microscopic observation of particles collected at the exhaust. An overview of the particle morphologies observed under ammonia and methane combustion with the different oils was also provided. Overall, this work provides new insights into lubricant degradation during ammonia combustion and its implications for engine operation and pollutant emissions. It highlights the need to adapt lubricant formulations to the specificities of ammonia.

Keywords: lubricant, engine oil, liquid phase oxidation, ammonia, particles

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Contents

Remerciements	i
Résumé en français	1
General introduction	13
1 Literature review: potential impacts of ammonia/hydrogen combustion on lubricants	19
1.1 Basics of lubricants in combustion engines	20
1.1.1 Roles of lubrication	20
1.1.2 Formulation of lubricants	21
1.1.3 Fuel-oil interactions	23
1.2 Effect of hydrogen and/or ammonia combustion on the aging of the lubricant .	25
1.2.1 Potential issues related to hydrogen and ammonia combustion charac-	
teristics	25
1.2.2 Liquid phase oxidation	27
1.2.3 Nitro-Oxidation	31
1.2.4 Compatibility with unburned fuel	40
1.2.5 Compatibility with water	47
1.2.6 Particle emissions	48
1.3 Lubricants characterization techniques	56
1.3.1 Monitoring oxidation	56
1.3.2 Accelerated aging protocols	56
1.3.3 Accelerated aging versus in-field aging	59
1.3.4 Analytical techniques	60
1.4 Conclusion	63
2 Material and methods—base oil oxidation under reference conditions	65
2.1 Experimental section	66
2.1.1 Base oils	66
2.1.2 Accelerated aging setup	67
2.1.3 Oil characterization techniques	72
2.2 <i>Operando</i> oxidation with headspace-GC	77

CONTENTS

2.2.1	<i>Operando</i> oxidation: proof of concept	77
2.2.2	Effect of the oil volume	78
2.2.3	Identification of degradation products	79
2.2.4	Effect of the heating time and temperature	82
2.3	Rancimat applied to lube oils	86
2.3.1	Characterization of the accelerated aging via Rancimat method	86
2.3.2	Comparison of the oils reactivity	88
2.4	Oxidation using a pressurized stirred reactor	91
2.4.1	Mineral oil under pure oxygen—assessment of the oxidation protocol and between-day repeatability	91
2.4.2	Comparison with the complex polyester base oil	92
2.4.3	Effect of the temperature	92
2.4.4	Total oxygen content	93
2.4.5	Viscosity	94
2.4.6	Simulated distillation	95
2.4.7	GC2D/MS analysis of the mineral oil oxidation products	96
2.5	Discussion—comparison of the accelerated aging setups	99
2.6	Conclusion	102
3	Investigating lubricants base oils reactivity under nitrogen oxides and ammonia	103
3.1	Experimental section	105
3.1.1	Gas mixtures	105
3.1.2	Summary of the experimental conditions	105
3.2	Effect of nitrogen oxides in air	106
3.3	Effect of ammonia in air	110
3.4	Speciation of nitrogen	112
3.4.1	GC2D/MS analysis	113
3.4.2	Specific detection of nitrogen-containing compounds	114
3.5	Effect of mixing with an ammonia solution	116
3.5.1	Reaction conditions	116
3.5.2	Monitoring of the reaction	117
3.5.3	Molecular analysis	118
3.5.4	Possible synthesis pathways for amides and nitriles	120
3.5.5	Corrosion and deposits	120
3.6	Discussion—interaction between oxygen, ammonia, and a mineral oil during accelerated aging	122
3.7	Conclusion	124
4	Investigating lubricants base oils evolution during engine operation	127

4.1	Experimental section	128
4.1.1	Engine test bench	128
4.1.2	Preparation of the pre-aged base oil	133
4.1.3	Properties of the pre-aged base oil and between-day repeatability . . .	134
4.2	Evolution of engine oils during engine operation with methane and ammonia .	135
4.2.1	Evolution at the macroscopic scale	135
4.2.2	Molecular evolution of the base oils	146
4.3	Discussion—evolution of base oils under engine conditions	149
4.4	Conclusion	151
5	Effect of the engine oil on engine operation and pollutant emissions	153
5.1	Experimental engine setup	154
5.1.1	Engine setup and combustion parameters	154
5.1.2	Diluter Fine Particle Sampler (FPS 4000)	155
5.1.3	Engine Exhaust Particle Sizer (EEPS)	157
5.1.4	FTIR spectroscopy	159
5.1.5	Mini Particle Sampler (MPS)	160
5.1.6	Methodology for engine test experiments and data processing	161
5.1.7	Microscopy imaging	163
5.2	Effect of the oil on engine operation and gaseous emissions	164
5.2.1	Effect of the engine oil under methane combustion	164
5.2.2	Effect of the engine oil under ammonia combustion	166
5.2.3	Effect of the engine oil under ammonia/hydrogen blends combustion .	171
5.3	Investigating particulate matter emissions with methane and ammonia: in-line analysis	173
5.3.1	Particle size distributions under methane combustion	173
5.3.2	Particle size distributions under ammonia combustion	177
5.3.3	Comparison between methane and ammonia	181
5.3.4	Discussion	182
5.4	Investigating particulate matter emissions with methane and ammonia: ele- mental and morphological analysis	183
5.4.1	Particles obtained with the fully-formulated lubricant	183
5.4.2	Particles obtained with the mineral base oil	189
5.4.3	Particles obtained with the pre-aged mineral base oil	192
5.4.4	Particles obtained with methane	194
5.4.5	Analysis and comparison of the particles observed	200
5.4.6	Discussion—particle emissions	202
5.5	Conclusion	204
	General conclusion and perspectives	205

CONTENTS

Appendices	209
Appendix A—Chapter 2	209
Appendix B—Chapter 3	214
Appendix C—Chapter 4	215
Appendix D—Chapter 5	225
List of acronyms	236
Bibliography	238

Résumé en français

Introduction

La combustion de carburants fossiles pour la production d'énergie, les procédés industriels et les transports constitue une source majeure d'émissions de gaz à effet de serre. Depuis l'avènement de l'ère industrielle, les émissions massives de ces gaz ont largement contribué, et contribuent encore aujourd'hui, au réchauffement climatique actuel. Le secteur du transport, avec 8.7 Gt CO_{2eq} émises en 2019, représente à lui seul 15 % des émissions nettes de gaz à effet de serre [1]. Face à cet enjeu majeur, la recherche sur l'électrification et les carburants alternatifs mobilise à la fois la communauté scientifique et les industriels. Si les moteurs électriques et les batteries offrent une solution pertinente pour les véhicules légers et le transport urbain, l'utilisation de moteurs à combustion interne alimentés par des carburants décarbonés apparaît mieux adaptée à certaines applications spécifiques exigeant de fortes puissances et/ou une longue autonomie, comme le transport longue distance ou non routier.

L'hydrogène est considéré comme un vecteur énergétique prometteur, intrinsèquement sans carbone, mais son développement fait face à plusieurs difficultés, notamment pour ce qui concerne son transport et son stockage [1]. L'ammoniac peut lui-même être envisagé comme un transporteur d'hydrogène, présentant plusieurs avantages. Cette molécule peut être stockée et transportée à l'état liquide à 10 bar à température ambiante, ou bien à -33 °C à pression atmosphérique, et elle a une plus grande densité d'énergie volumique par rapport à l'hydrogène dans ces conditions de stockage avec 11,3 GJ/m³ à 1,1 MPa/300K, contre à 4,7 GJ/m³ à 70 MPa [2]. L'ammoniac bénéficie par ailleurs d'infrastructures de stockage et d'échange déjà largement déployées dans les ports du fait de son utilisation massive dans la production d'engrais et comme base de synthèse chimique [2, 3]. Ces caractéristiques expliquent l'intérêt croissant pour l'ammoniac, à la fois comme vecteur d'hydrogène et comme carburant sans carbone potentiel, notamment pour le transport maritime. Cependant, cette molécule est difficile à inflammer et nécessite parfois l'utilisation de carburants pilotes tels que l'hydrogène [4–6] ou le diesel [7, 8].

Selon l'Agence Internationale de l'Energie (IEA), l'ammoniac pourrait représenter entre 25 % et 45 % de la consommation finale totale d'énergie de l'industrie maritime d'ici 2050 [3]. Les principaux fabricants de moteurs marins, tels que MAN, WinGD et Wärtsilä, prévoient de commercialiser des moteurs deux temps adaptés à l'ammoniac pour les porte-conteneurs d'ici fin 2025/2026 et multiplient les communications sur leurs avancées [9–12].

Le développement de tels moteurs s'appuie sur une expertise existante concernant les moteurs thermiques, qui doit cependant s'adapter pour prendre en compte les propriétés de combustion spécifiques de l'ammoniac et ses mélanges [2, 6]. En parallèle, la question de l'adaptabilité des lubrifiants se pose également. L'introduction de nouveaux carburants entraîne en effet de nouvelles contraintes chimiques, thermiques et mécaniques, qui modifient les conditions auxquelles les lubrifiants sont soumis. La comparaison des propriétés de combustion de l'ammoniac avec les connaissances actuelles sur les mécanismes de dégradation des lubrifiants met en évidence plusieurs défis pour l'intégrité de ces derniers et pour les performances associées du moteur, qu'il est nécessaire d'explorer. L'objectif principal de ce travail de thèse est d'étudier ces défis potentiels, ainsi que les effets réciproques du vieillissement des lubrifiants sur la performance du moteur et les émissions de polluants produites lors de la combustion de l'ammoniac.

Objectifs et stratégie de la thèse

Afin de mieux comprendre le vieillissement des lubrifiants directement dans le moteur, une approche multiéchelle et multitechnique a été mise en œuvre. Des expériences de vieillissement accéléré ont d'abord été conduites pour isoler différents mécanismes de dégradation et mieux contrôler les conditions de vieillissement. En particulier, les effets des NO_x et de NH_3 ont été étudiés dans le cadre de vieillissement accéléré en laboratoire dans cette thèse. Pour évaluer correctement la dégradation dans ces conditions modifiées, le comportement du vieillissement dans des conditions d'oxydation de référence a tout d'abord dû être examiné. Cette étape préliminaire essentielle a permis de développer une méthodologie pour caractériser à la fois les propriétés physico-chimiques et les compositions moléculaires et élémentaires des huiles moteur, et d'affiner progressivement la matrice expérimentale. La construction de cette méthodologie et de ce cadre de référence a par la suite rendu possible l'interprétation de résultats obtenus directement lors d'essais moteur.

Chapitre 1

Le premier chapitre présente tout d'abord des considérations générales sur les lubrifiants, en détaillant leur rôle et leur formulation. Il met ensuite en lumière plusieurs caractéristiques distinctives de la combustion de l'ammoniac et de l'hydrogène, susceptibles d'introduire de nouveaux mécanismes de dégradation au regard des connaissances actuelles sur les lubrifiants. En s'appuyant sur des résultats issus de domaines connexes, il rassemble les connaissances actuelles sur quatre points clés : la réactivité vis-à-vis des oxydes d'azote, la compatibilité avec l'ammoniac imbrûlé, la contamination par l'eau, ainsi que l'influence des lubrifiants sur les émissions polluantes. Enfin, les principales techniques de caractérisation utilisées pour étudier la dégradation des lubrifiants sont présentées.

Les lubrifiants sont essentiels pour garantir l'efficacité optimale et la durabilité des moteurs à combustion interne. Ce sont des produits chimiquement complexes, contenant une large

gamme d'additifs adaptés à des applications et des conditions de fonctionnement spécifiques. La transition actuelle vers des carburants alternatifs, en particulier l'ammoniac et l'hydrogène, soulève de nouveaux enjeux concernant leur compatibilité avec les lubrifiants.

La durée de vie des lubrifiants est généralement déterminée par leur résistance à l'oxydation et leur consommation lors de la marche du moteur. L'oxydation en phase liquide est l'un des mécanismes principaux de dégradation des lubrifiants qui se produit en raison de l'exposition des huiles à l'oxygène [13]. Ce mécanisme conduit à la dégradation de l'intégrité des lubrifiants, altérant leurs capacités de réduction des frottements ainsi que d'autres propriétés fondamentales. Dans le cas de l'ammoniac et des mélanges, d'autres contraintes sont susceptibles d'engendrer des mécanismes de dégradation additionels.

Plusieurs études montrent notamment des niveaux élevés de NO_x et d'ammoniac imbrûlé, en plus d'une teneur substantielle en vapeur d'eau à l'échappement de moteurs à l'ammoniac [4, 14–16]. Par conséquent, les lubrifiants sont susceptibles d'être en contact avec ces espèces sur les parois des cylindres ou dans le carter, en raison du mécanisme de blow-by, avec des effets potentiellement néfastes sur leurs propriétés [17–19]. En effet, de manière similaire à l'oxydation induite par l'oxygène, les oxydes d'azote peuvent se solubiliser dans les huiles et réagir avec les hydrocarbures, générant des radicaux et des produits de dégradation [18, 19]. Bien que ce processus de "nitro-oxydation" soit connu par les fabricants de lubrifiants et contrôlé par des normes spécifiques [20], il n'est pas encore entièrement compris et mérite d'être étudié plus finement. La nitro-oxydation pourrait être réduite en choisissant des conditions où les émissions de NO_x sont les plus faibles. Malheureusement, plusieurs études montrent que limiter les niveaux de NO_x et d'ammoniac imbrûlé à l'échappement constitue un compromis [4, 16].

L'interaction entre l'huile et l'ammoniac a été principalement étudiée dans le contexte des compresseurs à ammoniac dans les systèmes de réfrigération [21, 22]. Il apparaît que l'ammoniac, en tant que molécule polaire, peut être partiellement soluble dans les huiles en fonction de leur polarité, et engendrer une diminution de la viscosité [22]. De plus, l'ammoniac dissout pourrait ensuite réagir comme une base avec les composés acides dans l'huile —additifs acides ou produits d'oxydation —et former des boues et des dépôts, comme rapporté par des fabricants [21, 23]. Des études récentes [17, 24, 25] ont examiné cette réactivité potentielle entre l'huile moteur et l'ammoniac dans des conditions plus proches des conditions des moteurs. Agocs *et al.* [17] ont rapporté une aminification et une augmentation des tendances aux dépôts des huiles moteur exposées à de l'air contaminé avec 1000 ppm NH_3 et 21,7 % NH_3 . Xu *et al.* ont également mis en avant la formation de liaisons de faible énergie entre de l'ammoniac dissout et des constituants polaires de l'huile, modifiant la rhéologie du fluide [24].

De plus, l'eau produite par la combustion peut migrer vers le carter et condenser sur des surfaces plus froides. Des problèmes d'émulsification ont été rapportés dans les prototypes de moteurs à hydrogène et à ammoniac, bien que les conséquences pour l'intégrité du lubrifiant

et ses propriétés de friction restent floues [26]. Dans le secteur maritime, la contamination par l'eau du fait de l'environnement est redoutée car elle peut être associée à des problématiques d'oxydation, de corrosion, de croissance bactérienne et de cavitation [27]. Si des gouttelettes d'eau entrent dans le flux de circulation de l'huile, elles peuvent également déstabiliser le film d'huile et diminuer la capacité du lubrifiant à réduire les frottements [27]. Comme l'ammoniac, l'absorption d'eau semble dépendre de la polarité de l'huile de base et de ses additifs [26].

Tous ces facteurs sont susceptibles d'affecter les propriétés des lubrifiants, réduisant leur durée de vie utile. Enfin, puisque les lubrifiants contribuent aux émissions de particules [28,29], tout changement dans leurs propriétés pourrait influencer les émissions globales de polluants, ce qui est une préoccupation majeure pour le développement de nouveaux moteurs plus propres.

Les travaux sur la dégradation des lubrifiants reposent souvent sur des protocoles de vieillissement accéléré, menés dans des conditions éloignées de celles du moteur, mais apportant néanmoins des informations précieuses sur leur réactivité. L'étude de ces produits, lourds et aux compositions complexes, nécessite de combiner plusieurs techniques de caractérisation. Parmi les techniques les plus couramment employées dans la littérature scientifique, on trouve notamment la spectroscopie infrarouge, les mesures de viscosité, ainsi que le titrage des espèces acides et basiques. Obrecht *et al.* [25] ont suggéré que ce dernier ne s'avérerait pas pertinent dans le cadre de l'étude de l'ammoniac car le résultat pouvait être perturbé par la présence d'ammoniac dissout.

Les technologies de moteurs à ammoniac et hydrogène étant encore à un stade de développement, la plupart des conclusions présentées ont été extrapolées de domaines de recherche connexes. Des études approfondies dans des conditions représentatives des moteurs sont donc nécessaires pour comprendre pleinement les implications en termes de dégradation des lubrifiants et de performances à long terme des moteurs. À partir de ces conclusions, les chapitres suivants examinent l'évolution des lubrifiants dans des moteurs fonctionnant à l'ammoniac, ainsi qu'avec des mélanges ammoniac/hydrogène, en combinant protocoles de vieillissement accéléré et expérimentations sur banc moteur.

Chapitre 2

Pour préparer l'étude de l'évolution des lubrifiants dans des conditions de dégradation accélérées simulant la combustion de l'ammoniac, le comportement de différentes huiles de base a d'abord été examiné dans des conditions de référence, en présence d'oxygène. Étant donné que les propriétés et la réactivité des lubrifiants sont largement déterminées par les additifs, ce qui complique également l'analyse moléculaire détaillée, cette étude s'est concentrée sur des huiles de base sans additifs. Bien que ce choix réduise la représentativité des résultats vis-à-vis de la réactivité réelle des lubrifiants commerciaux, il permet de découpler les effets des additifs et des huiles de base, permettant ainsi de tirer des conclusions plus universelles. Ce deuxième chapitre présente le développement et la mise en œuvre d'une approche multitechnique visant à

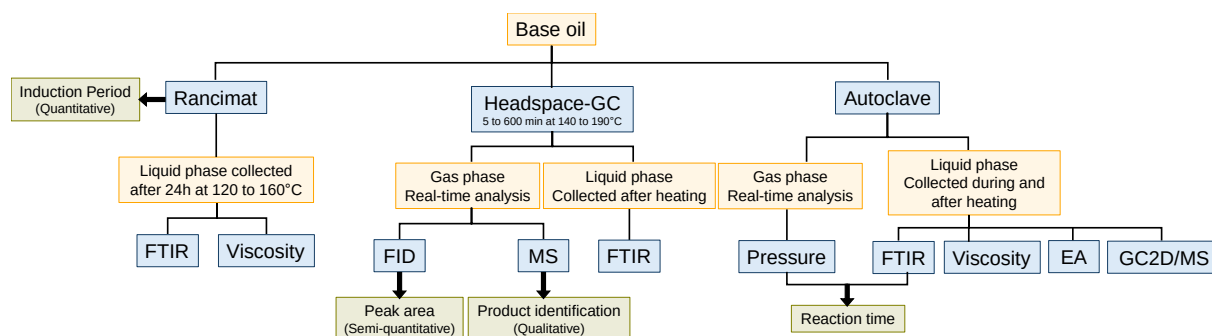


Figure 1: Schéma des dispositifs expérimentaux de vieillissement accéléré utilisés pour étudier le comportement à l'oxydation d'huiles de base, et les caractérisations associées

améliorer la compréhension de la dégradation des huiles de base et à identifier les paramètres pertinents pour son suivi. Trois protocoles ont été développés et appliqués pour oxyder et analyser huit huiles de base lubrifiantes d'origine minérale et synthétique; ils sont présentés en Figure 1. Le chapitre discute des avantages et de la nouveauté de chaque technique, et souligne les bénéfices de leur combinaison pour étudier un large éventail d'échantillons d'huile et obtenir une vue d'ensemble complète de leur comportement à l'oxydation.

La méthode Rancimat a d'abord été appliquée avec succès aux huiles de base. Les périodes d'induction des huiles ont été mesurées à trois températures différentes, et des échantillons d'huile ont été prélevés après 24 h pour être caractérisés à l'aide de mesures de viscosité et en spectroscopie FTIR. En parallèle, l'oxydation *operando* des mêmes huiles a été réalisée directement dans un échantillonneur automatique à espace de tête couplé à un instrument GC/MS. Les nombreux avantages de ce protocole, développé et mis en œuvre pour la première fois dans cette thèse, sont démontrés ici. Les huiles de base minérales, les naphthalènes alkylés et les huiles de base polyesters se sont toutes dégradées en six types principaux de produits : cétones, acides, aldéhydes, alcanes courts et dihydrofuranones. Certains produits supplémentaires, spécifiques à chaque huile de base, ont également été identifiés. Bien que les deux protocoles représentent des conditions d'oxydation différentes en termes d'apport d'oxygène, d'environnement ouvert/fermé, d'équilibre phase liquide/gaz, et reposent sur des principes de mesure différents, ils ont montré des tendances de réactivité similaires et ont fourni des informations complémentaires sur les produits étudiés. Les deux ont montré la forte réactivité des huiles minérales par rapport aux polyalphaoléfinés et la plus grande stabilité des naphthalènes alkylés. La combinaison de ces méthodologies a permis à la fois l'évaluation de l'évolution de propriétés clés de phase liquide (IR, viscosité) et l'identification des produits d'oxydation légers, grâce à des expériences faciles à mettre en œuvre. Cette approche a permis un premier criblage des huit huiles de base, dont deux ont été sélectionnées pour des expériences plus complexes. En s'appuyant sur ces résultats, une huile minérale et une huile polyester, désignées B et G respectivement, ont été sélectionnées pour une analyse plus approfondie, et ont subi un vieillissement accéléré sous oxygène pur dans un réacteur agité sous pression. Ces expériences préliminaires ont permis de définir une méthode de travail pour les expériences de vieillissement

et la caractérisation des huiles, et d'en évaluer la fidélité intermédiaire. En particulier, ce dispositif expérimental permet de procéder à des prélèvements réguliers d'huile qui peuvent être finement caractérisés, et d'exposer l'huile à différentes atmosphères gazeuses. La spectroscopie infrarouge, les mesures de teneur totale en oxygène et de viscosité ont été retenues comme descripteurs de l'évolution des huiles. De plus, une méthodologie pour l'analyse moléculaire utilisant le GC2D/MS a été développée.

L'étude de ces huit huiles de base à l'aide de trois configurations différentes et de multiples caractérisations nous a permis de définir un cadre pour l'évolution des propriétés des huiles de base dans des conditions contrôlées. Les expériences menées sous oxygène pur ont permis d'évaluer le protocole de vieillissement accéléré dans le réacteur dans des conditions standard. Cela a ouvert la voie à une meilleure compréhension de l'évolution des lubrifiants moteurs dans des conditions modifiées par rapport aux carburants conventionnels, qui fait l'objet du chapitre suivant.

Chapitre 3

Dans ce chapitre, la méthodologie de vieillissement accéléré dans un réacteur agité et sous pression, développée au chapitre précédent, a été appliquée avec des mélanges gazeux simulant ceux auxquels les lubrifiants peuvent être exposés lors du fonctionnement de moteurs alimentés à l'ammoniac pur ou à des mélanges. L'huile de base minérale et polyester complexe B et G ont été exposées à du dioxyde d'azote et de l'ammoniac dans l'air et caractérisées à différents temps de réaction.

Les résultats ont mis en lumière des effets contrastés des oxydes d'azote et de l'ammoniac sur les mécanismes de vieillissement des huiles. Le dioxyde d'azote se révèle puissant agent oxydant, accélérant l'initiation de la réaction d'oxydation, mais avec peu d'effet sur les produits de dégradation formés. À l'inverse, l'ammoniac semble ralentir la réaction d'oxydation en interagissant avec les produits oxygénés à mesure qu'ils sont formés. L'analyse d'échantillons collectés à des temps intermédiaires en chromatographie en phase gazeuse couplée à une détection spécifique des produits azotés a permis de mettre en évidence la solubilisation progressive de l'ammoniac dans la matrice hydrocarbure, puis la formation de produits de réaction azotés de tailles et types variés. Une analyse moléculaire plus approfondie a permis d'émettre l'hypothèse qu'il s'agissait en partie d'amides et de nitriles, issus de réactions avec les produits d'oxydation tels que les aldéhydes, acides ou alcools. La Figure 2 présente une représentation schématique du mécanisme d'interaction proposé entre l'oxygène, l'ammoniac et l'huile minérale.

Une expérience réalisée en ajoutant un petit volume de solution ammoniacale à l'huile minérale B dans le réacteur sous pression d'oxygène a également mis en évidence un phénomène de corrosion notable des parois du réacteur, attribué à l'action combinée de l'ammoniac, de l'eau et de l'oxygène. Ce résultat souligne l'importance d'évaluer soigneusement la compatibilité des matériaux dans des environnements riches en ammoniac.

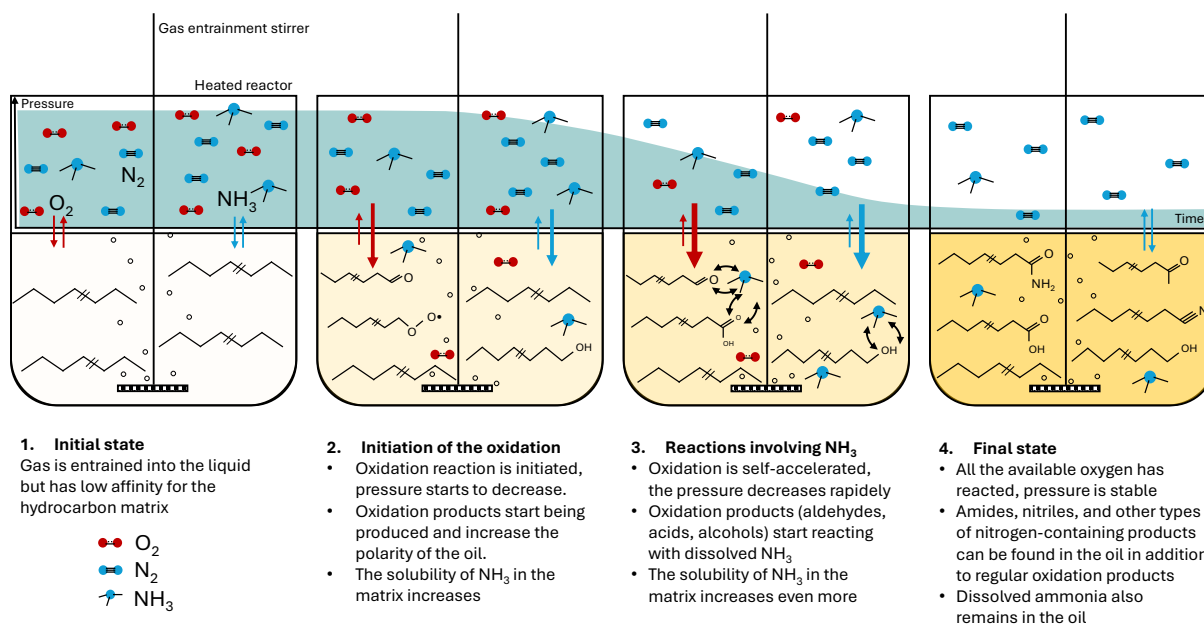


Figure 2: Illustration schématique du mécanisme de dégradation d'une huile minérale exposée à l'oxygène et l'ammoniac

En conclusion, cette étude met en évidence les effets distincts du dioxyde d'azote et de l'ammoniac sur la dégradation des huiles moteur. Alors que le dioxyde d'azote agit comme un accélérateur des processus oxydatifs, l'ammoniac joue un rôle plus ambivalent, modérant certaines réactions tout en favorisant la formation de nouveaux composés azotés. Ces résultats ouvrent des perspectives intéressantes pour adapter les formulations des lubrifiants aux carburants alternatifs comme l'ammoniac, tout en soulignant la nécessité de poursuivre les recherches sur les interactions entre gaz et huiles dans des conditions réelles de moteur.

Chapitre 4

Le chapitre 4 s'attache à étudier l'évolution de lubrifiants directement en conditions moteur. Un moteur monocylindre à allumage commandé a été alimenté alternativement à l'ammoniac et au méthane avec trois huiles différentes : une huile commerciale formulée, l'huile de base minérale B, et un échantillon de cette même huile minérale pré-vieillie en laboratoire afin de simuler un état de dégradation avancé. Le pré-vieillessement a consisté à exposer l'huile minérale à 140 °C à un mélange gazeux d'azote, oxygène et ammoniac dans le réacteur agité sous pression utilisé jusqu'à lors. Pour les essais moteur, un carter spécifique de 2 L a permis l'échantillonnage et l'analyse des huiles, qui ont été caractérisées par différentes techniques (analyse élémentaire, FTIR, viscosité, GC/NCD, ICP-OES, GC×GC/MS). Les résultats ont ensuite été comparés à ceux obtenus en vieillissement accéléré sous conditions contrôlées.

Malgré des durées de fonctionnement relativement courtes (4 h), une dégradation des huiles a été observée, avec des différences notables selon leur formulation et leur état initial. L'huile commerciale formulée a montré une stabilité relativement élevée vis-à-vis de l'oxydation, probablement grâce à ses additifs antioxydants. Toutefois, elle a accumulé de l'ammoniac dissous,

entraînant une diminution de viscosité et la corrosion de certaines pièces moteur (cuivre, fer). L'huile de base minérale sans additifs a présenté une augmentation modérée de ses teneurs en oxygène et en azote, sans toutefois d'évolution significative de la viscosité. Enfin, l'huile pré-vieillie a connu une évolution rapide dès la première heure d'utilisation : perte de composés volatils, forte absorption d'ammoniac, réactions avec les composants de l'huile et augmentation marquée de la viscosité. Cette huile s'est révélée particulièrement corrosive, notamment envers le cuivre et le fer, indiquant également un risque accru d'usure. Le tableau 1 synthétise les tendances d'évolution de paramètres clés des huiles lors des essais moteur.

Table 1: Résumé des tendances d'évolution des propriétés des différentes huiles sur 4 h cumulées de combustion sous NH_3 et CH_4 alternativement. "LUB" désigne le lubrifiant commercial utilisé, et huile B2 l'huile minérale de groupe III.

Huile	Viscosité cin. (mm^2/s)	Teneur oxygène	Teneur azote	Teneur soufre	Teneur eau	Teneur métaux
LUB	—	=	++	—	++	++
Huile B2	=	+	+	non mesuré	+	+
Huile B2 pré-vieillie	+	—	+++	non mesuré	++	+++

Ces observations soulignent l'intérêt de la méthodologie de pré-vieillessement : elle permet d'accéder plus rapidement à des stades avancés de dégradation et de comparer directement les mécanismes mis en évidence en conditions accélérées et en conditions moteur réelles. Néanmoins, certaines limites doivent être notées, telles que des contaminations résiduelles entre essais malgré les rinçages et la brièveté des durées d'opération, susceptibles d'influencer l'interprétation des résultats.

Ce travail met en évidence plusieurs points majeurs. Tout d'abord, l'ammoniac peut effectivement se solubiliser dans les huiles moteur au cours de la combustion, même dans des matrices peu polaires. Cette solubilisation est favorisée par la polarité de l'huile et la présence de produits d'oxydation, et peut avoir plusieurs conséquences délétères : modification des propriétés tribologiques, corrosion de pièces métalliques, ou encore réactions chimiques conduisant à de nouveaux produits de dégradation. Ces résultats montrent que, au-delà du vieillissement accéléré en laboratoire, l'ammoniac peut également affecter les lubrifiants dans des conditions moteur.

Ces conclusions soulignent la nécessité d'adapter les formulations de lubrifiants aux spécificités de la combustion de l'ammoniac. En particulier, il apparaît crucial de limiter la solubilisation de l'ammoniac dans l'huile et d'éviter l'utilisation d'éléments ou d'alliages à base de cuivre dans les moteurs alimentés à l'ammoniac. Enfin, des stratégies comme la mise en place de systèmes de ventilation pourraient contribuer à réduire le temps de résidence de l'ammoniac dans l'huile.

Chapitre 5

Le dernier chapitre de cette thèse s'intéresse aux effets réciproques de l'évolution de l'huile moteur sur les performances du moteur ainsi que sur les émissions de polluants. Ce chapitre décrit tout d'abord le dispositif expérimental mis en oeuvre pour monitorer les émissions gazeuses et de particules, au moyen d'un dispositif de dilution de l'échappement, auquel sont connectés une baie d'analyse de gaz FTIR, un analyseur de particules EEPS et un dispositif de collecte de particules directement sur des grilles de microscopie. Les performances du moteur ainsi que les émissions associées ont été étudiées avec les trois huiles présentées précédemment, à savoir le lubrifiant commercial additivé, l'huile minérale dans l'état frais et pré-vieilli.

L'étude des paramètres moteur a mis en avant que l'opération du moteur avec l'huile pré-vieillie était associée à une réduction de l'efficacité thermique lors de la combustion d'ammoniac pur et de mélanges ammoniac/hydrogène, mais pas du méthane. Dans le cas de l'ammoniac, cela était également associé à des différences dans les émissions gazeuses, avec une augmentation des émissions de NO et N₂O et une diminution de celles de CO. Le fait que le méthane ne soit pas impacté de la même manière, alors même que méthane et ammoniac ont été utilisés alternativement, suggère que ce résultat n'est simplement explicable par une dégradation générale de l'huile pré-vieillie, qui affecterait tout type de carburant. Il semblerait plutôt qu'une interaction spécifique entre l'ammoniac et l'huile directement pendant l'opération du moteur puisse être à l'origine de la réduction de l'efficacité thermique du moteur constatée. Plusieurs études récentes ont démontré que la présence d'ammoniac avait pour effet d'augmenter le coefficient de frottement d'huiles moteur mesuré en laboratoire, du fait de l'absorption d'ammoniac directement dans le film d'huile [30,31]. Un phénomène similaire pourrait se produire directement dans le moteur sur les parois du cylindres. Les caractérisations des huiles décrites dans le chapitre précédent ont en effet mis en avant une plus grande affinité de l'ammoniac pour l'huile pré-vieillie, ainsi qu'une teneur en fer plus importante, indiquant une usure accrue avec cette huile dégradée.

Les émissions de particules ont été étudiées en parallèle, au moyen d'un analyseur en ligne fournissant la distribution de taille en temps réel. L'influence importante des conditions de dilution de l'échappement sur le nombre total de particules, ainsi que sur l'allure de la distribution de taille a été mise en avant pour le méthane et l'ammoniac. Pour ces deux gaz, le nombre total de particules diminue fortement quand la dilution augmente, et ce même après qu'un facteur correctif de la dilution ait été appliqué. De même, à faible dilution, davantage de particules, dites du mode accumulation, sont observées. Cela est dû au fait qu'un faible facteur de dilution favorise la nucléation homogène d'espèces à l'échappement, ainsi que la condensation d'espèces sur des noyaux déjà existants, augmentant le nombre de particules plus larges, dites d'accumulation. Le fort impact des conditions de dilution sur le nombre total de particules met en évidence l'importante contribution d'espèces volatiles condensables dans les émissions associées à la combustion de l'ammoniac.

En parallèle, des particules obtenues avec les trois huiles moteur ont directement été collectées sur des grilles de microscopie. Une analyse morphologique a révélé des particules complexes, incluant des structures core-shell, des fragments amorphes, des fragments métalliques et des résidus de lubrifiants. Avec l'ammoniac, de nombreux objets de nature semi-volatile et très sensibles au faisceau d'électrons ont été observés. Avec le méthane, les particules carbonées directement issues de la combustion étaient majoritaires. L'analyse de la composition chimique de ces éléments a montré que les additifs influencent significativement la nature et la composition des particules, avec notamment une forte prévalence du soufre et calcium, provenant des additifs, dans les particules collectées avec le lubrifiant commercial. Pour la première fois, un panorama des types de morphologies de particules formées lors de la combustion de l'ammoniac a été dressé.

Ces observations soulignent les défis liés à l'évaluation des émissions de particules d'ammoniac, en raison de la prévalence des particules volatiles, souvent exclues des réglementations actuelles. Les résultats présentés dans ce chapitre mettent en avant la nécessité de développer des formulations spécifiques de lubrifiants permettant de préserver les performances du moteur lors de la combustion d'ammoniac et de minimiser les émissions associées.

Conclusion

Dans le cadre du développement de carburants alternatifs comme l'ammoniac, caractérisés par des propriétés de combustion et un comportement chimique différents des carburants conventionnels, cette étude avait pour objectif principal d'explorer les défis potentiels posés aux lubrifiants ainsi que les effets réciproques du vieillissement des lubrifiants sur la combustion et les émissions de polluants.

L'étude a été structurée en plusieurs étapes : identification des défis spécifiques liés à la combustion de l'ammoniac à travers une revue de la littérature; analyse du comportement à l'oxydation d'huiles de base dans des conditions de référence et développement d'une méthodologie expérimentale pour le vieillissement accéléré; exploration de l'évolution des huiles de base dans des conditions de vieillissement accéléré modifiées, incluant les effets des oxydes d'azote, de l'ammoniac gazeux et de l'ammoniac aqueux; étude de l'évolution des mêmes huiles directement lors d'essais moteur; et enfin analyse des effets de la dégradation des huiles sur les performances du moteur et les émissions polluantes, gazeuses et de particules.

Les résultats montrent que les lubrifiants jouent un rôle central dans le fonctionnement des moteurs à combustion interne et subissent des mécanismes de vieillissement spécifiques lorsqu'ils sont exposés à l'ammoniac. De nouveaux mécanismes de dégradation impliquant l'ammoniac et l'oxygène ont été identifiés, initiés par l'absorption d'ammoniac dans l'huile et conduisant à la formation de produits contenant de l'azote tels que des amides et/ou des nitriles notamment, en conditions de laboratoire. Par la suite, le suivi de l'évolution d'huiles directement pendant des essais moteur avec du méthane et de l'ammoniac a permis de mettre

en évidence une dégradation des huiles en seulement 4 h de combustion, au niveau moléculaire et avec des répercussions sur les propriétés des huiles. En outre, l'absorption d'ammoniac dans les lubrifiants, accentuée par leur polarité, semble être corrélée avec l'augmentation de leur corrosivité. Réciproquement, ces changements chimiques influencent la performance du moteur et les émissions associées, en particulier les émissions de particules dominées par des espèces volatiles provenant du lubrifiant. Ces travaux ont également montré que bien que la combustion d'ammoniac ne produise pas directement de carbone, des émissions de particules polluantes dérivées du lubrifiant ou de résidus métalliques peuvent être mesurées.

Cette étude ouvre la voie à de futures recherches sur les mécanismes de dégradation chimique, les propriétés tribologiques des huiles, l'optimisation des formulations d'huiles pour minimiser les effets de l'ammoniac, et l'amélioration des protocoles de mesure des émissions. Les principaux résultats soulignent l'importance d'examiner la compatibilité entre ammoniac et lubrifiants pour assurer une utilisation durable et sécurisée des futurs moteurs.

General introduction

Context of the study

The combustion of carbon-based fuels for energy production, industrial processes, and transportation is a major source of greenhouse gas emissions. Since the onset of the industrial era, the massive release of these gases has contributed significantly to the critical challenge of climate change. The transportation sector alone accounts for 15 % of net global greenhouse gas emissions, corresponding to 8.7 Gt CO_{2eq} [1]. In response, research on electrification and alternative fuels is mobilizing both scientists and industry. While batteries and electric motors are considered promising for light vehicles or urban transports, internal combustion engines appear better suited for applications requiring high power and long autonomy, such as long-distance and off-road transportation, provided they operate on carbon-free fuels [1].

In recent years, hydrogen has attracted growing interest and development as a carbon-free energy carrier, but it still faces major challenges, particularly regarding storage and transportation [1]. Ammonia itself can be seen as an efficient hydrogen-carrier with several advantages. This molecule can be stored under easier conditions, as it is under the liquid state at 10 bar at ambient temperature, or -33 °C at atmospheric pressure, and has a greater volumetric energy density compared to hydrogen, with 11,3 GJ/m³ at 1,1 MPa/300K, compared to 4,7 GJ/m³ at 70 MPa [2]. In addition, this molecule already benefits from important storage and transport infrastructures in ports due to its massive use for fertilizers and as a feedstock for the synthesis of various chemicals [2, 3]. For these reasons, it also attracts growing interest and is actively considered as a potential carbon-free fuel, especially for maritime transportation. However, this molecule is hard to ignite and sometimes requires the uses of co-fuels such as hydrogen [4–6] or diesel [7, 8].

Historically, hydrogen is mainly produced via the methane steam reforming process, which is based on fossil fuel energy [2]. Likewise, ammonia is currently mainly synthesized from hydrogen via the energy demanding Haber-Bosch process: $\text{N}_2 + 3\text{H}_2 \longleftrightarrow 2\text{NH}_3$, at 670 K, 10–30 MPa, with catalysts [2]. Worldwide, ammonia production accounts for around 2 % of the total final energy consumption, among which 40 % is consumed as feedstock and 60 % as process energy, and results in 450 Mt CO_{2eq} [3]. However, varied decarbonized production pathways are currently being developed, including electrolysis, methane pyrolysis and fossil-based routes associated with carbon capture and storage, as thoroughly reported in the review from Valera-Medina *et al.* [2].

According to the International Energy Agency (IEA), ammonia is projected to account for 25 % to 45 % of the total final energy consumption of the shipping industry by 2050 (Figure 3) [3]. Major engines manufacturers such as MAN, WinGD, and Wärtsilä, are planning to commercialize retrofitted ammonia-powered two-stroke engines for containerships by the end of 2025/2026 and multiply communications about their progress [9–12].

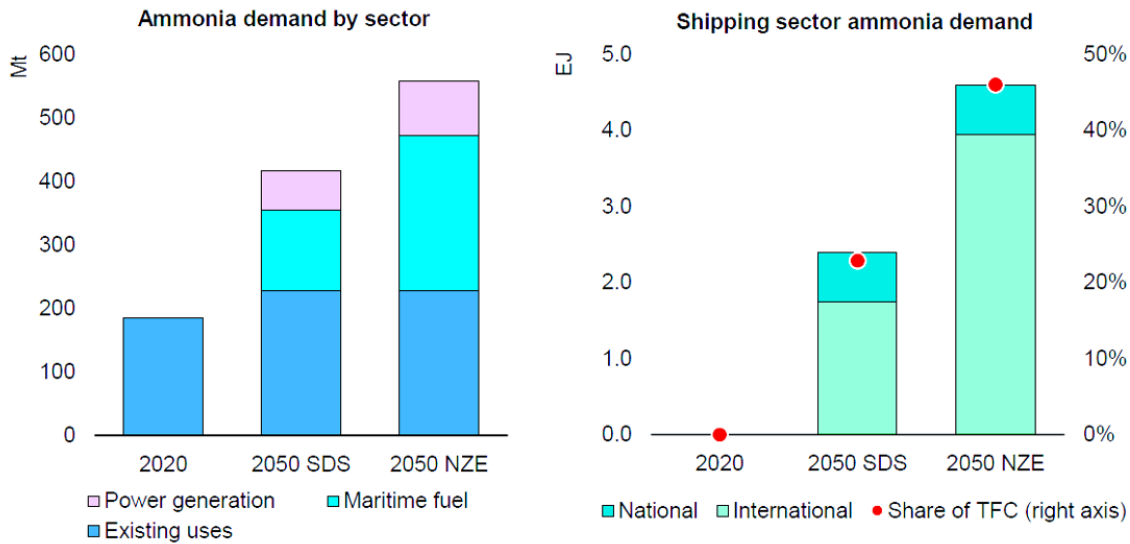


Figure 3: Ammonia use as an energy carrier in the Sustainable Development Scenario (SDS) and the Net Zero Emissions by 2050 scenario (NZE). Reprinted from [3]. TFC=Total Final energy Consumption

The development of such engines involves extensive efforts to adapt the engine design, injection strategies and burning conditions to the specific combustion properties of ammonia and its blends [2, 6]. Meanwhile, the adaptability of lubricants is also challenged. In internal combustion engines, lubrication is a key challenge to ensure moderate fuel consumption, high energetic yield, and durability of the engine. Engine oils are complex products, with formulations tailored to specific types of engines. The global market of automotive lubricants reached \$ 78.6 billion in 2023 [32]. Engine oils represent the largest market share before gear oil, brake fluid or transmissions fluids. Lubricants dedicated to passenger cars also represent the largest market share compared to light commercial vehicles and heavy commercial vehicles including busses, trucks, and heavy-duty machineries. In parallel, the global market of marine lubricants reached \$ 6.1 billion in 2022, among which 50 % for engine oils, and for a total of more than 56000 merchant ships [33]. These figures are expected to grow in future years as lubricants are considered critical fluids [32].

The lifetime of lubricants is usually determined by their resistance to oxidation and consumption rate. Liquid phase oxidation, the major degradation mechanism, occurs due to oil exposure to oxygen and combustion by-products such as nitrogen oxides [13]. This mechanism leads to the degradation of lubricants integrity, altering its friction reducing abilities as well as other fundamental properties. New fuels impose new chemical, thermal, and me-

chanical constraints, all modifying the conditions endured by lubricants. Therefore, assessing the fuel/engine oil compatibility is crucial to guarantee proper function and reasonable drain intervals.

The effect of ammonia, hydrogen and their blends on lubricants in internal combustion engines is a relatively new field of study [17, 34]. However, lubricants degradation processes have been studied in other contexts, with conventional fuels [13, 35], or in compressors using ammonia as a refrigerant for example [21]. The findings of these studies indicate that several combustion characteristic of ammonia and its blends might challenge the lifetime of lubricants.

Measurements at the exhaust of ammonia test engines conducted in several studies [4, 14–16] show potential high levels of NO_x and unburned ammonia before post treatment systems, in addition to substantial water content, as a function of the engine operating conditions and engine architecture. Hence, lubricants are likely to be in contact with these species on the cylinder walls or in the crankcase due to blow-by mechanism with possible detrimental effects on their properties [17–19]. Indeed, similarly to oxygen-driven oxidation, NO_x can solubilize in oils and react with hydrocarbons, generating radicals and degradation products [18, 19]. Even though this “nitro-oxidation” process is recognized by lubricants manufacturers and controlled with specific standards [20], it is not yet fully understood and deserves to be further studied. Nitro-oxidation could be reduced by choosing conditions where NO_x emissions are the lowest. Unfortunately, several studies show that limiting NO_x and unburned ammonia levels at the exhaust is a trade-off [4, 16]. The interaction between oil and ammonia was mainly studied in the context of ammonia compressors in refrigeration systems [21, 22]. It appears that ammonia, as a polar molecule, can be soluble in oils according to their polarity and cause a viscosity decrease [22]. Furthermore, dissolved ammonia may act as a base and react with acidic compounds in the oil—acidic functions of the base oil itself, acidic additives, or oxidation products—and form sludge and deposits, as reported by manufacturers [21, 23]. Recent studies [17, 24, 25] examined this potential reactivity between engine oil and ammonia under conditions closer to engines conditions. Agocs *et al.* [17] reported aminification and increased deposit tendencies of engine oils exposed to air contaminated with 1000 ppm NH_3 and 21.7 % NH_3 . Additionally, water produced during combustion can travel to the crankcase and condensate on cooler surfaces. Emulsification issues were reported in hydrogen and ammonia engine prototypes, though the consequences for lubricant integrity and friction properties remain unclear [26]. In the marine sector, water contamination is well-known as it can degrade the lubricant and damage engine itself through oxidation and corrosion, bacterial growth, and cavitation [27]. If water droplets enter the oil circulation flow, they can destabilize the oil film and decrease the friction-reduction ability of the lubricant [27]. Like ammonia, water uptake seems to depend on the polarity of the base oil and its additives [26]. All these factors are likely to affect lubricant properties, reducing their service life. Lastly, since lubricants contribute to particles emissions [28, 29], changes in their properties could influence overall pollutant emis-

sions, which is a key concern for the development of new, cleaner engines. These potential issues are largely inferred from adjacent research fields. Therefore, comprehensive investigations under engine-representative conditions remain necessary to assess the implications of ammonia combustion for lubricant degradation and long-term engine performance.

Objectives and strategy of the thesis

The emergence of alternative fuels such as ammonia, whose combustion characteristics and chemical reactivity differ from conventional fuels, raises new questions regarding fuel/engine oil compatibility. Comparison of these combustion properties with current knowledge about lubricant degradation mechanisms points out several challenges for lubricant integrity and associated engine performance that need to be addressed. The main objective of this work is to investigate these potential challenges for lubricants, as well as the reciprocal effects of lubricants aging on combustion and pollutant emissions during ammonia combustion.

To better understand lubricant aging directly in the engine, a multiscale and multitechnique approach was implemented. Accelerated aging experiments were first conducted to isolate different degradation mechanisms and have a better control of the degradation conditions. In particular, the effects of NO_x and NH_3 were investigated under laboratory accelerated aging conditions in this thesis. To properly assess degradation under these modified conditions, aging behavior under reference oxidation conditions first had to be examined. This essential preliminary step enabled the development of a methodological workflow to characterize both the physico-chemical properties and the molecular and elemental compositions of engine oils, and to iteratively refine the experimental matrix. Building this methodology and reference framework enabled the interpretation of results obtained directly from engine tests.

Outline of the manuscript

To report these different work phases, this manuscript is organized in five chapters.

- Chapter 1 first reviews the role of lubricants in internal combustion engines. Then, it presents how they could potentially be affected by the specific combustion characteristics of ammonia and its blends in addition to conventional aging mechanisms. Details about the usual techniques used to study lubricants degradation are also provided.
- Chapter 2 examines the oxidation behavior of base oils under reference conditions and introduces the characterization techniques applied throughout the rest of this manuscript.
- Chapter 3 investigates the effects of NO_x and NH_3 on two selected base oils using accelerated aging. New degradation pathways are discussed.
- Chapter 4 studies the evolution of a base oil in the fresh and pre-aged state, and a lubricant, directly in the engine. Degradation mechanisms are discussed and compared to accelerated aging.

- Chapter 5 focuses on the consequences of oil degradation on engine performance and pollutant emissions. It investigates the unexplored topic of particulate matter under ammonia combustion and discusses the effect of the engine oil and sampling conditions.

Figure 4 depicts the outline of the experimental chapters of this thesis.

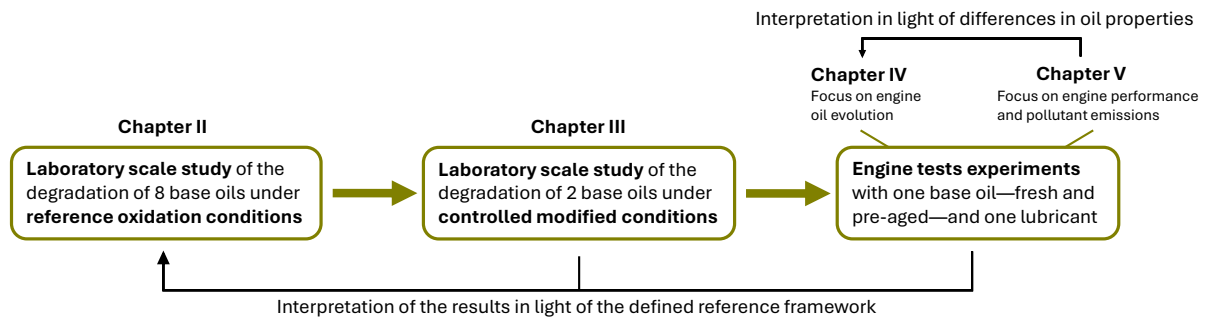


Figure 4: Outline of the experimental chapters of this manuscript

Chapter 1

Literature review: potential impacts of ammonia/hydrogen combustion on lubricants

1.1	Basics of lubricants in combustion engines	20
1.1.1	Roles of lubrication	20
1.1.2	Formulation of lubricants	21
1.1.3	Fuel-oil interactions	23
1.2	Effect of hydrogen and/or ammonia combustion on the aging of the lubricant	25
1.2.1	Potential issues related to hydrogen and ammonia combustion characteristics	25
1.2.2	Liquid phase oxidation	27
1.2.3	Nitro-Oxidation	31
1.2.4	Compatibility with unburned fuel	40
1.2.5	Compatibility with water	47
1.2.6	Particle emissions	48
1.3	Lubricants characterization techniques	56
1.3.1	Monitoring oxidation	56
1.3.2	Accelerated aging protocols	56
1.3.3	Accelerated aging versus in-field aging	59
1.3.4	Analytical techniques	60
1.4	Conclusion	63

As emphasized in the general introduction, the ongoing development of ammonia and its blends as alternative fuels for combustion applications, particularly in long-distance shipping, raises new questions regarding fuel/engine oil compatibility. The first chapter of this manuscript initially outlines the fundamental role of lubricants in internal combustion engines, describing how they are stressed during engine operation, their exposure to fuels and exhaust gases, and the complexity of their formulation to maintain engine durability and efficiency over extended periods of time. The following section presents the combustion characteristics of ammonia and hydrogen in relation to current knowledge of lubricant degradation mechanisms. High levels of nitrogen oxides, the presence of unburned fuel residues, interactions with water, and pollutant emissions are identified as the main challenges for lubricants in engines operating with ammonia/hydrogen blends. The state of the art regarding each of these degradation mechanisms is then reviewed in detail. Finally, the chapter concludes with an overview of the experimental techniques most commonly used in the literature to characterize and analyze lubricants.

Selected passages of this literature review have been published as a review paper with complete reference Doncoeur, C., L. Giarracca-Mehl, P. Cologon, and C. Mounaïm-Rousselle. Potential impacts of ammonia/hydrogen on engine lubricants: A review. *Frontiers in Energy*, 2025, 10.1007/s11708-025-1031-3 .

1. Basics of lubricants in combustion engines

1.1 Roles of lubrication

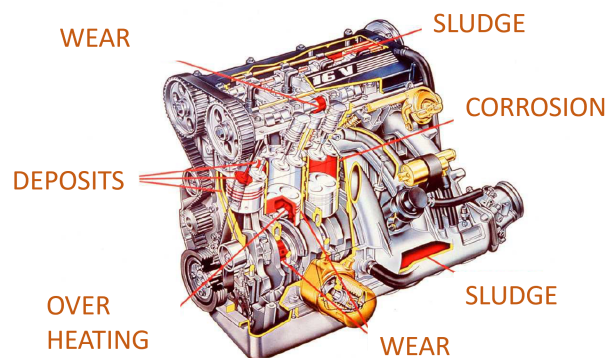


Figure 1.1: Roles of the lubricant and lubrication circulation system (yellow) in a four-cylinder engine [36]

In internal combustion engines, lubricants continuously circulate in a closed-loop circuit, as shown in yellow in Figure 1.1. The lubricant is collected in the crankcase, filtered through a strainer, and pumped to the top of the engine, from where it returns by gravity. A fraction of the oil is also injected directly under the piston crown through a special nozzle. A heat exchanger can be installed in the crankcase to maintain an average oil temperature of around 100 °C.

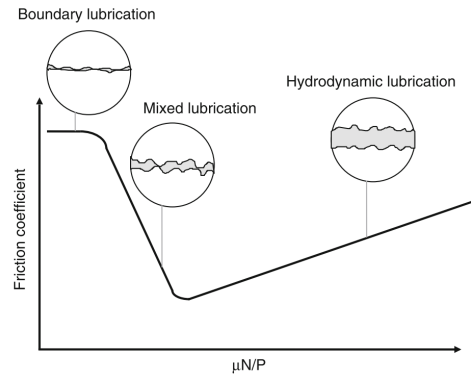


Figure 1.2: Stribeck curve. μ is the dynamic viscosity, N the relative speed and P the normal load applied. Reprinted from [37] with permission from Springer Nature.

Lubricants' primary role is to protect metallic surfaces from wear. This property is governed by the science of tribology. Theory behind oil film lubrication of rough surfaces is described by Stribeck's model and Hersey number. Hersey showed that friction coefficient due to viscous shear was a function of the lubricant's viscosity, multiplied by the relative speed of the surfaces, divided by the normal load applied [37]. It is then possible to represent friction coefficient in the whole lubrication range, depending on this number (Figure 1.2). This representation shows three distinct domains, called lubrication regimes. When the surface roughness is smaller than the oil film thickness, surfaces are completely separated, and lubrication is governed by the oil's viscosity: it is the hydrodynamic regime. On the contrary, when the two surfaces are in contact, lubrication is governed by the surface's properties: it is the boundary regime. Mixed regime is a combination of both situations, in which surfaces can be in contact around asperities. Depending on the engine part and the speed, lubricants experience all kinds of regimes in engines [38]. In addition to preventing wear, lubricants play several critical roles, essential for the optimized operation of engines (Figure 1.1) [39]:

- Preventing impurities deposition of sludge or varnish
- Protecting surfaces against corrosion
- Cooling the engine

Lubricants are thus high-technology products that must maintain effective friction-reducing properties under severe mechanical stress and varying pressure and temperature conditions over a long period of time, while fulfilling other complementary key roles. Some of these properties are directly linked to the hydrocarbon nature of lubricants, while others have to be fulfilled by additives [39].

1.2 Formulation of lubricants

Lubricants are usually composed of 80% of a base oil, complemented by 20% of additives, each component fulfilling one or more specific functions [39].

1.2.1 Base oils: origins and classification

Several types of base oils can be used to formulate lubricants, and they can have a mineral or a synthetic origin. Mineral oils are petroleum products obtained from the heaviest fractions of atmospheric distillation, called atmospheric residue. This residue can itself be submitted to vacuum distillation in order to be further fractionated. Isoparaffins, n-paraffins, naphthenics, and aromatics are the main molecules found in crude oil. It also contains impurities such as sulfur compounds, nitrogen compounds, oxygenated compounds and metals. The atmospheric residue contains molecules from all these families, with a high number of carbon atoms, typically between 20 and 50 [39, 40]. Among these molecules, linear paraffins have poor cold properties and tend to crystallize as wax, and naphthenics and aromatics lead to high variations of the viscosity depending on the temperature. Besides, sulfur and nitrogen compounds can lead to highly polluting sulfuric/nitric acid or sulfur/nitrogen oxides emissions. All these compounds have to be removed from distillates in order to produce high quality and standardized base oils. This is the aim of the dewaxing, solvent extraction and hydrotreatment steps endured by distillates. These processes can be processed in different orders and in more or less severe conditions. Different choices in distillate selection and refining process leads to a variety of qualities in the mineral base oils. To ensure shared standards, the American Petroleum Institute (API) classifies mineral oils in three types—group I, II, III—according to their final aromatics, sulfur and nitrogen contents, and their viscosity range [41] (Table 1.1). The viscosity variation with temperature is described via the Viscosity Index (VI). It is calculated from the kinematic viscosity at 40 °C and 100 °C according to the standards ASTM D2270 and ISO 2909.

Table 1.1: Classification of base oils by the API (1993) [41]

Group	Composition	Saturates, w%	Sulfur, w%	Viscosity index (VI)	Typical aromatics, w%
I	Solvent refined oils	<90	>0.3	80–119	15–35
II	Hydrotreated oils	≥90	≤0.3	80–119	≤7
III	Severely hydrotreated oils	≥90	≤0.3	≥120	≤5
III+	Fischer-Tropsch	≥90	≤0.3	≥120	—
IV	Polyalphaolefins	—	—	—	—
V	Every other type	—	—	—	—

On the other hand, synthetic oils result from petrochemical processes. They have the particularity of having a more tunable and reproducible composition. In the API classification, they represent groups IV and V (Table 1.1). Group IV is only composed of polyalphaolefins (PAO) which were historically the first synthetic oils. Group V contains every other type of oils, such as esters, alkylbenzenes, polyalkylene glycols, silicones and vegetable oils for instance. Group III+ is an intermediate category: oils have similar standards compared to group III, but they are obtained from the Fischer-Tropsch gas-to-liquid process. This chemical process converts syngas coming from coal gasification, natural gas or biomass into hydrocarbons [42].

1.1. BASICS OF LUBRICANTS IN COMBUSTION ENGINES

The choice of a base oil determines essential properties of lubricants such as the viscosity, polarity, and chemical stability. These, in turn, are respectively key properties for friction and wear reduction ability, volatility, solvency, and oxidation stability [39]. Yet, performance in terms of tribology, detergency and lifetime stability can be further improved by incorporating specific additives.

1.2.2 Additives

To improve the performance of base oils and add new functionalities to lubricants, additives are commonly incorporated in their formulations. According to the classification proposed by Minami *et al.* in [43], these additives can be grouped into three categories: those that improve the tribological properties of lubricants, those that enhance their rheological behavior, and those that extend their service life by introducing new functionalities, as summarized in Table 1.2. A detailed review of the chemistry and functions of these additives can be found in [43–48].

Table 1.2: Main types of engine lubricants additives and examples

Type	Additive	Examples
Tribo-improvers	Friction modifiers	Alkyl chain connected to a polar head: acid, amine or amide, MoDTC
	Anti-wear agents	Phosphates
	Extreme pressure agents	ZnDTP
Rheo-improvers	Pour-point depressants	Polymethacrylates
	Viscosity modifiers	Styrene-diene copolymers
Maintainers	Antioxidants	Aromatic amines, phenols
	Detergents	Sulfonates, salicylates and phenates
	Dispersants	Polyisobutadiene
	Demulsifiers	Oleic acid
	Anti-foam agents	Polymethylsiloxane
	Anti-bacterial agents	Phenols, acetals
	Fragrances, coloring agents	Perfumed essential oil

Additives are tailored to meet the specific requirements of each application, with some compounds exhibiting multifunctional properties. In engine oils, the main additives usually include aminic and phenolic antioxidants, along with zinc dithiophosphate (ZnDTP) [44]. Oils dedicated to marine engines may also contain dispersants and overbased detergents to neutralize acidic species due to the high sulfur content of heavy fuels used in large ships, and deal with water contamination [49].

1.3 Fuel-oil interactions

An internal combustion engine is not a completely sealed system. Several oil and gas transport mechanisms lead to contacts between lubricants and fuels or combustion gases [50].

1.1. BASICS OF LUBRICANTS IN COMBUSTION ENGINES

On the one hand, combustion gases can pass through the sides of the piston and enter the crankcase, carrying oil droplets on the way [50]. This blow-by phenomenon is due to the pressure difference between the combustion chamber and the oil pan (Figure 1.3 c). As a result, nitrogen oxides, oxygen, and unburned fuel residues are transported into the crankcase. Once solubilized, these gases can take part in reactions in the liquid phase, such as oxidation and nitro-oxidation, which degrade the lubricant, as will be discussed further. On the other hand, as it is distributed near the pistons crown and next to the injection valves, the lubricant can be in contact with fuels and exhaust gases, and may even contribute to combustion if transported into the combustion chamber. Several oil consumption mechanisms were identified (Figure 1.3) [50,51]:

- Spraying of oil into the chamber by piston inertia (a)
- Draining of oil accumulated in the piston rings by reverse blow-by (b)
- Evaporation of the oil film (d)
- Leakage around intake valves (e)

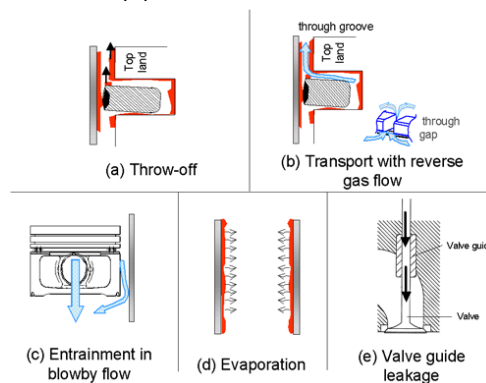


Figure 1.3: Different oil transport mechanisms in an engine, near the segments (a, b, c), on the cylinder wall (d) and near the intake valve (e). Reprinted with permission from [51], copyright 2004, SAE International

Various parameters affecting the relative contribution of each mechanism under different operating conditions, such as regime, and temperature, have been identified by Yilmaz *et al.* [51]. The amount of lubricant entering the combustion chamber depends on the thickness of the film oil on the cylinder walls, which in turn is influenced by the viscosity of the oil [51]. Besides, evaporation occurs mainly at high loads, probably due to an increase in wall temperature under these conditions [51]. The evaporation rate is also related to the oil's volatility and the residence time of the oil film on hot surfaces, as might be expected [52]. Any change of these properties can affect oil consumption, engine operation and pollutant emissions [53,54]. Because of these oil and gases transport mechanisms, engine oils are likely to be in contact with both fuels and combustion gases. Fuel/oil compatibility therefore needs to be addressed at two levels: chemical reactivity in the crankcase (liquid phase), and co-combustion in the chamber. When exploring alternative fuels, fuel/oil compatibility seems to be a critical issue.

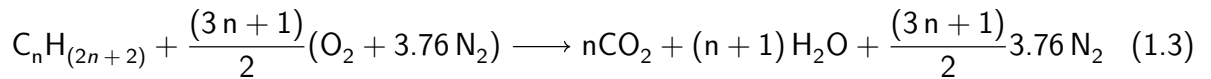
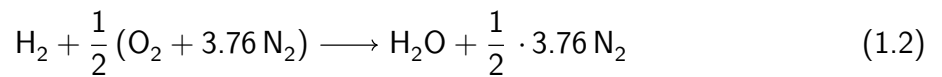
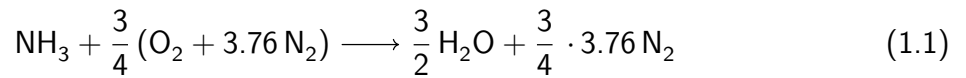
In this section, the role of lubricants in engine applications and the mechanical, thermal and chemical constraints they endure during their service-time was presented. These constraints are directly related to the fuel used and its combustion byproducts. A brief overview of different oil formulations and types of additives was also provided, pointing out that lubricants' formulations are complex and tailored for each type of applications. Therefore, the development of alternative fuels raises new issues of fuel/oil compatibility. In order to adapt lubricant formulations to ammonia and its blends, especially with hydrogen, it is necessary to first understand the unique aging mechanisms involved in engines operated on this fuel. The following section examines the combustion characteristics of ammonia and hydrogen, and how they differ from conventional fuels, with the aim of identifying potential challenges they may raise for lubricants, with consequences on proper engine operation and pollutant emissions.

2. Effect of hydrogen and/or ammonia combustion on the aging of the lubricant

2.1 Potential issues related to hydrogen and ammonia combustion characteristics

Table 1.3 summarizes the main combustion characteristics of ammonia and hydrogen in comparison to standard gasoline.

The global stoichiometric combustion reactions for these fuels are:



Gasoline, ammonia and hydrogen have different properties in terms of energy density and combustion properties (Table 1.3). Therefore, extensive research has been conducted and continues to be undertaken to adapt engine design and operating conditions for ammonia and hydrogen [4–6, 55]. In order to achieve maximum engine performance, lubricants formulations must also be tailored to accommodate the characteristics of these new fuels. Among the data from Table 1.3, several features can be highlighted. The combustion of hydrogen is characterized by a wide flammability domain [56], high burning velocity [58] and high flame

1.2. EFFECT OF HYDROGEN AND/OR AMMONIA COMBUSTION ON THE AGING OF THE LUBRICANT

Table 1.3: Ammonia, hydrogen and gasoline properties at 300 K and 0.1 MPa [2, 4, 55–57].

	Ammonia	Hydrogen	Gasoline (iso-octane)
Formula	NH ₃	H ₂	C _{5–12}
Storage	liquid	compressed	liquid
Storage temperature (K)	300	300	300
Storage pressure (MPa)	1.1	70	0.1
Density (storage conditions) (kg.m ⁻³)	600	39	740
Lower heating value (MJ.kg ⁻¹)	18.8	120	44.5
Volumetric energy density (GJ.m ⁻³)	11.3	4.7	33
Mass stoichiometric air-fuel ratio	6.05	34.6	15
Laminar burning velocity ^a (m.s ⁻¹)	0.07	3.51	0.34
Auto-ignition temperature (K)	930	773–850	503
Adiabatic flame temperature (K)	2073 ^b	2390 ^b	2200–2400
Min. quenching distance ^c (mm)	7	0.64	3.5
Flammability limits in air (%)	15–28	4.7–75	0.6–8
Materials compatibility	alkaline molecule, corrosive	can permeate in steel	X

[a] Given at $\phi = 1$ at 300 K, 0.1 MPa, with ϕ the equivalence ratio, defined as the molar fuel-to-oxidizer ratio normalized by the fuel-to-oxidizer ratio under stoichiometric conditions.

[b] Measured in air at $\phi = 1$ [56].

[c] Minimal at stoichiometry for hydrogen [56].

temperature. In contrast, the combustion of ammonia is more restricted by a narrower flammability domain [57] and higher resistivity to ignition. Hydrogen is known to facilitate ammonia's ignition and stabilize its combustion, which is why these two fuels are often considered as co-fuels [4, 59, 60]. Compared to gasoline, high temperatures and short quenching distance [56] in the case of hydrogen, might increase the thermal degradation of the lubricant film on engine walls, thereby accelerating lubricant degradation and promoting reactivity in the liquid phase. Another issue with these alternative fuels is the composition of their combustion products. First, for both fuels, water is the principal combustion product, comprising more than 30 % of burned gases in volume at stoichiometry. Exposure to water vapor can have several deleterious consequences on lubricants, as further discussed in Section 1.2.5. Second, they can produce high level of nitrogen oxides, particularly NO and NO₂, designed as NO_x, which are highly toxic molecules causing health and environmental issues such as respiratory diseases, and acid rains (NO₂ with water giving nitric acid HNO₃) [61]. When in contact with the lubricant, they can also solubilize and react with hydrocarbons leading to sludge in the crankcase [18], as further detailed in Section 1.2.3. Another concern is nitrous oxide (N₂O) emissions from ammonia combustion, which, despite its limited reactivity with hydrocarbons, has a high global warming potential [62]. The formation of nitrogen oxides occurs mainly from several pathways [63]:

- Thermal-NO_x: Arise from the reaction $\text{N}_2 + \text{O}_2 \longrightarrow 2\text{NO}$, involving nitrogen atoms from the air. This reaction is initiated by the decomposition of nitrogen due to the effect of oxygen radicals. Nitrogen being a highly stable molecule, this can only happen at high temperatures, typically above 1800 K [56].
- Prompt-NO_x: Result from N₂ reacting with CH free-radicals formed at very high temper-

1.2. EFFECT OF HYDROGEN AND/OR AMMONIA COMBUSTION ON THE AGING OF THE LUBRICANT

atures, leading to nitrogen containing functions on hydrocarbons and N radicals. Oxides are then formed as fuel-NO_x [63].

Moreover, in the case of nitrogenated fuel:

- Fuel-NO_x: Involve nitrogen atoms directly contained in the fuel (amines, nitriles), which are more reactive than nitrogen molecules, but less concentrated. This reaction can happen at temperatures below 1200 K [64].

In the case of ammonia combustion, De Soete [65] proposed a global kinetic mechanism for NO production from NH₃ oxidation, with reactions $\text{NH}_3 + \text{O}_2 \longrightarrow \text{NO} + \text{H}_2\text{O} + \frac{1}{2} \text{H}_2$ and $\text{NH}_3 + \text{NO} \longrightarrow \text{N}_2 + \text{H}_2\text{O} + \frac{1}{2} \text{H}_2$. According to the calculated reaction rates, this mechanism is responsible for significant NO production even at temperatures below the 1800 K threshold required for the thermal route. More detailed pathways involve NH₂ and NH radicals, and HNO as intermediate species [8, 66]. Besides, N₂O can be formed from the reactions $\text{NH}_2 + \text{NO}_2 \longrightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$, or $\text{NH} + \text{NO} \longrightarrow \text{N}_2\text{O} + \text{H}$ at temperatures below 1400 K [8]. Westlye *et al.* showed that the first reaction was dominant in the case of abundant NH₂ production from ammonia pyrolysis [67, 68]. On the contrary, Sako *et al.* showed that the second reaction was dominant in the case of ammonia/methane/air combustion [66]. In the case of hydrogen combustion, high temperatures can promote the thermal-NO formation. Although in the case of ammonia, one origin of NO_x is attributed to the fuel-NO pathway [5], the addition of H₂ in NH₃ combustion strongly increases NO in lean conditions in [60] and [59] when the hydrogen fraction reaches 10 % and 15 %. Even if optimized post-treatment systems can reduce final NO_x emissions, lubricants are exposed to these species inside the engine and during different phases of the combustion development. Therefore, lubricant degradation due to increased nitrogen oxide concentrations needs to be addressed. Additionally, due to its poor ignitability, a fraction of the ammonia may remain unburned and be in contact with lubricants.

In summary, ammonia and hydrogen combustion present several challenges: degradation of the lubricant due to its exposure to higher temperatures, degradation due to high exposure to nitrogen oxides, compatibility with unburned fuel, and compatibility with water. These concerns are addressed in detail in the following sections, which review the current state of knowledge on each topic.

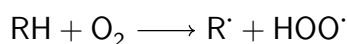
2.2 Liquid phase oxidation

2.2.1 Oxidation mechanism

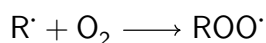
The auto-oxidation of hydrocarbons is a free-radical chain reaction happening in the liquid phase, differently described depending on whether it occurs at low temperature or high temperature. At temperatures below 120 °C, the mechanism can be depicted as follows:

1.2. EFFECT OF HYDROGEN AND/OR AMMONIA COMBUSTION ON THE AGING OF THE LUBRICANT

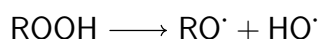
1. Initiation step:



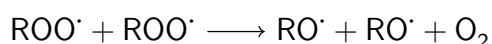
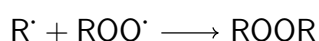
2. Propagation step:



3. Chain Branching:



4. Termination:



At low temperatures, hydroperoxide production is the rate-limiting step in the oxidation process, typically represented by the reaction $\text{ROO}^\cdot + \text{RH} \longrightarrow \text{ROOH} + \text{R}^\cdot$ [13,69]. At higher temperatures, both hydroperoxide production and decomposition are much faster. In the case of n-decane auto-oxidation, Le *et al.* showed that hydroperoxide cleavage, generating two radicals from one neutral compound ($\text{ROOH} \longrightarrow \text{RO}^\cdot + \text{HO}^\cdot$), was the kinetically determinant reaction for experiments conducted at 140 °C [70]. The oxidation process can be divided in two distinct stages [13]:

1. Primary phase: Initiation and propagation reactions accelerate compared to low temperatures. This phase is characterized by the proliferation of $\text{HO}^\cdot$ radicals, and formation of light products such as carboxylic acids, esters and ethers (the latter formed via intramolecular reactions)
2. Secondary phase: This stage involves the polycondensation of bifunctional oxygenated intermediates and subsequent polymerization, leading to the formation of high-molecular weight degradation products

Liquid phase oxidation is a continuous process, where oxidation intermediates and termination products can themselves take part in further oxidation reactions. In early stages, light oxidation products, such as alcohols, ketones/aldehydes and light hydrocarbons are first produced. As they accumulate, these products compete with the initial hydrocarbon for oxidation, which can lead to second order products such as carboxylic acids, esters or bifunctional products [71, 72]. Bifunctional products can then undergo polycondensation and polymerization, resulting in large hydrocarbon chains which are sludge and deposits precursors. Figure 1.4 summarizes these different processes [13].

Liquid phase oxidation affects the properties of hydrocarbons. While light oxidation prod-

1.2. EFFECT OF HYDROGEN AND/OR AMMONIA COMBUSTION ON THE AGING OF THE LUBRICANT

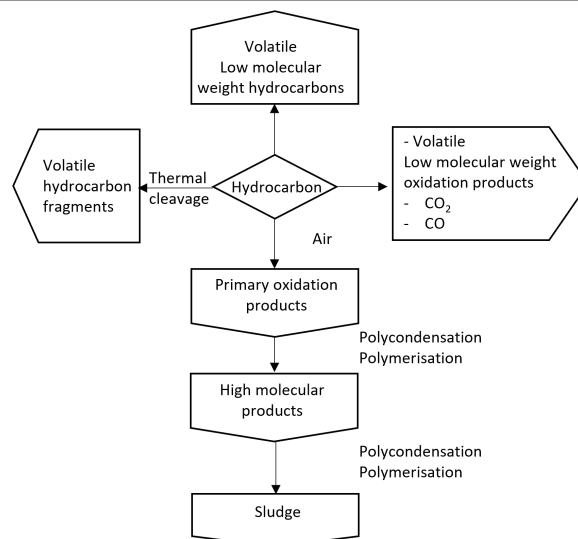


Figure 1.4: Scheme of lubricant degradation at high temperatures. Reprinted from [13] with permission from Springer Nature

ucts can evaporate, heavy products and low energy interaction between polar products can increase the viscosity of the oil and/or lead to the formation of sludge, varnishes and deposits on the hottest surfaces [13]. Acidic compounds formed tend to make the oil corrosive towards the metallic parts of the engine [44, 69]. Suspended metal particles can then act as catalysts, self-accelerating the process. To prevent this phenomenon and increase the stability of lubricant properties, different kinds of antioxidant additives with complementary modes of action are employed. Scavengers, such as aromatic amines and phenols, trap radicals under stable and less reactive forms. Their action prevents propagation reaction to occur [44]. Scavengers act in a stoichiometric way, meaning they are no longer effective once they trapped a radical. Their concentration decreases through time, until the engine oil has to be drained [44]. Besides, species such as sulfur polybutenes can react with hydroperoxides, preventing their decomposition [44]. On the other hand, ZnDTP or molybdenum dithiocarbamate (MoDTC) can also catalytically decompose hydroperoxides. Chelating agents can also be added to trap metals and limit their catalytic activity. Finally, basic species can be added as antiacids to limit acidification of the oil. Most common antiacids are alkaline organometallic salts, such as calcium alkylarylsulfonates/phenates/salicylates [45, 46, 73].

2.2.2 Oxidation parameters

Different parameters influence the lubricants oxidation rate: reactivity of the base oil, temperature, oxygen availability and the presence of catalysts [69]. Therefore, ammonia and hydrogen combustion characteristics might change some of these parameters influencing the oxidation rate.

1.2. EFFECT OF HYDROGEN AND/OR AMMONIA COMBUSTION ON THE AGING OF THE LUBRICANT

First, for base oils, reactivity towards initiation is determined by the speed of radicals initiation by oxygen attack, which follows the ranking of radicals stability as suggested by Rasberger *et al.* [13]:

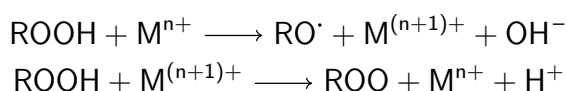


This comes from the fact that radicals are delocalized and stabilized on aromatic rings and double bonds; and preferentially on hindered carbons. Propagation of the hydroperoxide radical follows the same ranking. Branched molecules counting a lot of tertiary carbons are then less resistant to oxidation [13]. Chatelain *et al.* [69], and Venegas-Reynoso *et al.* [74] studied molecular features determining the oxidation stability of hydrocarbons. Their results show that stability decreases with the increase in chain length for n-paraffin and napthenic [69, 74]. The number of insaturations increases stability of the cyclic molecules, but decreases stability of linear species. Hydroprocessing of base oils increases their resistance to oxidation by removing impurities, with group III being more stable than group II, than group I. However, sulfur compounds and aromatics can sometimes act as natural antioxidants, making group I oils more resistant to oxidation [13].

Second, oxidation reaction follows an Arrhenius law, meaning that reactivity increases exponentially with temperature [69, 70].

Then, reactivity depends on the oxygen availability in the liquid phase [69]. Oxidation happens at the interface between air in the crankcase, coming from the blow-by gases, and oil. Foam can increase the surface area accessible to air, increasing the oxidation rate.

Finally, metals can act as catalysts. Iron surfaces act as heterogeneous catalysts, and wear and corrosion suspended particles act as homogeneous catalysts [13]. They can accelerate the hydroperoxides decomposition [44]:



Metals also act as catalyst for chain branching reaction (homolytic scission of hydroperoxide $ROOH \longrightarrow RO\cdot + HO\cdot$) which self-accelerates the oxidation [13].

Mathai *et al.* [75] found that the addition of 18 % H_2 to natural gas resulted in a significant change in the viscosity of the lubricant compared to the reference conditions over a 60-h running time in an engine test bench. They also observed a faster increase in the Total Acid Number (TAN), which means a faster accumulation of acidic oxidation products, which the authors attributed to an increase in combustion temperature due to hydrogen. These changes were accompanied by a higher concentration of wear metals.

1.2. EFFECT OF HYDROGEN AND/OR AMMONIA COMBUSTION ON THE AGING OF THE LUBRICANT

To conclude, high temperatures, high exposure to oxygen and increased wear result in a higher oxidation rates. While the chemical nature of the base oil does not change with alternative fuels, all other parameters are likely to be different from conventional fuels and modify the oxidation kinetics. Moreover, lubricant aging due to oxidation can even be more severe in the case of engine running on ammonia and/or hydrogen, due to the presence of nitrogen oxides as combustion by-products.

2.3 Nitro-Oxidation

2.3.1 NO_x production

Nitro-oxidation is another free-radical degradation reaction caused by the reactivity of nitrogen oxides with hydrocarbon chains, with ester nitrates (RONO₂) as key intermediates, acting similarly as hydroperoxides in oxidation [18]. Nitrogen oxides can react with fuel residues around the injectors, promoting sludge formation [76], and can also react directly with the lubricant in the cylinder or if they are transported by blow-by gases (Section 1.1.3). The detrimental impact of nitrogen oxides on both fuels and oils, as well as on the accumulation of deposits have long been recognized by lubricant and engine manufacturers, as it has been studied since the first half of the twentieth century [77]. However, knowledge is missing on the precise reaction mechanism and relative contribution compared to oxidation.

As hydrogen combustion induces high temperatures (Table 1.3), this can lead to high thermal-NO_x production. However, this can be mitigated by operating under very lean equivalence ratio, ϕ , i.e. with a very large excess of air compared to hydrogen [56] or by using high dilution strategies. Doing so, the flame temperature is reduced and nitrogen oxide production can be almost reduced to zero, by preventing N₂ dissociation. Verhelst *et al.* [56], found that for equivalence ratios below 0.5, NO_x emissions were negligible, but increased exponentially above this value in correlation with the increase in combustion temperature. Therefore, with hydrogen, nitrogen oxides can be reduced or even avoided by selecting appropriate combustion conditions. Meanwhile with ammonia, as the fuel itself contains nitrogen atoms, the production of fuel-NO_x could be significant and difficult to reduce in the context of engines without an excess of unburned ammonia [5, 60, 78]. In the case of ammonia/diesel dual fuel engines, adding ammonia up to 40 % still reduced NO and NO₂ emissions compared to diesel alone in the work of Hiraoka *et al.* and Xiang *et al.* [8, 78]. This was attributed to a reduction of the combustion temperature with ammonia addition, and de-NO_x reactions. Table 1.4 summarizes NO_x levels reported in different studies, with measurements conducted using in-line Fourier Transform Infrared (FTIR) spectroscopy [4, 14–16, 79], and dedicated gas analyzers [5, 55, 64] at the exhaust.

1.2. EFFECT OF HYDROGEN AND/OR AMMONIA COMBUSTION ON THE AGING OF THE LUBRICANT

Table 1.4: Extreme values of nitrogen oxides emissions from the combustion of ammonia and blends in literature

Ref.	Fuel	NO _x Level (min and max)	Eq. ratio	Conditions
[64]	pure H ₂	350 ppm 7000 ppm	$\phi = 1.8$ $\phi = 1.18$	4-cylinder, 1500 rpm 4-cylinder, 2500 rpm
[14]	pure NH ₃	1300 ppm 4300 ppm	$\phi = 1.1$ $\phi = 0.9$	Monocylinder, 1000 rpm Monocylinder, 1000 rpm
[4]	NH ₃ -H ₂ /95-5	≤ 500 ppmv 5000 ppmv	$\phi = 1.2$ $\phi = 0.8-0.9$	Monocylinder, 1500 rpm Monocylinder, 1500 rpm
[4]	NH ₃ -H ₂ /40-60	≤ 500 ppmv 9000 ppmv	$\phi = 1.3$ $\phi = 0.7$	Monocylinder, 1500 rpm Monocylinder, 1500 rpm
[55]	NH ₃ -H ₂ /11-89	2750 ppm 4500 ppm	$\phi = 1$ $\phi = 1$	4-cylinder, 1300 rpm (SI -25 °CA) 4-cylinder, 1300 rpm (SI -5 °CA)
[16]	NH ₃ -H ₂ /90-10	500 ppm 3750 ppm	$\phi = 1.1$ $\phi = 0.9$	Monocylinder, 2000 rpm Monocylinder, 2000 rpm
[14]	NH ₃ -H ₂ /50-50	1300 ppm 6900 ppm	$\phi = 1.1$ $\phi = 0.9$	Monocylinder, 1000 rpm Monocylinder, 1000 rpm
[79]	NH ₃ -diesel/98-2	1000 ppm 5000 ppm	$\phi = 1.1$ $\phi = 0.8$	Monocylinder, 1000 rpm Monocylinder, 1000 rpm
[15]	NH ₃ -diesel/98-2	2500 ppm 4900 ppm	$\phi = 1$ $\phi = 0.85$	Monocylinder, 1000 rpm Monocylinder, 1000 rpm
[15]	NH ₃ -diesel/95-5	1900 ppm 4600 ppm	$\phi = 1$ $\phi = 0.75$	Monocylinder, 1000 rpm Monocylinder, 1000 rpm
[25]	NH ₃ -diesel/85-15	2590 ppm	unknown	4-cylinder, 2000 rpm

Although absolute NO_x levels measured under different operating conditions and with different engine types cannot be directly compared, a consistent trend across studies shows that lower emission levels are achieved with rich blends, i.e. $\phi > 1$ for premixed ammonia/air spark ignition (SI) engines. Valera *et al.* [80] attributed this to the promotion of the termination reaction: $\text{NH}_2 + \text{NO} \longrightarrow \text{H}_2\text{O} + \text{N}_2$, which suppresses radical chain propagation in rich conditions. Besides, Li *et al.* [5] showed that although fuel-NO_x become dominant as the ammonia increases in ammonia/hydrogen blends, the overall amount of NO_x decreases as the flame temperature decreases. Similar conclusions were reported by Lhuillier *et al.* [4], who observed a consistent NO reduction across a wide range of NH₃ contents in the mixture (from 20 % to 100 % by volume). Comparable NO_x concentration ranging between 200 and 2000 ppm could be obtained with gasoline and diesel engines with various set-ups, as indicated Pochopien [81]. Rousselle *et al.* [16] compared the maximum NO_x level of 3750 ppm for a NH₃-H₂/90-10 fuel blend with $\phi=0.9$, to three times what is emitted with a similar engine fueled with gasoline. Hiraoka *et al.* [78] measured NO+NO₂ levels 2.5 times higher with a 5-95/diesel-ammonia blend compared to neat diesel. Regarding the speciation of these nitrogen oxides, several studies show that NO is dominant at the exhaust with ammonia. For instance Mercier *et*

1.2. EFFECT OF HYDROGEN AND/OR AMMONIA COMBUSTION ON THE AGING OF THE LUBRICANT

al. found that only 70 ppm were NO₂ among 4200 ppm of total NO_x measured with pure ammonia [14]. Similarly in [16], the NO₂/NO ratio ranged between 0.02 % and 0.75 % of the total NO_x emission at $\phi=0.9$ and 1.1 respectively. Xiang *et al.* [8] measured a maximum NO₂ fraction of 10.9 % compared to NO in a diesel-ammonia dual-fuel engine, while Westlye *et al.* [67] reported a fraction of 3–4 % NO₂ with a ammonia/hydrogen engine.

2.3.2 Structure of nitrogen oxides

NO and NO₂ have a radical structure by nature (Figure 1.5), which explains their high reactivity, especially towards other radicals [82,83].

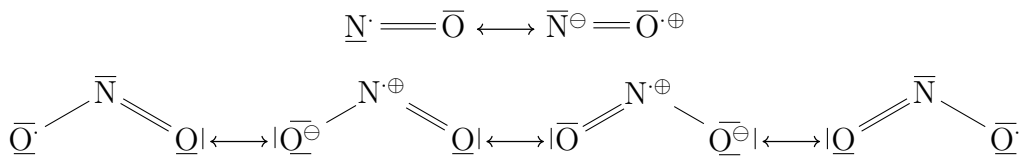


Figure 1.5: Mesomers of NO and NO₂

In contrast, N₂O does not have a radical structure and is not included in the NO_x designation. Controlling its emissions is a challenge, as this gas has a global warming potential 265 times higher than CO₂ [16], but no studies have investigated its potential reactivity with hydrocarbons, in particular lubricants.

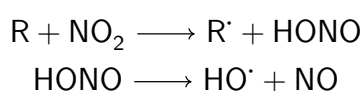
2.3.3 Nitro-oxidation mechanism

The chemical mechanism by which nitrogen oxides degrade lubricants is not yet fully understood. Many studies assess the degradation consequences of nitrogen oxides on lubricants [17, 35], but few directly explore the underlying chemical reactions involving NO_x and hydrocarbons. Some possible reactions involving NO, NO₂, hydrocarbons and oxidation intermediates can be found in [18, 81, 84, 85]. From kinetics and thermodynamic standpoints, authors as Johnson and Korcek (1991) [18] and Coultas [19] (2015), proposed theoretical models. Johnson and Korcek conducted experiments in a batch reactor at 160 °C, using a continuous gas flow composed of 20 % O₂ and 0 to 792 ppm NO₂ over hexadecane for up to 3 h, and analyzed exhaust gases. They also monitored the hydroperoxide concentration in the liquid phase by iodometry. However, they did not identify reaction intermediates or products analytically, limiting the validation of their mechanism. Coultas used FTIR to quantify nitration products in lubricants used in real engines at different temperatures. However, this methodology was not able to identify key species precisely. Later, the theoretical mechanisms have been confronted to experimental results and product identification thanks to the work of Pochopien and Harris [81, 82]. Pochopien studied the reactivity of phenolic and aminic antioxidants in squalane, using an autoclave at 180 °C, with the following gas mixtures: 100% O₂, 1000 ppm NO₂ in N₂, and 1000 ppm NO in N₂. Two-dimensional Gas Chromatography

1.2. EFFECT OF HYDROGEN AND/OR AMMONIA COMBUSTION ON THE AGING OF THE LUBRICANT

(GC) followed by a Nitrogen Chemiluminescence Detector (NCD) was used to identify reaction products [81]. Harris studied the reactivity of squalane directly at 150 °C, using a similar methodology [82]. Squalane is a C₃₀ molecule considered a good surrogate for lubricants as it has a high molecular weight and a similar ratio of tertiary carbons [81] compared to mineral base oils. Recently, Slavchov *et al.* [76] explored the reactivity between iso-octane and nitrogen oxides to better understand nitro-oxidation process leading to fuel deposits near the injectors [76]. They used a pressurized autoclave at 160 °C, 10 bar to reproduce the injector nozzle conditions. Conclusions from these different studies are presented below, following the different steps of the radical reaction.

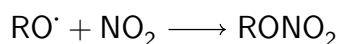
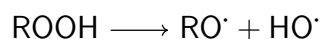
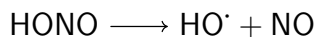
Initiation As for oxidation, the radical chain reaction in nitro-oxidation starts with the initiation of a radical, by proton abstraction from a hydrocarbon chain. Whether the abstraction is initiated by O₂ or NO₂, the most likely proton to be abstracted is the one which will result in the formation of the most stable radical, i.e on tertiary carbon atoms (Section 1.2.2) [81,82]. There seems to be consensus on the fact that proton abstraction is caused by NO₂, rather than NO directly under engine conditions [76,82]. However, NO can still indirectly contribute to the initiation step, by being oxidized to NO₂ via the reaction $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$, as exhaust gases travel to colder and oxygen-rich zones [18]. Besides, according to Slavchov *et al.*, NO₂ has a higher rate of radical initiation compared to O₂ in the range 100–220 °C [86]. This is consistent with the reduction in inhibition time observed in the presence of nitrogen oxides in [18], both with and without antioxidants. The nitrous acid formed during this proton abstraction is highly unstable [18] and readily decomposes into two radicals, thereby propagating the chain reaction. Initiation step can then be written as:



Propagation and branching For the propagation step, Harris proposed the reaction $\text{R}' + \text{NO}_2 \longrightarrow \text{RONO} \longrightarrow \text{RO}' + \text{NO}$ based on the products identified by gas chromatography [82]. Although alkyl nitrites RONO are highly unstable, and could not be detected in his study, the subsequent formation of RO' radicals due to its decay was supported by the identification of secondary oxidation products such as ketones [82]. These ketones arise from alkoxy radicals which undergo β -scission [82]. Based on the measurement of the concentration of NO and NO₂ in the exhaust gas of a batch reactor at 150 °C, Johnson and Korcek found that this reaction $\text{R}' + \text{NO}_2 \longrightarrow \text{RONO}$ or RNO_2 was likely to happen, but only without oxygen. With oxygen in the gas flow exposed to hexadecane, the measured consumption rates of NO and NO₂ no longer aligned to this reaction pathway. As a radical reaction rate is determined by the probability of a collision between the radicals, R' are more likely to meet O₂ molecules, which are more concentrated, than NO₂ in the liquid phase. Then, in the presence of oxygen, they propose that propagation reaction is rather dominated by $\text{R}' + \text{O}_2 \longrightarrow \text{RO}_2'$, resulting in

1.2. EFFECT OF HYDROGEN AND/OR AMMONIA COMBUSTION ON THE AGING OF THE LUBRICANT

peroxy radicals [18]. This would mean that radicals generated by nitrogen oxides also contribute to hydroperoxide formation, thereby accelerating the oxidation process. This hypothesis was followed by Coultas, who proposed the following simplified mechanism, showing how oxidation and nitro-oxidation are entangled (reactions 1 to 4) [19]:



Recent experimental findings support this hypothesis. Agocs *et al.* found that adding 1000 ppm of nitrogen dioxide to synthetic air and exposing commercial oil to this gas flow at 170 °C resulted in accelerated aging of the oil compared to exposure to air alone. This was evidenced by higher concentration of acidic compounds and a greater viscosity increase [17], even though nitrated products could not be identified.

Field tests conducted by Coultas at varying temperatures further supported this conclusion. He found that the nitration peak, at 1630 cm⁻¹ decreased between experiments conducted at 130 °C and 150 °C, while oxidation peak continued to increase. He proposed the following explanation, depicted in Figure 1.6:

- Below 110 °C, only few RO[·] radicals formed, resulting in slow ester nitrates production
- Around 130 °C, a lot of ester nitrates are formed, and have a long life time, leading to their accumulation in the oil.
- Above 150 °C, a lot of RO[·] radicals are generated, accelerating ester nitrate formation. However, these compounds decompose quickly due to the high temperatures, making them more difficult to detect with IR spectroscopy.

Precaution must be taken as tests at different temperatures were conducted with different engine types. Nevertheless, Besser *et al.* [87] also found that the nitration peak was decreasing after oxidized oils have been heat treated at 170 °C for 2 h, while oxidation continued to increase. This finding could be consistent with the hypothesis that ester nitrates decompose rapidly at higher temperatures, whereas oxidation products are more thermally stable. In [35], tests conducted in a passenger car for 20 000 km with oil samples collected every 1000 to 3000 km showed that oxidation and nitration seemed to increase in parallel. It might be due to the fact that engine temperatures remained below 150 °C during the field test, thereby allowing ester nitrates to accumulate without rapid thermal degradation.

1.2. EFFECT OF HYDROGEN AND/OR AMMONIA COMBUSTION ON THE AGING OF THE LUBRICANT

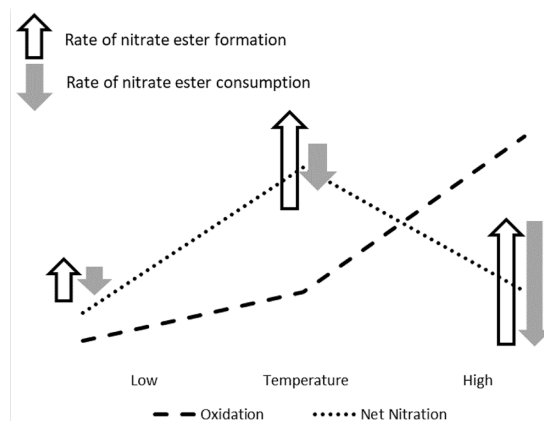


Figure 1.6: Schematic explanation of oxidation and nitro-oxidation: net nitration being the equilibrium between the formation and consumption rates of nitrate esters. Reprinted with permission from [19], copyright 2020, SAE

While NO is generally considered unreactive towards hydrocarbons in standard engine conditions, it might still participate in radical chain reactions by reacting with peroxy radicals regenerating NO_2 as follows: $\text{RO}_2^\cdot + \text{NO} \longrightarrow \text{RO}^\cdot + \text{NO}_2$. This pathway is supported by Slavchov *et al.* based on the analysis of isooctane degradation products using GC in the presence of NO, NO_2 or pure air. Johnson and Korcek also found evidence of this reaction, as they could not observe any measurable NO accumulation despite the nitrous acid decomposition. This suggests that nitrogen monoxide was actively consumed by another reaction, likely through its reaction with $\text{RO}_2^\cdot$ [18]. In parallel, hydroxy radicals $\text{HO}^\cdot$ formed by the decomposition of nitrous acid can be involved in the oxidation reaction $\text{HO}^\cdot + \text{RH} \longrightarrow \text{H}_2\text{O} + \text{R}^\cdot$, thereby propagating the radical chain reaction on another alkyl chain.

Termination The termination products formed during nitro-oxidation depend on the previous reaction pathways, and experiment conditions. $\text{R}^\cdot$ radicals may recombine to form alkanes of various chain lengths, but they can also react with alkoxy and peroxy radicals, or with nitrogen dioxide, or nitrogen monoxide, producing a wide range of functionalized molecules. Seeing that almost all of the nitrogen dioxide introduced was retained by hexadecane, Johnson *et al.* concluded that it was retained in nitrogen-containing termination products such as alkyl nitrites and ester nitrates, but could not isolate them [18]. Interestingly, Slavchov *et al.* did not find any nitrogen-containing products after 2 h at 150°C when they used a gas flow composed of 5% O_2 and 100 ppm NO_2 [76]. They could only identify nitrogen-containing products when 500 ppm of NO was added to the gas flow. Using GC/MS (Mass Spectrometry), they identified nitromethane, methylethyl and 3,3-dimethylpropylesters of nitric acid, 2,2,4-trimethyl-4-nitropentane, nitromethane and 2-methyl-2-nitropentane. Nitroalkanes are supposed to come from the reaction $\text{R}^\cdot + \text{NO}_2 \longrightarrow \text{RNO}_2$, while ester nitrates from the reaction $\text{ROO}^\cdot + \text{NO} \longrightarrow \text{ROONO} \longrightarrow \text{RONO}_2$ [76, 88]. They concluded that this last termination reaction was particularly important as it scavenged two radicals simultaneously,

1.2. EFFECT OF HYDROGEN AND/OR AMMONIA COMBUSTION ON THE AGING OF THE LUBRICANT

and could have a strong impact on the nitro-oxidation rate. However, this is compensated by the decomposition $\text{ROO}^\bullet + \text{NO} \longrightarrow \text{ROONO} \longrightarrow \text{RO}^\bullet + \text{NO}_2$ which generates new radicals and perpetuates the chain reaction [76]. Using GCxGC/MS to study the liquid phase of squalane exposed to 1000 ppm NO_2 and 10% O_2 for 2 h, Harris was not able to detect nitrogen-containing products but only found alkanes, alcohols, ketones and lactones [82]. However, nitroalkanes could be detected despite the absence of NO thanks to a NCD detector which has a detection level below ppb. This highlights the challenge of detection limits and choosing appropriate detection techniques. This result questions the fact that Slavchov *et al.* did not find any nitrogen-containing products with NO_2 with the protocol they used [76].

Interestingly, Slavchov *et al.* also observed that degradation occurred in the presence of 100 ppm NO_2 and 5% O_2 , whereas 5% O_2 alone did not result in any degradation [76]. This confirms that NO_2 still participates in oil accelerated degradation compared to pure oxygen, even if no nitrogen-containing products are identified in the end [76]. Combining the findings of Harris and Slavchov, it appears that products with nitro groups are less abundant than oxygenated products in the presence of NO_2 only, making them hard to detect. This might be explained by the fact that termination products containing nitrogen involve mainly NO molecules, which have to be produced by the reaction $2\text{NO}_2 \longrightarrow 2\text{NO} + \text{O}_2$, in the absence of oxygen [18]. Thus, termination reactions directly involving NO_2 are unlikely to occur ($\text{NO}_2 + \text{R}^\bullet \longrightarrow \text{RONO}$ or RNO_2 and $\text{NO}_2 + \text{RO}^\bullet \longrightarrow \text{RONO}_2$). Nonetheless, NO_2 participates to initiating radicals and accelerate the oxidation rate.

Interestingly, Harris found that squalane exposed to NO_2 without oxygen resulted in less degradation products than when NO_2 and O_2 are combined. Figure 1.7 shows the results obtained, the large spot corresponds to unreacted squalane, while small spots to degradation products. This is consistent with the fact that NO_2 reacts with oxidation intermediates and accelerates the reaction, even though no nitrogen compounds can be found in the end.

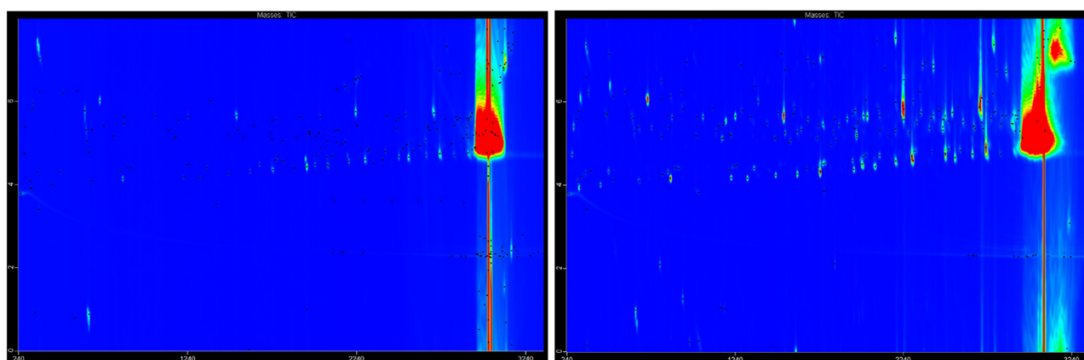


Figure 1.7: GCxGC-TOF/MS of nitration (left) and nitro-oxidation (right) of squalane–150 °C 2 h. Reprinted with permission from [82]

1.2. EFFECT OF HYDROGEN AND/OR AMMONIA COMBUSTION ON THE AGING OF THE LUBRICANT

In summary, results from the studies reviewed above show that NO_2 readily abstracts protons from hydrocarbon chains to initiate radical reaction. It participates in producing ester nitrates as intermediates, and can also participate indirectly in forming hydroperoxides. As the reaction proceeds, oxidation products accumulate rapidly, which suggests that oxidation takes over, even if nitrogen dioxide can be responsible for the chain initiation. Meanwhile, NO can react with intermediates to form nitroalkanes and ester nitrates, or regenerate NO_2 . Overall, oxidation and nitro-oxidation appear to be tightly coupled processes, and should be studied in conjunction. Despite progress, several challenges remain in fully understanding the nitro-oxidation mechanism. Precise kinetics and energy calculations would allow for better prediction of the reactions and intermediates species. Experimental studies should consider both NO and NO_2 , as they seem to play different roles. Moreover, analytical techniques are crucial for addressing this topic, since the detection of unstable intermediates or low-concentration products directly constrains the hypotheses that can be formulated.

2.3.4 Impact of oxidation and nitro-oxidation on additives

Nitro-oxidation and oxidation degrade lubricant integrity via reactions involving hydrocarbons. Depending on the conditions, these processes can lead to changes in the viscosity, sludge or varnish deposition, altering the performance of oils. Several studies have attempted to evaluate whether nitro-oxidation could also affect tribo-improver additives, in parallel to altering hydrocarbon chains. Bouchet *et al.* [89] studied the effects of nitro-oxidation and oxidation consequences on MoDTC and ZnDTP additives using X-ray Photoelectronic Spectroscopy (XPS) and Liquid Chromatography (LC). Tribological performance was assessed using a ball-on-disk tribometer. They showed that these additives were also affected by oxidation and nitro-oxidation, which led to ligand exchange between the two additives. After 12 h in a 140 °C bath under oxygen and nitrogen dioxide gases, additives concentration decreased by 80 %. Higher friction coefficient but medium wear were measured. They suggested that some compounds had lost their sulfur atoms, cancelling their friction reduction ability. After 16 h, additive depletion was completed, which led to poor performance of the lubricant. More recently, Besser and Dörr studied bench and in-field aging of ZnDTP in gasoline engines [35,87]. Using GC/MS, they identified more precisely ZnDTP and degradation products at different time scales. They confirmed that this component was also oxidized, leading to sulfur substitution by oxygen atoms and alkyl chains loss, as suggested in [89]. Additionally, they showed that free sulfur atoms could recombine to form sulfuric acid (Figure 1.8). Fresh oil had the lowest friction coefficient and wear while aging below 8 h led to reduced wear compared to oil in the fresh state. However extensive wear was observed after two days of artificial aging, attributed to the corrosive effects of phosphoric and sulfuric acids formed by additive depletion. In related

1.2. EFFECT OF HYDROGEN AND/OR AMMONIA COMBUSTION ON THE AGING OF THE LUBRICANT

experiments, aged lubricants originally containing MoDTC had the same friction coefficient as their base oil without any additives after similar aging protocol, as reported in [90]. This confirms that additive depletion, especially the loss of sulfur-containing functionalities, leads to substantial loss of friction-reducing capability.

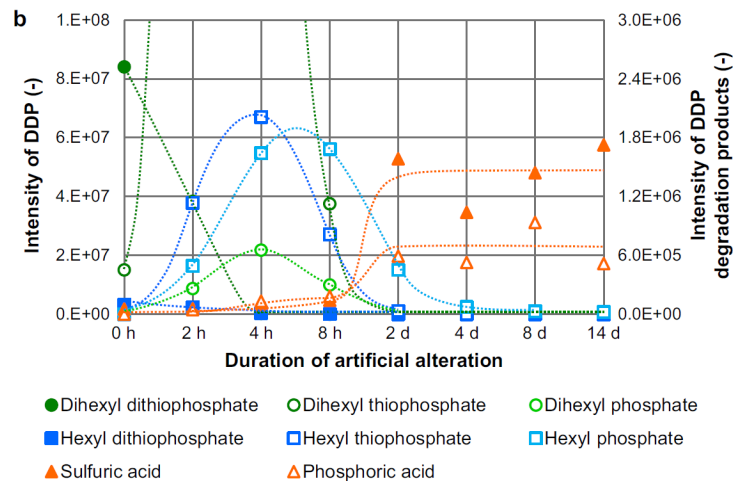


Figure 1.8: Evolution of dihexyldithiophosphates (left) into subproducts (right), leading to sulfuric and phosphoric acids production quantified by high resolution MS, after aging in air ovens at 180 °C. Reprinted from [91] with permission from Springer Nature

Numerous studies on this topic concluded that friction modifiers such as MoDTC and ZnDTP act as antioxidants and are gradually consumed during lubricant aging. The tribological performance of the lubricant is then degraded with time, as these additives can no longer form low frictions films. One study tried to isolate the role of oxidation versus nitro-oxidation in this process by varying the relative concentration of gases in NO_x /air atmospheres [92]. Interestingly, they found that at high temperatures, such as 160 °C, NO_x concentration had no significant influence on the rate of friction loss, suggesting oxidation was the major cause of degradation under these conditions. In contrast, NO_x concentration was highly correlated to the loss of friction properties at 100 °C [92]. This means that at low temperatures, radicals generation by NO_x species is a relative important degradation mechanism, while at high temperatures, oxidation happens so fast that nitro-oxidation is no longer dominant. This is in agreement with NO_x reactivity discussed in previous paragraphs.

Pochopien studied the impact of NO_2 on phenolic and aminic antioxidants [81] by exposing squalane enriched with antioxidants to 1000 ppm NO_2 in N_2 at 180 °C. She found that the phenolic antioxidant octadecyl 3-(3,5-di-tert-butyl-4-oxo-cyclohexa-2,5-dien-1-ylidene) propanoate used alone conferred the longest inhibition period (130 min), outperforming the aminic antioxidant 4,4'-dioctyl diphenylamine (60 min) and even a mix of both (90 min) [81]. The reaction between NO_2 and the phenolic antioxidant resulted in quinone derivatives due to NO_2 addition followed by β -scission, as nitro-phenols were not stable at 180 °C. The aminic antioxidant resulted in nitrated amines and cyclo-imines. Two new products were obtained when both kinds of antioxidants were combined, suggesting simultaneous inhibition pathways.

1.2. EFFECT OF HYDROGEN AND/OR AMMONIA COMBUSTION ON THE AGING OF THE LUBRICANT

Both nitro-oxidation and oxidation have negative effects on base oils, and their additives. However, the relative contribution to degradation of these processes to overall degradation is not fully understood, and in the case of nitro-oxidation, no consensus exists on the exact chemical mechanism. Considering that large amounts of NO_x are expected to be in contact with the lubricant with ammonia and/or hydrogen combustion, a better understanding of nitro-oxidation process is essential.

2.4 Compatibility with unburned fuel

2.4.1 Compatibility with ammonia

Nitro-oxidation could be reduced by choosing operating conditions where NO_x production is the lowest. Unfortunately, several studies showed that limiting NO_x and unburned ammonia levels at the exhaust remains a trade-off: increasing the equivalence ratio decreases NO_x emissions, while increasing the fraction of ammonia in the exhaust [4,14,16,78,93]. According to Westlye *et al.*, NH_3 emissions are due to the accumulation of the gas in the crevice volume of the combustion chamber [67]. Liu *et al.* [94] also suggest that the ammonia measured at the exhaust might come from its desorption from the oil film. Typical orders of magnitudes for residual ammonia are 1000 to 16 000 ppm in [4], with respective conditions: NH_3/H_2 -40/60 fuel blend, $\phi=0.6$ and NH_3/H_2 -95/5 fuel blend, $\phi=1.2$, at the exhaust of a monocylinder at 1500 rpm. Consistently, NH_3 at the exhaust was found to be between 0.7 % (NH_3/H_2 -90/10 fuel blend, $\phi=0.9$) and 1 % (pure NH_3 , $\phi=1.1$) in [16]. In another study with a monocylinder operated at 1000 rpm [15], NH_3 at the exhaust was between 1 % from equivalence ratios between 0.7 and 1 with ammonia/diesel-98/2 blends, and reached 5.5 % at $\phi=0.45$ and with 2.5 % diesel. In [59], adding 15 % of hydrogen led to divide by two the NH_3 emissions, ranging from 7000 ppm to 3000 ppm, in a single-cylinder at 1000 rpm. Ammonia concentrations in the exhaust are just an indicator of the ammonia which can be in contact with lubricants. Obrecht *et al.* highlighted this in a 1.5 L 4-cylinder engine test bench fueled with ammonia and diesel (85/15) where they measured concentrations of 9000 ppm of ammonia in the exhaust and 23 000 ppm in the blow-by circuit at 2000 rpm [25].

Unfortunately, unburned ammonia in the exhaust is a major challenge for the development of ammonia engines due to its adverse environmental and health issues [62]. Besides, it might induce new reactivity for lubricant degradation, as studied in the field of compressors using ammonia as a refrigerant [21]. The effect of ammonia on engine oils is not an abundant topic in literature. To date, only few academic studies have focused on this concern recently [17,24]. In parallel, engine manufacturers and lubricant suppliers have recently begun to develop in-

1.2. EFFECT OF HYDROGEN AND/OR AMMONIA COMBUSTION ON THE AGING OF THE LUBRICANT

house protocols to determine whether ammonia engines require new lubricant formulations, as in [95, 96]. As a first approach, it is worthwhile to examine the existing literature on the solubility of ammonia in organic solvents that exhibit similarities with lubricant base oils.

Solubility of ammonia in organic solvents The first question to be answered is whether this gaseous unburned ammonia can be considered soluble in engine oils. Fundamental thermodynamic studies provide enlightening results on this topic. The solubility data sheets from the International Union of Pure and Applied Chemistry gather, among other results, experimental measurements of the solubility of ammonia in organic solvents, including pure hydrocarbons [97]. The reported values clearly indicate that the solubility of ammonia in hydrocarbons decreases with the chain length of the solvent, and significantly increases if the solvent contains aromatic rings. The partition coefficient, which is the molar ratio of ammonia dissolved in the solvent over ammonia as a gas, at 293 K and atmospheric pressure, is 4.16 in hexane, 1.84 in hexadecane, but reaches 7.23 in methylbenzene. The solubility is also significantly improved in solvents with alcohol or other polar groups, which is explained by the formation of hydrogen bonds. These thermodynamic tables do not provide values for hydrocarbons above C16. Besides, Rehbein *et al.* used a calculation method based on quantum chemistry to estimate the solubility of ammonia in various solvents, which could potentially be used as co-fuels in combustion applications [98]. They studied solvents up to C8, which is significantly shorter than lube oil typical chain length. However, it remains interesting to see that alcohols and carboxylic acids exhibit higher solubility compared to alkanes, esters, aldehydes or ketones. For all types of molecules, the solubility of ammonia decreases with the chain length, and the completely apolar alkanes showed a maximum solubility for ammonia of 0.001 g/g at ambient pressure and temperature. These studies provide valuable information for a better understanding of the solubility of ammonia in hydrocarbons, but the results remain limited to short chain lengths. Questions about the interaction with longer hydrocarbons is of specific interest in the domain of compressors using ammonia as a refrigerant and compressor oil.

Oil/ammonia interactions in compressors The compatibility between ammonia and lubricants has mainly been studied in the context of compressors using ammonia as a refrigerant [21]. As seen with fundamental solubility studies, gaseous ammonia solubility can be expected to be very low in non-polar base oils made of long hydrocarbon chains. Takahashi *et al.* studied the miscibility of liquid ammonia in different base oil matrices. They found that ammonia could be miscible in oils enriched with polar compounds, such as esters or polyalkylene glycols [21]. The evaluated miscibility by measuring phase separation temperatures of oil/ammonia mixtures at a 5 to 1 ratio and observed that miscibility resulted in viscosity reduction at -50 °C. More recently, Feja *et al.* studied viscosity changes in oils exposed to ammonia comparing different kinds of oils under different pressure and temperature conditions (up to 50 bar and 140 °C) [22]. Miscibility was measured by vapor pressure measurements

1.2. EFFECT OF HYDROGEN AND/OR AMMONIA COMBUSTION ON THE AGING OF THE LUBRICANT

to prevent bias due to emulsification. In agreement with the findings of the previous study, they found that ammonia could be dissolved in the oils, causing decrease in viscosity. The maximum observed ammonia solubility was around 6 % at 50 bar. At 40 °C and 15 bar the viscosity decrease reached 80 % for alkylbenzene with (4 % uptake), 50 to 55 % for mineral oil and 50 to 45 % for polyalphaolefin (with 3 % NH_3 uptake) (Figure 1.9). At 90 °C and 10 bar, the ammonia solubility in PAO was around 1 %, leading to a 11 % viscosity decrease (Figure 1.9). The authors explained that the higher miscibility in alkylbenzene was attributed to the increased polarity brought to the oil by aromatic rings. Although polyolefin oils are often considered by manufacturers to be the most suitable lubricants for ammonia compressors [23] due to their low miscibility, some ammonia might still be dissolved in these oils under usage conditions of a compressor.

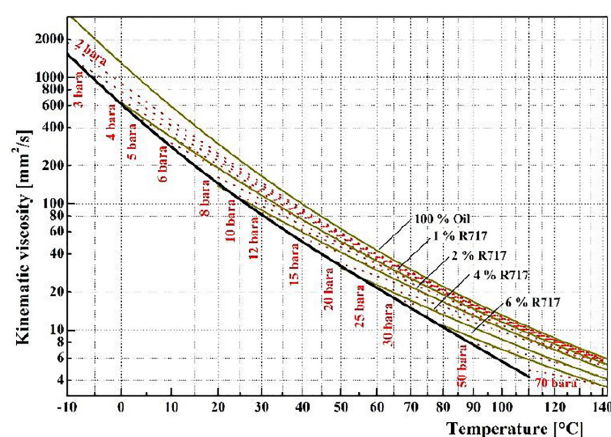


Figure 1.9: Kinematic viscosity of a PAO oil at different temperatures and with different ammonia uptakes. Dissolved ammonia fractions are indicated in black and constant along a khaki line. The black line represents the critical miscibility point below which ammonia and oil are not miscible at indicated pressure (in red). Reprinted from [22], copyright 2018, with permission from Elsevier

The second issue is the alkalinity of ammonia. Once solubilized in the lubricant, ammonia can react with acidic components such as additives, oxidation products, or the acidic functions of the base oil. Takahashi *et al.* observed the formation of sediments in oils treated under ammonia atmosphere in autoclaves, which they tentatively identified as amides [21], although no chemical analysis was shared to support this identification. There seems to be a consensus on the link between ammonia solubilization and amide sludge in compressors, although no specific scientific studies have been carried out on this point. Only Eurofins and Fluitec studies supporting this with examples of sediments analysis showing the identification of amides could be found [99, 100]. Reports of floodings next to ammonia compressors leading to large amounts of sludge tend to suggest that reactivity might be increased with the coupled presence of water [23]. More detailed knowledge on the reactivity of ammonia and identification of the degradation products then appears as an important challenge for ammonia engines.

The findings of these studies are in line with fundamental studies on shorter hydrocarbons. Even if the main constituent of lubricants is usually non-polar mineral base oil, the presence of

1.2. EFFECT OF HYDROGEN AND/OR AMMONIA COMBUSTION ON THE AGING OF THE LUBRICANT

acidic groups in the additives, or in oxidation products could enhance the solubility of ammonia in such fluids. Although pressure and temperature conditions in these studies are not engine-like conditions, these results motivate the study of ammonia and lubricant compatibility in the context of engines.

Oil/ammonia interactions in engines The interaction between oil and ammonia under typical engine conditions has only begun to be studied in recent years, with the emergence of ammonia-fueled marine engines. Liu *et al.* [94] measured NH_3 concentrations higher than 100 ppm in lubricants used in ammonia/gasoline and ammonia/hydrogen dual-fuel engines, showing that some ammonia could accumulate in the lubricant during engine operation. Agocs *et al.* further studied the effect of ammonia exposure on the aging of lubricants with a 2 L reactor [17], where a group II mineral oil with a specific additive package was maintained under a constant gas flow containing synthetic air and ammonia for up to 100 h, at 170 °C. In addition to conventional oxidative degradation which could be monitored using FTIR, the authors reported the accumulation of aminic compounds in the oil exposed to both trace (1000 ppm in air) and stoichiometric (21.7 % in air) concentrations of ammonia. This accumulation contributed to an increase in the viscosity [17]. Furthermore, oils exposed to ammonia had a higher propensity to form deposits in static micro-coking tests (Figure 1.10), even when exposed to trace amounts, and showed lower load-bearing capabilities compared to oil exposed to air only. These results suggest that ammonia is likely to react with lubricants in conditions reproducing engine environment, and that it could lead to both accelerated chemical aging and diminished tribological performance.

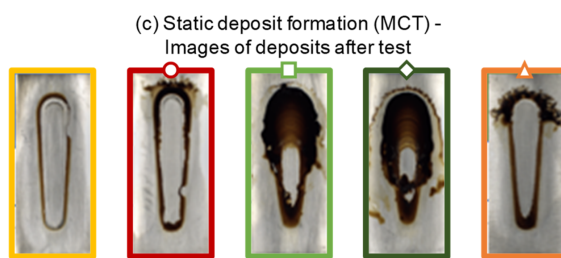


Figure 1.10: Deposits images after static micro-coking tests for the fresh (yellow) and aged oils (red: air–green: air and trace ammonia–dark green: air and stoichiometric ammonia–orange: air and trace nitrogen dioxide). Reprinted with permission from [17]

Using the same experimental setup, several lubricant types with different additives packages were tested by Obrecht *et al.* [25]. The evolution of the kinematic viscosity at 40 °C with increasing ammonia exposure times, appeared to be highly dependent on both base oil chemistry and additive composition (Figure 1.11). A similar trend was observed when the failure loads were measured. All tested oils had a lower failure load after being exposed to ammonia instead of pure air, though the extent of this reduction varied significantly between formulations. The authors also observed a correlation between the failure load and micro-coking

1.2. EFFECT OF HYDROGEN AND/OR AMMONIA COMBUSTION ON THE AGING OF THE LUBRICANT

behaviors, with oils which tend to produce more deposits having lower failure loads [25]. The study also reported measurements of the Total Acid and Base Numbers (TAN and TBN) at different aging times, which yielded unexpected results, such as a decreasing TAN and increasing TBN. Indeed, with oxidation, TAN should increase along with the accumulation of acidic products in the oil, while TBN, measuring the basic reserve due to additives, should decrease as additives are consumed [35]. According to the authors, these results could be explained by the accumulation of some ammonia in the liquid oil, which increased the basic reserve, or neutralized acidic products. These finding suggests that unlike in conventional fuels, TBN and TAN do not seem to be highly reliable indicators of lubricant degradation when ammonia is present. Overall, this study highlights significant chemical interaction between ammonia and lubricants under these experimental conditions. A similar experimental setup was used by

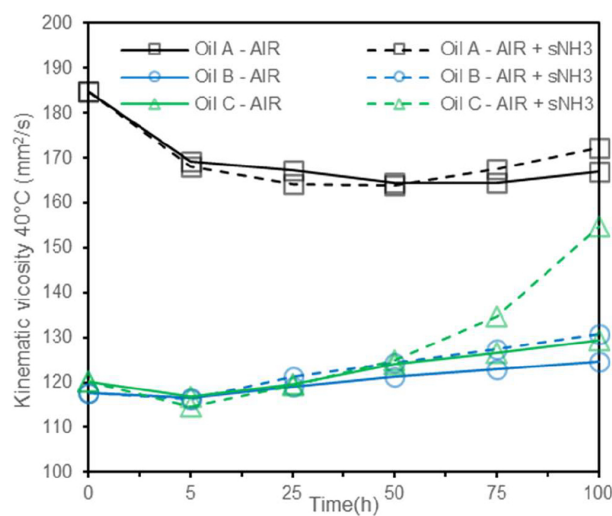


Figure 1.11: Kinematic viscosity at 40 °C for group II oils with unknown additive packages, at different aging times under air (continuous lines) and air with stoichiometric ammonia (dashed lines). Reprinted with permission from [25], copyright 2023 SAE International

Chevron Oronite to study the impact of ammonia on lubricants, as presented in [96]. They exposed a group I mineral oil and a plant-based branched hydrocarbon oil, each formulated with additives leading to a TBN of 40, to gaseous ammonia at 180 °C until the nitrogen content of the oil reached 600 ppm. They also measured the deposit tendency, using the Komatsu hot tube test at 330 °C, the kinematic viscosity, and the oxidation onset temperature using Differential Scanning Calorimetry (DSC). The Komatsu deposit test involves flowing oil into a tube at elevated temperature and rating the lacquer formation. This method is different from the micro-coking test performed by Agocs *et al.* [17], which involves heating a small volume of oil at 230 °C (center of the plate in Figure 1.10) and 285 °C (edges of the plate in Figure 1.10) for 90 min and rating the lacquer formed under static conditions. Compared to the fresh oil, these characteristics were not significantly different for the aged oils. The difference between the conclusions of those two studies might come from differences in aging duration, ammonia concentrations or the specific additive package used.

1.2. EFFECT OF HYDROGEN AND/OR AMMONIA COMBUSTION ON THE AGING OF THE LUBRICANT

A different experimental setup has been developed by MAN, who designed a test rig comprising pressurized cylinders in which engine parts or oil can be immersed in liquid or gaseous ammonia at room temperature, as described in [95]. They exposed different lubricants in liquid ammonia for one week. After the ammonia was allowed to evaporate, the oils were characterized for changes in color, deposit tendency, cold flow properties and kinematic viscosity. The tested oil included mineral-based system oils, base oils, and lubricants for steam turbines, refrigeration compressors, gas turbines and piston oils. Among these, a synthetic base oil formulated for ammonia refrigeration exhibited the most stable performance, showing a minimal interaction with ammonia. No quantitative results were provided, but this finding implicitly suggested that other types of lubricant were, in contrast, affected by ammonia.

Xu *et al.* [24] generated liquid ammonia-oil emulsions and water-oil emulsions which they studied after different storage times under heating between 20 °C and 100 °C. As in [17], they measured very high TBN values with ammonia. Below 70 °C, the viscosity of ammonia-oil emulsions was significantly higher than the pure oil, and even than the water-oil emulsion, indicating a specific interaction with ammonia. They showed evidence of the formation of an H-bond network at low temperatures, between ammonia, water and polar additives, which did not affect the lubricating properties. Similarly, Rao *et al.* [31] mixed a marine lubricant with ammonia solution at 80 °C to investigate the combined exposure to ammonia and moisture. After 288 h, the lubricant had a higher turbidity, viscosity and a lower thermal stability, which the authors attributed to amidation of the carboxylic acid additives and complexation of Ca^{2+} and Mg^{2+} from the additives with both NH_3 or OH^- , depending on the ammonia concentration.

To evaluate lubricant behavior under more realistic conditions, Obrecht *et al.* performed long-duration engine tests using a 1.5 L 4-cylinder engine fueled with diesel/ammonia (15/85 in vol. %) with three lubricants, tested over 250 h at 2000 rpm and high load [25]. Kinematic viscosity at 40 °C, TAN and TBN did not appear to follow any clear trends, indicating limited degradation of lubricant or inappropriate characterization protocols, as suggested by the authors. The impact on tribology was monitored by targeting specific trace metals with Induced Coupled Plasma Optical Emission Spectrometry (ICP-OES):

- Copper, usually found in engine bearing alloys such as conrod bearings or turbocharger bearings, was considered as a sign of corrosive wear.
- Iron, considered as a sign of adhesive or abrasive wear.
- Nickel, used as a sign of wear in the ring/piston/cylinder region, as it is used in cylinder liner coatings.

Obrecht *et al.* observed increasing concentrations for those three metals with rates function of oil chemistry. The copper concentration reached 600 ppm in the worst case, that is, one order of magnitude higher than the results obtained with neat diesel [25]. This is consistent with the corrosiveness of ammonia towards copper and brass [2]. The iron concentration

1.2. EFFECT OF HYDROGEN AND/OR AMMONIA COMBUSTION ON THE AGING OF THE LUBRICANT

did not exceed the values expected with neat diesel, and the content did not depend on the oil chemistry. This also agrees with the literature, as iron theoretically passivates in the presence of ammonia [2]. Both metals can act as catalysts for liquid-phase oxidation. The authors observed that the increase of the nickel content was correlated with an increase in the blow-by flowrate, indicating a reduced sealing of the engine around the piston rings due to significant wear in this region. Visual inspection of the engine after the tests confirmed this hypothesis [25]. However, it remains unclear whether it is due to the direct interaction of gaseous ammonia with engine parts, or to ammonia uptake in the oil. The results from artificial aging could not be exactly reproduced with the engine test bench. This discrepancy might be due to the fact that the blow-by gas mixture contains less ammonia than stoichiometric proportion, but water, NO_x and diesel combustion by-products in addition. In engines, oil also undergoes varying temperatures and might contain metals acting as catalysts. Moreover, they also indicated that some oil samples were found to contain water, which may have altered the measured properties.

In summary, these results clearly indicate that lubricants chemically interact with ammonia under laboratory and engine-like conditions. Depending on the additive package, ammonia exposure seem to affect lubricant properties and tribology, which highlights the need for better understanding the degradation mechanisms involved in ammonia engines and developing ammonia-compatible engine oils.

2.4.2 Compatibility with hydrogen

Although hydrogen is a highly diffusive gas which could easily travel to the crankcase with blow-by gases, its uptake into the lubricant seems unlikely in an engine. First, it is unlikely that any unburned hydrogen will remain, due to its high reactivity. Second, The reactivity of hydrogen towards unsaturations is well-established and exploited in refineries for hydrotreatment processes, but such reactions occur at very high temperature and pressure typically around 400°C and up to 200 bar pressure, along with specialized catalysts [40]. Obrecht *et al.* also studied the effect of hydrogenation on the main properties of lubricants [101]. They exposed 800 g of a commercial engine oil to a constant flow of 2 mL/min of hydrogen at 20 bar and 80°C for 48 h and performed standard characterizations including kinematic viscosity, oxidative stability, TBN, and micro-coking behavior. No measurable changes were observed in any of these properties before and after hydrogenation. Furthermore, GC/MS analysis revealed no evolution of the oil at the molecular level [101]. To the best of our knowledge, no other studies have addressed this question, and no additional data are available to validate or challenge these findings.

2.5 Compatibility with water

Like ammonia, water, a polar molecule, produced during ammonia and hydrogen combustion, can travel to the crankcase by blow-by gases and partially dissolve into engine lubricants. However, in contrast to ammonia, water can condensate and exist in the liquid state under the temperature and pressure conditions of the crankcase. It can first dissolve in oils, up to a threshold where emulsification happens, resulting in water droplets dispersed and stabilized in the oil phase [27]. Over time, this emulsion can destabilize, leading to phase separation and accumulation of free water at the bottom of the crankcase [39].

The problem of water contamination arises in ships where poor storage conditions can lead to water accumulation in large tanks, and leaks of refrigerating systems can happen. Here is a list of possible bad consequences associated with water contamination reported from [27, 102]:

- Oxidation promotion and antioxidant neutralization leading to sludge and deposits
- Hydrolysis of lubricant additives into acids (especially esters in detergents, dispersants, and friction modifiers)
- Rust and corrosion, with increased abrasive wear due to metal particles
- Impaired lubrication from a discontinuous oil film
- Overflowing due to emulsification and/or foam
- Cavitation if vapor bubbles form in critical regions
- Hydrogen embrittlement from reduction of water into hydrogen, and diffusion through metal causing blistering and cracking
- Bacterial growth, which further increases acids formation and oil degradation [103]

The Chevron branch dedicated to industrial marine lubricants recommends a complete drain when the water content is greater than 0.5 w/w% [102].

One critical question is the water residence time in lubricants, as they are heated during engine operation. Under controlled conditions (80 °C), Cen *et al.* observed that the water content decreased from 1 w/w% to less than 0.4 w/w% in two weeks, suggesting that water uptake was partially reversible [26]. This timescale is long considering the possible repetitive exposure to water in an engine, but higher temperatures (especially above 100 °C) would probably lead to faster evaporation. The uptake and evaporation rate depend on the polarity of the base oils: with ester bases, a larger quantity of water is dissolved, but it takes longer to evaporate than with PAO, as expected based on polarity [26]. In the same study, water uptake correlated with an increased TAN and accelerated depletion of ZnDTP additives, suggesting that water promotes oxidation and other ways of acids formation (ester hydrolysis, bacteria). The same results were obtained by Shishigin *et al.*, who measured a TBN decrease of 58 % after 100 h on engine test benches with a constant 1 w/w% water content in the oil, versus only

1.2. EFFECT OF HYDROGEN AND/OR AMMONIA COMBUSTION ON THE AGING OF THE LUBRICANT

22 % drop without water [104]. Under these conditions, no significant difference was obtained with tap water, sea water and distilled water. In the same study, viscosity increased by 190 % after a 36 h laboratory wear test with ball bearings, and the mass loss from bearing inserts was 70 % higher than with fresh oil [104]. On the other hand, Cen *et al.* did not measure any impact of water contamination on the evolution of the viscosity. Using a rolling ball on a disk, they measured similar friction coefficients with and without water for a polyester and a PAO oil with the same ZnDTP additive, but aging with water was associated with slightly higher wear for both oils. They attributed this result to the accelerated degradation of ZnDTP with water, evidenced by the depletion of the bands associated with P=S, P–O and S–O in FTIR [26].

In marine oils, additives are used to limit these processes [27, 44]. Overbased detergents increase the initial basic reserve, demulsifiers promote phase separation, and anti-foaming agents counterbalance foam formation. These additives are usually not found in engine oil formulations for heavy duty or passenger cars.

As shown earlier, water uptake seems to be influenced by the base oils and its additives, like ammonia. The accumulation of acidic products in the oil with time might facilitate further water and ammonia uptake. Experimental results suggest that water may contribute to oil aging with conventional fuels, but the effect of larger amounts of water in the case of ammonia and/or hydrogen combustion is not well explored. Besides, water uptake can amplify the accumulation of ammonia—considering the high solubility of this gas in water—or nitric oxides, leading to the accumulation of nitric acid. This issue was never addressed.

Altogether, previous sections have highlighted the potential chemical and rheological changes in lubricants used in internal combustion engines fueled with ammonia/hydrogen blends, particularly when exposed to nitrogen oxides, unburned ammonia and water at high temperatures. Moreover, lubricants are known to contribute to particle emissions, with direct influence of their properties, such as chemical composition and viscosity. Next section clarifies the role of lubricants in particle emissions with hydrocarbon fuels and present recent studies on particulate matter from the combustion of carbon-free fuels.

2.6 Particle emissions

With increasingly stringent regulations on the emission of pollutants, researchers have explored all potential sources of particulate matter and found that lubricants also contributed to particle emissions [28]. This contribution is expected to be greater with carbon-free fuels, as lubricants become the primary source of carbon in the system [28, 29, 101]. Oil-derived solid

1.2. EFFECT OF HYDROGEN AND/OR AMMONIA COMBUSTION ON THE AGING OF THE LUBRICANT

particles are believed to come from lubricant droplets which are transported into the combustion chamber where they are partially oxidized, leading to the formation of carbonaceous particles and inorganic nucleation particles [28,29,105]. In addition, evaporation of the oil film on the cylinder liner can lead to volatile emissions of heavy hydrocarbons and organic matter [106]. Besides, recent studies [107] tend to show that hydrogen and ammonia as exhaust gases can modify the number and morphology of soot particles emitted with dual-fuel engines.

2.6.1 General considerations about engine exhaust particles from carbon-based fuels

Engine exhaust particle formation was thoroughly described in [108–110]. Particle formation during and after combustion of hydrocarbon fuels results from the condensation of Poly-Aromatic Hydrocarbons (PAHs) into nucleation germs, growing by condensation and coalescence [109,110]. Usually with hydrocarbon fuels and especially diesel, particles are classified as a function of their diameter in three groups which also correspond to different possible stages of formation and growth: the smallest ones, 'nucleation mode', correspond mainly to mostly volatile condensates such as sulfuric acid and hydrocarbons, the medium ones, 'accumulation mode', have higher solid content, carbon and metallic ash mixed with condensates, and the biggest ones, 'coarse mode' are for very large agglomerates, formed mainly after deposition at the exhaust (Figure 1.12). The distribution between these three groups depends on the operating conditions of the engine such as its speed, load, and whether it is cold start or stabilized running conditions (Figure 1.12) [108]. In parallel, official standards are based on the total mass of particles with a distinction based on diameters, distinguish fine particles PM_{2.5} and PM₁₀, with respective diameters below 2.5 and 10 μm from even smaller types.

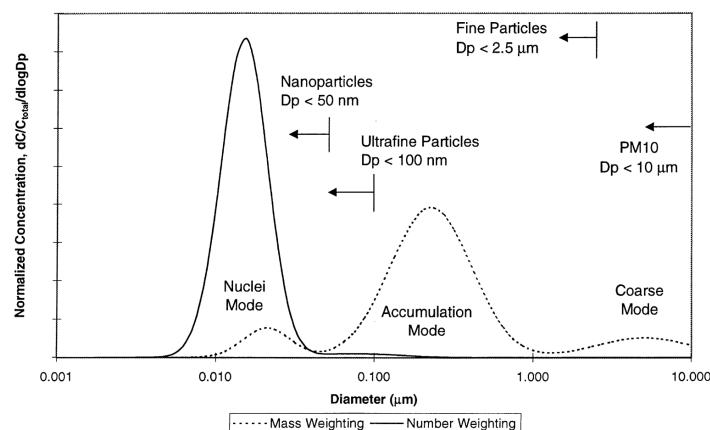


Figure 1.12: Theoretical mass and number distribution of particles with diesel fuel. Reprinted from [108], Copyright 1998, with permission from Elsevier

Lubricants are also a source of particle emissions, generating both soot and condensed inorganic species, especially when additives contain significant amounts of sulfur and nitrogen [106].

2.6.2 Lubricant contribution to particulate matter with hydrocarbon fuels

Lubricants contribution to particle formation is thought to be linked to different oil consumption mechanisms, identified by Yilmaz *et al.* [51] as being transport into the combustion chamber, evaporation of the oil film wetting the cylinder liner and, to a lesser extent, carrying of oil mist by reverse blow-by gases. The direct transport mechanism was estimated to account for up to 50 % of the total oil consumption [51]. It leads to hydrocarbons, metals and inorganic ashes from the additives being transported to the combustion chamber, where they can undergo partial combustion and pyrolysis and generate nuclei. Evaporation of the oil film only concerns hydrocarbons and not metals [106]. Lubricants are thought to contribute to both nucleation and accumulation mode particles via these transport mechanisms and during post-combustion reactions [29, 110]. The vaporized fraction can condensate on nuclei or on mineral particles in the exhaust, where temperature decreases [110]. Several studies have concluded that lubricants mostly contribute to the Soluble Organic Fraction (SOF) of particles obtained with conventional fuels, as a high proportion of unburned heavy hydrocarbons from the oil can condensate on soot precursors [111–114]. Sulfur and phosphorous atoms contained in oil additives in the lubricant further contribute to the SOF and can be found as sulfates and phosphates, as in [113, 114]. Depending of their concentrations, metals and sulfur can also undergo the formation of oxides and salts, themselves generating nucleation particles [106]. Oil-derived soot particles also seem to have a more disordered structure. Raman and XPS characterizations show higher proportion of tertiary carbons and C–H groups, indicating a less graphitic character in [114], which is consistent with microscope observations showing larger interlayer distances between carbon crystallite layers [112]. The disordered structure offers more reactive sites for particles post-oxidation as confirmed by oxidation studies [112, 115]. Particle characteristics also vary with lubricant formulations. Wang *et al.* compared the emissions when using two different base oils [112], and found that it led to variations in the size of particles, structure, volatile fraction and oxidation reactivity (Figure 1.13). Higher viscosity oils seem to result in particles with a higher volatile fraction, which is attributed to promoted condensation of heavy hydrocarbons [106]. Lubricants with similar viscosity values also produced similar particle number distributions, but different size distributions in [116]. Similarly, six oils with similar viscosity but different additive packages resulted in different PN10 emissions (number of particles above 10 nm) from a hydrogen-fueled engine in [101], confirming that both lubricant characteristics and composition had an influence on particulate matter emissions. A more in-depth analysis can be found in the recent review by Lyu *et al.* [106], focusing on this topic of the influence of lubricants on the emission of particulate matter from internal combustion engines.

1.2. EFFECT OF HYDROGEN AND/OR AMMONIA COMBUSTION ON THE AGING OF THE LUBRICANT

	150 base oil	350 base oil
Condensation point (°C)	−30	−24
Flash point (°C)	190°C	222°C
Viscosity index	108.27	99.69
Kinematic viscosity at 100 °C (mm ² /s)	5.15	8.38
Kinematic viscosity at 40 °C (mm ² /s)	28.88	64.10

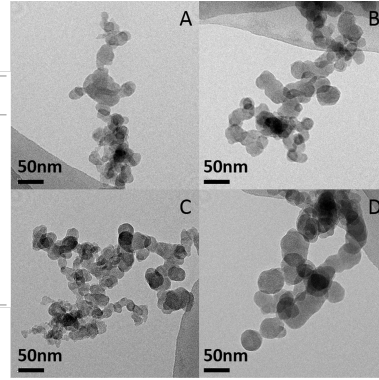


Figure 1.13: Oils characteristics and microscope observation of the resulting particles. A and C correspond to base oil 150–B and D to base oil 350. Reprinted from [112], copyright 2016, with permission from Elsevier

2.6.3 Lubricant contribution to particulate matter with zero-carbon fuels

Particulate matter in hydrogen engines Lubricants also contribute to particulate emissions in engines fueled with carbon-free fuels such as ammonia and hydrogen, which needs to be addressed as underlined by Lyu *et al.* [106]. A recent study by Apicella *et al.* analyzed the SOF of particles collected using GC/MS at the exhaust of a hydrogen-fueled monocylinde engine, revealing the presence of large PAHs, clear evidence that some oil underwent severe thermal degradation in the combustion chamber [29]. Similarly, Thawko *et al.* studied particulate emissions from a hydrogen-rich reformat blend (75 %mol H₂ and 25 %mol CO₂), focusing on the number distribution and chemical composition of particles [105]. They found a higher number of accumulation mode particles with the lubricant containing the highest metal content, although the total number of ultrafine particles (<100 nm) was greater with the oil containing fewer metals. Particle mass distribution peak was found to be twice as high with the metal-rich oil. They also found that all trace elements from the lubricants did not have the same recovery yield in the particles: significant amounts of silicon, iron, sodium and potassium were found in the particles compared to calcium, zinc, phosphorous and molybdenum. The authors suggested that elements with higher boiling points tend to remain in the combustion zone and act as precursor for nucleation [105]. This hypothesis is consistent with the findings of Miller *et al.*, who studied particulate emissions in hydrogen-fueled engines in 2007 [28] to isolate the effect of the lubricant in particulate matter by filling the engine with a carbon-free fuel. They classified four different types of particles by size and morphology: nanoparticles (<50 nm), core-shell particles (core <20 nm), dense spheres (100 nm) and agglomerates (300 nm). They studied the elemental composition of each type of particles and showed that agglomerates were mostly made of carbon, dense spheres mostly Ca (along with Na, K, S, P), iron dominated the particle cores, and shells contained P, K, Zn, and Na [28]. Their hypothesis posits that combustion evaporates the most volatile elements (P, K, Na, Zn), while high-boiling-point elements (e.g. T_b=2860 K for Fe, 1484 K for Ca) act as precursors for nucleation. During the expansion stroke and subsequent cooling of the

1.2. EFFECT OF HYDROGEN AND/OR AMMONIA COMBUSTION ON THE AGING OF THE LUBRICANT

chamber, vapors condensate on nucleation cores, or nucleate independently. Dense spheres would then result from oil droplets from which it would only remain the non-volatile residues, while core-shell structures would originate from condensation of vapor on iron and/or calcium nuclei [28]. Recently, the work of Lagana *et al.* [117] provided new insights on this emerging topic with few references to date. As the studies above, they studied particulate matter from a spark-ignited engine fueled with hydrogen. Real-time measurements of total particle number and size distributions were combined with particles collection on microscope grids for steady-state conditions (high speed-low load and low speed-high load), and transient conditions. A catalytic stripper was used to remove the volatile fraction of particles before the analyzer. Detailed analysis of the particle size, morphology and chemical composition via Transmission Electronic Microscopy and Energy Dispersive X-ray Spectroscopy (EDX) led them to conclude that particulate matter with hydrogen engines mainly had three origins: lubricants (typically identified by a high S, Zn or Ca content), wear (typically identified by a high Fe or Ni content) and engine coolant. The latter was indeed hypothesized because elements such as K, Na or Cl were found, with no other possible origin identified by the authors. High speed-low load resulted in a higher number of particles, and types of morphologies with particles ranging from small particles (10 nm–90 nm) to large agglomerates (> 500 nm, $1\text{ }\mu\text{m}$), with amorphous and crystallized regions. High levels of emissions were attributed to the combination of low loads promoting oil consumption and high speed promoting high temperatures. On the contrary, low speed-high load resulted in fewer particles and types of morphologies, as in that case, only large agglomerates were found. Another interesting finding of this study is that changing the piston rings led to an immediate reduction of the total solid particle number by reducing oil consumption. A smaller engine with equal power was operated with diesel as a reference under the high speed-low load conditions. The total solid particle number obtained with diesel was two orders of magnitude above the level with hydrogen after engine improvement, but was the same order of magnitude than with hydrogen before the improvement. Overall, these studies highlight that particulate matter requires to be studied even with zero-carbon fuels such as hydrogen as they can reach non-negligible levels. In particular, the absence of abundant soot production resulting from the combustion of carbon-based fuels brings out new types of particles. Both the lubricant formulation and engine design seem to be relevant levers for reducing particle emissions in hydrogen engines.

Particulate matter in ammonia engines The same concern can be raised about particulate matter at the exhaust of ammonia engines. To date, only one study focusing on this topic could be found. Patil *et al.* [118] conducted a comprehensive study of particulate matter at the exhaust of a research engine operated with 100% NH_3 . Combining Transmission Electronic Microscopy (TEM) observations, with EDX chemical analysis, Raman, FTIR and XPS spectroscopy, they demonstrated the formation of ammonium nitrate salts under their operating conditions. Numerical simulation and real-time analysis of the

1.2. EFFECT OF HYDROGEN AND/OR AMMONIA COMBUSTION ON THE AGING OF THE LUBRICANT

exhaust gases show levels of NO_x and NH₃ which could enable nitrate formation via the reaction $2\text{NO}_2 + 2\text{NH}_3 \longrightarrow \text{N}_2 + \text{H}_2\text{O} + \text{NH}_4\text{NO}_3$, which can undergo decomposition above 175 °C [119], resulting in NH₃ and HNO₃, supporting their demonstration. Elements originating from the lubricant were also found, such as sulfur, magnesium and calcium. The observed particles mainly consisted of nitrate cores encapsulated in inorganic material derived from the lubricant. This first study calls for others to determine whether ammonium nitrate or other types of nitrogenated particles are also measured under different conditions and with different engines.

To summarize, lubricants contribute to particulate matter not only in conventional engines but also in hydrogen and ammonia engines. Ammonia combustion might also lead to the emission of specific nitrated species. The metal content of lubricants influences particle mass and distributions, whereas sulfur and phosphorus derived from the additives increase the soluble organic fraction of the particles. In addition, lubricants contribution depends on oil transport mechanisms and injection type. Aging of the lubricant might induce physical and chemical changes, such as increased metal content or changes in viscosity, and thus alter particle emissions. Investigating particulate matter associated with ammonia and hydrogen combustion is essential for the development of ensure these new engines comply with emission standards and are authentic carbon-free fuels.

2.6.4 Effect of NH₃ and H₂ on soot formation

Additionally, as exhaust gases can condensate on particle precursors, variations in their composition can affect particle structure, mass, and morphology. In their fundamental work on soot formation, Haynes and Wagner investigated the influence of various fuel additives [120], including H₂, NH₃, and H₂O in premixed flames. They reported that the addition of NH₃ to ethylene decreased the total amount of particles, while water vapor had negligible effects at concentrations below 10 % [120]. In another more in-depth study in which the soot volume fraction, the mean particle size, and the particle number density were measured on flat premixed flames of ethylene air at atmospheric pressure, they found that NH₃ reduced the soot volume fraction while H₂ promoted soot under these conditions [121]. Although H₂ promoted the onset of soot formation, it did not appear to affect its aspect or number density at molar fractions below 3 %. They also found a shift in the soot production zone, with the onset of soot formation occurring farther from the burner in the case of ammonia was present [121]. More recently, Boyette *et al.* studied soot formation in ethylene/nitrogen turbulent flames with varying nitrogen substitution degrees. They concluded that replacing nitrogen with ammonia

1.2. EFFECT OF HYDROGEN AND/OR AMMONIA COMBUSTION ON THE AGING OF THE LUBRICANT

reduced the soot volume fraction by a factor of three in flames containing 75 % C_2H_4 by volume [122]. They also showed that soot production started farther from the burner in the case of ammonia substitution (Figure 1.14). According to Haynes *et al.*, this shift was associated with a slight increase in flame temperature, between 10 to 20 K, due to ammonia substitution [120]. However, H_2 substitution resulted in a higher soot volume fraction along the flame centerline (Figure 1.14). Interestingly, when H_2 and NH_3 were mixed, soot volume fraction still decreased, suggesting the soot inhibiting effect of ammonia is more efficient than the promoting effect of hydrogen. However, the effect on particle growth dynamics appears to differ between studies. Haynes *et al.* found that there is no effect on surface growth rate or coagulation of particles in their ethylene flat flames, while Boyette *et al.* observed that ammonia substitution in ethane flames (0–25 % NH_3) resulted in smaller particles [122].

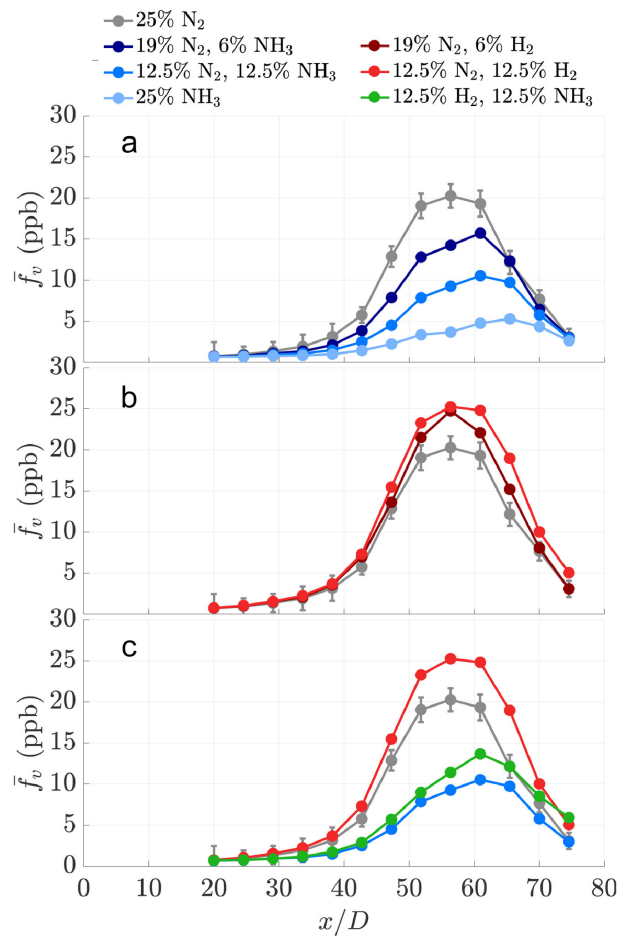


Figure 1.14: Mean soot volume fraction along the a flat flame centerline for flames with 75 % C_2H_4 and various NH_3 and H_2 proportions. Reprinted from [122], copyright 2020, with permission from Elsevier

Zaher *et al.* studied soot obtained in laminar co-flow flames with ethylene doped with up to 50 % NH_3 , using XPS and Raman spectroscopy [107], and concluded that nitrogenated species interact with the surface of soot particles, preventing soot growth by blocking carbon addition pathways. Their analysis revealed that the nitrogen content on the particles surface increase linearly with increasing NH_3 concentrations (Figure 1.15). This was attributed to

1.2. EFFECT OF HYDROGEN AND/OR AMMONIA COMBUSTION ON THE AGING OF THE LUBRICANT

the ability of nitrogenated species to bond with graphitic carbon defects, since the sp²/sp³ carbon ratio was higher when ammonia was added, meaning that the particles have a more organized structure overall, with fewer defect sites [107]. In their recent review, Chen *et al.* [123] summarize current knowledge on the effect of ammonia addition on soot formation, supporting these conclusions.

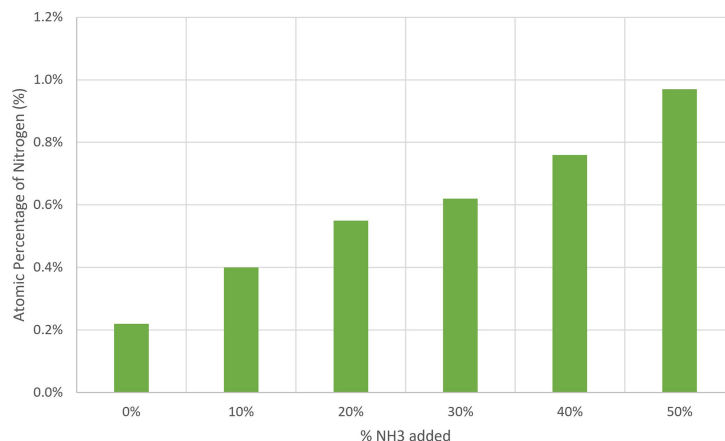


Figure 1.15: Atomic percentage of nitrogen on the soot surface using XPS for laminar flames with up to 50 % NH₃ blended with C₂H₆. Reprinted from [107], copyright 2023, with permission from Elsevier

Burner studies clearly demonstrated that the addition of hydrogen to hydrocarbon fuels, and even more importantly, ammonia, affects soot formation. Although the experimental conditions in these studies differ substantially from those of internal combustion engines, the influence of unburned gases on particulate emissions should be considered when studying oil-derived particles. Exploring particle formation in ammonia-fueled and dual-fuel engines is therefore essential for the deployment of these technologies.

This section explored how the specific combustion characteristics of ammonia and hydrogen may influence lubricant degradation mechanisms. The conditions driving well-established thermo-oxidative degradation may change—particularly due to the high temperatures associated with hydrogen combustion—which could lead to more severe degradation processes. Elevated NO_x levels may also promote nitroxidation reaction, which remains insufficiently understood. Moreover, novel degradation mechanism could occur, such as interactions with unburned ammonia, as suggested by studies on ammonia compressors and recent research on ammonia-fueled engines. Additionally, lubricants can significantly contribute to particulate matter emissions, especially in the context of carbon-free fuels, with a direct impact of their formulation and properties. Altogether, these aspects point to the need for studies about the lubrication of next generation engines operated with ammonia and/or hydrogen. The following section reviews the principal characterization techniques and experimental protocols reported in the literature for studying lubricant degradation.

3. Lubricants characterization techniques

3.1 Monitoring oxidation

The known consequences of oxidation are changes in the viscosity, accumulation of oxygenated, acidic and unsaturated products [13, 44]. Therefore, various characterization techniques can be used to monitor the degree of oxidation, for in-field analysis or accelerated testing. The main techniques, and references in which they are used are summed-up in Table 1.5.

Table 1.5: Usual parameters used to monitor oxidation

Technique	Principle	Examples of references
Fourier Transform Infrared (FTIR) Spectroscopy	Absorbance measurements to quantify oxidation products and antioxidant consumption	[19, 35, 124–126]
Kinematic viscosity	Viscosity and specific gravity measurements to show the accumulation of heavy and/or polar products	[19, 35, 124]
Total Acid Number (TAN)	Potentiometric titration to quantify the formation of acid species	[124, 125]
Ultra-Violet (UV) Spectroscopy	Absorbance measurements to identify specific chemical groups	[81, 127]

Depending on the engine type and size, the quality of the oil and the operating conditions, recommendations for service life of lubricants can be found between 5000 km (for light diesel engines operating mostly in cities) and up to 100 000 km For heavy duty engines. On the other hand, the Conseil International des Machines à Combustion (CIMAC) provides precise criteria concerning the above properties for drain interval recommendation [128]. For reciprocating gas engines, the criteria are summarized in Table 1.6, these are very close to criteria for diesel engines, presented in [129].

Each characterization technique involves different timescales and degradation scales. In [91] for instance, FTIR spectroscopy shows antioxidant depletion and oxidation products from 1 h, but viscosity only increases after 6 days in an open air oven at 180 °C. This is because the increase in viscosity is actually a consequence of multiple reactions between oxidation products.

3.2 Accelerated aging protocols

Lubricant maintenance is essential to preserve machineries. The most direct method to study engine oil degradation is to characterize oil samples from real engines or with engine test benches, at different times. This kind of study enables to be as close as possible to real aging conditions. For instance, Levermore *et al.* and Dörr *et al.* studied in-situ oxidation of an engine oil, after respectively 8 376 miles and 19 800 km with regular sampling [35, 130].

1.3. LUBRICANTS CHARACTERIZATION TECHNIQUES

Table 1.6: CIMAC criteria for precautionary and mandatory action regarding lubrication of reciprocating gas engines [128]

Physical Property	Unit	Method	Advisory action limit	Mandatory action limit
Kin. Viscosity at 40 °C	mm ² /s	ISO 3104–ASTM D7279/D2270	±25 %	±35 %
Kin. Viscosity at 100 °C	mm ² /s	ISO 3104–ASTM D7279/D2270	±15 %	±25 %
TBN depletion	mg KOH/g	ISO 3771–ASTM D2896	≤ 60 % of fresh oil	≤ 50 % of fresh oil
TAN	mg KOH/g	ASTM D664	+1.5 increase	+2.5 increase
Water	%v/v	DIN 51777–ASTM D6304/ E2412	≥ 0.15	≥ 0.30
Oxidation	A/cm	DIN 51453–ASTM E2412/D7414	≥ 15	≥ 25
Nitration	A/cm	ASTM E2412/D7624	≥ 15	≥ 25
Flash point (open cup)	°C	ISO 2719–3679	≤ 190	≤ 170
Flash point (closed cup)	°C	ISO 2592	≤ 210	≤ 190

However, in-field tests are costly and time consuming. For upstream research, and in order to reduce analysis costs and time, standardized methods and norms using the setups presented in Table 1.7 are used by manufacturers and laboratories. These tests reproduce specific constraints: heating, oxidizing atmosphere and/or catalytic activity of metals to accelerate the evolution of the lubricants and thus assess the service time of the product and ensure reasonable drain intervals. One important parameter considered is the oxidation stability, usually quantified via the Induction Period (IP) which has different definitions depending on the protocol used. This parameter corresponds to the setting point from which the oxidation reaction is self-accelerated following the accumulation of hydroperoxides.

Accelerated aging tests show several major differences from in-field degradation. One of them is the temperature variation. In real engine, the lubricant sees cyclic temperatures: it is severely heated during very short times around the piston, and then cooled down in the crankcase, before being pumped again in hot regions. Lab tests generally happen at relatively high and constant temperatures to accelerate degradation processes without risking thermal cracking. To our knowledge, no study investigated the residence time of lubricants in hot regions and the determination of a representative exposure to cyclic variations. Another difference is the metal content, due to wear and corrosion. Standardized manufacturers tests are usually done with metal spiking, to reproduce the catalytic effect of wear metals (ASTM D4742). Finally, these tests ignore other degradation phenomena such as fuel or water contamination. With real engines, special caution must be paid to the drain between lubricants, as residues might stay on the wall and contaminate following samples [35].

1.3. LUBRICANTS CHARACTERIZATION TECHNIQUES

Table 1.7: Different instruments and methods to study and characterize accelerated oxidation

Principle	Measure	Advantages	Drawbacks
PetrOxy from Anton Paar			
25 mL pressurized reactor, filled with oxygen	Oxygen pressure is measured. IP is defined as the time for a 10% pressure drop	Easily implemented; small quantity of sample; standard conditions enabling comparison	Possible leaks; no in-process sampling; biased if formation of volatile compounds; no bubbling; no stirring
Rancimat [131] from Metrohm			
Air is bubbled into the sample, volatile products are entrained in a water beaker	The conductivity of water is measured. IP is defined as the inflexion point of the conductivity curve	Easily implemented; good contact between air flow and oil	Only atmospheric pressure; conductivity measurement only quantifies soluble species; oxidation under air only
Autoclave [69, 81]			
Pressurized reactor	Numerous ways possible to follow the reaction, such as pressure monitoring, FTIR or titration	Highly tunable (volume, temperature, pressure, gas); possibility of in-process sampling; good contact with stirring	Method which requires development; limited amount of reactive gas
Three-neck round flask [124]			
Heated round flask with refrigerant	Numerous ways possible to follow the reaction, such as FTIR, titration	Highly tunable (volume, temperature, gas composition and flowrate); possibility of in-process sampling; requires no specific instrument	Only atmospheric pressure; less reproducible; high gas consumption
DSC [132, 133]			
A small volume of oil (≤ 20 mg) is exposed to oxygen and a temperature ramp	Oxidation is an exothermic reaction, DSC shows a peak after induction time	Small amount of sample; very fine measurement	No analysis possible on the liquid or gas phase
TGA [115, 134]			
Thermobalance	Quantification of the mass loss rate due to volatiles	Small amount of sample; measures the oxidation rate; tunable oxidative atmosphere	No analysis possible on the liquid or gas phase

3.3 Accelerated aging versus in-field aging

As a reference, the CIMAC criteria reported in Table 1.6 can be used to evaluate the degradation stage of artificially aged oils, and establish a link between the timescales of artificial aging compared to in-field aging. Besser *et al.* tried to compare in-lab and in-field aging for two different oils, using artificial aging in a 250 L stirred reactor, and a 1 L three-necked round flask, both heated at 180 °C [124]. Samples were taken periodically, and compared to a reference oil after 30 000 km, with characteristics close to the limit values reported in Table 1.6. In the small scale test, the target oxidation level was reached after 950 h for one oil, but only 150 h for the other (Figure 1.16). For these oils, antioxidants were almost completely consumed after 600 h and 175 h, respectively. In the larger scale experiment, the target oxidation level was reached after 350 h and less than 100 h for the same oils. This was attributed to thorough stirring and a proportionally higher air flow rate in the large scale experiment. In another study, characteristics similar to an oil after 20 000 km in a passenger car were obtained after 400 h of aging in a 200 L reactor at 180 °C [87], giving an equivalence of 50 km for a 1 h experiment for the large scale setup at 180 °C, equal to what can be deduced from the study [124] for oil A.

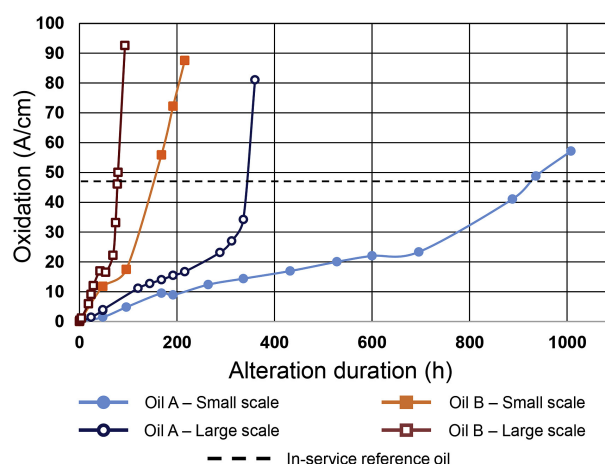


Figure 1.16: Comparison of two oil aging protocols to reproduce the target properties of a reference used oil. Reprinted from [124], copyright 2019, with permission from Elsevier

Dörr *et al.* also studied the degradation of a fully formulated oil by simply putting it in an oven at 180 °C, with open air [91]. The targets defined by CIMAC were reached in 6 days for oxidation, between 6 and 8 days for the viscosity at 100 °C, and antioxidant were severely depleted after 4 days. The evolution of these parameters was similar to what was observed in [35] over 19 800 km, with a kind of induction period until 6 000 km. Despite interesting results, working with an open beaker does not seem to be the best solution, as information about volatile products is lost, and corrections due to evaporation must be applied for quantification measurements [91]. Agocs et Obrecht also conducted parallel experiments with artificial aging in a 2 L reactor at 150 °C for up to 100 h and an engine test bench running up to 250 h [25]. Unlike the precedent cited works, they could not unambiguously reproduce

1.3. LUBRICANTS CHARACTERIZATION TECHNIQUES

the same trends than with artificial aging for TAN and kinematic viscosity. In [125], aging protocol was only 2 h at temperatures between 150 and 300 °C in a 500 mL autoclave, to reproduce temperature exposure of aviation engine oils. For samples above 250 °C, they could observe color changes, viscosity decrease, and TAN and pour point increase despite the short aging period.

In summary, establishing a link between accelerated degradation conditions and in-field degradation is not straightforward. Numerous parameters including temperature, gas composition and flow rate, volumes, and lubricant formulations have a major influence on the evolution of lubricant properties. Nevertheless, the purpose of small scale experiments is to provide faster results as a first approach and to have a better control of the degradation conditions.

Similar characterizations are commonly conducted to study the evolution of lubricants: oxidation and nitro-oxidation via FTIR spectroscopy, acidity via the TAN, kinematic viscosity. In more detailed studies, gas chromatography and mass spectrometry are used to analyze engine oils at a molecular level. Analytical techniques which enable product identification are required to provide in-depth comprehension of the chemical reactions occurring.

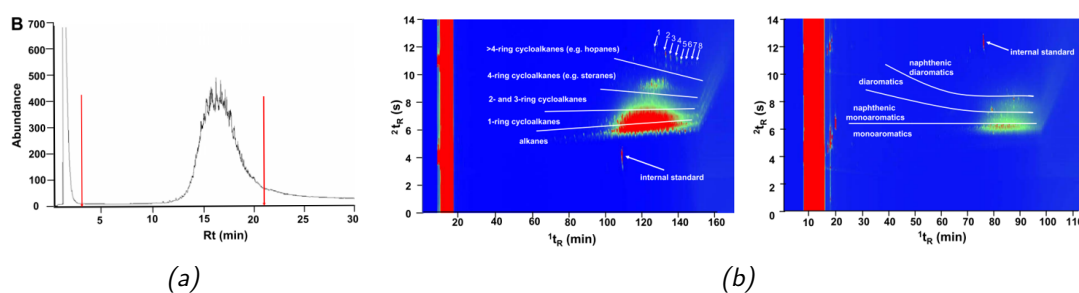
3.4 Analytical techniques

Considering their high molecular weight and complexity, the composition of lubricants is not easily retrieved. Associated to chromatography, mass spectrometry is nonetheless highly interesting to study aging at a molecular level. Chromatography is a separation technique which isolate different components from a mixture. Mass spectrometry is a technique where molecules from a sample are ionized and detected according to their mass/charge ratio. Coupling both enables to pre-fraction different components before they are ionized and decomposed into numerous sub-products. Many different methodologies to analyze base oils and additives have been developed in the literature [82, 135–137].

Some studies used High Performance Liquid Chromatography (HPLC) as a first approach to characterize base oils and/or additives. This technique is not limited by the boiling point of the compounds, but does not sufficiently separate heavy compounds. Similar results were obtained in [135, 136]: HPLC could be used to quantify different categories of compounds (saturates, naphthenics) and discriminate molecules containing one aromatic ring or more for example, but base oil analysis remained quite limited. On the other hand, Kreisberger *et al.* could identify antioxidants and their degradation products with HPLC coupled to a quadrupole Time-of-Flight (ToF) mass spectrometer [137].

1.3. LUBRICANTS CHARACTERIZATION TECHNIQUES

Besides, simple GC is not sufficient either to separate base oils compounds. It requires high injection temperatures ($\geq 300^{\circ}\text{C}$) to vaporize lubricants. Typical profile of a lubricant can be called a "hump", as can be seen in Figure 1.17a, corresponding to a mass of different heavy products which are not well isolated. More successful results were obtained by Harris *et al.* who used two-dimensionnal GC, with one column eluting products according to their polarity and the other one according to their volatility, and could identify squalane degradation production up to C22 [82], and especially nitro-oxidation products thanks to a NCD detection, specific of nitrogen-containing molecules (Figure 1.7). To improve sample vaporization, he diluted it in toluene (1:20). Even better results were obtained by adding a third separation dimension with HPLC before GC2D in [135], as shown in Figure 1.17b and [136]. This type of analysis gives a more detailed profile of the type of hydrocarbons and the different chain lengths. In order to obtain detailed analysis of this kind of complex mixtures, separation techniques and dimensions have to be multiplied.



Red arrows correspond to n-alkanes C10 and C40 respectively.

Figure 1.17: Different analysis of the same 15W40 oil. a) Conventional GC/FID analysis. b) HPLC followed by GC2D/FID. Reprinted from [135], copyright 2009, with permission from Elsevier

Another way to overcome the difficulty of lubricant analysis is to partially vaporize it and study its gaseous fraction. Headspace analysis consists in heating the sample in a closed vial, letting each species at equilibrium between the liquid phase and the gas phase, and collecting directly the gas phase, as shown in Figure 1.18.

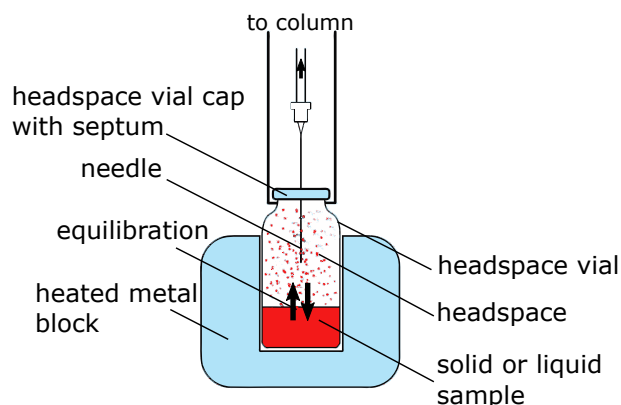


Figure 1.18: Scheme of headspace sampling principle. Reprinted with permission from [138]

1.3. LUBRICANTS CHARACTERIZATION TECHNIQUES

It is not appropriate for quantification as it is based on phase equilibrium, but seems a relevant technique to indirectly study a complex sample. Proof of concept for the examination of oxidized oils was done by Levermore *et al.* [130]. Oil from a real engine was collected at different mileages. Samples were then heated up to 140 °C, and the gas phase was collected by solid phase microextraction for 2 minutes. The collected fraction was desorbed and injected in a gas chromatography column, and analyzed by a mass spectrometer. Different light oxidation products such as benzaldehyde, 1-pentanol or benzoic acid could be identified. Using the same type of desorbable trap, Holse *et al.* [139] used dynamic headspace GC/MS analysis to monitor oxidation degree of marama bean oil, mainly composed of oleic and linoleic acid. They collected the volatile fraction of oil samples kept under different light and temperature conditions over a period of seven months by heating samples at 30 °C during one hour. They identified up to 25 degradation products, all below C8, among which alcohols, aldehydes, ketones and volatile esters. Antioxidant depletion was also studied by heating oil samples at 95 °C for 15 min by Del Nogal *et al.* [140]. Targeting previously identified species, they compared concentrations in new and aged oils of nine antioxidants, up to C14. Headspace-GC/MS then appears as a relevant technique to study altered oils. These studies have all used headspace chromatography to analyze oils which were already degraded, by vaporizing their lightest fraction. The main advantages of headspace analysis is that it requires no sample preparation, and can be conducted in-line with a direct coupling to gas chromatography, thereby avoiding losses induced by heated transfer line for example.

To date, one of the most comprehensive analytical work was done by Lacroix-Andrivet *et al.* in the study [141]. They used high-resolution MS to perform direct infusion, without prior prefractionation of the compounds by gas chromatography. By combining two ionization modes and precisely analyze mass losses, they managed to unambiguously identify numerous kinds of additives, structures and chain lengths: aromatic amines and phenolic antioxidants, ZnDTPs, stearic acids, succinimide dispersants, sulfonate detergents. It required in-depth analysis to get this level of precision.

It can be concluded that no single technique is sufficient to fully characterize the exact composition of a lubricant's base oil, additives and degradation products. A combination of complementary methods is often required. The choice and complexity of these methods should be aligned with the level of detail or resolution required by the study.

This section detailed the usual characterization techniques used to monitor the evolution of lubricants properties. In this field, accelerated aging tests are common to avoid costly and time consuming engine experiments. Therefore, the main protocols and conditions used for accelerated aging were also presented, and compared with in-field aging.

4. Conclusion

Lubricants are essential to ensure the optimal efficiency and durability of internal combustion engines. They are chemically complex products, containing a wide range of additives tailored to specific applications and operating conditions. The current transition toward alternative fuels, particularly ammonia and hydrogen which are increasingly studied as these carbon-free fuels gain attention for long-distance and off-road applications, raises challenges regarding new fuel/oil compatibility. This chapter first presented general considerations about lubricants, detailing their role and formulation. Then, it highlighted several distinctive characteristics of ammonia and hydrogen combustion that may introduce new degradation mechanisms, according to current knowledge on lubricants. Drawing on existing knowledge from related domains, it compiled current insights on four key topics: reactivity with nitrogen oxides, compatibility with unburned ammonia, water contamination, and the impact of the lubricant on pollutants emissions. Finally, the main characterization techniques to monitor and study lubricants degradation were presented. The main takeaways and perspectives can be summarized as follows:

- High nitrogen oxide concentrations measured in the exhaust gases, and by implication, in contact with lubricants, can accelerate nitro-oxidation, reducing the lifetime of lubricants. Future research is needed to examine more precisely the role of NO and to identify reaction intermediates involved in the degradation mechanism.
- Lubricants can also be in contact with unburned ammonia. This could be associated to new degradations mechanisms involving base oils and/or additives which remain to be fully investigated.
- Water contamination might also necessitate the use of new additives. Additionally, the solubilization of ammonia and nitrogen oxide in accumulated water could be investigated to address the potential production of nitric acid into the oil.
- Although ammonia and hydrogen are carbon-free fuels, lubricant-derived soot and particulate matter can still be emitted. Future studies should be conducted to characterize particulate emissions from engines operating on these fuels and to evaluate the influence of lubricant properties.
- Studies focusing on lubricants degradation often rely on accelerated aging protocols, often under conditions that are far removed from engine conditions but still provide valuable insights into oil reactivity.
- Due to their heavy nature and complex composition, the study of lubricants poses analytical challenges.

As ammonia and hydrogen engine technologies remain in early stages of deployment, most conclusions herein are extrapolated from adjacent research fields. Comprehensive studies under engine-representative conditions are then required to fully understand the implications for

1.4. CONCLUSION

lubricant degradation and long-term engine performance. Drawing from these conclusions, next chapters investigate the evolution of lubricants in engine operated with ammonia, and ammonia/hydrogen blends, using accelerated protocols combined with engine bench experiments.

Chapter 2

Material and methods—base oil oxidation under reference conditions

2.1	Experimental section	66
2.1.1	Base oils	66
2.1.2	Accelerated aging setup	67
2.1.3	Oil characterization techniques	72
2.2	<i>Operando</i> oxidation with headspace-GC	77
2.2.1	<i>Operando</i> oxidation: proof of concept	77
2.2.2	Effect of the oil volume	78
2.2.3	Identification of degradation products	79
2.2.4	Effect of the heating time and temperature	82
2.3	Rancimat applied to lube oils	86
2.3.1	Characterization of the accelerated aging via Rancimat method	86
2.3.2	Comparison of the oils reactivity	88
2.4	Oxidation using a pressurized stirred reactor	91
2.4.1	Mineral oil under pure oxygen—assessment of the oxidation protocol and between-day repeatability	91
2.4.2	Comparison with the complex polyester base oil	92
2.4.3	Effect of the temperature	92
2.4.4	Total oxygen content	93
2.4.5	Viscosity	94
2.4.6	Simulated distillation	95
2.4.7	GC2D/MS analysis of the mineral oil oxidation products	96
2.5	Discussion—comparison of the accelerated aging setups	99
2.6	Conclusion	102

2.1. EXPERIMENTAL SECTION

To prepare for the study of lubricant evolution under accelerated degradation conditions simulating ammonia combustion, the behavior of various base oils was first examined under reference conditions, in the presence of oxygen, to establish a baseline behavior. Given that lubricant properties and reactivity are largely determined by additive formulations, which also complicate detailed molecular analysis, this study focused on additive-free base oils. Although this choice reduces the representativeness of the results with respect to the actual reactivity of commercial lubricants, it enables the decoupling of additive and base oil effects, thereby allowing more universal conclusions to be drawn. This chapter presents the development and implementation of a multitechnique approach designed to improve the understanding of base oil degradation and to identify relevant parameters for its assessment. First, a novel methodology based on *operando* oxidation in a headspace autosampler is introduced. The same oil samples are then analyzed using the Rancimat method. A third experimental setup, involving a pressurized stirred reactor enabling exposure to reactive gases other than oxygen, is also described. The chapter discusses the advantages and novelty of each technique, but more importantly, it underlines the benefits of combining them to study a broad range of oil samples and gain a comprehensive view of their oxidation behavior.

The combination of Rancimat and *operando* oxidation using a headspace autosampler was published as a research paper with complete reference: Doncoeur, C., P. Cologon, C. Mounaïm-Rousselle, and L. Giarracca-Mehl. "Molecular Characterization of Lubricant Base Oil Oxidation Using Operando Headspace Chromatography and Rancimat, 2025, *Energy Fuels*, 2025, 10.1021/acs.energyfuels.5c02751 .

1. Experimental section

1.1 Base oils

Table 2.1: Characteristics of the base oils used in this study

Name	Supplier	Type	Carbon chain length	Viscosity 40°C (mm ² /s)	VI *
A	1	Mineral oil grp II	Unknown	100	104
B	1	Mineral oil grp III	C20–50	48	128
C	2	Polyalphaolefin (PAO)	C10 based	66	135
D	2	Alkylated Naphthalene	C4–22	109	109
E	3	Alkylated Naphthalene	Unknown	102	101
F	4	Pentaerythrithol ester	C32–48 // C6–10 branches	94	90
G	4	Trimethylolpropane ester of carboxylic acid	C27–40 // C6–10 branches	72.4	164
H	5	Dimerate 2-ethylhexyl esters	C18 unsaturated dimers	94	146

*VI = Viscosity Index

2.1. EXPERIMENTAL SECTION

Eight base oils, both mineral and synthetic and commonly used in engine lubricants formulations, with comparable viscosity grades but differing polarities, were selected from five suppliers. They are presented in Table 2.1. Molecular structure of the different ester types is displayed in Figure 2.1.

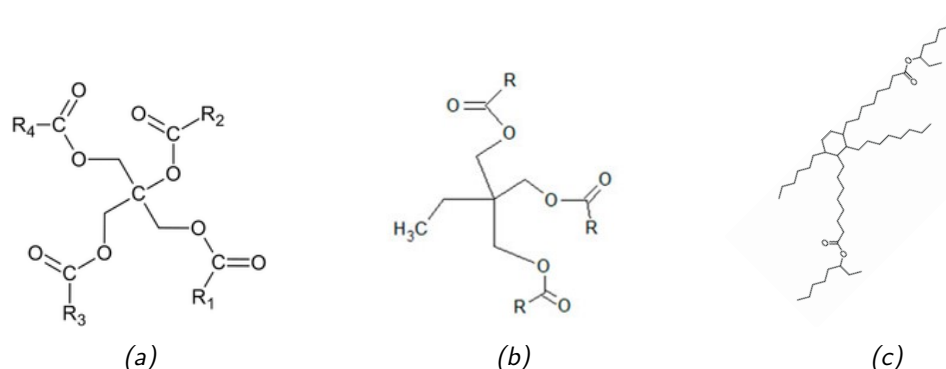


Figure 2.1: Three types of complex polyester. a) Oil F: Pentaerythritol ester $R = C6$ to $C10$. b) Oil G: Trimethylolpropane ester of carboxylic acid $R = C6$ to $C10$. c) Oil H: Dimerate 2-ethylhexyl esters

1.2 Accelerated aging setup

1.2.1 Headspace-Gas Chromatography

The principle of headspace-GC was explained and illustrated in Figure 1.18. Here, experiments were conducted with 0.5 mL of oil in 20 mL sealed vials, filled with ambient air. This volume was selected after preliminary tests conducted with 1 mL of oil showing lower peak intensity (Figure 2.8). For each temperature, several vials were prepared, corresponding to various heating durations. This approach prevents from piercing the septum several times, which can lead to losses of volatile species and non representative subsequent analysis. After the sample was heated, 1 mL of the headspace phase was collected automatically using a syringe and introduced to the column via a heated transfer line. The parameters for the GC/FID analysis are summed in Table 2.2. Peak areas were calculated with Chromeleon software from ThermoFischer. In order to enable precise product identification, this protocol was replicated on a second instrument equipped with a mass spectrometer. The configuration and columns were exactly the same; parameters are summed up in Table 2.3. Products were identified using the 2017 NIST library and peak matching on GC/FID chromatograms was carried out with the help of retention times, considering chromatographic separation took place under the same conditions. For each product and heating temperature, the order of analysis at increasing heating times was performed in a random order to prevent any bias due to progressive system contamination. In addition, the blank level was measured regularly to verify that the system was not contaminated.

2.1. EXPERIMENTAL SECTION

Table 2.2: Parameters of the headspace-GC/FID analysis

Instrument	Parameter	Conditions
Agilent Headspace Sampler 7897A	Oven temperature	120 –190 °C
	Vial equilibration	0-680 min
	Carrier gas	Helium
Transfer line	Temperature	Oven temperature+50 °C
	Carrier gas speed	10 mL/min
Agilent GC 7890B	Column	HP-5 30 m x 320 µm x 0.25 µm
	Oven	5 min at 30 °C-5 °C/min to 270 °C-10 °C/min to 320 °C-2 min
	Flow rate	1 mL/min
	Split ratio	25:1
	Detector	FID

Table 2.3: Parameters of the headspace-GC/MS analysis

Instrument	Parameter	Conditions
Thermo Scientific headspace TriPlus500	Oven temperature	120–190 °C
	Vial equilibration	0-680 min
	Carrier gas	Helium
Thermo Scientific Trace 1310	Column	HP-5 30 m x 320 µm x 0.25 µm
	Oven	5 min at 30 °C-5 °C/min to 270 °C-10 °C/min to 320 °C-2 min
	Flow rate	1.5 mL/min
	Split flow	5 mL/min
	Detector	MS
ISQ Series Mass Spectrometer	Type	Quadrupole
	Ionization mode	Electronic Impact
	Energy	70 eV
	Source temperature	240 °C
	Resolution	40.0-600.0

The experimental error associated to the measurement of the peak area on FID chromatograms was evaluated using the results of tests conducted with the oils D and E, which showed no evolution at 160 °C. Each heating time corresponded to a different vial. The error, Δ , was evaluated on the total peak area and the peak area of an impurity in the sample, identified as naphthalene (Table 2.4). The confidence intervals of 95 % reported in Table 2.4 were calculated based on the Student's t-distribution (Equation 2.1), and normalized to calculate the relative error. The relative error, including sample preparation, heating of the sample and peak area calculation, was below 5 %, considered as threshold value for identifying sample evolution.

$$\Delta x = t_{n,\alpha} \cdot \frac{s}{\sqrt{n}} \quad (2.1)$$

with $t_{n,\alpha}$ the Student coefficient for n measurements and s the standard deviation,

$$s = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2}$$

2.1. EXPERIMENTAL SECTION

Table 2.4: Evaluation of the experimental error on headspace experiments, including sample preparation, heating of the sample and calculation of the peak area

Heating time (min)	Total peak area (pA*min) D	Naphthalene peak area (pA*min) D	Naphthalene peak area (pA*min) E
20	10.09	1.80	0.072
30	10.19	1.81	0.075
60	NA	NA	0.071
90	NA	NA	0.073
120	10.31	1.82	0.071
240	10.46	1.83	0.066
480	10.13	1.74	NA
Mean value (pA*min)	10.24	1.80	0.071
std. dev (pA*min)	0.15	0.04	0.003
Δ (pA*min)	0.19	0.05	0.004
rel. error (%)	1.9	2.5	5

1.2.2 Rancimat

The Rancimat instrument, developed by Metrohm, is initially dedicated to study the oxidation stability of fatty acids in the food and cosmetic industry. This instrument enables to implement a method based on the quantification of light acidic compounds produced during early stages of oxidation, through the measure of the conductivity of a small water volume in which the degradation products are solubilized (Figure 2.2). The induction period, defined as the inflection point of the conductivity curve, is the key parameter provided by this method. Several studies applied the Rancimat method to study oxygenated oils [131, 142–144]. Yet, the oxidation of non-oxygenated hydrocarbons is also known for resulting in light acidic compounds [13]. The study of Nowotny et al. is to our knowledge the only one showing the benefits of using the Rancimat instrument to study the oxidation stability of mineral oils [145]. Here, the instrument was not only used to determine the inductions periods at 120, 140 and 158 °C, but also to collect oil samples after 24h-long experiments for further characterization.

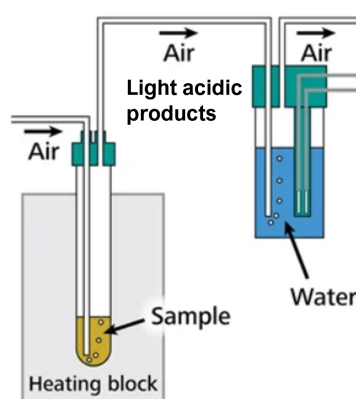


Figure 2.2: Scheme of the Rancimat instrument—credit: Metrohm

2.1. EXPERIMENTAL SECTION

In particular in this study, Rancimat 893 was used to measure the induction period of the samples and expose oils to air and heat. The principle of the measurement is illustrated in Figure 2.2: the sample is heated, with a continuous air bubble introduced in the sample at a fixed flow rate via a plunger tube. Light oxidation products are transported to a beaker filled with 50 mL of Milli-Q water, thanks to an iso-versinic tube. Iso-versinic tubes are made of fluoroelastomers showing high resistance to strong acids, alcohols and aromatics. Oxidation products are mostly acidic compounds that solubilize in the water in the form of charged ions. The subsequent increase in water conductivity is measured through the test. The induction period is determined at the maximum of the second derivative of the conductivity, calculated by the associated software Stabnet.

In this work, 3 g of samples were weighted directly in the glass tubes. Induction periods were measured at 120, 140 and 158 °C with an air flow at 20 L/h. A temperature correction to compensate the cooling effect of the introduced air was applied according to Metrohm's instructions: +1.6, +1.8 and +2 °C, respectively. Experiments were repeated at least three times, and oil samples from the same reference were mixed before further characterization. A reference experiment was carried out with an empty tube to measure the effect on the conductivity of the accumulation of carbonates from the air into the beaker, and showed the associated conductivity increase was negligible over 24 h. To better evaluate the error, taking into account the low number of repetitions, IP values are reported with a 90 % confidence interval, calculated using the Student's t-distribution (Equation 2.1).

1.2.3 Autoclave reactor

Additionally, a 250 mL reactor made of Hastelloy was used to expose the oils to different gas mixtures. It was filled with 50 mL of oil, allowing 200 mL for the gas phase. A gas entrainment stirrer enhanced the contact between both phases, and its speed was fixed at 1000 rpm to minimize the temperature difference between the gas and liquid phase. The pressure and temperatures of both liquid and gas phases were monitored throughout the experiments. After heating of the system under inert nitrogen atmosphere, gas mixtures were introduced in three cycles of filling/venting, to reach more than 99 % purity of the final composition. The first gas injection defined the initial time of the experiment. Regular liquid samplings via a three-way valve were performed to characterize oils at different reaction times. Samples were placed in the fridge at 4 °C immediately after collection to stop reactions. The reactor was only opened after complete cooling to collect the final oil. A description of the set-up is displayed in Figure 2.3.

The decrease in pressure with time, occurring as reactive gases react with the liquid phase, was normalized by the initial pressure and calculated as a percentage, as follows:

$$\text{Residual Pressure (t)} = \frac{P(t)}{P_{\text{initial}}} * 100$$

2.1. EXPERIMENTAL SECTION

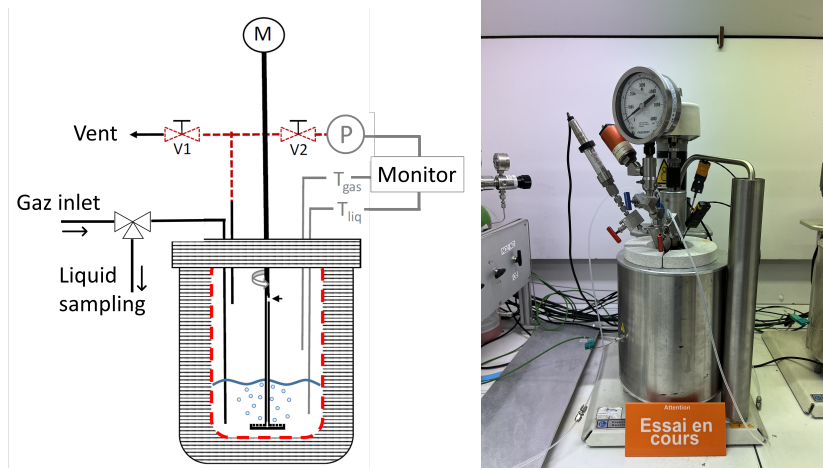


Figure 2.3: Scheme and photo of the autoclave set-up

Sudden drops on residual pressure curves are due to the liquid samplings.

Calculation of the gas purity To start an experiment, the reactor was filled with 50 mL of oil, and tightly closed. After closing the reactor, nitrogen was flown into the oil sample and the reactor to remove the remaining air and oxygen. After 10 min, the reactor was filled with 2 bar of nitrogen and heated up. It reached a pressure P_{init} . After heating, the filling/venting steps consisted in filling the reactor with reactive atmosphere at a higher pressure than target pressure, P_{high} , and venting it at P_{low} , approximately $P_{init} + 1$ bar, three times in a row. The reactor was finally filled with the reactive gas, at target pressure, P_{final}). The theoretical purity of the final gas phase can be calculated as follows:

According to Dalton's law,

$$P_i = x_i * P_{total}$$

The final N_2 concentration is then:

$$x_{N_2, final} = \frac{P_{N_2, final}}{P_{final}}$$

Going from P_{low} to P_{high} , at cycle n, we have

$$x_{N_2, n} = \frac{P_{N_2, n-1}}{P_{high}} = \frac{x_{N_2, n-1} * P_{low}}{P_{high}}$$

For n=1,

$$x_{N_2, 1} = \frac{P_{N_2, 0}}{P_{high}} = \frac{P_{N_2, init}}{P_{high}}$$

For n=2,

$$x_{N_2, 2} = \frac{x_{N_2, 1} * P_{low}}{P_{high}}$$

2.1. EXPERIMENTAL SECTION

For $n=3$,

$$x_{N_2,3} = \frac{x_{N_2,2} * P_{low}}{P_{high}} = x_{N_2,1} * \left(\frac{P_{low}}{P_{high}}\right)^2 = P_{N_2,init} * \frac{(P_{low})^2}{(P_{high})^3}$$

After three filling/venting cycles, the reactor was filled at requested pressure, P_{final} , and:

$$x_{N_2,final} = \frac{x_{N_2,3} * P_{low}}{P_{final}} = \frac{P_{N_2,init}}{P_{final}} * \left(\frac{P_{low}}{P_{high}}\right)^3$$

Considering $P_{init}=3.5$ bar; $P_{low}=4.5$ bar; $P_{high}= 15$ bar; $P_{final}= 10$ bar,

With only two filling/venting cycles, $x_{N_2,final} = 2.7\%$

With three filling/venting cycles, $x_{N_2,final} = 0.7\%$

Three filling/venting cycles were sufficient to reduce the residual nitrogen concentration to below 1%, which was considered acceptable.

1.3 Oil characterization techniques

1.3.1 FTIR spectroscopy

Infrared absorption spectra were measured with a Bruker Vertex 70 instrument in Attenuated Total Reflectance (ATR) configuration, between 400 and 4000 cm^{-1} with a resolution of 2 cm^{-1} . Using the software OPUS, the carbonyl peak area was measured by integrating each spectrum between 1600 and 1800 cm^{-1} , after subtracting the spectrum of the fresh oil for the mineral oils. As the polyester base oil G already showed a strong absorption band in this region due to the C=O double bond in the ester groups, the method was adapted. The spectrum was integrated between 1650 and 1730 cm^{-1} after subtraction of the fresh oil, in order to isolate the newly formed carbonyl groups, as depicted in Figure 2.4. The instrument error was calculated by repeating FTIR spectrum acquisition of one sample (oil G after 24 h at 160 °C with Rancimat), as reported in Table 2.5. For single measurements, the error on peak area calculation due to the instrument repeatability was considered 2 %.

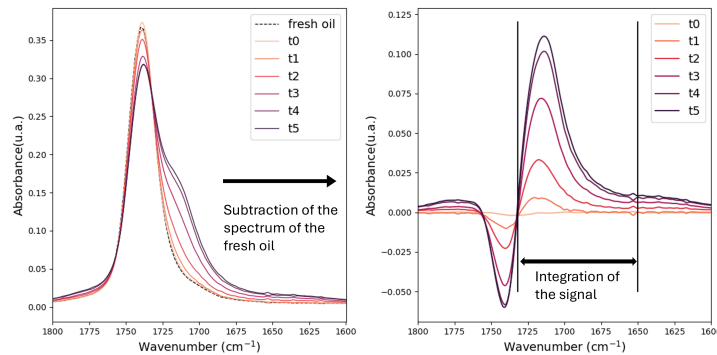


Figure 2.4: Integration method applied to oil G-FTIR spectra after 0, 1.7, 2.7, 3.8, 4.7, 5.7h at 140 °C under 10 bar oxygen

2.1. EXPERIMENTAL SECTION

Table 2.5: Repeated measurements of the carbonyl peak area of oil G after 24 h at 160 °C in Rancimat and evaluation of the instrument error associated with FTIR spectrum acquisition

Measurement	1	2	3	4	5	6	7	8	9	10	Mean value
Peak area (A/cm)	4.92	4.90	4.89	4.87	4.88	4.84	4.87	4.62	4.95	4.94	4.85
std. dev											0.11
rel. error											2 %

1.3.2 Viscosity

Kinematic viscosity of the samples was measured using a Stabinger viscosimeter SVM 3001 from Anton Paar. It consists of a tube, filled with the sample and thermoregulated in a copper housing, in which a rotor is maintained via centrifuge forces. Rotation of the cylinder induces shear forces of the fluid on the rotor, while a magnet inside the rotor induces a induction brake with the surrounding copper housing. Viscosity is determined by measuring the torque resistance at equilibrium. Density of the fluid is simultaneously determined with a measurement based on an oscillating U-tube, also integrated in the copper thermoregulator. This measure relies on the principle that the eigenfrequency of the tube depends on the mass of fluid inside. Dynamic viscosity and density were measured at 20, 40, 60, 80 and 100 °C, allowing direct calculation of the kinematic viscosity as a ratio of these values, as detailed in Equation 2.2. These whole cycle lasted 1 h for each sample, allowing the temperature to equilibrate between each measurement. Prior to viscosity measurements, oil samples were sonicated for 10 min to release residual gas bubbles.

$$\nu = \frac{\mu}{\rho} \quad (2.2)$$

with ν , the kinematic viscosity in m²/s, μ the dynamic viscosity in Pa.s and ρ the density in kg.m⁻³.

The instrument error was calculated based on repeated viscosity measurements of oil C on different dates (Table 2.6). For single measurements, the error due to the instrument repeatability was considered 1 % on viscosity measurements and 0.01 % on density measurements. As a widely used parameter in the lubricants' scientific community, the kinematic viscosity at 40 °C was especially considered.

1.3.3 Elemental Analysis (EA)

The total oxygen and nitrogen contents were determined using respectively pyrolysis and nitrogen chemiluminescence. Measurements were performed by the Analysis Department of IFPEN. The experimental error associated to this method is 5 %. This is close to the variation of the total oxygen content induced during autoclave experiments with the polyester base oil G, with an initial oxygen content superior to 16 %. Thus, only the nitrogen content was considered for oil G.

2.1. EXPERIMENTAL SECTION

Table 2.6: Evaluation of the instrument error associated with viscosity measurements (evaluated with oil C on different dates)

Measurement	Dynamic viscosity (mPa.s)	Kinematic viscosity (mm ² /s)	Density (g/cm ³)
1	160.34	192.45	0.83315
2	159.15	191.01	0.83321
3	159.26	191.13	0.83326
4	159.39	191.29	0.83324
5	159.25	191.12	0.83327
6	159.21	191.06	0.83329
Mean value	159.43	191.34	0.83324
std. dev	0.45	0.55	5*10 ⁻⁵
rel. error	0.3 %	0.3 %	6.10 ⁻³ %

1.3.4 Simulated distillation

The samples were diluted 1:5 in dichloromethane and analyzed using a MXT-1HT column associated, either to a FID, detecting all kinds of hydrocarbons, or a NCD detector, only detecting nitrogen-containing molecules. The column was heated from 100 to 400 °C with a ramp of 50 °C/min. Retention times obtained with the FID detection can be compared with the retention times of a standard paraffin blend to establish a link between retention times and ebullition temperatures. Analysis were performed by the Analysis Department of IFPEN.

The FID chromatograms of the base oils A, B, C, G and H in the fresh state and corresponding simulated distillation curves are displayed in Figure 2.5.

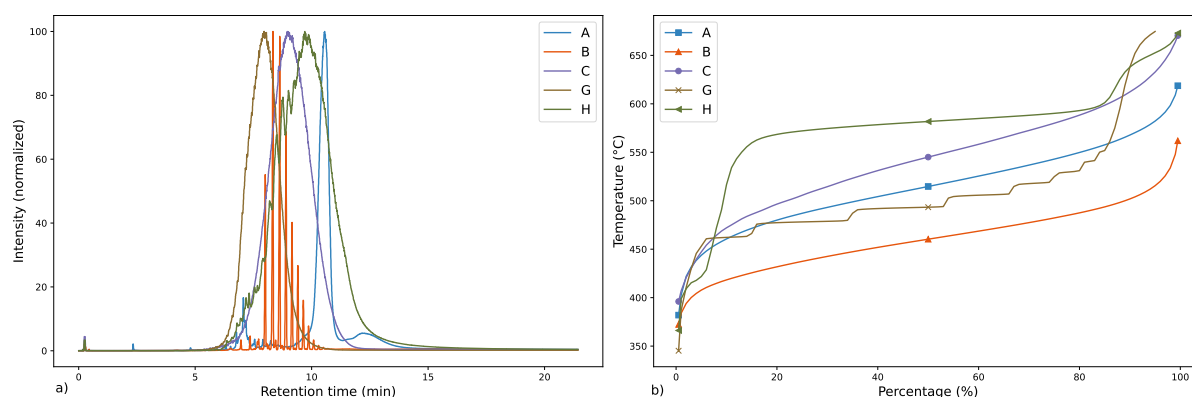


Figure 2.5: FID chromatograms of the base oils (a) and the corresponding simulated distillation curve (b)

1.3.5 Water content–Karl Fisher

Water content was determined using potentiometric titration, according to the NF ISO 6296 standard. Measurements were subcontracted to SGS Laboratory.

1.3.6 ICP-OES

Analysis were performed by the Analysis Department of IFPEN. Samples were digested in acidic solution and introduced into a high-temperature plasma. In this technique, excitation of the atoms and ions emits electromagnetic radiation at specific wavelengths, characteristic of the elements in the sample. Intensity of these radiation can be used to quantify target elements.

1.3.7 GC2D/MS analysis

GC2D/MS analysis were conducted using a 78908 GC from Agilent equipped with a LECO modulator, and coupled to a high resolution ToF mass spectrometer PEGASUS GC-HRT+ 4DLECO. The parameters used for the two dimensional separation and mass detection are summarized in Table 2.7. These analyses were conducted by the Analysis Department of IFPEN.

Table 2.7: Parameters of the GC2D/MS analysis

Parameter	Conditions
Configuration	Normal (apolar × polar)
Columns	PONA 20 m × 0.2 mm × 0.5 μm BPX50 1 m × 0.1 mm × 0.1 μm
Carrier gas	Helium
Flow rate	1 mL/min
Temperature gradient	60 °C for 2 min, 2 °C/min up to 350 °C
Injector temperature	300 °C
Injected volume	1 μL
Cryogenic modulation	Second dimension time: 8 s Hot pulse time: 0.6 s Cool time between stages: 3.4 s
Ionization source	Electronic impact
Collision energy	70 eV
m/z range	20–600

To avoid any contamination of the column with residues of heavy products, samples with high final boiling points underwent preparative distillation, with a cut at 520 °C. The distillation was made under vacuum according to ASTM 1160 standards. The sample was progressively heated up to 520 °C, and the lightest fraction was collected via condensation.

Even though acidic and basic titrations with TAN and TBN measurements are widely used techniques to characterize the oxidation of lubricants, they were not used in this thesis. Obrecht *et al.* indeed showed that the result of these measurements could be altered by the presence of ammonia, acting as a base and interfering in the titration reaction. The diagram in Figure 2.6 depicts the experimental workflow implemented in this chapter, detailing the samples characterized and different techniques used.

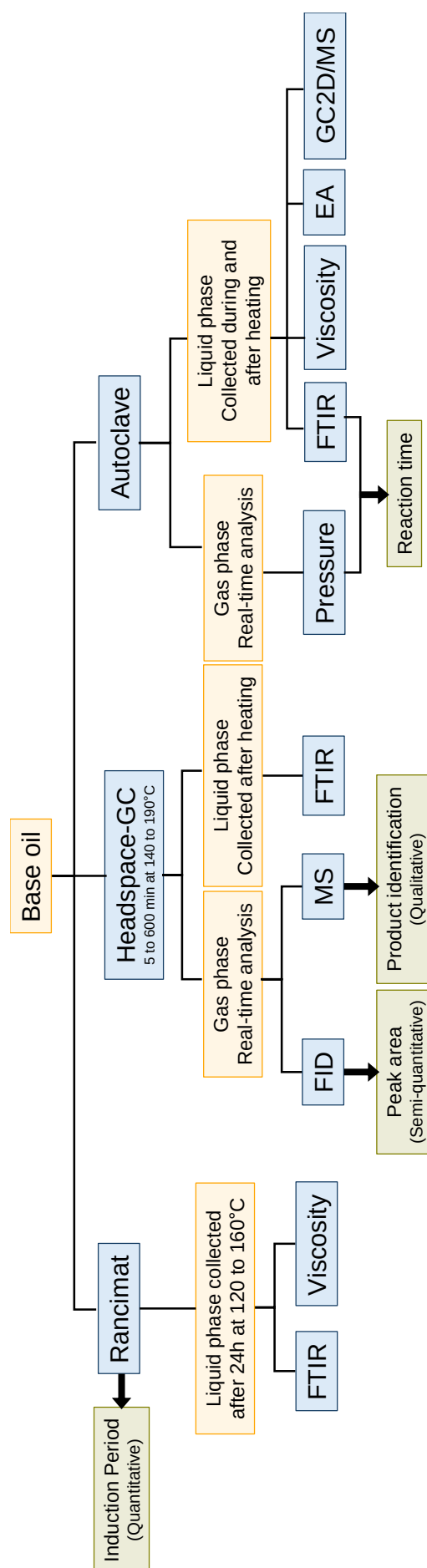


Figure 2.6: Diagram of the experimental workflow

2. Operando oxidation with headspace-GC

2.1 Operando oxidation: proof of concept

In this study the principle of headspace sampling was diverted. The instrument was used not only as a means of analysis, but also as an integrated coupling of heating/aging and analysis. Exposure to high temperatures in a sealed vial enabled to oxidize the oil *operando*: the lighter oxidation products were directly vaporized in the headspace and analyzed via gas chromatography. It is in that sense an *operando* study, as the observed phenomenon occurs simultaneously as it is characterized, and is generated by the analysis instrument itself. In contrast, the water conductivity monitoring in the Rancimat experiment is an *in-situ* measurement, as the conductivity probe measures in real-time the solubilization of acidic species without influencing this phenomenon.

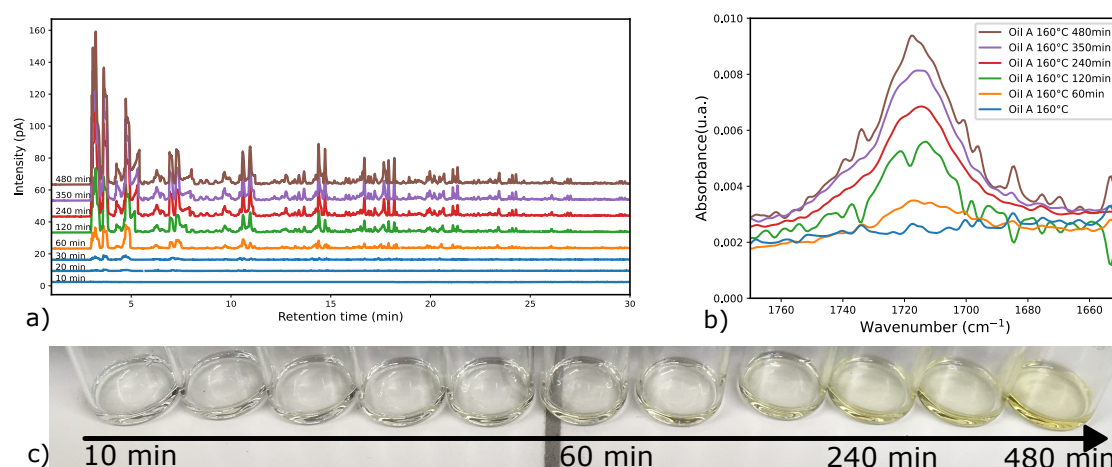


Figure 2.7: Operando oxidation of oil A at 160 °C. a) Superposition of the chromatograms for oil A at 160 °C. b) Partial IR spectrum of oil A at different heating times at 160 °C. c) Aspect of the oil with crescent heating times at 160 °C

Here, the vial was used as a small reactor, where oxygen comes from ambient air and can react with the sample. Along with the increase in the heating time, the number of peaks on the chromatogram and their area increased (Figure 2.7 a). This is due to the increase in light oxidation products being generated, both in diversity and quantity. Associated with color changes (Figure 2.7 c), and apparition of a peak at around 1715 cm⁻¹ in IR spectroscopy (Figure 2.7 b), which can be attributed to the carbonyl functional group found in oxidation products, this indicates that the detection of oxidation products in the gas phase is an indirect witness of liquid phase oxidation happening during oil heating. Color changes toward yellow/brownish are caused by the apparition of unsaturations, whereas carbonyls and aromatics tend to absorb in the UV region, between 250 and 400 nm [127]. The evolution of these parameters is frequently used in oil oxidation studies [13, 35]. 140, 160, and 190 °C are well below the initial boiling points of the oils, measured with simulated distillation (Figure 2.5),

indicating that oils remained in the liquid phase during vial heating. Figure 2.7 shows only the results obtained with oil A, but similar trends were observed with the other types of samples. All these observations confirm that the experimental conditions induce oil oxidation.

2.2 Effect of the oil volume

The theory underlying headspace sampling is governed by three fundamental laws that establish a connection between a compound's concentration in a liquid matrix and its concentration in the gas phase based on phase equilibrium. These laws include Dalton's law, which relates the partial pressure of a molecule to the total pressure, Raoult's law, which determines the partial pressure based on the concentration in the liquid phase, and Henry's law, which provides the partial pressure of a diluted compound above a liquid matrix at a specific temperature [146]. Elevated concentrations in the liquid phase result in higher headspace concentrations, thereby leading to higher signal-to-noise ratios. The optimal liquid volume is expected to represent half of the vial's volume [146]. While increasing the sample volume enhances the amount of vaporized compounds and facilitates their detection, it is crucial to allow sufficient space for the compounds to reach their vapor pressures.

However, in this study, the sample reacted with ambient air, which modified the typical conditions for headspace sampling. In Figure 2.8, the evolution of the total peak area for oil C at 190 °C is plotted for a vial filled with 1 mL of oil (dashed line) and a vial filled with 0.5 mL of oil (continuous line). Error on the peak area was set at 5 % as explained in Section 2.1.2.1. The plateau reached with a 1 mL sample was lower than with 0.5 mL. In this experiment, higher volume led to smaller peak intensity. This contradiction with the literature can probably be explained by the fact that headspace collection usually happens under inert atmosphere, with no reaction between the gas phase and the liquid phase. In the experiment presented here, the products identified come from a reaction between the original gas atmosphere and the liquid sample. The more oxygen is added, the more it can react with the oil. However, despite a difference of total oxygen availability due to a 0.5 mL difference of air, it seems insufficient to explain such a decrease of the maximum peak area. One possible explanation could be that, as the total amount of oxidation products formed is likely to be very similar as the air/oil contact surface is the same, the resulting concentration of oxidation products was higher in the smaller volume, leading to a favored equilibrium shift towards the gas phase. This hypothesis was supported by the difference between areas of the carbonyl peak in IR spectroscopy after 2 h at 190 °C, which were equal to 0.147 A/cm⁻¹ and 0.243 A/cm⁻¹ for 1 mL and 0.5 mL respectively, suggesting a higher concentration of acidic products in the smaller volume sample. All the experiments were then conducted with 0.5 mL of oil, in order to maximize the signal-to-noise ratio.

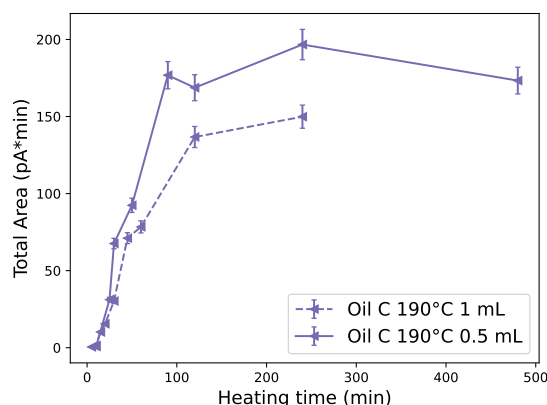


Figure 2.8: Peak area for oil C at 190 °C, with 0.5 mL (continuous line) or 1 mL (dashed line)

2.3 Identification of degradation products

As a non-polar column was used, products were eluted according to their boiling point, related to their molecular weight. The chromatograms obtained with the different oils, displayed in Figure 2.9, show that different kinds of degradation products, with increasing chain lengths were detected. Interestingly, the chromatogram aspects showed a lot of similarities, especially at short retention times, except for oil F.

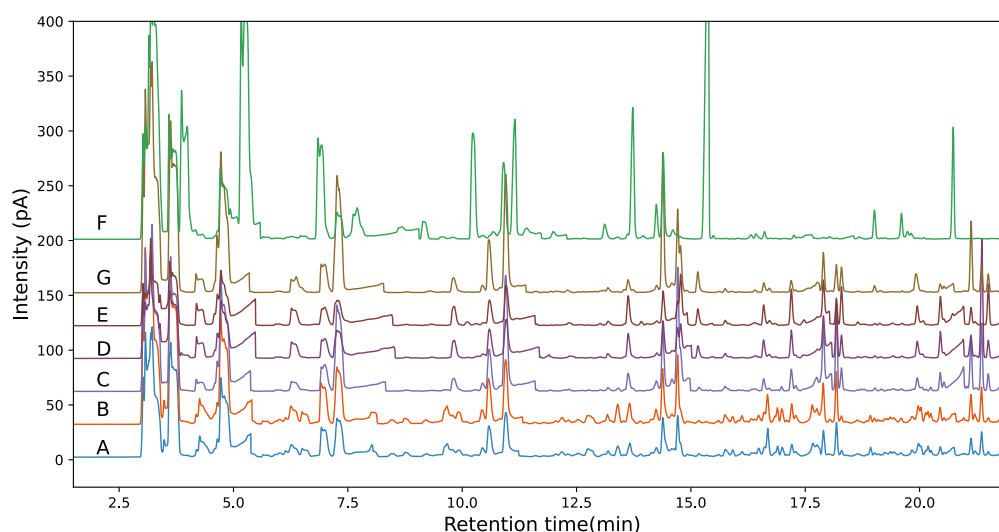


Figure 2.9: Headspace chromatograms after 480 min at 190 °C—focus on short retention times. A: Grp II mineral oil, B: Grp III mineral oil, C: PAO, D/E: Alkylated naphthalene, F: Pentaerythrithol ester, G: Trimethylolpropane ester of carboxylic acid, H: Dimerate, 2-ethylhexyl ester

Coupling with a mass spectrometer (quadrupole type) enabled accurate product identification. After 8 h at 160 °C, products from six main families were identified in the gas phase: short alkanes (C4 to C14), alcohols (C4-C9), ketones (C5-C12), acids (C2-C12), aldehydes (C5-C11) and dihydrofuranones (with an alkyl ramification between C1 and C5). The FID profile of oil C after 8 h at 160 °C, with peak identification is displayed in Figure 2.10.

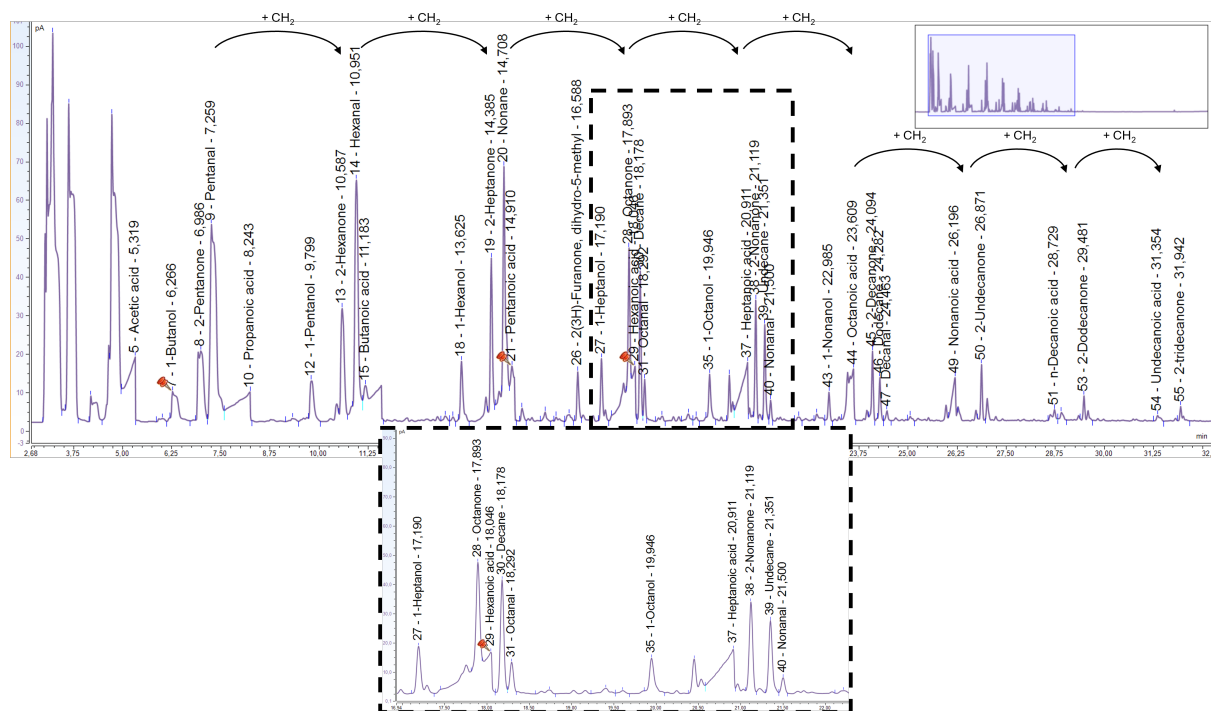


Figure 2.10: Headspace chromatograms of oil C (PAO) after 8 h at 160 °C

It shows the different product types, and the clear repetitive pattern with increasing chain lengths. C_n ketones and aldehydes have similar retention times as C_{n-2} carboxylic acids, and C_{n+2} alkanes. For other oils, products are reported in Appendix A.1. The same products were found in oils A, B, C, G and H, confirming the observation that the FID profiles are superimposable (Figure 2.9). These products were also found with oils D and E, though with a little delay because these oils had to be heated to 190 °C to generate the same kind of products. This indicates some similarities in the oxidation chemistry despite the varied nature of the base oils. The fact that no peak appeared at 160 °C with oils D and E might be due to the naphthalene rings, which could trap radicals and inhibit the propagation of the oxidation chain reaction [13,74]. Some products specific to one base oil were also identified, as presented in Appendix A.2. The group II mineral oil (A) was the only sample where branched oxidation products were identified, consistent with the fact that this base oil contains more branched alkanes. For oil H, the products identified were mainly 2-ethylhexyl esters, derived directly from the main constituent of the fresh base oil. Molecules identified in oil G can also be easily identified as fragments of the molecular structure of the fresh oil, retaining the quaternary carbon. Finally, oxidation products from oil F were different from other oils, but can be classified into the same six categories. Their structure derived from the original structure of the base oil, with the characteristic tert-butyl fragment containing a quaternary carbon (Table A.2). With this oil, a fragment identified as tert-butylhydroperoxide could be detected, certainly thanks to the +I inductive effect of the tert-butyl group which increases the stability of this peroxide compared to other types.

The types of products identified are in agreement with what is expected considering hydrocarbons oxidation [13, 71, 72, 147]. As seen in section 1.2.2, primary carbons are less reactive than secondary and tertiary carbons regarding H-abstraction, as the radical formed is less stabilized [13]. This is followed by chain propagation which leads to hydroperoxides production, via the reaction: $\text{ROO}^\bullet + \text{RH} \longrightarrow \text{ROOH} + \text{R}^\bullet$. Alcohols, ketones and aldehydes are considered first order products, as they derive directly from the decomposition of hydroperoxy radicals. They mainly come from the termination reactions $\text{ROO}^\bullet + \text{ROO}^\bullet \longrightarrow \text{ROH} + \text{R}(\text{C}=\text{O}) + \text{O}_2$ and $\text{ROO}^\bullet + \text{ROO}^\bullet \longrightarrow \text{RO}^\bullet + \text{RO}^\bullet + \text{O}_2$ [70], with $\text{RO}^\bullet$ resulting in alcohols as in Figure 2.11 a). Aldehydes and ketones come from secondary and tertiary radicals, such as those illustrated in Figure 2.11 b, c) [70–72].

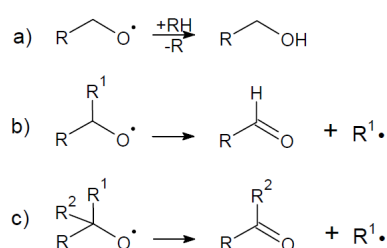


Figure 2.11: Chain branching steps leading to alcohols, aldehydes and ketones in hydrocarbon oxidation

Carboxylic acids are second order products which are only formed at higher temperatures (above 120 °C according to [13]), and imply several oxidation steps. Several mechanisms can be found to explain their formation, such as the Bayer-Villiger reaction between peracids and aldehydes, aldehyde oxidation (Figure 2.12 a) or via keto-hydroperoxide cyclization (Figure 2.12 b), as presented in [13, 69, 71, 81].

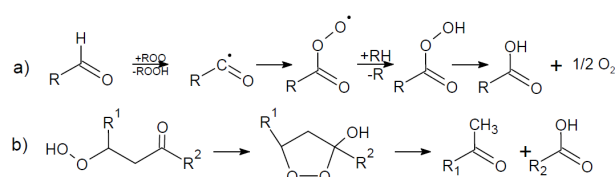


Figure 2.12: Two proposed mechanisms for the formation of carboxylic acid during hydrocarbon oxidation

Dihydrofuranones are also second-order products, which were also observed in Webster *et al.* [148], who studied the oxidation of a mix of *n*-alkanes in a PetroOxy device at 140 °C, and Goosen *et al.* [72] who studied decane oxidation at 160 °C. Several mechanisms were proposed for the formation of dihydrofuranones in [81, 149]. All are based on an intramolecular Fischer reaction, as shown in Figure 2.13.

Short alkanes can be obtained via direct chain cleavage due to the temperature, or be byproducts of the above reactions, where small $\text{R}^\bullet$ fragments are formed [69]. Finally, the

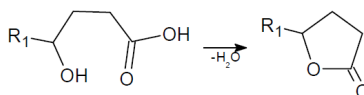


Figure 2.13: Intramolecular Fischer reaction leading to dihydrofuranones

esters detected in this study were only fragments from the original polyesters, and were not resulting from oxidation reactions.

This methodology mainly detected products with a relatively low boiling point, which is why certain oxidation mechanisms were not considered here. Other types of products, such as those with more complex structures, might be present in the liquid phase but remained undetected. For instance, dihydrofuranones were the only products resulting from an intramolecular reaction which were identified, but heavier products with higher boiling points could potentially persist in the liquid phase. The product with the highest boiling point that could be detected under considered experimental conditions was 2-tridecanone, with a boiling point of 263 °C.

2.4 Effect of the heating time and temperature

As an example of oxidation products, the total peak area of all the compounds identified as ketones (C5-C12) was plotted against reaction time at different temperatures in Figure 2.14. With this technique, the peak area of a specific compound is correlated to the detected amount of this compound, itself correlated its concentration in the headspace. In Figure 2.14, it can be observed that the peak area of ketones increased with time until it reached an upper limit, and that this increase was quicker at higher temperatures. The maximum amount of ketones which could be detected was higher at higher temperatures. This is the result of thermodynamics and kinetics effects: higher temperatures shift the phase equilibrium toward the gas phase, enhancing the vaporization of degradation products, and higher temperatures accelerate the oxidation rate. Oxidation indeed follows an Arrhenius law, meaning its rate increases exponentially with the temperature [69]. At relatively low temperatures, 140 and 160 °C, some chromatograms remained unchanged for a certain period of time before products, and especially ketones, could be observed. This was the case for example with oil C at 160 °C, where a kind of induction period could be observed for approximately 90 min. At 140 °C, no ketones were detected with oils B and C, even after more than 10 h of heating. Oils F and G showed a slight increase in the peak area respectively between 240 and 480 min, and 240 and 380 min. On the other hand, ketones were more rapidly detected with oils A and H at 140 °C, as the peak area started to increase after less than 60 min of heating with both samples. For oils D and E, ketones were only detected after at least 90 to 120 min of heating at 190 °C, and could not be detected after more than 10 h of heating at 160 °C.

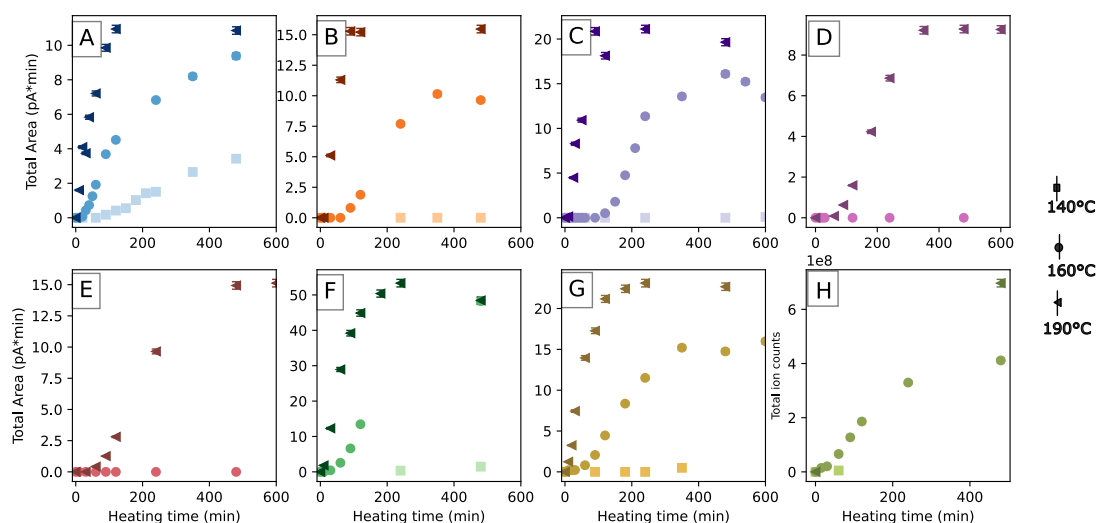


Figure 2.14: Total amount of ketones as a function of the reaction time and temperature

These observations are consistent with what could be expected regarding the oxidation stability of the different oils. Group II mineral oil (A) is expected to have a lower oxidation stability than group III (B), as they contain aromatics, and impurities such as trace metals acting as catalysts, or sulfur compounds, prone to accelerate oxidation [150]. In the same way, PAO base oils (C) are known to have a better resistance to oxidation compared to group III mineral oils, as they are even more pure due to their synthetic nature and contain less tertiary carbons [13, 74, 150]. On the other hand, alkylated naphthalenes showed excellent oxidation stability compared to the other samples. This was expected, as they contain naphthalene groups that tend to form highly stable radicals and prevent oxidation propagation. The reactivity of the complex polyesters is harder to predict and compare with non-oxygenated oils. The relative contribution of each type of molecule to the total peak area was calculated at different temperatures with increasing times. Results are presented in Figure 2.15 and Appendix A.1.

For oil A, it can be noticed at 140 °C that alcohols and dihydrofuranones were only detected after 180 and 150 min respectively, contrary to acids, ketones and aldehydes which could be detected in the gas phase after only 90 min. This delay was reduced at 160 °C where alcohols and dihydrofuranones were identified after 60 and 50 min respectively, compared to 20 min, and reduced to very short times at 190 °C (Figure 2.15). This can also be observed with oils B and C at 160 °C with a delay between 90 and 120 min, and with oil E where oxidation products started to be detected after 90 min, while alcohols and furanones could only be detected after 150 and 120 min at 190 °C, respectively (Appendix A.1). This is consistent with the fact that dihydrofuranones are second order oxidation products, as seen previously, and with the fact that alcohols come from primary alkoxy radicals, whose production is less promoted than tertiary or secondary radicals. In fact, proton abstraction is more likely to occur on a tertiary

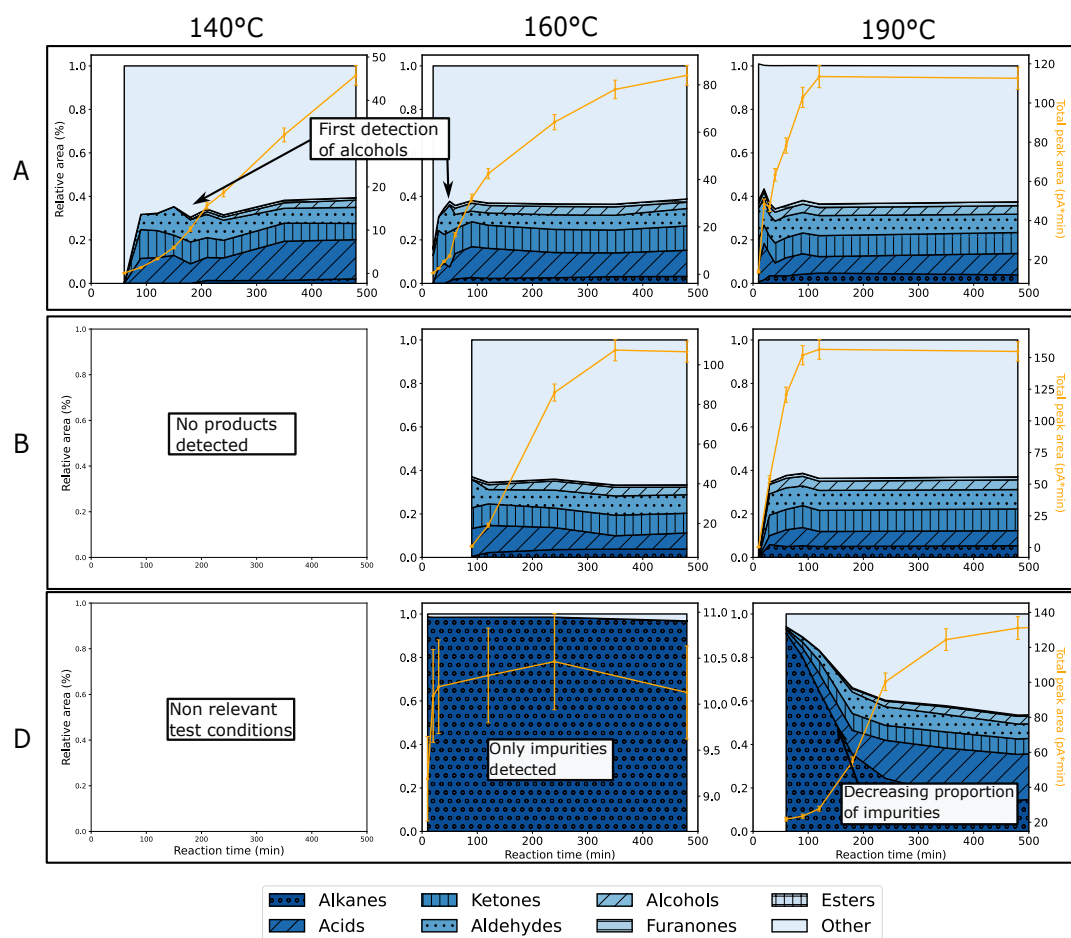


Figure 2.15: Relative contribution of each category of product (left axis) to the total peak area (orange–right axis) at different temperatures and increasing times

carbon, which tends to form a more stable radical [13]. Increasing the temperature reduces this selectivity of the initialization step of the chain reaction. At higher temperatures, all types of products seemed to appear simultaneously, and with constant proportions for all the oils. The decreasing fraction of alkanes for oil D is related to the presence of naphthalene and other short chain impurities (nonane, decane, undecane, and dodecane) in the fresh product, which were almost immediately vaporized. The decrease of the relative area of these impurities is one supplementary argument which indicated that the increase in the total peak area was not simply due to progressive vaporization of products, but in fact depicted the accumulation of oxidation products directly in the heated vial. This was the same for oil H, which contained a large fraction of 2-ethylhexanol coming from the hydrolysis of the fresh ester, leading to an important and decreasing fraction of alcohols (Figure A.1). The large contribution of aldehydes for oil C at short times was due to the fact that even though several peaks started to appear, they were not considered significant before 200 min, unlike pentanal and hexanal (Figure A.1). The important proportion of non-identified components was mostly due to the significant peak area of the first peaks, which corresponded to a mix of several not well separated light

products. For instance, formic acid, butane, and alkanes shorter than C4 could be identified in these peaks at very short retention times. The fact that these types of products kept constant proportions in these experiments suggests that light oxidation products did not further react under these conditions. For instance, the results shown here do not show an accumulation of acidic products at high temperatures, as Rasberger suggested in his work [13]. These results, however, only reflect one fraction of the oxidation chemistry through the lighter products.

Within each product category, the distribution between chain lengths was also investigated. Figure 2.16 shows the evolution of the peak area of 2-ketones depending on their chain length in oil A for experiments at 140, 160, and 190 °C. Boiling points of these compounds are indicated in parallel, and it can be noticed that some of the compounds were above their boiling points while others were below but could still be detected due to partial vaporization. Whether it was at 140, 160, or 190 °C, all sizes of ketones seemed to appear simultaneously, even though shorter molecules resulted in higher peak areas, consistent with their lower boiling points. As illustrated and discussed in Figure 2.14, the maximum peak area reached, all ketones considered together, resulted from a combination of kinetics effects for product formation, and thermodynamic effects for product vaporization and further detection. This also applies for each individual product, meaning that heavy molecules resulted in lower peak areas, without implying that they were present in lower concentrations in the liquid phase. This illustrates that peak areas of individual compounds within a chemical family cannot be quantitatively compared. In addition, the response factor of individual molecules depends highly on their type, meaning that relative proportion of one chemical family compared to another cannot be directly compared either. Nevertheless, this methodology can be applied to compare the evolution with heating time of each family (Figure 2.15) and chain lengths (Figure 2.16) to show that both follow linear trends, meaning that no specific chain length was promoted and that no secondary reaction occurred under these experimental conditions.

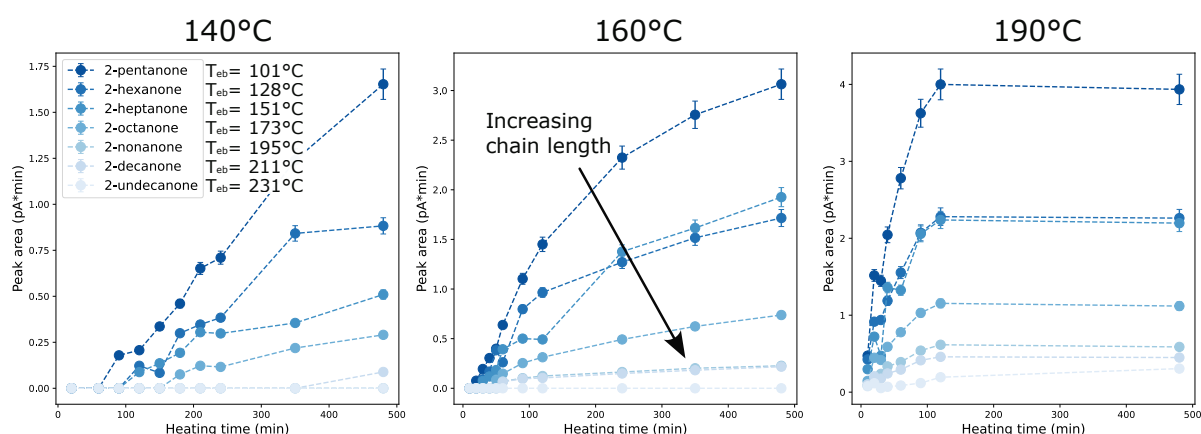


Figure 2.16: Peak area of the individual ketones for oil A as a function of the heating time, at 140 °C, 160 °C and 190 °C

To conclude, *operando* oxidation of different base oils was performed using a headspace autosampler, and enabled the analysis of around a hundred light oxidation products from eight base oils. To the best of our knowledge, no comparable study using a headspace autosampler as a minireactor to simulate oxidation was found in the literature. With this technique, the effects of the heating time and temperature were examined. This protocol shows various advantages: it requires a small amount of sample, prevents sample manipulation and is highly repeatable. The direct injection via a heated transfer line prevents any condensation of products, and the versatility in the choice of the column allows to separate products according to various parameters (polarity, volatility). In addition, this technique allows an indirect examination of changes of heavy products (up to C15) present in the liquid phase. Despite the variability of the samples studied, common descriptors could be found to allow comparison. As FID has a low detection limit, this technique is useful to detect early stages of oxidation. On the other hand, as vials contain a limited quantity of oxygen, and because the vapor pressure of each molecule is determined by phase equilibrium, peak areas reach a limit after only a few hours. This technique is therefore not pertinent to study severe states of oxidation, such as sludge formation. Besides, this technique does not give access to heavier thus not vaporized compounds. The oxidation behavior of the selected base oils was then also examined with a different technique based on a continuous air flow circulation in a heating station.

3. Rancimat applied to lube oils

3.1 Characterization of the accelerated aging via Rancimat method

The reactivity of each base oil was studied at 140 and 158, and 120 °C for the most reactive samples. Experiments at 190 °C could not be conducted due to limitations of the maximum temperature of the heating station.

As an example, results from oil A are presented in Figure 2.17. The induction period increased as the temperature decreased, as could be expected. Higher temperatures increase the cleavage of hydroperoxides $\text{ROOH} \longrightarrow \text{RO}^\bullet + \text{}^\bullet\text{OH}$, propagating the oxidation reaction, and increase the collision probability between radicals leading to termination products [13]. The increase in the conductivity of the water (Figure 2.17 a) was correlated with the apparition of common oxidation descriptors. In Figure 2.17 c), the IR spectrum of aged oils is presented after subtraction of the spectrum of the fresh oil. The region evolving were typical of oxidation products:

- $1300\text{-}1000\text{ cm}^{-1}$: stretching of C—O bond in esters, acids and alcohols

2.3. RANCIMAT APPLIED TO LUBE OILS

- 1600 – 1800 cm^{-1} : stretching of C=O double bond in acids, aldehydes and ketones
- 2700 cm^{-1} : stretching of C–H bonds in aldehydes
- 2900 – 3000 cm^{-1} : stretching of C–H, CH₂ and CH₃ groups (decrease with oxidation of the hydrocarbon chains)
- 3200 – 3600 cm^{-1} : stretching of the O–H bond in alcohols, acids and water

In addition, the color of the oils evolved (b), and their kinematic viscosity increased (d). Similar trends were obtained with all the samples, although not to the same extent, except oil F which showed no change in the color. For polyester base oils, similar regions of the FTIR spectra can be looked at to characterize their evolution, the only difference being the region associated to C=O double bonds. The associated band broadened with the accumulation of different oxidation products. In particular, a shoulder peak appeared at lower wavelengths with the ester hydrolysis into acids and the formation of aldehydes and ketones (Figure 2.4), as observed in [151]. For oil F, oxidation also led to the depletion of the C–O bond of the esters at 1136 cm^{-1} , reversely to a significant increase in the C–O bond of primary alcohols at 1055 cm^{-1} . Duong *et al.* observed the same evolution in [151], where similar type of neopolyol ester was oxidized using a PetroOxy device. All the results are summarized in Appendix A.2.

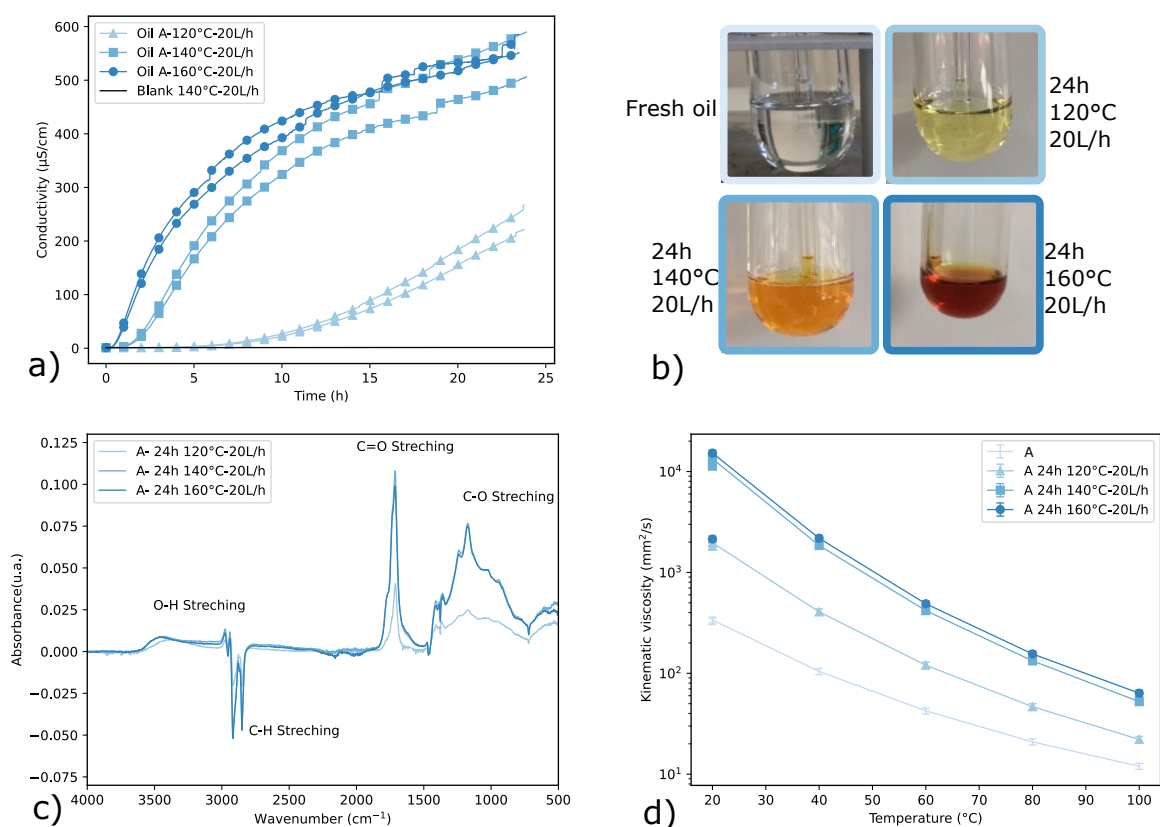


Figure 2.17: Characterization of oil A after Rancimat experiments. a) Evolution of the conductivity of the water at different temperatures. b) Aspect of the oils after 24h at different temperatures. c) IR spectra after 24h at different temperatures, fresh oil subtracted. d) Kinematic viscosity of oil A after 24h at different temperatures

Concerning the evolution of conductivity, three stages could be observed for all the samples: a steady regime called induction period, then a high rate increase in the conductivity, and finally a lower rate increase. The induction period corresponds to the accumulation of hydroperoxides in the liquid phase. The decomposition of hydroperoxides into two radicals via the chain branching reaction $\text{ROOH} \longrightarrow \text{RO}^\cdot + \cdot\text{OH}$ then self-accelerates the reaction and contributes to the massive formation of light oxidation products. The conductivity increases more rapidly. Then, secondary products and termination products are formed, and the oxidation rate becomes slower. The secondary products can be less volatile and less soluble in water and do not result in ionic species, which reduces their contribution to the increase in the total conductivity. Examination of the composition of the collected water with oxidation products with time could confirm these hypotheses.

24 h at 140 or 158 °C led to more significant viscosity and carbonyl peak area increases, compared to 120 °C: not only the induction period was shorter at higher temperatures, but the oxidation degree after 24 h was more severe at higher temperatures, consistent with what could be expected (Figure 2.17 b, c, d). Along with the peak area of the carbonyl region in IR, used as a marker of the oxidation degree, the kinematic viscosity increased due to the accumulation of heavier termination products and polymerization of bifunctional oxygenated products. It was measured at different temperatures (20, 40, 60, 80 and 100 °C), both before and after aging. The viscosity increase was even more significant at low temperatures, it was multiplied by a factor 45 for oil A at 20 °C versus a factor 4.3 at 100 °C (Figure 2.17 d), diminishing the viscosity index. This is probably due to the accumulation of acidic and oxygenated products which are involved in low energy interactions, such as hydrogen bonding, which only contribute to the viscosity increase at low temperatures. Karis *et al.* [152] had already measured a viscosity increase despite a stable molecular weight when studying the oxidation of complex polyesters similar to oil F.

3.2 Comparison of the oils reactivity

Oils D and E, for which oxidation products could only be detected at 190 °C in headspace *operando* oxidation, were particularly stable in the Rancimat, at 158 °C under continuous air flow. Experiments up to more than 100 h at 158 °C were conducted, and yet the conductivity increase remained very low (less than 30 µS/cm, 10 times lower than for other oils after only 24 h). IR examination of the oil samples after 30 h and 75 h at 160 °C indicated very low oxidation degree, when compared to IR examination of the same oils after reaction at 190 °C in the headspace sampler (peak areas of 0.036 A/cm and 0 after 75 h at 160 °C, respectively, for oils D and E, versus more than 0.3 A/cm after 8 h at 190 °C with *operando* headspace oxidation). In addition, similar volatile degradation products were expected with these oils, as shown previously. This proved that this result can be attributed to an important stability regarding oxidation, and highlighted the consistency of the results obtained by the various approaches (Rancimat, headspace-GC oxidation, and FTIR spectroscopy).

2.3. RANCIMAT APPLIED TO LUBE OILS

The measured induction periods are summarized in Table 2.8 and Figure 2.18, and their logarithm is plotted against temperature in Figure A.3. The experimental uncertainty is given as a 90 % confidence interval, based on the results of three measurements. A linear correlation between the logarithm of the induction period measured with Rancimat and temperature was several times reported in the literature, for vegetable oils [131,142,153]. The authors of these publications did not give any explanation for this observation. The linearity is indeed difficult to interpret as it is the result of several phenomena and reflects several chemical mechanisms happening at the same time. In this work, linearity could only be established with oils A, G and H, with correlation coefficients larger than 0.99. For other samples, the induction period at lower temperatures was too long to be measured. For example, samples B and C did not reach the end of the induction period at 120 °C after 103 h of heating. This is more than the induction period which could be hypothesized with the values at 140 and 158 °C, indicating that the linearity was not verified with these oils.

Table 2.8: Induction periods measured with Rancimat method

Sample	120 °C-20 L/h	140 °C-20 L/h	158 °C-20 L/h
A	11.5±3.2 h	1.8±0.2 h	0.35±0.01 h
B	≥103 h	12.8±0.5 h	2.5±0.4 h
C	≥103 h	13.1±1 h	2.6±0.2 h
D	NA	NA	21.0±1.6 h
E	NA	NA	18.3±2.5 h
F	≥31 h	11.6±1 h	0.8±0.4 h
G	19.5±1.3 h	6.3±0.7 h	1.4±0.3 h
H	35.2±1 h	5.2±0.2 h	1.2±0.1 h

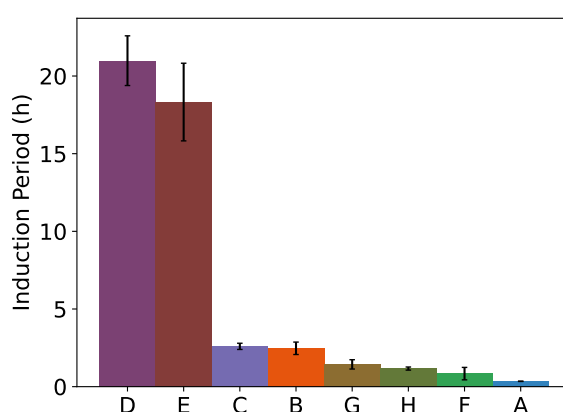


Figure 2.18: Induction periods at 158 °C-20 L/h measured with Rancimat

Considering the induction periods measured with the Rancimat at 158 °C, the following ranking in terms of reactivity could be established: $A \sim F \sim H \sim G \leq B \sim C \leq E \sim D$. Results for oils F, G and H were inverted at lower temperatures. The main advantage of the Rancimat method is that oxygen is continuously renewed and put in close contact with the oil, allowing

2.3. RANCIMAT APPLIED TO LUBE OILS

accelerated oxidation of the samples. Acceleration of the reaction kinetics is also due to the enhanced vaporization of oxidation products, which shifts the equilibrium toward the formation of new products. This method is easy to put into practice and provides fast results but is not fully representative of the in-field conditions. It is suitable to study and compare the stability and behavior of different base oils. As it is a standard and commercial apparatus, quantitative results from different studies can be compared, as soon as the experimental conditions are similar. Finally, 3 g of oil was used in this study, which is small but still allowed to further characterize the aged oils. However, the standard errors obtained on the measurements of the induction periods were quite high, typically around 10 % and up to 20 % for oil A at 120 °C. Finally, regarding the oxidation monitoring, experiments conducted with headspace chromatography showed that oxidation resulted in a variety of light oxidation products, in agreement with the literature [13]. These products are also formed in Rancimat, but do not necessarily contribute to the increase in the conductivity (short hydrocarbons, ketones, and esters) and thus the determination of the induction period. The latter is then only attributed to the production of soluble charged species, especially acids. Nevertheless, results from headspace chromatography showed that acidic products are among the first to be detected in the gas phase at early stages of oxidation.

Both techniques appear to be highly complementary to understand the oxidation behavior of a matrix of base oils of different types. The characterizations conducted on oils exposed to a continuous air flow and heating in the Rancimat instrument mostly provided information about the evolution of the heavy fraction of degradation products. Meanwhile, the *operando* headspace-GC enabled precise product identification of the lightest fraction of degradation products, formed in a sealed vial filled with air. Using the Rancimat for hydrocarbons such as mineral oil was firstly conducted in this study and proved to be relevant. Similarly, the diverted use of a headspace autosampler to generate and identify oxidation products was a very innovative means of combined production and identification of such products. Combining both techniques enabled to draw a comprehensive overview of the reactivity of eight diverse base oils and investigate the effects of parameters such as reaction temperature as part of a preliminary study. However, the principle of both experiments only enabled to study the aging under air. Besides, the small oil volumes used, which can be seen as an advantage, are a limit for the characterizations which can be implemented on oil samples. For further study of the reactivity of base oils under different gaseous atmospheres, representative of what they could be exposed to in ammonia combustion, a third experimental set-up was used. It consists in a pressurized stirred reactor in which a custom gas mixture can be injected. The following section presents the reference experiments conducted with the autoclave set-up.

4. Oxidation using a pressurized stirred reactor

From the matrix of eight base oils, only two were selected for further study: the group III mineral oil, B, and the trimethylolpropane ester of carboxylic acid, G. Oil B was chosen because group III mineral oils are the most widely used base for lubricants dedicated to engines such as the one used later in this thesis. In addition, it represented a compromise between the group II mineral oil A with a complex chemistry and the PAO oil C with a higher oxidation stability, therefore requiring longer reaction times. Besides, among the polyesters, oil G was chosen because it resulted in similar products as oil B, as opposed to oil F. A preliminary study was conducted to assess the autoclave experimental conditions and robustness, and to study the evolution of these oils under oxygen as a reference case before studying their evolution under different gaseous atmospheres.

4.1 Mineral oil under pure oxygen—assessment of the oxidation protocol and between-day repeatability

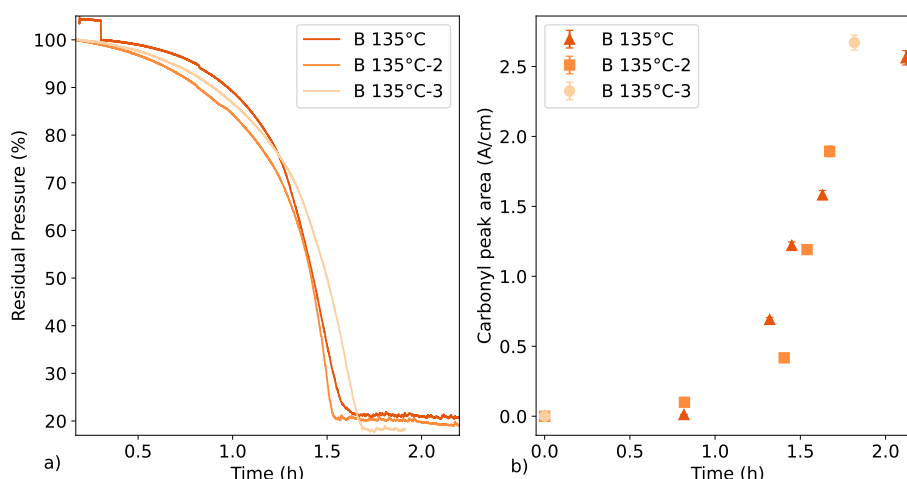


Figure 2.19: Repetitions of the experiment conducted at 135 °C under 10 bar of O₂. a) Residual pressure with reaction time. b) Carbonyl peak area with reaction time

The initial time corresponds to the injection of O₂ in the reactor at target pressure, 10 bar here. The residual pressure in the reactor is calculated as described in Section 2.1.2.3. As can be seen in Figure 2.19 a), the global pressure in the reactor decreased with time when the oil was exposed to oxygen and temperature. This decrease was caused by the consumption of gas molecules through reactions with hydrocarbons in the liquid phase. According to the ideal gas law, the reactor pressure depends on the number of gas moles in the gas phase. Therefore, a decrease of the pressure at constant temperature is an indicator of the ongoing reactivity between the reactive gas mixture and the oil. The evolution of the pressure was non-linear under these conditions: it was rather stable at short times, corresponding to the induction period in which the first radicals were initiated by proton abstraction by O₂ and hydroperox-

2.4. OXIDATION USING A PRESSURIZED STIRRED REACTOR

ides accumulated; followed by a rapid pressure drop as the propagation self-accelerated the reaction. The reaction rate decelerated as less fresh oxygen became available. The pressure was finally stabilized once most of the available oxygen had reacted. It can be noticed that the residual pressure was stabilized around 20 % of the initial pressure and not 0 %, despite the filling/venting cycles ensuring a 99 % purity of the oxygen inside the reactor at the beginning of the experiment. This can be explained by the vaporization of some oxidation products, which are lighter than the original oil. Figure 2.19 b) shows in parallel the increase in carbonyl peak area in FTIR spectroscopy. This confirmed the accumulation of oxidation products along with the pressure decrease, confirming the chemical conversion of gaseous oxygen to molecular oxygen in the liquid phase. The three repetitions of this experiment gave highly comparable results, confirming the robustness of the protocol. It can be noticed that carbonyl peak area kept increasing after 1.5 h, despite the stabilization of the pressure. After 2 h, it remained stable. This delay might be due to a delay between the solubilization of the oxygen and its conversion into molecular oxygen. Besides, deprived of unreacted oxygen, oil components can continue to evolve via intramolecular reactions or polycondensation reactions between bifunctional products, but this was not monitored here.

4.2 Comparison with the complex polyester base oil

Under the same experimental conditions, the reaction time of oil G was significantly higher than oil B (Figure 2.20 a and b). This was unexpected, as the measured IP values for oil G at 120 °C, 140 °C and 158 °C were shorter than for oil B (Table 2.8), and because light oxidation products could be detected at 140 °C in *operando* oxidation via headspace-GC (Figure 2.14).

4.3 Effect of the temperature

Figure 2.20 a) b), and c) d) show respectively the evolution of the pressure at different reaction temperatures, and resulting evolution of the carbonyl peak area for both oils. It highlights that the temperature has a significant influence, as a variation of +5 °C almost doubled the total reaction time for both oils B and G. The temperature also influences the final residual pressure in the reactor, as it shifts the phase equilibrium towards the gaseous state. For oil B, the residual pressure after oxygen consumption was indeed higher at 140 °C, than at 135 °C, itself higher than at 130 °C, suggesting that a higher fraction of oxidation products were vaporized. The reaction at 135 °C for oil G was not complete when the experiment was stopped which prevents comparison with 140 °C. Oils were collected after complete cooling of the reactor to ensure recondensation of this fraction of products. At fixed pressure, higher temperatures also correspond to fewer oxygen molecules introduced. The amount of oxygen injected in the reactor is indeed controlled by the pressure, and the same oxygen molar quantity will result in a higher pressure at 140 °C than at 130 °C. All these elements point out the fact that temperature should be precisely monitored to make experiments comparable.

2.4. OXIDATION USING A PRESSURIZED STIRRED REACTOR

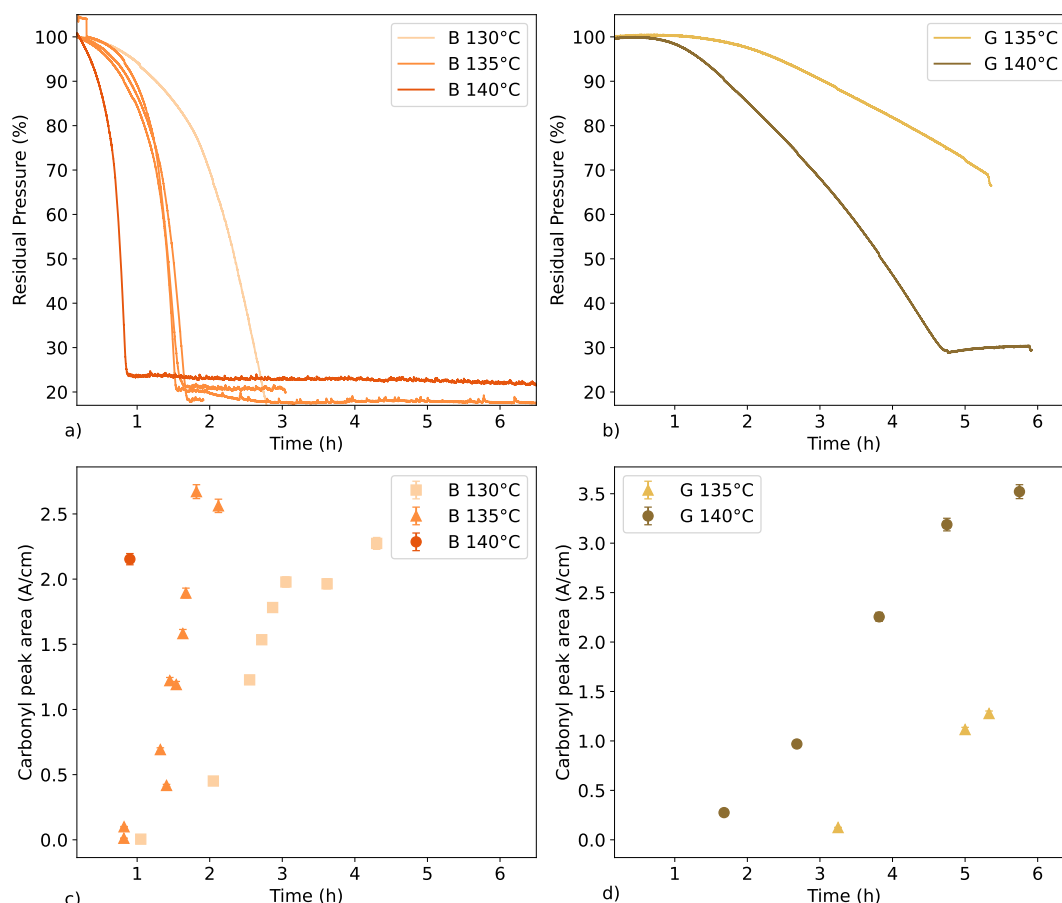


Figure 2.20: Residual pressure for oils B (a and c) and G (b and d) at 130 °C, 135 °C and 140 °C, under 10 bar O_2

4.4 Total oxygen content

In addition to FTIR, the total oxygen content of oil B samples was also analyzed, as described in Section 2.1.3.3. The result is given as a mass fraction of oxygen in the sample, and knowing the density of the latter, the corresponding amount of oxygen atoms can be calculated. Calculations showed that the final oxygen content and the initial gaseous oxygen were between 80 and 99% when all experiments are considered. This confirmed that the stabilization of the pressure corresponded to the consumption time of the oxygen initially introduced in the reactor, and that they were few losses due to volatiles vaporization during the sampling and cleaning steps. The total oxygen content was measured at different reaction times and under different conditions, but always with an initial total pressure of 10 bar. It is represented against the carbonyl peak area of corresponding samples in Figure 2.21.

A correlation between the carbonyl peak area and the total oxygen content could be observed, despite the variety of oxidation conditions and times. This showed that the carbonyl peak area was a good descriptor of the accumulation of oxygenated products inside oil B. It also showed that the total oxygen content measured corresponded to covalently bonded oxygen contained in oxygenated degradation products, especially with C=O bonds. This sug-

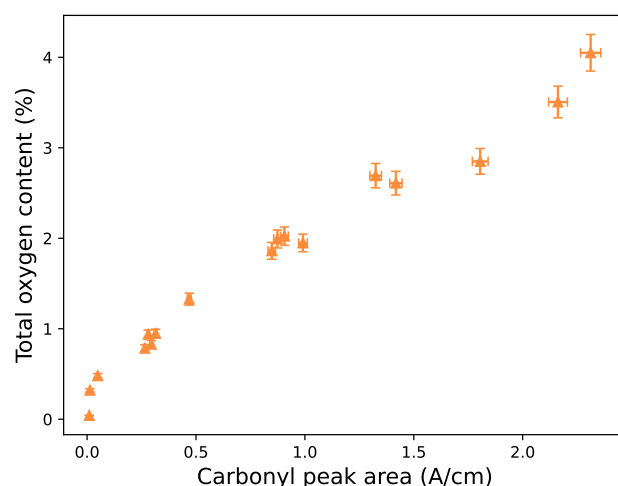


Figure 2.21: Total oxygen content as a function of the carbonyl peak area for samples of oil B at different reaction times and conditions (both 135 °C and 140 °C, under air, air with 50 % O_2 and pure O_2)

gests a great contribution of ketones, aldehydes, acids, and furanones compared to alcohols, consistent with headspace results. Such a correlation could not be verified for oil G as the total oxygen content was not measured because its variation was negligible compared to the initial oxygen content in this oil.

4.5 Viscosity

As seen in the Rancimat experiment, the accumulation of oxidation products also resulted in viscosity changes. Figure 2.22 shows the evolution of the dynamic viscosity (a), density (b) and the resulting kinematic viscosity (c), which was calculated by taking the ratio of the other two values (Equation 2.2). Viscosity values at 100 °C were not measured due to the presence of water in the sample, generating gas bubbles preventing accurate measurement. Like after aging in Rancimat, the dynamic viscosity of oil B increased after exposure to O_2 in the autoclave reactor. The increase was more significant at low temperatures, due to the increase in low energy interactions between oxidation products prone to form hydrogen bonds. The kinematic viscosity followed a similar trend. The behavior of oil G differed from oil B, and from the behavior of the same oil measured after aging in the Rancimat. Here, despite the density increase like for oil B, the dynamic and kinematic viscosity after aging in a closed reactor under pure oxygen decreased, especially at high temperatures. This can be attributed to the production of shorter chains during oxidation, which remain in the oil due to the pressure conditions, as opposed to Rancimat experiment in which light products are continuously vaporized. Such a viscosity decrease with oxidation was already observed in [25, 154].

2.4. OXIDATION USING A PRESSURIZED STIRRED REACTOR

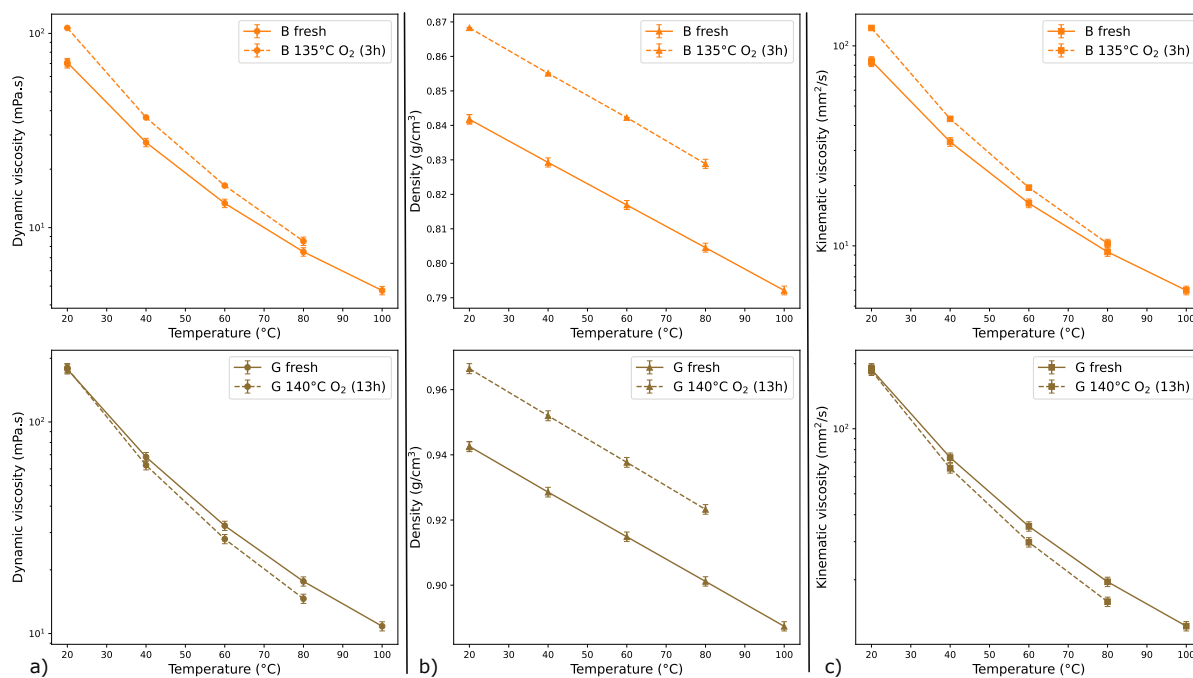


Figure 2.22: Dynamic viscosity (a), Density (b) and kinematic viscosity (c) of oils B and G, fresh and after exposure to O₂, respectively at 135 °C, 10 bar and 140 °C, 10 bar

4.6 Simulated distillation

Simulated distillation of oil B after 24 h under 10 bar of oxygen at 135 °C (Figure 2.23) confirmed the presence of both light oxidation products and heavy molecules. The starting boiling point indeed shifted from 372 to 180 °C, and the final boiling point from 542 to 643 °C.

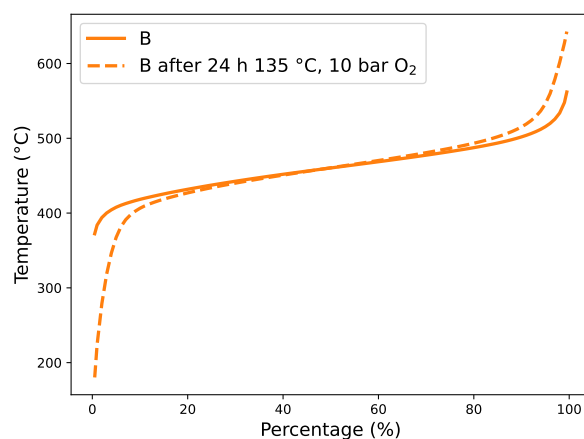


Figure 2.23: Simulated distillation curve of oil B fresh (continuous line) and after 24 h at 135 °C, 10 bar O₂

Elemental analysis, viscosity and simulated distillation measurements provide valuable information about the oil samples, but only at a macroscopic scale. GC2D/MS analysis were also conducted for a more in-depth characterization.

4.7 GC2D/MS analysis of the mineral oil oxidation products

Following the method described in Section 2.1.3.7, oil B after 24 h in the autoclave reactor under 10 bar of oxygen at 135 °C was analyzed using GC2D/MS. For this sample, the total oxygen content was $3.4 \pm 0.2\%$. Products were first separated according to their boiling point, and then according to their polarity. The two dimensional chromatograms of oil B before and after aging are respectively displayed in Figure 2.24 a) and b). Analysis of the fresh oil revealed that it contained mostly isoparaffins, olefins, polyunsaturated hydrocarbons and monoaromatics, as could be expected in a group III mineral oil. After aging, various oxidation products, lighter than the base oil itself could be detected. Interestingly, the same six families which could be identified using headspace-GC/MS were also present here: oxidation products mainly consisted of ketones, carboxylic acids, short paraffins, aldehydes, alcohols, and lactones. Only very few 1-alcohols could be detected, as with headspace-GC/MS and consistent with the fact that alcohols result from alkoxy radicals which can only generate 1-alcohols. It can also be noticed that the polycyclic hydrocarbons present in the fresh base oil could not be found after aging. As stated in [74], such molecules have a lot of tertiary carbons, prone to be oxygen attack sites. In the previous study, the induction period of decalin measured with petroOxy device at 140 °C was only 1 h, when it was more than 2.5 h for C14 to C20 n-alkanes. As with headspace, a pattern was repeated with increasing chain lengths (Figure 2.25 a) and Figure 2.10). The order of elution in one group of the pattern was also similar compared to headspace, with the C_{n-2} carboxylic acids having a very close but slightly lower boiling point than the C_n 2-ketones followed by the C_n aldehydes (Figure 2.10). It also corresponded to the boiling point of C_{n+2} alkanes, as seen with headspace-GC/MS, but the latter were well better separated here thanks to the second separation dimension. The few lactones detected were the same kind of di-hydrofuranones as in headspace-GC/MS. Adding one separation dimension enabled here to clearly isolate alkanes from oxygenated products, but also acids and ketones, which can have very similar boiling points and could sometimes be co-eluted, as in Figure 2.10. It also enabled to detect different isomers of ketones, even if the linear 2-ketones remained majoritarian. Although n-paraffins only could be detected in headspace GC/MS, GC2D/MS after aging in the autoclave showed a variety of branched and iso-paraffins with short chain lengths. In addition to the main types of products, other types could be detected in this analysis, especially complex products such as methyl esters, diketones or bifunctional products. These products are likely to result from second order reactions. Cross comparison of these results indicate that the oxidation products formed and detected using *operando* headspace-GC/MS oxidation and after exposure to oxygen in pressurized stirred reactor followed by GC2D/MS analysis were highly similar. Identifying the same product types using a more conventional accelerated aging protocol highlights the great interest and potential of a more innovative technique as *operando* oxidation using a headspace autosampler. It also confirmed that the products identified using headspace-GC/MS were effectively products from the liquid phase, after vaporization. It is one supplementary argument

2.4. OXIDATION USING A PRESSURIZED STIRRED REACTOR

to state that the detected gaseous products are an indirect indicator of the reactivity in the liquid phase. Heavy oxidation products brought to light by simulated distillation in Figure 2.23 were not identified in GC2D/MS analysis. This might be a consequence of their very high boiling points preventing vaporization at the head of the column.

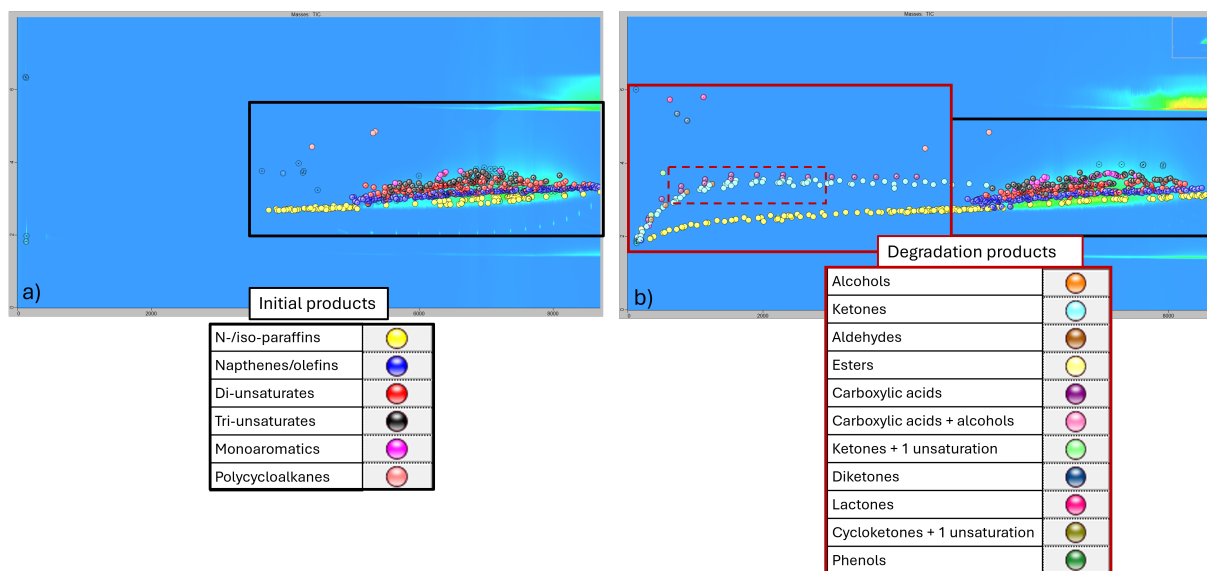


Figure 2.24: GC2D/MS analysis of oil B after 24 h under 10 bar O_2 at 135 °C. a) GC2D/MS of the fresh oil-b) GC2D/MS after aging.

In this section, the development and assessment of accelerated aging using a pressurized stirred reactor and the associated characterizations was described. Two oils, one mineral and one polyester were considered for this more detailed study. Their reactivity under pure oxygen as a function of the temperature was studied, showing a great dependency on this parameter. Characterization of oil samples taken at different reaction times using FTIR showed that the evolution at a molecular level was consistently correlated to the evolution of the pressure inside the reactor. This confirmed that monitoring the pressure drop in the reactor is a valid and effective way to monitor the reaction, even though it is biased by the partial vaporization of light products. Calculating the carbonyl peak area also showed a good correlation with the measurement of the total oxygen content, showing this parameter is a good indicator of the progressive degradation of the oil. Finally, a molecular analysis methodology was developed using GC2D/MS to identify precise degradation products. A very interesting parallel could be drawn between these analyses and the *operando* oxidation in a headspace autosampler. Performing these tests under pure oxygen conditions enabled us to assess the accelerated aging and the evolution of the oils under reference conditions, setting the baseline before further experiments involving ammonia and nitrogen oxides. This setup will then be used to study the influence of reactive gases such as nitrogen dioxide and ammonia.

2.4. OXIDATION USING A PRESSURIZED STIRRED REACTOR

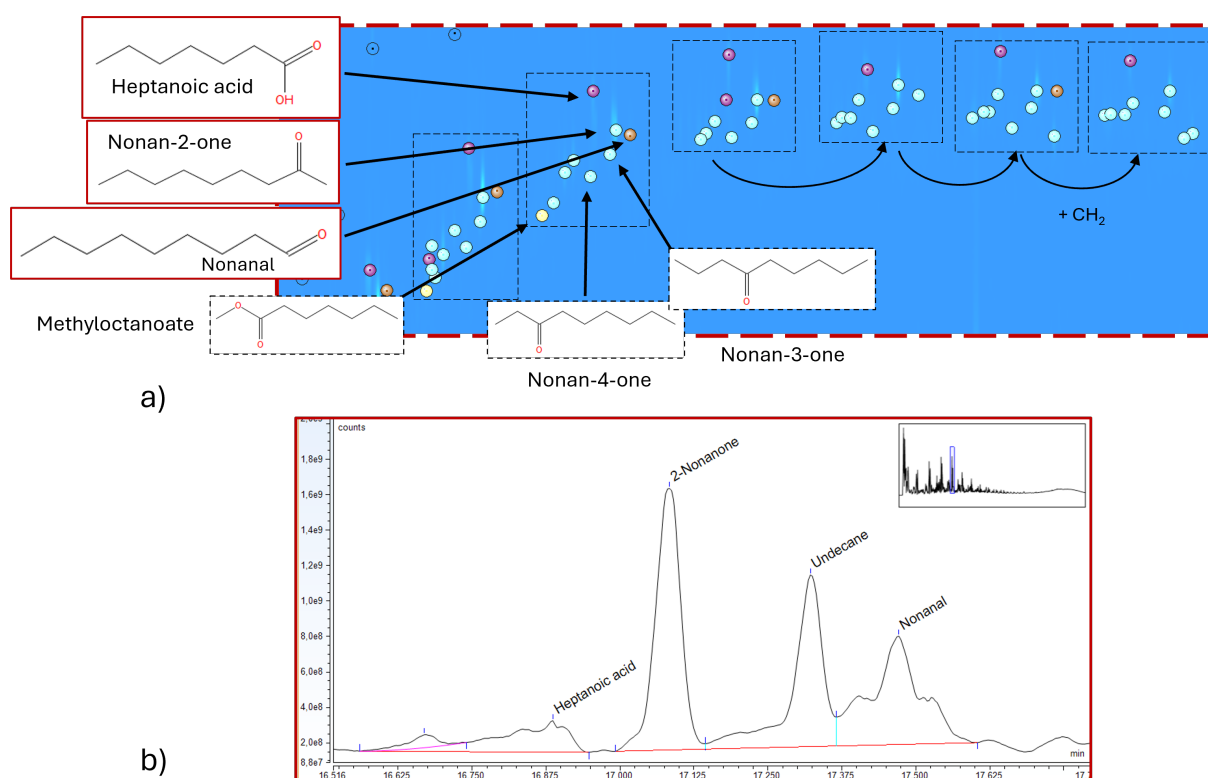


Figure 2.25: Comparison of GC2D/MS analysis of oil B after 24 h under 10 bar O₂ at 135 °C (a) and operando headspace-GC/MS oxidation after 20 min at 190 °C b). a) Zoom on the two dimensional chromatogram and precise product identification. Compounds in red were also found using headspace-GC/MS. b) GC/MS peak attribution of oil B after operando oxidation in the headspace sampler

5. Discussion–comparison of the accelerated aging setups

As a first approach, two different methods were developed and applied to study the oxidation stability of varied lubricant base oils. These two methods, Rancimat and *operando* headspace-GC, are based on different principles, and do not correspond to the same oxidation conditions but appeared to be highly complementary for a comprehensive approach of the liquid phase oxidation chemistry of different oil types. Besides, both techniques appeared to be relevant for studying the oxidation of both non-oxygenated hydrocarbons and complex polyester base oils. The main difference is the continuous oxygen supply and stirring due to the air flow in the Rancimat, while oxidation in the headspace sampler happens only with a small quantity of oxygen and a limited reactive surface area. As one technique enables one to focus on the lightest fraction of oxidation products in the gas state, while the other enables a deeper characterization of the evolution of the liquid phase, both techniques are highly complementary and provide a global overview of the oxidation behavior of the products. Both techniques resulted in similar reactivity trends. Alkylated naphthalenes (D, E) had longer induction periods with Rancimat and reacted at higher temperatures in the headspace, indicating high oxidation stability, as it could be expected considering the stabilization provided by the naphthalene group. On the contrary, the mineral oil from group II (A) had the shortest induction period and formed oxidation products at 140 °C in headspace chromatography as opposed to other oils, indicating an overall lower oxidation stability. The mineral oil from group III (B) and the PAO oil (C) showed comparable behaviors with both protocols. A significant amount of short alkanes was produced during *operando* oxidation in the headspace sampler, this might be due to chain scission of C-C bonds. Such a scission requires a higher activation energy compared to oxidation, yet it can be favored if oxygen supply is limited, as it is the case in headspace oxidation [134]. Short alkanes were also formed with Rancimat, as oil droplets were observed at the surface of the water.

Thanks to this preliminary study, two oils (B and G) were selected for further studies. A more tunable experimental setup for accelerated aging using a pressurized reactor was developed. Experiments conducted under pure oxygen resulted in a different reactivity trend between oils B and G, probably because working in a close environment modified the oxidation kinetics of these products. GC2D/MS analysis of aged oil B showed great similarity in terms of chemical nature of products and size with molecules detected using headspace-GC/MS. Quantitative characterization techniques such as FTIR spectroscopy and viscosity measurements could be conducted with the different setups and allowed comparison of the oxidation degrees. FTIR of the liquid phase was used after all three experiments to establish a link between the techniques and their effects on oil degradation. The carbonyl peak areas for oil B and G after experiments conducted at 140 °C are displayed in Figure 2.26.

It highlights that only early stages of oxidation were reached with *operando*-headspace-GC

2.5. DISCUSSION–COMPARISON OF THE ACCELERATED AGING SETUPS

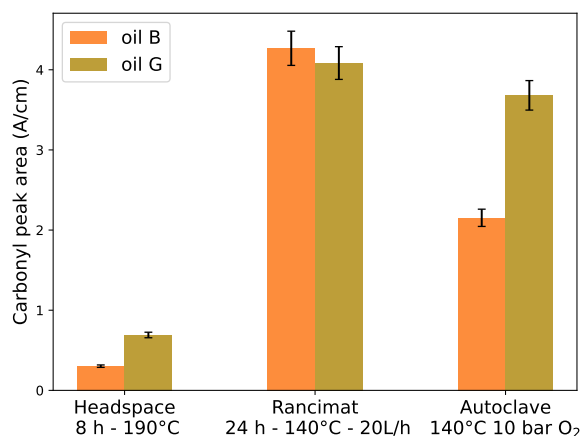


Figure 2.26: Carbonyl peak area of oils B and G after three accelerated aging experiments.

oxidation, as the total amount of oxygen in the vial was limited. Thanks to the continuous gas bubbling, severe stages of oxidation could be reached in the Rancimat, despite the fact that oxidation happened under air. The viscosity of samples after aging in the Rancimat or the autoclave can also be measured and compared, as in Figure 2.27. Is it interesting to notice that Rancimat led to a significant increase in the dynamic viscosity (a), density (b) and kinematic viscosity (c). On the contrary, the viscosity increase after exposure to oxygen in a closed reactor was more limited, and even showed a reversed trend for the polyester oil, showing a slight decrease. As discussed above (Figure 2.22), such a decrease after oxidation was already observed for oil which contain polyester additives, as in [25]. This difference, despite similar carbonyl peak areas, can be explained by the fact that lightest products are vaporized in the Rancimat. The remaining oil after 24 h was mainly composed of heavy products. On the contrary in the autoclave, light degradation products stay in the liquid phase, as confirmed by GC2D/MS, and contribute to a lower viscosity of the final sample. This major difference could explain the change regarding the oxidation stability of the polyester base oil.

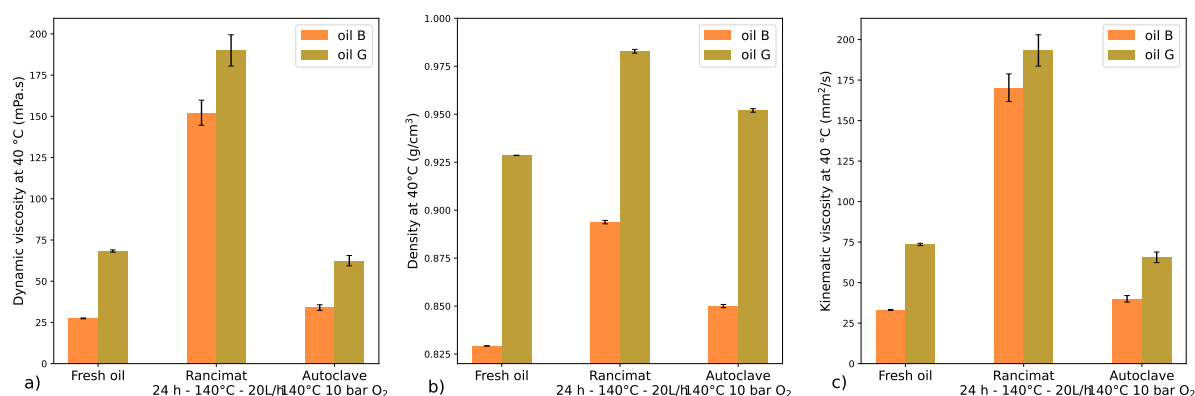


Figure 2.27: Kinematic viscosity at 40 °C for oils B and G before and after two accelerated aging experiments.

The main features, advantages and drawbacks of the two methods are summed up in Table 2.9.

2.5. DISCUSSION–COMPARISON OF THE ACCELERATED AGING SETUPS

Table 2.9: Characteristics of the accelerated oxidation setups and conditions used in this study

	Operando oxidation headspace sampler	Rancimat	Autoclave
Sample size	0.5 mL	3 g	50–100 mL
Oxidizing atmosphere	Limited amount of air	Continuous air flow	Fixed volume of a custom gas mixture
Time scale (in this work)	10 min–12 h	Up to ≥ 100 h	Up to ≥ 100 h
Temperature range	35–250 °C*	50–158 °C	Up to 350 °C 135/140 °C here
Oxidation monitoring	Detection and identification of light degradation products	Monitoring of the light acidic products produced during oxidation	Monitoring of the pressure in the reactor
Studied mechanism	Early stages of oxidation– Focus on light oxidation products	More severe stages of oxidation– Focus on heavy oxidation products	Early to severe degradation degree
Scale	Molecular identification of oxidation products	Macroscopic scale, quantification of the total amount of light acidic compounds	Multiscale characterization
Repeatability	Highly repeatable: less than 5 % uncertainty on the peak area	Up to 20 % uncertainty on the IP value	Good repeatability: 4 % repeatability on the carbonyl peak area and viscosity
Complementary techniques	MS coupling, FTIR	FTIR, viscosity	FTIR, viscosity, elemental analysis, GC2D/MS

*Limit of the oven of the headspace autosampler. The experiment is actually limited by the maximum pressure to which the vial can resist.

Working with the autoclave reactor gives a great flexibility when it comes to choosing the reactive gas mixture, and enables to perform multiple types of characterizations due to relatively important oil volume used. For the remainder of this study, the autoclave setup was used to expose oils B and G to gaseous atmosphere reproducing what they could be exposed to during the combustion of ammonia/hydrogen blends.

6. Conclusion

In this chapter, the methods used to characterize oils samples were described. In parallel, three protocols were developed and applied to oxidize and analyze eight lubricant base oils of mineral and synthetic types. The Rancimat instrument was successfully newly applied to mineral base oils. Induction periods of the oils were measured at three different temperatures, and oil samples were collected after 24 h to be further characterized using FTIR and viscosity measurements. This study points out that this instrument can be used to study mineral base oils as well as oxygenated hydrocarbons. In parallel, *operando* oxidation of the same oils was conducted directly in a headspace autosampler coupled to a GC/MS instrument. The numerous advantages of this protocol, developed and implemented in this work for the first time are demonstrated here. Mineral, alkylated naphthalenes and polyester base oils all degraded into six main types of products: ketones, acids, aldehydes, short alkanes and dihydrofuranones. Some additional products, specific to each base oil, were also identified. Despite the fact that both protocols represent different oxidation conditions in terms of oxygen supply, open/closed environment, liquid/gas phase equilibrium, and rely on different measurement principles, they showed similar reactivity trends and resulted in complementary information about the studied products. Both showed the high reactivity of mineral oils compared to polyalphaolefins and the higher stability of alkylated naphthalenes. Combining these methodologies enabled both the evaluation of key liquid phase properties (IR, viscosity) and the identification of light oxidation products, managing easy to implement experiments. This approach enabled an initial screening of the eight base oils, from which two were selected for more complex experiments. Considering these results, a mineral one and a polyester one were selected for further analysis, and underwent accelerated aging under pure oxygen in a pressurized stirred reactor. Preliminary experiments were conducted to assess the between-day repeatability of this experiment, and define a workflow for aging experiments and oil characterization. In particular, this experimental setup enables to proceed to regular oil samplings which can be finely characterized. FTIR, total oxygen content and viscosity measurements can be performed to characterize the evolution of the oil under controlled conditions. In addition, a methodology for molecular analysis using GC2D/MS was developed. Studying these eight base oils using three different setups and multiple characterizations led us to define a framework for the evolution of base oils properties under controlled conditions. Experiments conducted under pure oxygen enabled to assess the accelerated aging protocol under standard conditions. Global pressure inside the reactor, carbonyl peak area, total oxygen content and kinematic viscosity were selected as monitoring parameters of the evolution of the oils B and G. This paved the way to a better understanding of the evolution of engine lubricants under modified conditions compared to conventional fuels, which is the subject of the next chapter.

Chapter 3

Investigating lubricants base oils reactivity under nitrogen oxides and ammonia

3.1	Experimental section	105
3.1.1	Gas mixtures	105
3.1.2	Summary of the experimental conditions	105
3.2	Effect of nitrogen oxides in air	106
3.3	Effect of ammonia in air	110
3.4	Speciation of nitrogen	112
3.4.1	GC2D/MS analysis	113
3.4.2	Specific detection of nitrogen-containing compounds	114
3.5	Effect of mixing with an ammonia solution	116
3.5.1	Reaction conditions	116
3.5.2	Monitoring of the reaction	117
3.5.3	Molecular analysis	118
3.5.4	Possible synthesis pathways for amides and nitriles	120
3.5.5	Corrosion and deposits	120
3.6	Discussion—interaction between oxygen, ammonia, and a mineral oil during accelerated aging	122
3.7	Conclusion	124

As detailed in the first chapter of this study, several challenges are raised by the use of ammonia, hydrogen and blends as fuels regarding lubrication. In particular, one important issue is the compatibility of the engine oil with exhaust gases, which can be in contact with the lubricant due to the blow-by phenomenon. The studies [4, 5, 14, 15, 60] show that high levels of nitrogen oxides, and especially nitrous oxide, and unburned ammonia can be found at the exhaust, and thus be in contact with lubricants inside the engine. If liquid phase oxidation remains one of the main mechanisms by which lubricants are degraded, these gases could be associated to additional degradation mechanisms. The oxidation behavior of the products used in this study was investigated and thoroughly characterized in Chapter 2. Several studies investigated and improved knowledge about the nitro-oxidation reaction [17–19, 86, 87]. Nevertheless, experimental data and reaction intermediates identification are still missing to have a better understanding of the nitro-oxidation phenomenon and mechanism. Moreover, the compatibility between ammonia and engine oil remains largely unexplored. Although studies from other fields suggest potential interactions and reactivity between the two [21, 22], very few studies addressed this topic in the context of engines [17, 24, 25, 94]. Many questions remain to achieve a comprehensive understanding of the interaction between lubricants and ammonia in internal combustion engines. It remains unclear whether the ammonia only dissolves in the oil matrix, or really reacts with its components, and whether the interaction is limited to acidic additives or if the base oil itself can show a specific reactivity. Another issue is the potential reactivity between the acidic oxidation products and ammonia over time and as the lubricant degrades. Although the most direct method of studying oil degradation is to characterize oil samples from engine test rigs at different times, engine testing is expensive, time consuming and leads to limited understanding due to the high number of parameters. However, accelerated aging tests have proven to be relevant to reproduce the degradation mechanisms of lubricants [87, 155]. Based on the methodology of accelerated aging using a pressurized reactor developed in Chapter 2, the aim is now to investigate the interactions between different gaseous mixtures reproducing what lubricants could be exposed to during ammonia combustion and two types of base oils. These tests under controlled conditions pave the way for a better understanding of the evolution of lubricants directly during engine operation. To isolate the effect of each gas, two base oils, one mineral and one polyester, were exposed successively to nitric oxide, nitrogen dioxide and ammonia and the results obtained are presented in this chapter.

Part of the findings presented in this chapter were presented at the KSAE Powertrains, Energy and Lubricants conference in June 2025, and selected to be published as an article: Doncoeur, C., Giarracca, L., Cologon, P., and Rousselle, C., "Investigating Lubricants Base Oils Reactivity in Ammonia Engines via Accelerated Aging," SAE Technical Paper 2025-01-0240, 2025, 10.4271/2025-01-0240 .

1. Experimental section

As explained in Chapter 2, oil B and G were selected for further investigation (Table 2.1). They have different chemical properties, especially in terms of polarity, and do not contain any additives. They were exposed to nitrogen dioxide and ammonia with air in a pressurized stirred reactor under continuous heating, using the setup presented in Section 2.1.2.3 and Figure 2.3. Oil samples were characterized, following the techniques and workflow implemented in Chapter 2.

1.1 Gas mixtures

In addition to oxygen, three on-demand gas mixtures were purchased to Air Products, as detailed in Table 3.1. The different gas contents were requested considering values measured at the exhaust in different studies from the literature, as reported in Table 1.4.

Table 3.1: Gas mixtures composition

Gas	Composition
Nitrogen dioxide	1000 ppm NO ₂ in synthetic air (20,9 % O ₂)
Nitrogen monoxide	3000 ppm NO in N ₂
Ammonia	15 000 ppm NH ₃ in synthetic air (20,9 % O ₂)

In addition, an ammonium hydroxide solution with a concentration of 50 %v/v was purchased from ThermoScientific. This solution has a final ammonia concentration of 14 %w/w.

1.2 Summary of the experimental conditions

Table 3.2 summarizes the experimental conditions for the tests that we present in this chapter. For experiments conducted with NO, the reactor was first filled with 7.9 bar of the NO in N₂ mix, and 2.1 bar of O₂ were then added.

Table 3.2: Experimental conditions of the autoclave experiments

N°	Short name	Gas mixture					Pressure bar	Temperature °C
		O ₂ (%)	N ₂ (%)	NO ₂ (ppm)	NO (ppm)	NH ₃ (%)		
1	air	20.9	79.1	X	X	X	10	135
2	air + NO ₂	20.9	79.0	1000	X	X	10	135
3	air + NO	20.9	78.9	X	2370	X	10	135
4	air + NH ₃	20.9	77.6	X	X	1.5	10	135

Reference experiments conducted under pure oxygen in Chapter 2 showed that the oxygen uptake could still increase after the stabilization of the pressure. Therefore, experiments were stopped 1 h after the stabilization of the pressure. The oxygen quantity was kept equal for all the experiments conducted in this chapter, while the nitrogen content was adjusted considering

3.2. EFFECT OF NITROGEN OXIDES IN AIR

the addition of NO_2 , NO or NH_3 . This approach ensured that the effects of these contaminant gases were isolated, enabling a more reliable comparison of the results.

Figure 3.1 outlines the experimental workflow implemented in this chapter to investigate the reactivity of two base oils under nitrogen oxides and ammonia.

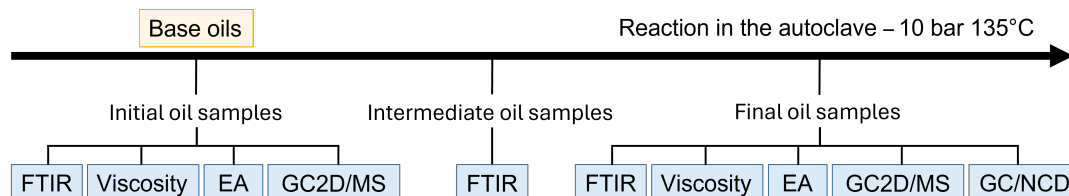


Figure 3.1: Diagram of the experimental workflow implemented in chapter 3

2. Effect of nitrogen oxides in air

Oils B and G were first exposed to NO and NO_2 in air, under the conditions summarized in Table 3.2.

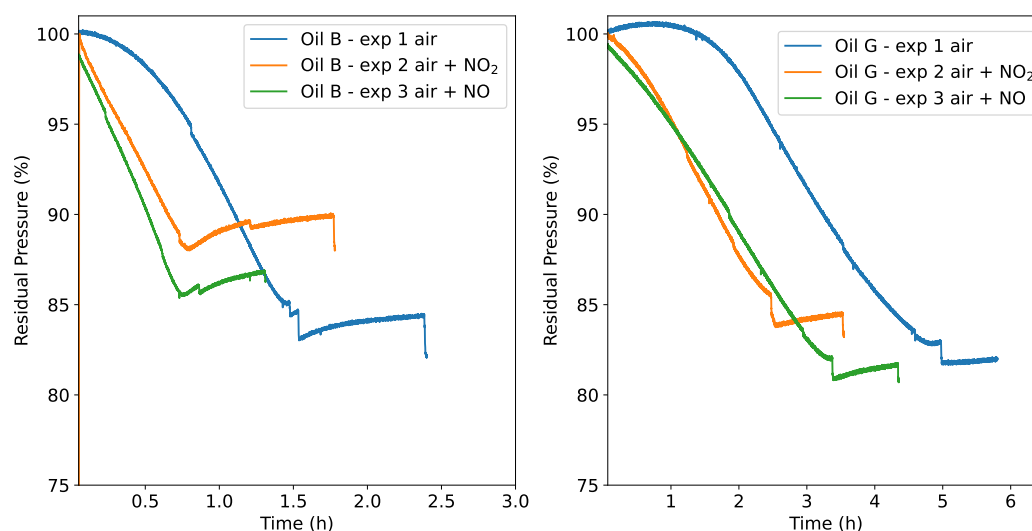


Figure 3.2: Residual pressure with time for experiment conducted under air, air + 1000ppm NO_2 and air + air + 2370ppm NO at 135°C –10 bar. Oil B = group III mineral base oil, oil G = trimethylolpropane ester of carboxylic acid

Figure 3.2 shows the evolution of the pressure for both oils, when exposed to NO , NO_2 and when exposed to neat air. Sudden pressure drops are due to liquid samplings. Both contaminants clearly accelerated the decrease of the pressure, especially at the very beginning of the reaction. Here, the exposure to NO and NO_2 seemed to result in comparable effects, despite their difference in concentrations. This is consistent with the fact that under these experimental conditions in an oxygen-rich environment, NO is quickly converted into NO_2 . The evolution of a original mix reproducing the experimental conditions 3 (Table 3.2) was simulated using the software Chemkin and the mechanism of Mei *et al.* [156]. The evolution

3.2. EFFECT OF NITROGEN OXIDES IN AIR

of the concentrations of both gases with time are represented in Figure 3.3: in less than 2 min, NO is almost completely oxidized into NO₂. Similar simulations performed with different temperatures, pressures and oxygen contents showed that no experimental conditions adapted to the aging setup ensured stable NO concentrations with time when combined with oxygen, even in small amounts. This is why, even if nitric oxide is mainly produced during ammonia combustion, as opposed to nitrogen dioxide, studying the effect of nitrogen dioxide on the oil is still relevant. The reactivity of nitric oxide alone without oxygen towards oils B was assessed. Oil B showed no evolution after 2 h at 135 °C with 10 bar of N₂ and 3000 ppm NO (Appendix B.1).

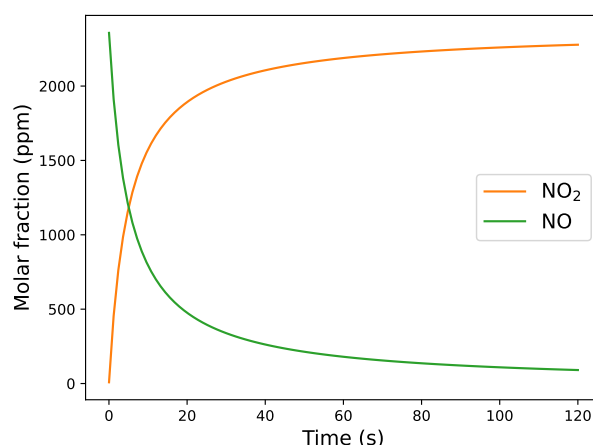


Figure 3.3: Simulation of the evolution of NO and NO₂ molar fractions in a perfectly stirred reactor at 135°C filled with 10 bar of air using Chemkin

For both oils, the rate of the pressure decrease with air and nitrogen dioxide greatly differed at the very beginning of the reaction, but then tended to align (Figure 3.2). The total reaction time was in the end decreased by 25 % with both oils with nitrogen oxides. This would be in line with the fact that nitrogen dioxide accelerates the initiation of the oxidation reaction, shortening the induction period, as suggested in [82,86]. This seemed to be confirmed by the evolution of the peak area of both oils (Figure 3.4), which increased rapidly for oils exposed to NO₂ and reached similar values at the end of the experiment when almost all the oxygen had been consumed. FTIR spectra showed no absorption bands characteristic of nitro groups, particularly around 1630 cm⁻¹, as defined in the standard for nitro-oxidation quantification [20].

The final oxygen and nitrogen contents are summarized in Table 3.3. For oil B, calculation of the ratio between the final content of oxygen in the oil and the amount of oxygen introduced in the reactor was close to 98 % for the three experiments under air, indicating that nearly all the available oxygen had each time reacted, as suggested by the stabilization of the pressure. The oxygen content of oil G was measured but its variation during the experiment was within the quantification error range, due to the already high initial oxygen content as a polyester oil. The final nitrogen content of the oils exposed to nitrogen dioxide suggests that some nitrogen atoms can be found in the oil phase and might have reacted with the hydrocarbons, and in

3.2. EFFECT OF NITROGEN OXIDES IN AIR

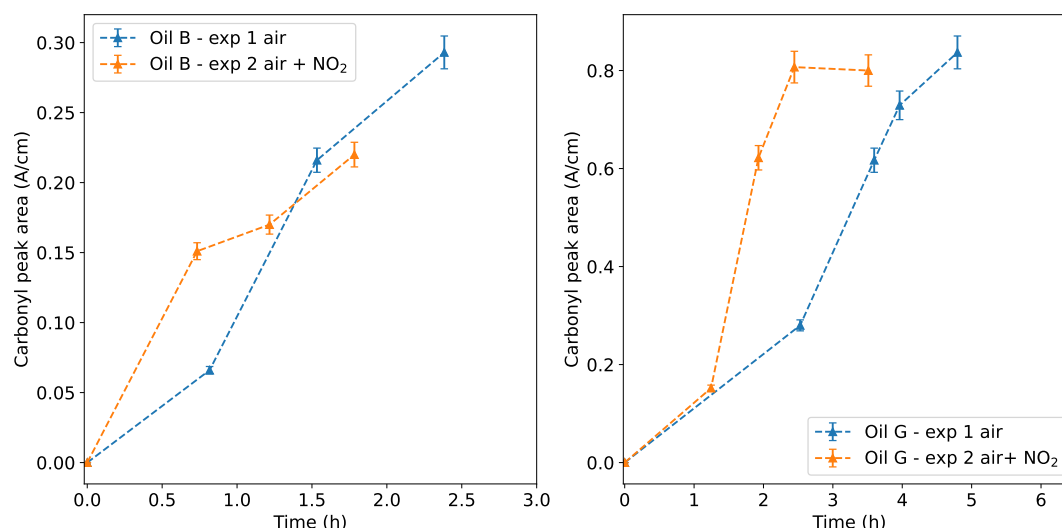


Figure 3.4: Increase in carbonyl peak area with time, under air and air + 1000 ppm NO₂ at 135 °C–10 bar. Oil B = group III mineral base oil, oil G = trimethylolpropane ester of carboxylic acid

greater amounts with the polyester oil. The low amounts of nitrogen contained in the oils after being exposed to air can be attributed to residual air bubbles trapped into the liquid.

Table 3.3: Total oxygen and nitrogen contents in oils B and G after exposure to three gas mixtures

Oil	Gas	Fresh Oil	Air	Air + NO ₂	Air + NH ₃
Oil B	Oxygen (%w/w)	≤ 0.0420	0.95 ± 0.05	0.83 ± 0.04	0.86 ± 0.04
	Nitrogen (mg/kg)	1.2 ± 0.1	5.7 ± 0.4	27 ± 2	214 ± 20
Oil G	Nitrogen (mg/kg)	0.8 ± 0.1	3.2 ± 0.2	47 ± 3	327 ± 20

For both oils, the final pressure was higher with nitrogen dioxide than with air, even though same amounts of oxygen had been introduced and measured in the final oils (Figure 3.2). This might be explained by a more important production of light oxidation production in the early stages of oxidation with nitrogen dioxide, counterbalancing the decrease of pressure due to oxygen consumption. The fact that the initiation of the oxidation reaction, via the abstraction of a proton on the hydrocarbon chain, is quicker with nitrogen dioxide than with oxygen might promote multiple initiation reactions and radical proliferation with a low selectivity towards stable tertiary carbon radicals. This might promote β -scission reactions over termination reactions and lead to higher amount of light first order oxidation products such as aldehydes or acids. This hypothesis could be verified using gas-chromatography analysis of the gas phase throughout the reaction.

The respective viscosity increase and decrease of oil B and G exposed to air with 20.9 % oxygen are lower than when exposed to pure oxygen under similar conditions, but still enable to discriminate aged oils from the fresh ones. Figure 3.5 shows that the viscosity of the oil B and G after exposure to air or NO₂ in air were similar. This means that the potential

3.2. EFFECT OF NITROGEN OXIDES IN AIR

effect of NO_2 on the oxidation and nitro-oxidation product types was not sufficient to have a significant impact on the viscosity under these conditions. However, it should be noticed that similar viscosities were obtained even though the reaction time was shorter by 25 % with NO_2 . A continuous air and NO_2 supply would surely result in an accelerated evolution of the viscosity with time, as it is the case in [17].

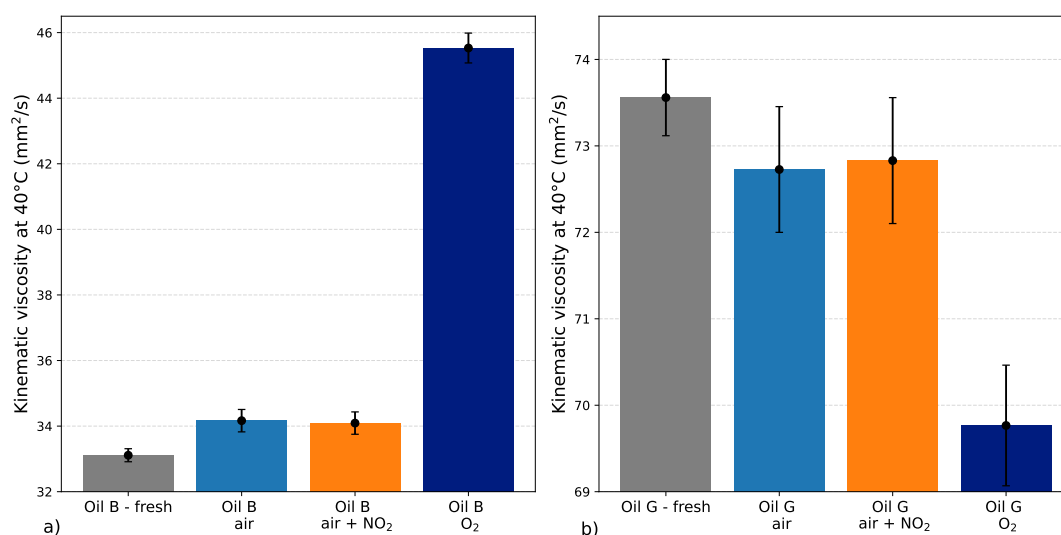


Figure 3.5: Kinematic viscosity at 40 °C of the fresh oils B and G and after aging under air, air + 1000 ppm NO_2 and pure O_2 at 135 °C–10 bar, samples collected 1 h after pressure stabilization. Oil B = group III mineral base oil, oil G = trimethylolpropane ester of carboxylic acid

These results show a clear impact of nitrogen dioxide on the oxidation rate of the base oils, and especially on the initiation step. Exposure to nitrogen dioxide even in trace amounts led to accelerate the initiation of the oxidation reaction, thus reducing the reaction time between a determined oxygen amount and oil volume. The rapid proliferation of radicals in the presence of NO_2 seems to promote the production of light oxidation products, as shown by a higher residual pressure and a lower carbonyl content in the liquid phase at the end of the experiments. Nitrogen dioxide greatly affects the liquid phase oxidation reaction even though few or no nitrogen-containing degradation products are found in the oils. This agrees with the work of Slavchov *et al.*, Coultas and Harris [19, 82, 86] in which they suggest that nitrogen dioxide accelerates the oxidation reaction by contributing to the production of radicals via the formation ester nitrates radical precursors. As the latter are unstable, they rapidly form and decompose, thus accelerating the propagation of radicals. They would also rarely be involved in termination reactions, explaining why few nitrogen-containing molecules are produced. Here, the mineral and polyester base oils were similarly affected. Under the experimental conditions of this study, nitrogen dioxide had no effect on the kinematic viscosity measured at the end of the experiments. Since the experiments

3.3. EFFECT OF AMMONIA IN AIR

were conducted in a closed reactor, this result can be attributed to the fact that the final viscosity was especially determined by the presence of oxygenated products in the liquid phase, which were found in same amounts with or without nitrogen dioxide. However, this suggests that a continuous gas supply, as in an engine, would result in a quicker increase in the viscosity with time. In the lubricant community, nitro-oxidation is quantified via the increase in the height of the absorption peak associated to N=O double bond [20], which was not observed here. Conclusions from these experiments point out that NO₂ can have deleterious impact even without producing nitro products.

3. Effect of ammonia in air

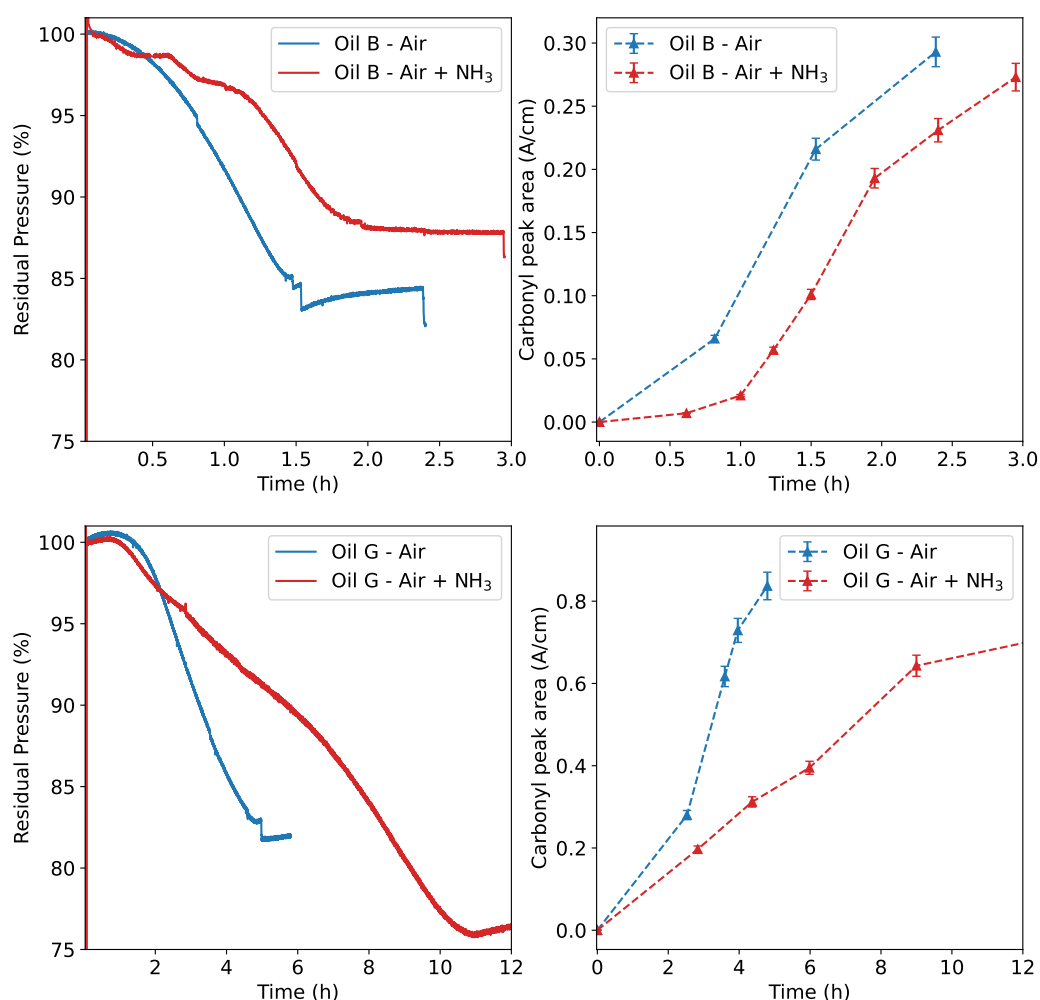


Figure 3.6: Residual pressure (left) and carbonyl peak area (right) with time for experiment conducted under air and air + 1.5% NH₃ at 135°C–10 bar. Oil B = group III mineral base oil, oil G = trimethylolpropane ester of carboxylic acid

3.3. EFFECT OF AMMONIA IN AIR

Subsequently, base oils were also exposed to gaseous ammonia in air to investigate how it could alter the standard liquid phase oxidation and/or modify the properties of the oils. As opposed to nitrogen dioxide, adding 1.5 % ammonia to the air mixture decreased the oxidation rate for both oils. This is deduced from both the slower evolution of the pressure, and the slower increase in carbonyl peak area (Figure 3.6). The reaction times were multiplied by 1.2 and 2.4 respectively for oils 1 and 2, indicating the polyester base oil was affected even more significantly. Agocs *et al.* had also measured slower oxidation rates for lubricants under ammonia atmosphere in [17]. In their work however, it was attributed to a lower oxygen content of the gas due to the high ammonia fraction (21.7 % in air). Here, the retarding effect can be attributed to ammonia unambiguously, as experiments were conducted with the same oxygen fractions.

As opposed to experiments with nitrogen dioxide, the evolution of the pressure with and without ammonia seemed to be similar at the beginning of the experiments, before diverging after a decrease of around 2.5 %. It might suggest that ammonia does not affect the initiation of the oxidation reaction but mainly reacts with acidic oxidation products or oxidation intermediates as soon as they start to be produced. The final nitrogen contents in both oils (Table 3.3) were significantly greater after exposure to ammonia. Like oxygen, the ratio between this final concentration and the nitrogen quantity introduced in the reactor as ammonia can be calculated. For oil B, this final quantity represented nearly 60 % of the nitrogen introduced. For oil G, the calculated ratio was greater than 1, which can be attributed to the error associated with calculating percentages with small figures. As the oils were sonicated for 10 min to remove gas bubbles prior to the elemental analysis, this high nitrogen content can be attributed to dissolved ammonia, or new kinds of nitrogen-containing degradation products. FTIR spectroscopy did not show any new absorption band characteristic of nitrogen-containing groups. However, adding ammonia to the reactive gas mixture resulted in a more advanced evolution of the viscosity for both oils (Figure 3.7). This indicates that in both cases, the final composition of the oil was different than when it was exposed to neat air. Oils might contain nitrogen-containing molecules, such as amides as it is hypothesized in [21], or dissolved ammonia taking part in low energy interactions, as suggested in [24]. One other hypothesis is that, as the oxidation reaction was slower, different oxidation products were formed, and in different proportions, affecting the final viscosity despite a very close total oxygen content. Besides, the final nitrogen content was higher for the polyester base oils, which could be explained by a higher affinity between ammonia and a more polar matrix.

3.4. SPECIATION OF NITROGEN

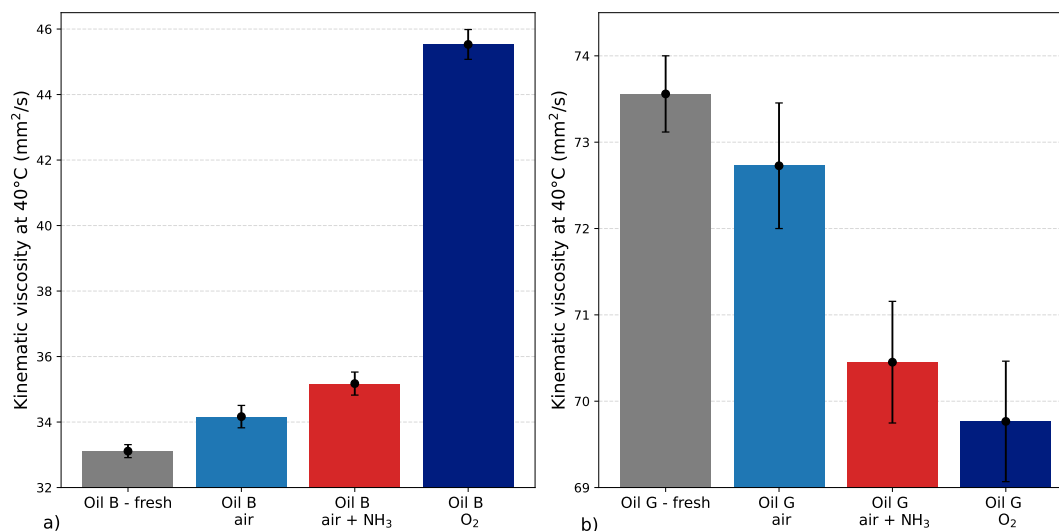


Figure 3.7: Kinematic viscosity at 40 °C of the fresh oils B and G and after aging under air, air + 1.5 % NH₃ and pure O₂ at 135 °C–10 bar. Oil B = group III mineral base oil, oil G = trimethylolpropane ester of carboxylic acid

Overall, these results clearly demonstrate that ammonia affects the process of liquid phase oxidation of both apolar mineral base oils, and polyester base oils. Ammonia seems to have an antioxidant effect, slowing down the oxygen conversion from gas into covalently bonded oxygen, as shown by both analysis of the pressure of the gas phase and the FTIR of the liquid phase. In addition, high final nitrogen contents and altered viscosity of the oils after exposure to ammonia compared to neat air indicate that some ammonia dissolves or reacts with the base oils as they undergo thermo-oxidative degradation. Both cases are deleterious as dissolved ammonia could increase the corrosivity of the oil towards metallic parts, and new types of degradation products could alter the friction coefficient, deposit tendency and other properties.

4. Speciation of nitrogen

The total nitrogen content in both oils increased after exposure to either NO₂ or NH₃ (Table 3.3). However, the concentrations remained very low, making it difficult to detect the associated nitrogenated molecules. For instance, no new absorption regions could be observed in FTIR in either case. To elucidate the nature of the nitrogen content in the oils after exposure to NO₂ and NH₃, oil samples were analyzed using GC2D/MS. As this in-depth analysis is time-consuming, it was carried out exclusively on samples of oil B, in anticipation of future engine tests planned with this specific oil.

4.1 GC2D/MS analysis

Using the methodology described in Section 2.1.3.7, molecular analysis was conducted on samples from oil B. Two dimensional chromatograms are displayed in Figure 3.8.

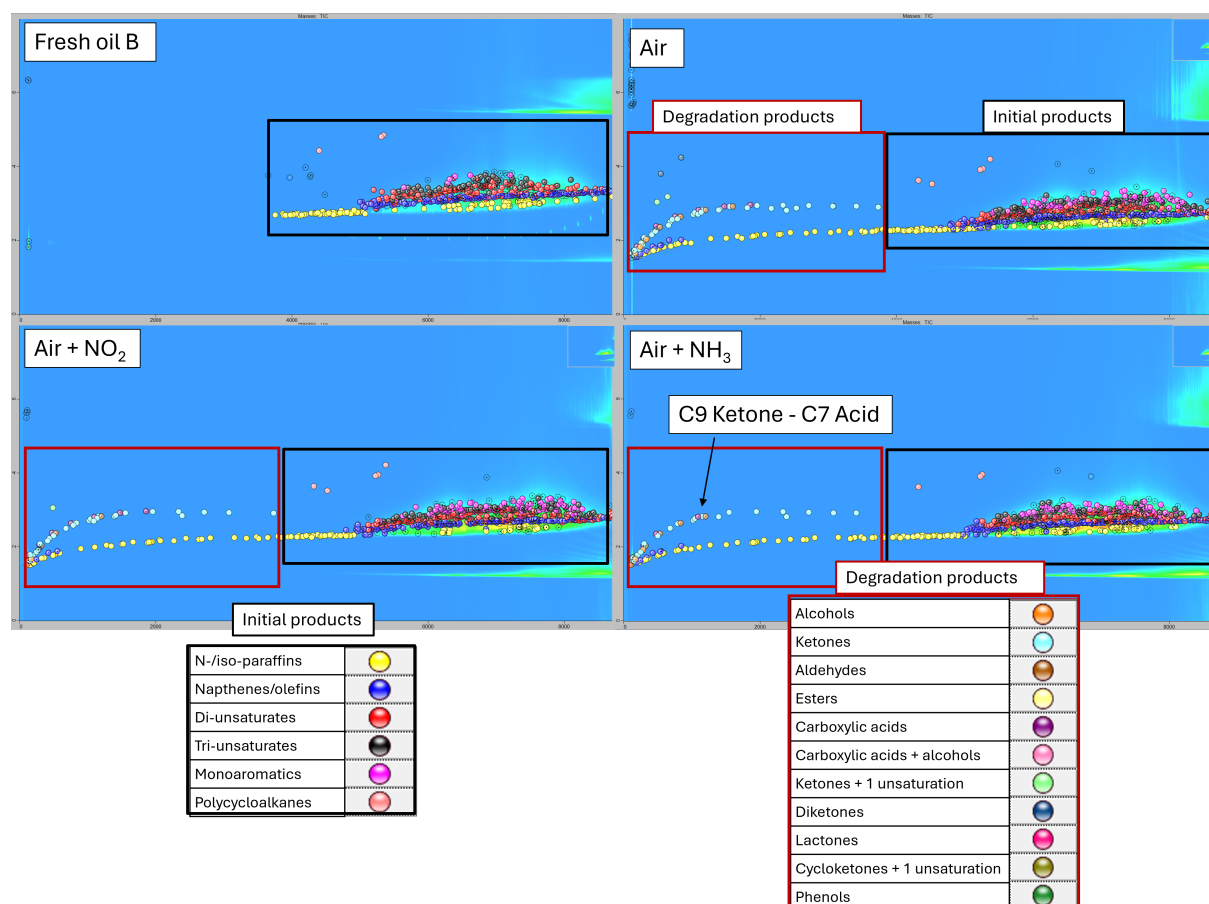


Figure 3.8: Total ion count chromatograms and product identification of oil B

Compared to aging under pure oxygen (Figure 2.24), aging under air resulted in similar types of products. Nonetheless, aging under air led to lower oxygen content and oxidation degree which results in several noticeable differences. Fewer ketones isomers could be detected after experiments under air, especially for ketones larger than C10, which were all identified as 2-ketones. This can be attributed to the lower oxygen availability in the reactive atmosphere, promoting a higher selectivity regarding radical formation. After experiments under oxygen, acids up to C16 could be detected, whereas only short acids up to C9 were detected here. Polycycloalkanes could still be detected after aging under air, as opposed to the experiment under oxygen, indicating the reaction was not sufficiently advanced for them to be completely depleted. Eventually, fewer complex products, such as diketones or cycloketones could be detected. Such products are likely to be formed under severe oxidizing atmosphere only. Similarly, no dihydrofuranones could be detected. This may be due to the fact that, during aging under oxygen, the oil remained in the reactor for 24 h, even though all the oxygen had reacted within the first 2 h. This prolonged exposure likely promoted intra- and intermolecular reactions between oxidation products in the absence of oxygen.

3.4. SPECIATION OF NITROGEN

With NO_2 or NH_3 very few differences could be noticed compared to neat air, and especially no nitrogenated product, could be detected. The sample exposed to NH_3 showed only shorter acids (up to C7) and fewer ketones types than other samples. This could be consistent with a slower reactivity. A targeted research of fragment ions characteristic of nitrogenated functions was implemented and led to hypothesize that nitriles may be present in the sample after aging with NH_3 (Appendix B.2). GC2D/MS analysis did not enable to identify specific nitrogenated degradation products.

4.2 Specific detection of nitrogen-containing compounds

In order to elucidate the speciation of nitrogen in oil B, and investigate its evolution during the reaction, elemental analysis was conducted on oil sampled at intermediate reaction times. Oil samples were analyzed with gas chromatography coupled to a Nitrogen Chemiluminescence Detector (GC/NCD). Figure 3.9a shows that the total nitrogen content increased with reaction time, along with the total oxygen content. For both gases, the uptake was gradual. After one hour, circa 19 % and 33 % of the nitrogen added as ammonia and oxygen were respectively found in the liquid phase. Regarding oxygen, this gradual increase correlated with the increase in carbonyl peak area, highlighting the benefits of using this parameter as an indicator of the oxidation reaction. GC/NCD analysis of the oil samples 1, 2 and 3 enabled to separate products according to their molecular weight while limiting the detection to the products containing nitrogen atoms. Chromatograms are displayed in Figure 3.9b. Interestingly, the chromatogram of the first sample taken after one hour showed a very intense first peak and a rather flat signal for longer retention times. As products were eluted according to their volatility, short retention times correspond to light products. Therefore, it suggests that, at this intermediate reaction time, most of the nitrogen-containing molecules in oil 1 were very light. It could be dissolved ammonia or light gases, accounting for a total nitrogen content of $59 \pm 3 \text{ mg/kg}$. For sample 2, collected 12 min later, this first peak was even more intense, but a growing “hump” on the chromatogram indicated that a wide diversity of larger products also contained nitrogen atoms. After 3 h, the intensity of the first peak was significantly reduced—divided by 20—and the chromatogram clearly indicated that the sample contained a wide variety of nitrogen-containing products. The large range of retention times suggested the presence of both small and large degradation products. Heavy nitrogen-containing molecules could be partly responsible for the significant viscosity increase observed in Figure 3.7. Given the chromatograms obtained at different reaction times with a detection specific to nitrogen-containing molecules, it is clear that the nitrogen speciation evolved from dissolved gaseous molecules at intermediate reaction times to molecular nitrogen. The great variety of products with nitrogen groups evidenced here partly explains why the detection of these products using GC2D/MS was particularly challenging, considering each molecule type was only present in very low concentration. These findings contributed to a more precise interpretation of the global nitrogen content and gave a deeper understanding of the interaction between ammonia and the mineral base oil in the presence of oxygen under heating.

3.4. SPECIATION OF NITROGEN

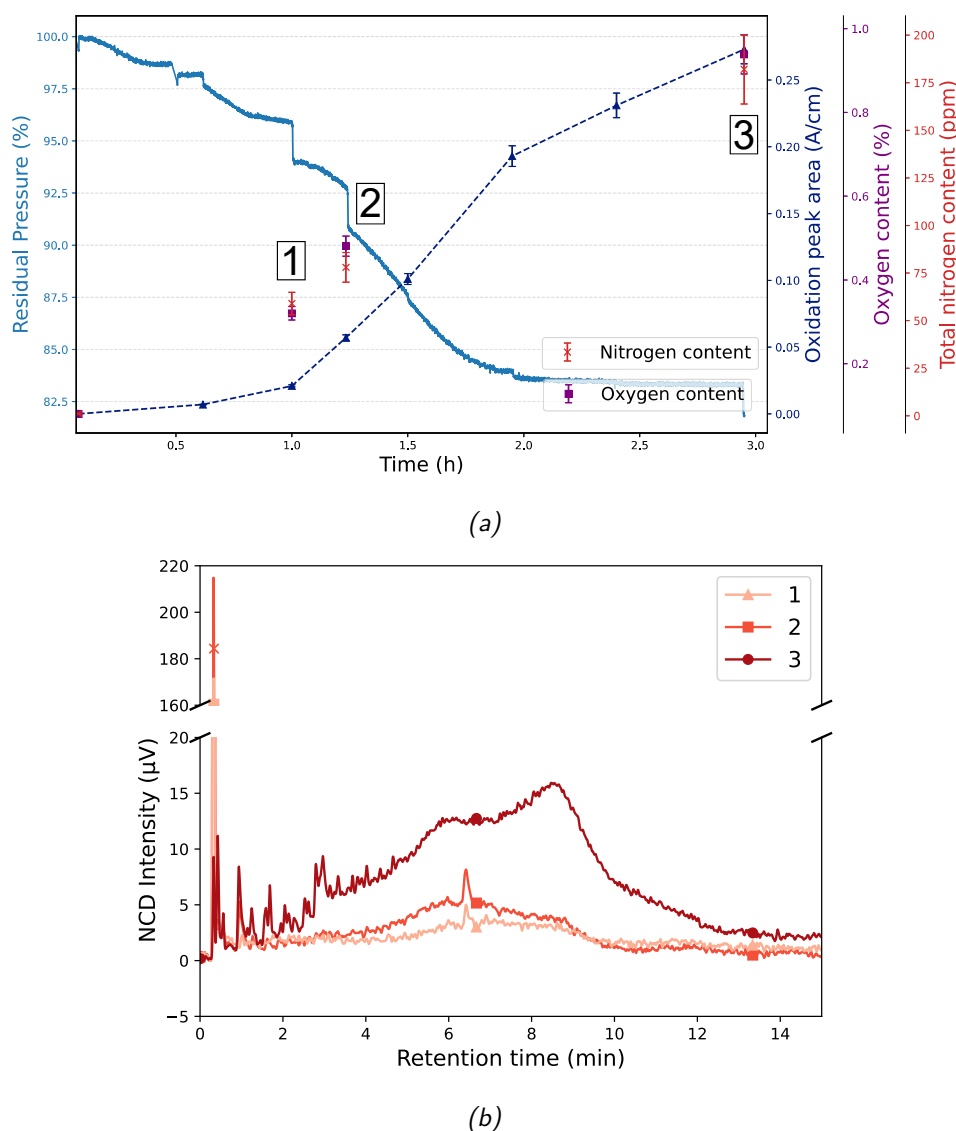


Figure 3.9: Evolution of the nitrogen content and its speciation in oil B with time, experiment under 10 bar air + 1.5 % NH_3 at 135 °C. a) Evolution of the total nitrogen and oxygen content along with the pressure decrease. b) GC/NCD at three reaction times, specific detection of nitrogen containing compounds

The same analysis was conducted on the oil sample exposed to NO_2 and with a total nitrogen content of 27 ± 2 mg/kg of nitrogen. The NCD chromatogram in Figure 3.10, compared with the sample after exposure to ammonia, showed the presence of nitrogen containing molecules in this sample two. The very low concentrations of these products in the considered sample make it difficult to proceed to identification with GC2D/MS. As the low nitrogen content obtained here is the result of the small amount of reactive NO_2 under the selected experimental conditions, nitrooxidation products could surely be identified in oil samples exposed to a continuous flow of NO_2 and O_2 , or higher NO_2 concentrations, boosting their concentration.

3.5. EFFECT OF MIXING WITH AN AMMONIA SOLUTION

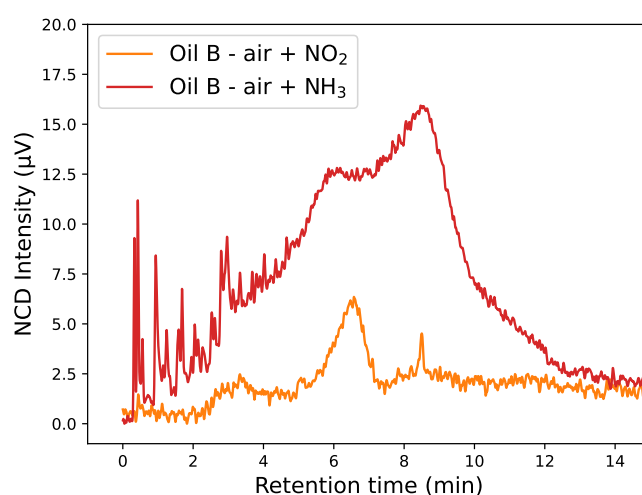


Figure 3.10: GC/NCD of oil B after exposure to air + 1000 ppm NO_2 at 135 °C–10 bar and air + 1.5 % NH_3

Coupling GC to a detector specific of nitrogen molecules enabled to evidence the progressive formation of nitrogen-containing degradation products when a mineral oil was exposed to ammonia and oxygen under heating. However, due to the low concentration of these products under the experimental conditions chosen, they could not be detected and identified using GC2D/MS, and no specific absorption band could be observed with FTIR spectroscopy.

In order to increase the nitrogen content in the samples, experiments under more severe degradation conditions were conducted. Pressure in the reactor was first increased to 16 bar, the maximum of the gas pressure regulation valve. It led to a total nitrogen content of 344 ± 25 mg/kg, which corresponds to 1.6 times the final content obtained with 10 bar, but was still insufficient to detect nitrogen-containing degradation products. An experiment was then conducted with oil B, directly mixed with 2 mL of a 14 %w/w ammonia solution, in order to further increase ammonia exposure. Moreover, mixing with an ammonia solution also allowed us to reproduce the combined effect of moisture and ammonia in the engine. Experimental results and details about this experiment are presented in the following section.

5. Effect of mixing with an ammonia solution

5.1 Reaction conditions

The regular protocol had to be adapted for this experiment with aqueous ammonia. As usually done, 50 mL of oil were loaded in the reactor, which was subsequently closed, purged and filled with 2 bar N_2 at room temperature. After heating, it reached a final pressure of 4 bar. In order to prevent ammonia to be vented out during the purges usually conducted after the heating step (Section 2.1.2.3), 2 mL of ammonia solution at 14 % w/w were directly

3.5. EFFECT OF MIXING WITH AN AMMONIA SOLUTION

introduced in the reactor using a syringe when target temperature of 135 °C was reached. 10 bar of O₂ were then immediately filled in the reactor, reaching a total final pressure of 14 bar. Under these conditions, water remains in the liquid state [157]. According to the work of Clifford *et al.* on aqueous ammonia solutions [158], at 14 bar and 135 °C, about 75 % w/w NH₃ of an ammonia solution should be in the gas phase. This would imply that the ammonia partial pressure could reach up to 14 % of the gas phase, ten times more than in previous experiments. However, their data cannot directly be applied to the system presented here, as it does not take into account the oil matrix and the gas entrainment stirrer. A reference test was also conducted with 2 mL of pure water.

5.2 Monitoring of the reaction

Figure 3.11 shows the evolution of the total pressure in the reactor during the reference test under pure oxygen, and tests conducted with 2 mL of pure water or ammonia solution in pure oxygen atmosphere. For tests conducted with ammonia solution or water, the total pressure was initially 14 bar, of which 10 bar of O₂. For the three conditions, the pressure reached a plateau after 2 h indicating the consumption of most of the oxygen. The residual pressure at the end of the test was higher for tests with water, as inert N₂ remained in the gas phase. In parallel, carbonyl peak area evolved similarly under all conditions (Figure 3.11 b). In this experiment, ammonia did not retard the oxidation, possibly because the oxygen concentration was so high that it determined the kinetic rates of radical initiation and propagation. However, carbonyl peak area in the final sample was significantly lower for the experiment with ammonia, and slightly lower for the experiment with water. This is consistent with the final oxygen content, which was lower for the oil with ammonia (Table 3.4). This was attributed to corrosion happening during the experiment, as will be discussed in Section 3.5.5. Besides, no specific evolution of the FTIR spectrum was observed with NH₃ or H₂O compared to pure O₂.

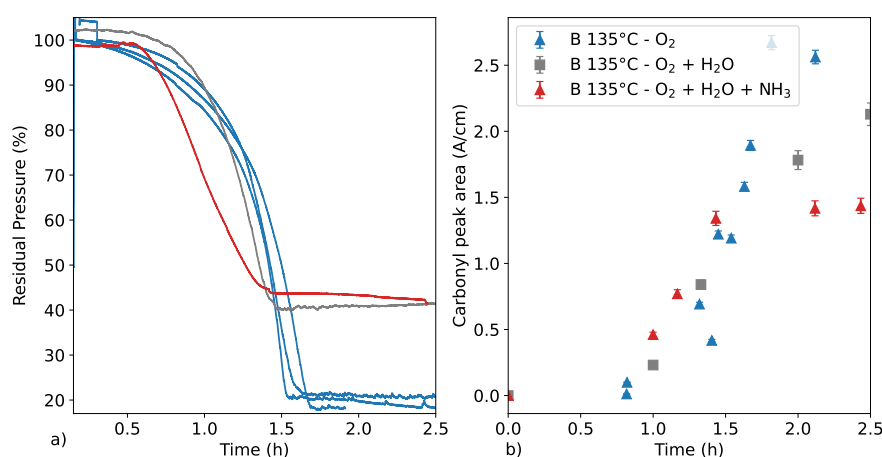


Figure 3.11: a) Residual pressure and b) carbonyl peak area with time for experiments conducted under O₂ at 135 °C–10 bar O₂ (blue), 2 mL water (gray) and with 2 mL ammonia solution (red)

3.5. EFFECT OF MIXING WITH AN AMMONIA SOLUTION

Table 3.4: Total oxygen and nitrogen contents in the oil after experiments under pure oxygen and with 2 mL of water or aqueous ammonia solution

Gas	Fresh Oil	O ₂	O ₂ + H ₂ O	O ₂ + NH _{3(aq)}
Oxygen (%w/w)	≤ 0.0420	3.42 ± 0.17	3.51 ± 0.18	2.61 ± 0.13
Nitrogen (mg/kg)	1.2 ± 0.1	≤ 1.13	not measured	1170 ± 70

5.3 Molecular analysis

After exposure of the mineral oil to a higher concentration of ammonia, its nitrogen content reached more than 1000 mg/kg (Table 3.4). Similarly to when the sample was exposed to gaseous ammonia, the formation of a large variety of nitrogen-containing products exceeding the size range of the molecules of the fresh oil was demonstrated using GC/NCD (Figure 3.12).

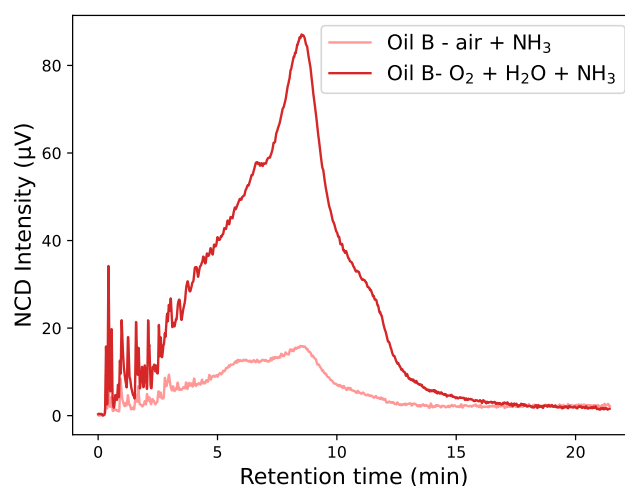


Figure 3.12: NCD Chromatogram of oil B after aging at 135 °C–10 bar O₂ with 2 mL ammonia solution

Despite the high nitrogen content, nitrogenated molecules could not unambiguously be detected and identified using GC2D/MS (Figure 3.13). Some differences compared to aging under pure oxygen under similar conditions (Figure 2.24) could however be noticed: more complex products could be detected, such as cyclic ketones, and more lactones ; a greater diversity of ketones could also be detected ; eventually, short olefins were also detected in addition to short paraffins. This might be attributed to the catalytic activity of metals.

To underline the potential presence of nitrogen-containing compounds, a targeted research of ions specific to nitrogenated molecules was then implemented. Table 3.5 summarizes the researched target ions. As can be seen in Figure 3.14, regular patterns with increasing chain lengths were observed for the combination of ions characteristic of amides, and the ion characteristic of nitriles, as observed in the sample exposed to air and 1.5 % NH₃. The intensity of the signal of the ions characteristics of amines was the same as noise level and

3.5. EFFECT OF MIXING WITH AN AMMONIA SOLUTION

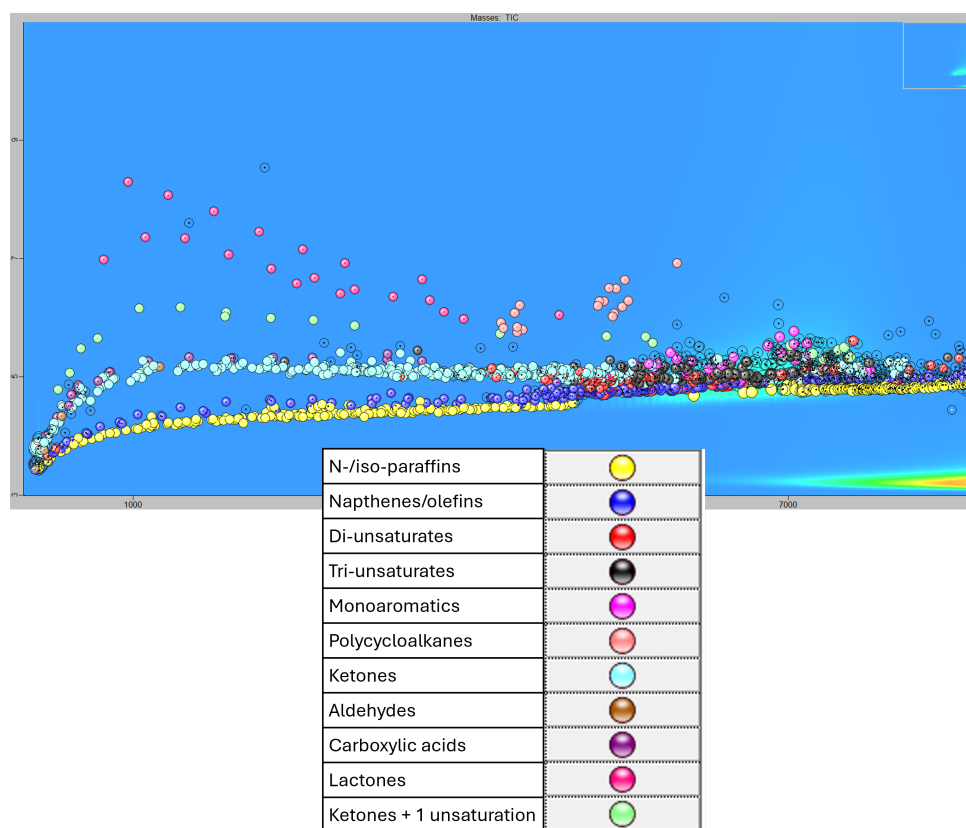


Figure 3.13: Total ion count chromatogram of oil B after aging at 135 °C–10 bar O_2 with 2 mL ammonia solution

Table 3.5: Mass-to-charge ratios selectively searched to investigate the presence of fragments specific to nitrogen compounds

Family	Researched ion	Formula	Ref.
Amides	m/z 59.0366	C ₂ H ₅ NO	[159]
	m/z 72.0444	C ₃ H ₆ NO	
Nitriles	m/z 82.065	C ₅ H ₈ N	[159]
Amines	m/z 72.081	C ₄ H ₁₀ N	[160]
	m/z 58.065	C ₃ H ₈ N	
	m/z 44.049	C ₂ H ₆ N	

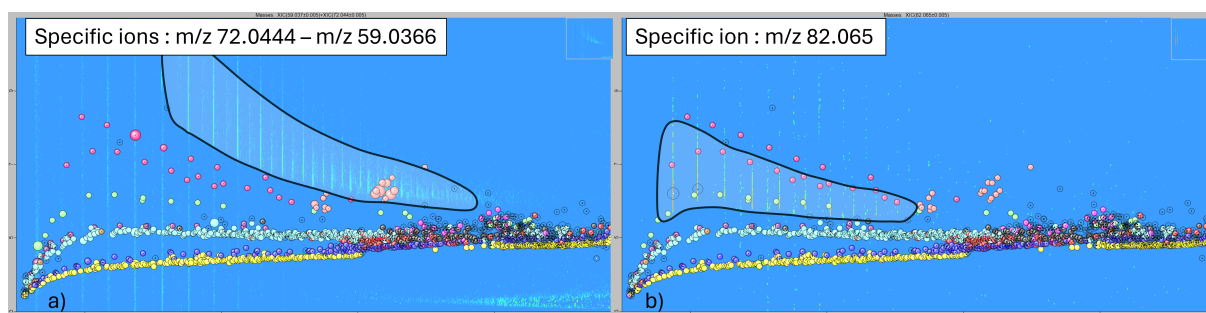


Figure 3.14: Target research of specific ions of a) amides b) nitriles

3.5. EFFECT OF MIXING WITH AN AMMONIA SOLUTION

showed no specific cluster or pattern. Still, their presence cannot be completely excluded, as detecting amines with GC/MS can be challenging because they tend to rapidly lose their nitrogenated fragment, and thus result in similar ions as a hydrocarbon chain. Elution zones where ions specific to amides and nitriles were found were consistent with what could be expected considering the polarity of such molecules. We could therefore make the assumption that, under these experimental conditions, amides and nitriles were probably formed. Evidence of amides formation was also found by Rao *et al.* [31] when they exposed a fully-formulated lubricant with ammonia solution at 80 °C over 288 h. In this study, they were originated from the carboxylic acids in the additives, but in our study, carboxylic acids from the oil oxidation were also present and likely to react.

5.4 Possible synthesis pathways for amides and nitriles

In order to appraise this hypothesis of amides and nitriles production, synthetic pathways on these compounds were investigated in the literature. Li *et al.* and Takashi *et al.* [5, 161] described the multiple synthetic routes for amides: depending on the experimental conditions, they can derive from the hydration of nitriles, aminolysis of esters, oxidative amidation of aldehydes and alcohols, and the amidation of carboxylic acids, involving amines or ammonia. All these reactions require the use of specific catalysts to optimize the yields, which generates active research [162–164]. However, catalytic effect of the reactor wall in our experiment, even though not optimized, cannot be excluded. Several amide synthetic pathways, involving different oxidation products and ammonia can then be considered plausible. Regarding nitriles, they can also derive from a reaction between alcohols and ammonia, but with a very low yield [165]. The use of an oxidant is required to promote the reaction, and oxygen can play this role, as in [165]. One possible synthesis route for nitriles is then an aerobic oxidative route involving alcohols or aldehydes, ammonia and oxygen, with catalysts. If amides can be obtained from nitriles, the inverse reaction is also possible under different conditions [166]. The above studies were conducted under controlled reaction conditions, in specific solvents and with the use of complex catalysts. However, the temperature ranges of these synthetic routes are consistent with the 135 °C reached in our reactor, and metals from the reactor wall could probably act as catalysts, especially considering corrosion occurred during this experiment. For both families, plausible synthetic pathways involving oxidation products and ammonia can then be considered. Synthesis of these products could also involve radicals directly. For instance, Erman *et al.* [167] patented a synthesis of nitriles from aldehydes and ammonia, promoted by hydroperoxides.

5.5 Corrosion and deposits

During the test conducted with ammonia solution under oxygen, it was noticed that the color of oil samples evolved more rapidly than under pure oxygen and that samples seemed

3.5. EFFECT OF MIXING WITH AN AMMONIA SOLUTION

to contain impurities (Figure 3.15 a and b). Indeed, at the end of the reaction, the reactor wall was covered with reddish deposits insoluble in organic solvents, while it was clean in other experiments. Figure 3.15 c) shows the empty reactor after the experiment with water: one can notice a layer of remaining oil, and dark regions corresponding to clusters of highly polar products, as usually observed under other conditions. In contrast, Figure 3.15 d) is a picture of the reactor after the experiment with aqueous ammonia showing important deposits.

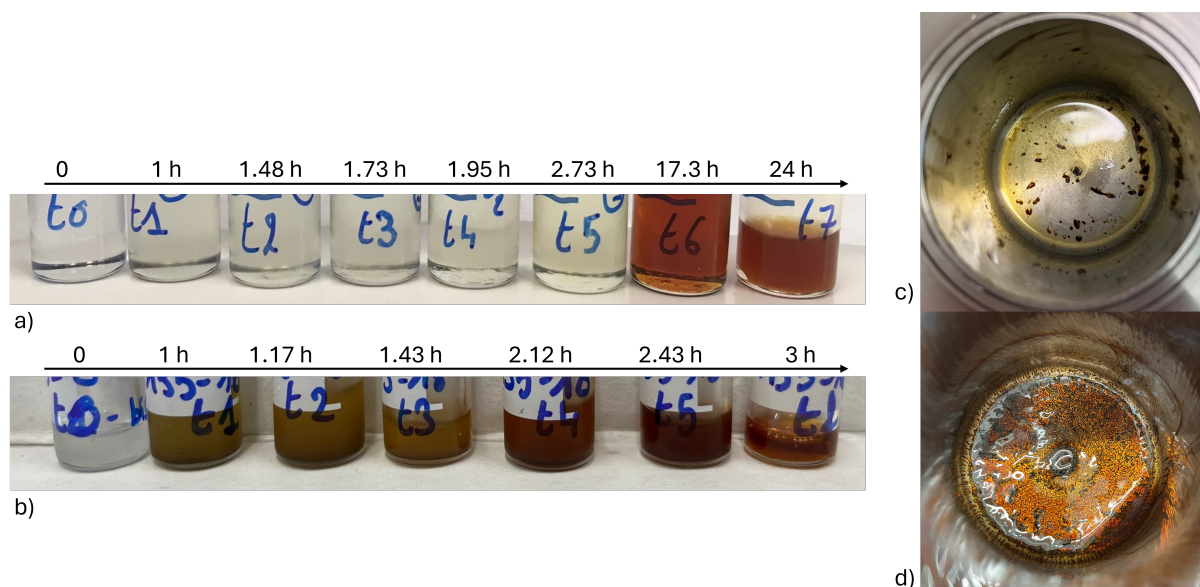


Figure 3.15: Aspect of oil samples a) under pure O₂, b) under O₂, and mixed with 2 mL ammonia solution. Aspect of the reactor after c) O₂ with 2 mL water, d) O₂ with 2 mL ammonia solution

ICP-OES of the oil samples confirmed the high metal content in the oil after the aging, and in the deposit (Table 3.6). Constitutive elements of Hastelloy, which the reactor is made of, were especially looked for. In particular, nickel, chromium and molybdenum, the main constituents of the alloy, were found in large amounts, both in deposits and in the oil. Iron and tungsten were also found in significant amounts. Even some titanium, coming from the stirrer helix was detected. Corrosion and formation of metal oxides on the walls could explain the lower oxygen content in the oil aged under O₂ and the ammonia solution compared to experiments under O₂ alone and with water, where no corrosion was observed (Table 3.4). When corrosion occurs, oxygen is indeed involved in the formation of metal oxides, leaving less oxygen available for the oxidation of the liquid base oil.

To conclude, at 135 °C, in the presence of 10 bar of O₂ and 2 mL of ammonia aqueous solution, corrosion of the reactor wall and stirrer was observed, even though Hastelloy is considered resistant to ammonia. This is probably due to a cocktail effect between ammonia, water and oxygen, as corrosion was neither observed when water was added under similar conditions, nor in experiments with gaseous ammonia. At low concentrations, and in dry conditions, ammonia is not corrosive towards nickel-chromium alloys such as Hastelloy [168, 169]. However, high oxygen pressure can lead to promote corrosion and solubilization of metallic ions. These ions

3.6. DISCUSSION–INTERACTION BETWEEN OXYGEN, AMMONIA, AND A MINERAL OIL DURING ACCELERATED AGING

Table 3.6: Metal content in oil B and collected deposits after experiments under O_2 with 2 mL ammonia solution

Metal	Fresh oil	Oil–final sample	Deposit
Co ($\mu\text{g/g}$)	≤ 5.1	≤ 4.7	65 ± 5
Cr ($\mu\text{g/g}$)	≤ 7.7	67.8 ± 4	2800 ± 200
Fe ($\mu\text{g/g}$)	≤ 5.1	37.4 ± 5	1120 ± 80
Mo ($\mu\text{g/g}$)	≤ 3.6	96 ± 6	2610 ± 180
Ni ($\mu\text{g/g}$)	≤ 5.1	451 ± 33	14100 ± 1000
Ti ($\mu\text{g/g}$)	≤ 3.6	8.2 ± 4	274 ± 19
W ($\mu\text{g/g}$)	≤ 10.2	26.5 ± 10	214 ± 15

may form stable complexes with ammonia, such a $[\text{Ni}(\text{NH}_3)_6]^{2+}$, which can enhance the ion solubilization and result in severe corrosion. This highlights the necessity to assess material compatibility in systems operating in contact with ammonia, especially in humid environment, as it is the case in engines. For following experiments, another reactor was used in order to prevent any catalytic effect of the degraded metallic wall.

6. Discussion–interaction between oxygen, ammonia, and a mineral oil during accelerated aging

During accelerated aging tests conducted under air and gaseous ammonia, an antioxidant effect of ammonia was observed, leading to a slower oxygen consumption by reactions in the liquid phase. This was quantified by a slower decrease of the pressure inside the reactor along with a slower increase in carbonyl peak area and other regions associated with oxidation products. Analysis of the elemental composition of the mineral oil at different reaction times showed that both nitrogen and oxygen progressively migrated from the gas phase to the liquid phase. FTIR was not sufficient to identify and monitor the evolution of nitrogen-containing chemical groups in the oil, leaving unresolved the speciation of the measured nitrogen content at this stage. However, a more detailed chromatography analysis with specific detection of nitrogen-containing molecules enabled to refine this result. We showed nitrogen speciation was evolving from dissolved ammonia and light species towards molecular nitrogen over a size range larger than the original mineral oil. Meanwhile, experiments conducted under pure O_2 and with 2 mL of ammonia solution also resulted in the production of nitrogen-containing molecules. Molecular analysis of the sample led us to hypothesize that amides and nitriles of different chain lengths were formed. Several plausible synthesis pathways for such molecules could be found in literature. They involve different oxidation products, ammonia and oxygen, and might also involve hydroxyl or hydroperoxy radicals. Taking into account these findings led us to formulate following hypothesis about the interaction between oil and gaseous ammonia: at short times, gaseous ammonia is insoluble in the oil due to a large polarity difference, and it does not seem

3.6. DISCUSSION-INTERACTION BETWEEN OXYGEN, AMMONIA, AND A MINERAL OIL DURING ACCELERATED AGING

to affect the initiation of the oxidation reaction. Then, ammonia's affinity for the hydrocarbon matrix increases with time as polar and acidic products start to accumulate in the oil under heating and exposure to oxygen. This leads to a progressive ammonia uptake, increasing along with the oxygen uptake. Dissolved ammonia can then react as a base with oxidation products or with radicals. These reactions do not seem to be selective, as suggested by the numerous peaks on the GC/NCD chromatogram indicating the detection of varied nitrogen-containing molecules. Some of these products might contain amides and nitriles groups, but other families might also be present. Reactions between oxidation intermediates and ammonia could explain the slower oxidation rate. Ammonia could have a scavenging effect towards the hydroxyl and peroxy radicals, slowing down the radical propagation. Besides, as the synthesis of nitrile from alcohols or aldehydes and ammonia requires oxygen, it might also compete with oxygen attack on hydrocarbons. In addition, reactions between oxidation products and ammonia could stabilize these products and prevent further chain reaction. Finally, if amines were produced, they could also act themselves as aminic antioxidants, whose chemistry is described in [170]. The production of new types of degradation products is probably associated with the greater viscosity evolution measured with ammonia than with air, despite similar oxygen contents. The retarding effect and the final nitrogen contents were more important for the polyester base oil. This might be explained by a higher affinity of ammonia with this slightly polar matrix even before the initiation of the oxidation reaction.

Figure 3.16 presents a schematic summary of the proposed degradation mechanism of a mineral base oil exposed to oxygen and ammonia in a closed, stirred, and heated reactor.

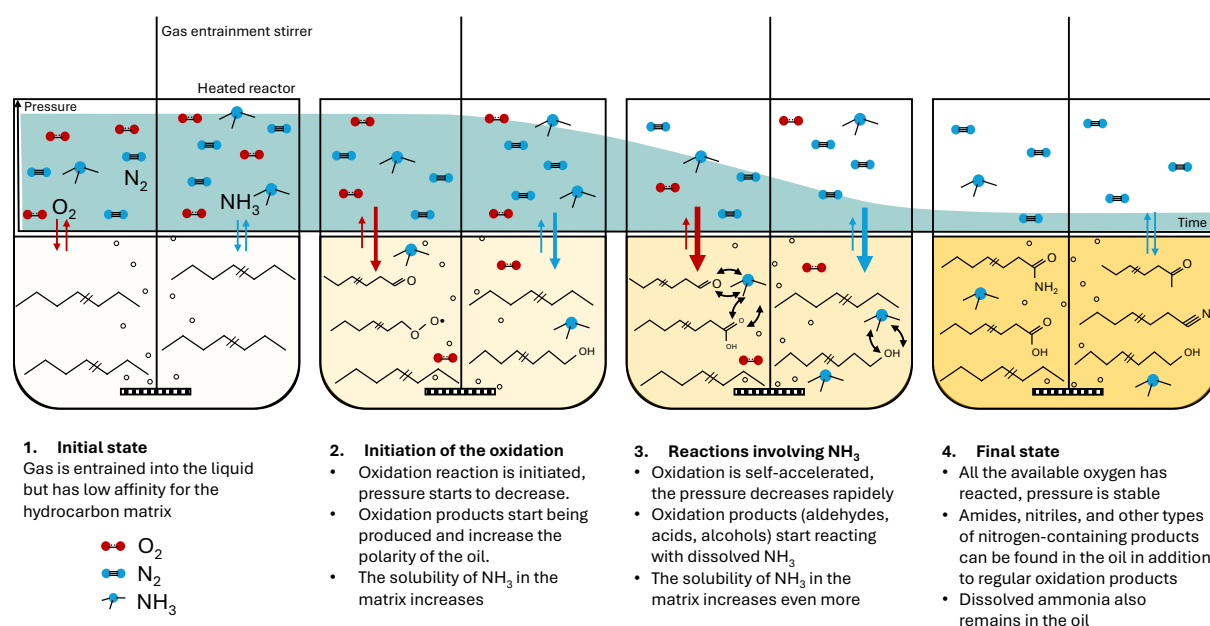


Figure 3.16: Proposed degradation pathway of a mineral base oil under ammonia and oxygen exposure

7. Conclusion

In Chapter 2, a methodology to implement accelerated aging of engine base oils had been developed and assessed under reference conditions with pure oxygen. In this chapter, the methodology was applied with gas mixtures representative of what lubricants could be exposed to during the operation of engines fueled with pure ammonia and blends. A mineral base oil and complex polyester were exposed to nitric oxide, nitrogen dioxide and ammonia in air in a pressurized stirred reactor, and characterized at different reaction times. The main outcomes of this chapter can be summarized as follows:

- NO_2 accelerates the oxidation rate, especially the initiation, promoting the production of light oxidation products,
- NO_2 is an important player in the oxidation reaction even though very few to no termination products accumulate,
- On the other hand, NH_3 can partly be dissolved in hydrocarbon base oils and progressively react with its components forming products of different types and size,
- The reaction between NH_3 and oxidation intermediates leads to slower oxidation rate,
- The presence of new nitrogen-containing products results in more advanced viscosity evolutions compared to neat air.

Further studies would be beneficial to improve understanding of the consequences of the high production of NO during ammonia combustion on the degradation of engine oils. The setup developed here could be used to proceed to more favorable nitro-oxidation conditions to try and identify reaction intermediates and termination products, to refine the reaction mechanism. To do so, several parameters could be modified: aging could be conducted under higher nitrogen oxide contents, at lower temperatures, or with a continuous gas supply. The implementation of a gas phase analysis to monitor the reactive gases and light oxidation products would also enable a deeper comprehension. Meanwhile, it is one of the first study to demonstrate new base oil degradation mechanisms associated to ammonia exposure under lab conditions. This brings out the need for further work on the topic of ammonia reactivity with oils in the context of ammonia engines. As the chemical composition of lubricants is directly linked to their tribological properties and the way they can ensure efficiency and durability of the engines, gaining knowledge on this topic is critical for the launch and safe operation of ammonia engines. This work points out that apart from the reactivity between some additives and ammonia, which could be handled via a change in the additives' chemistry, base oils themselves can be affected by ammonia contamination. As nitrogen dioxide and ammonia seem to have opposite effects on the oxidation rate, it would be interesting to expose the oils to a mix of both gases. It is likely that effects would not counterbalance but rather mutually worsen. Nitrogen dioxide could indeed accelerate the production of oxidation products, accelerating the ammonia uptake, but this remains to be tested.

3.7. CONCLUSION

The major advantage of accelerated aging is to enable to control the experimental conditions and thus isolate different phenomena. However, said conditions are sometimes quite different from the application conditions. Here, as discussed in Section 1.3.2, the implemented conditions do not exactly reproduce the engine conditions. This is why, to confront the obtained results with real applications and to evaluate the consequences on an evolution of the oil on the engine operation, engine tests experiments were conducted to pursue this work. Next chapter presents the evolution of three oils in an ammonia research engine: a fully formulated lubricant, the group III mineral oil B, and oil B after a pre-aging step performed in laboratory conditions.

Chapter 4

Investigating lubricants base oils evolution during engine operation

4.1	Experimental section	128
4.1.1	Engine test bench	128
4.1.2	Preparation of the pre-aged base oil	133
4.1.3	Properties of the pre-aged base oil and between-day repeatability	134
4.2	Evolution of engine oils during engine operation with methane and ammonia	135
4.2.1	Evolution at the macroscopic scale	135
4.2.2	Molecular evolution of the base oils	146
4.3	Discussion—evolution of base oils under engine conditions	149
4.4	Conclusion	151

4.1. EXPERIMENTAL SECTION

In Chapter 3, the reactivity of base oils was investigated under accelerated aging conditions. In particular, studying literature on lubricant degradation mechanisms alongside ammonia combustion characteristics revealed that nitrogen oxides and unburned ammonia could have deleterious effects on lubricant properties over time. A mineral and a polyester base oils were then exposed to oxygen, nitrogen oxides and ammonia in laboratory conditions. Their evolution with time under such conditions was investigated. It showed that nitrogen dioxide could significantly accelerate the oxidation process, while ammonia could have an antioxidant effect. Degradation mechanisms involving a mineral oil, oxygen and ammonia, hitherto poorly documented in literature, and leading to nitrogen-containing functional groups were uncovered. In this chapter, the evolution of oils during engine test experiments was investigated. A single-cylinder, spark-ignited engine was operated with ammonia and methane alternatively with three different oils. A specific 2 L crankcase was designed to enable oil sampling, and facilitate the detection of possible contaminants and degradation products. A commercial fully-formulated lubricant and a group III mineral base oil were tested in this study (oil B). In order to study more severe degradation degrees, and thereafter assess the impacts of a degraded oil on engine operation while limiting operating hours, a sample of the group III mineral base oil was also pre-aged under laboratory conditions and directly used in the engine. Oil samples were characterized overtime using the analytical workflow implemented in Chapters 2 and 3. Results were interpreted in light of what was learned during accelerated aging under controlled conditions. This chapter successively describes the engine setup and engine operating conditions, the pre-aging of the mineral base oil, and finally presents results depicting the evolution of the oils during the engine tests.

1. Experimental section

1.1 Engine test bench

1.1.1 Engine characteristics

The engine used for the experiments is a large stroke spark ignition single-cylinder with the specifications compiled in Table 4.1.

Table 4.1: Engine specifications

Model	PSA EP6
Stroke	115 mm
Bore	77 mm
Connecting rod length	177 mm
Axis offset	0.5 mm
Compression Ratio	12:1
Displacement Volume	535.5 cm ³
Ignition	Spark Ignition

4.1. EXPERIMENTAL SECTION

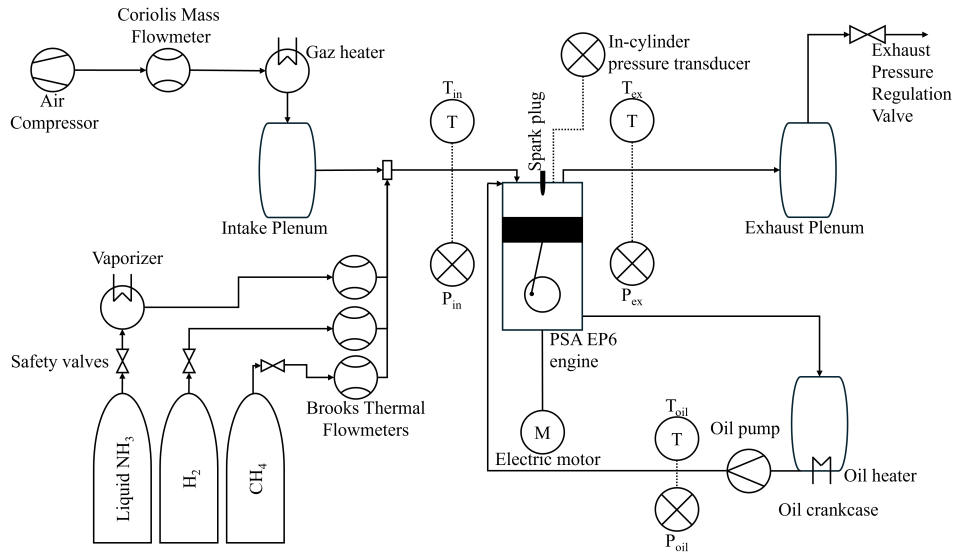


Figure 4.1: Schematic diagram of the engine setup

The schematic diagram of the engine is shown in Figure 4.1. An electric motor imposed the engine speed, which ranged between 1000 and 2000 rpm. Intake and exhaust pressures and temperatures were monitored using absolute pressure transducers and type K thermocouples. A cooled piezoelectric pressure transducer measured the in-cylinder pressure with a 0.1 CAD resolution. The absolute in-cylinder pressure was retrieved by equalizing it with the mean absolute intake pressure 20 CAD after intake valve opening. Liquid ammonia, from Air Liquide, was vaporized thanks to an evaporator at 60 °C. The spark plug used was the original one, with a coil charging time set to 2 ms, corresponding to an energy of about 80 mJ. The air flows, preheated to the intake temperature, were measured and controlled using Brooks thermal mass flow meters, with an accuracy of $\pm 0.7\%$. The spark ignition timing was optimized for each operating conditions. The temperature and pressure of the oil before it entered the engine was also monitored. It was set to 5 bar, and the temperatures reached 78 °C as the crankcase was kept at 90 °C.

1.1.2 Crankcase

For the means of this study, a small crankcase was specifically designed. It required a tenth of the oil usually required (2 L instead of 20) which showed two major advantages: minimizing the pre-aged oil volume to supply, and increasing the concentration of degradation products and metals, facilitating their detection. A photo of the crankcase is shown in Figure 4.2. The oil was heated on the bottom of the container with a heating resistance maintained between 90 °C and 100 °C, pumped and filtered before being sent to the usual lubrication network of the engine. Under the effect of gravity, the oil fell back at the top of the container. The container was a glass cylinder, enabling visual inspection of the oil aspect and level.

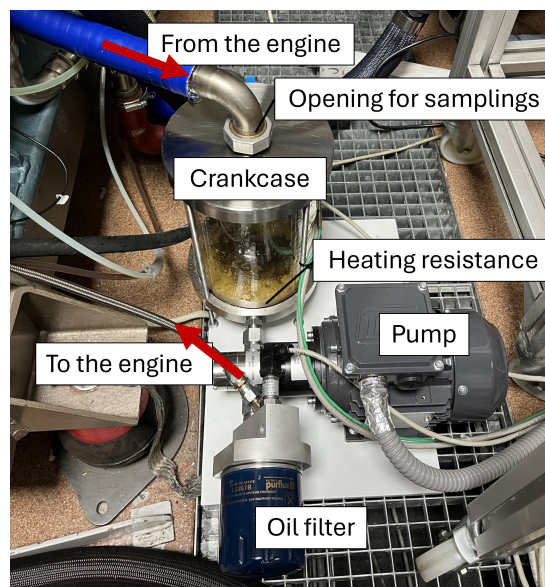


Figure 4.2: Photo of the 2 L crankcase installed for this study

1.1.3 Engine oils

The engine was successively operated with three oils. The workflow is depicted in Figure 4.3. The first oil was a commercial fully-formulated lubricant, referred to as "LUB" here, used during previous experiments on the same engine. This oil was mainly composed of a group III mineral base oil, enriched with bis(nonylphenyl)amine and benzenesulfonic, mono-C20-26-alkyl-derivatives additives. Then, the group III mineral base oil B (Table 2.1) was used. It is referred to as "Oil B2" because even though the same commercial reference as oil B was used, this second batch had slightly different properties compared to the first batch, especially for the simulated distillation curve and in terms of viscosity. Eventually, an oil pre-aged under laboratory conditions was also used. 2 L of Oil B2 were indeed exposed to oxygen and ammonia before being used in the engine. This oil is referred to as "Oil B2 pre-aged". Viscosity values at 40 °C and 100 °C of the three oils are reported in Table 4.2. Their aspect in the crankcase is shown in Figure 4.4. The group III mineral base oil was selected for engine experiments as it is a widely used base for engine lubricants, and because it was the closest to the commercial lubricant regarding the viscosity among the original matrix of eight base oils.

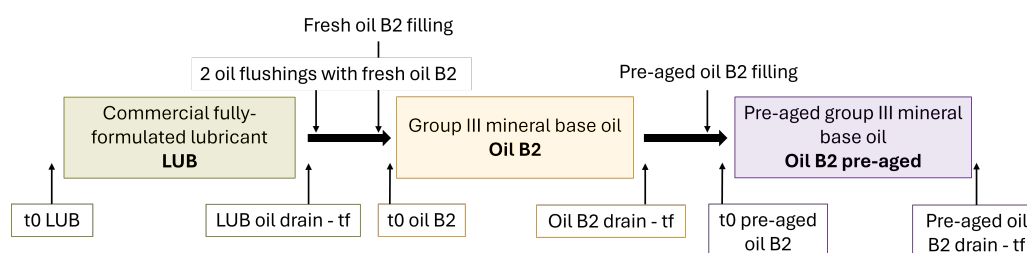


Figure 4.3: Schematic diagram of the experimental workflow implemented to operate the engine with three oils successively

4.1. EXPERIMENTAL SECTION

To switch from one oil to the next, the oil was first drained out as much as possible by leaving it flow down during one night. During this time, the oil filter was also put in reverse position to allow trapped oil to fall down. Between the commercial oil and the fresh base oil, the crankcase was twice in a row flushed with a new volume of fresh oil, and pumped into the lubrication system to remove residues of the fully-formulated lubricant. The crankcase was finally filled again with fresh oil a third time. This state of oil, after drainage and blending with residues was called "t0" and represented the initial state of the oil. Between the fresh base oil and the pre-aged one, the oil circuit was drained as much as possible but no flushing could be performed as it would have required large volumes of pre-aged oil which could not be supplied. The "t0" state of the pre-aged oil B2 corresponds to a sample taken after complete drainage of oil B2, refilling with the pre-aged base oil and homogenization of the system.

Table 4.2: Initial viscosity of the three oils used for engine experiments

Engine oil	Viscosity at 40 °C		Viscosity at 100 °C	
	Dynamic (mPa · s)	Kinematic (mm ² /s)	Dynamic (mPa · s)	Kinematic (mm ² /s)
LUB	54.4 ± 0.6	65.1 ± 0.7	9.4 ± 0.1	11.7 ± 0.2
Oil B2	41.9 ± 0.9	50 ± 1	6.17 ± 0.07	7.76 ± 0.08
Oil B2 pre-aged	46.6 ± 0.5	55.2 ± 0.5	6.31 ± 0.07	7.87 ± 0.07



(a) Commercial oil LUB



(b) Oil B2



(c) Oil B2 pre-aged

Figure 4.4: Aspect of the three different oils

1.1.4 Engine operating conditions

The engine was operated on ammonia and methane alternatively, under various regimes. Methane was used as a reference for engine experiments. With both fuels, the intake pressure was generally fixed at 1 bar and the equivalence ratio was mostly kept equal to 1. The engine was operated at 1000 rpm, 1500 rpm, and 2000 rpm. Appendix C.2 details the engine operating

4.1. EXPERIMENTAL SECTION

conditions. The combustion durations for each condition were recorded and used to calculate the cumulative total for each gas, as shown in Figure 4.5. Oil B2 fresh and pre-aged were both used for up to 4 h of combustion time, among which 2.6 h under ammonia combustion and the rest with methane. This does not take into account the total operation time including motoring conditions. During engine operation and at the oil changes, oil samples were collected, directly via a pipette plunged into the crankcase, and characterized. Oil samples were usually collected at the end of a running sequence, and therefore not necessarily at the same combustion times for all oils. Figure 4.6 summarizes the characterization techniques used on different samples. Appendix C.3 provides further information about collection times and the characterizations conducted.

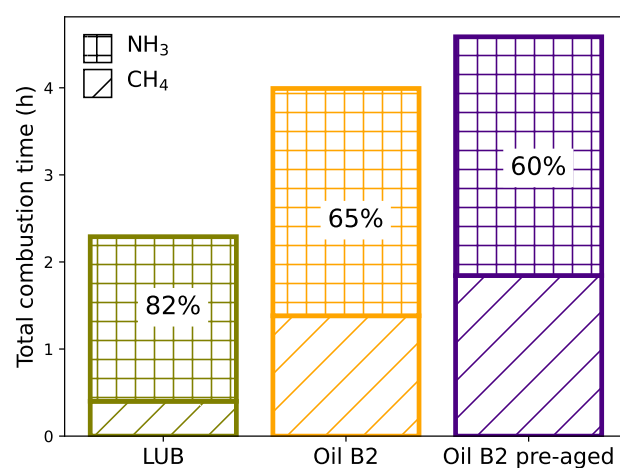


Figure 4.5: Cumulative combustion times with oil, under methane and ammonia conditions

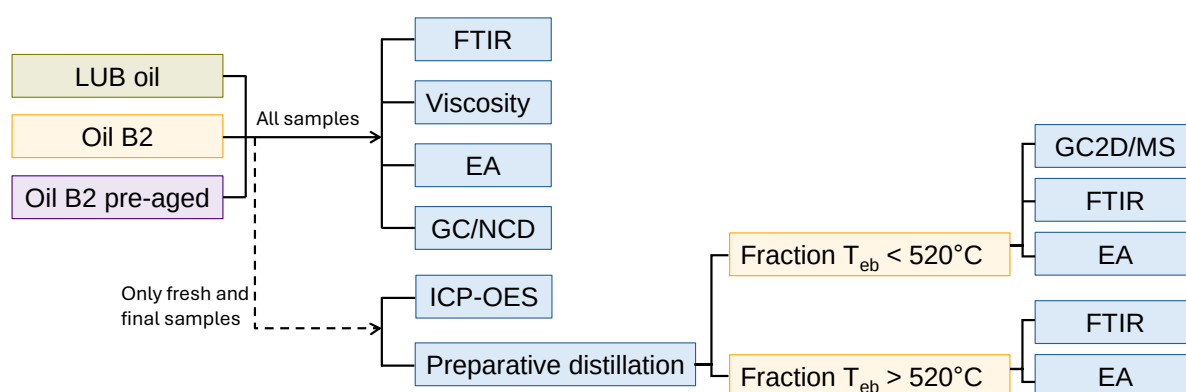


Figure 4.6: Summary of the characterization techniques used on oil samples collected from engine experiments

1.2 Preparation of the pre-aged base oil

1.2.1 Criteria for establishing the aging protocol

The pre-aged oil was produced using the autoclave reactor presented in Section 2.1.2.3. As this reactor was only 250 mL in total for both the gas and the liquid, the aging experiment had to be reproduced multiple times to reach a total pre-aged volume of 2 L. Several aging conditions were explored and the final aging protocol was selected based on following criteria:

- Aging volume: 100 mL of oil per batch,
- Aging time: less than 1 day per batch,
- Aging conditions: exposure to NH_3 and O_2 ,
- Intermediate evolution of key properties

The "intermediate evolution" of key properties was evaluated considering drain criteria given by the CIMAC (Table 1.6), and especially the criteria concerning the kinematic viscosity at 40 °C. They recommend to drain engine oils after a evolution of $\pm 25\%$ of the kinematic viscosity measured at 40 °C. In order to implement sufficiently advanced degradation, but allow for a more advanced degradation during the engine operation, the target increase was fixed at $+15\%$.

1.2.2 Aging protocol

The protocol meeting the criteria established in the previous paragraph is described here. The reactor was filled with 100 mL of oil B2 and purged with nitrogen. It was heated up to 140 °C and filled with 14.5 bar of NH_3 in air at 1.5 % according to the procedure in Section 2.1.2.3. Immediately after, 9.5 bar of pure oxygen were added, to reach a total pressure of 24 bar and a O_2 content close to 50 % (Table 4.3). Consumption of the reactive gases took approximately 3 h, and experiments were stopped 15 min after the stabilization of the pressure. After complete cooling of the reactor, the oxidized oil was collected in a 125 mL glass bottle and kept in the fridge at 4 °C. This protocol was replicated multiple times: Figure 4.7a shows the overlaid curves of the residual pressure, and Figure 4.7b the picture of the individual batches. They were all eventually blended and stored in a larger container one month before use in the engine.

Table 4.3: Composition of the gas blend used for pre-aging of oil B2 (at 140 °C)

Gas	Pressure (bar)	Volume fraction
O_2	3 + 9.5	0.52
N_2	11.3	0.47
NH_3	0.2	0.01
Total	24	1

4.1. EXPERIMENTAL SECTION

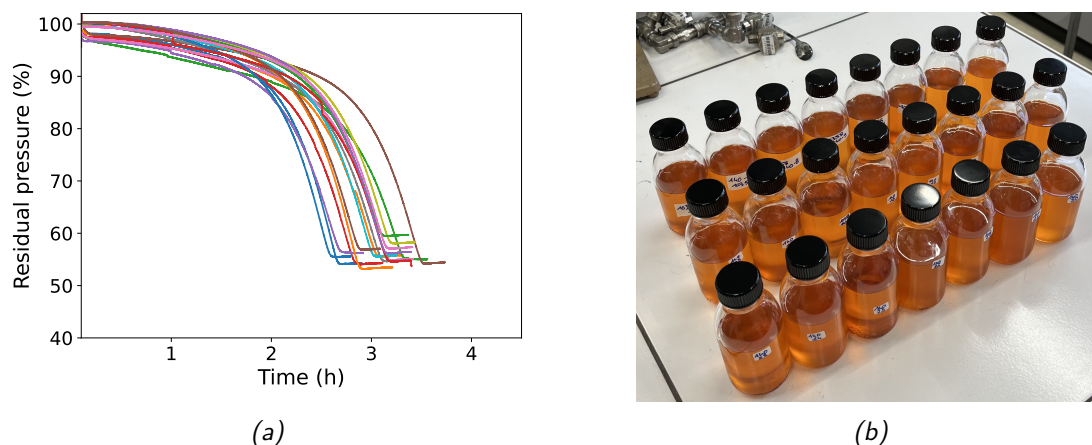


Figure 4.7: Repetition of the pre-aging experiment. a) Overlaid evolution of the pressure with time for all pre-aging batches. b) Pre-aged oil batches kept separately

1.3 Properties of the pre-aged base oil and between-day repeatability

Before blending, the viscosity of each batch was measured. Measured values are reported in Appendix C.1. Compared to the fresh oil B2, the kinematic viscosity at 40 °C was 15 % higher, in accordance with the target established. The overall error on the final viscosity was below 2 %. In addition, four oil samples randomly selected were more deeply characterized. FTIR spectra are displayed in Figure 4.8, and elemental analysis are reported in Table 4.4. IR absorption signals were highly similar, showing similar evolution as in Figure 2.17. Relative errors for these four measurements on the oxygen content, nitrogen content, and carbonyl peak area, calculated as described in Section 2.1.3.1, were below 5 %. For each characterization, the mean values obtained were very close to the values measured after blending of all the batches. This suggested a good between-day repeatability of the whole protocol including the pre-aging step, sampling methodology and characterization technique.

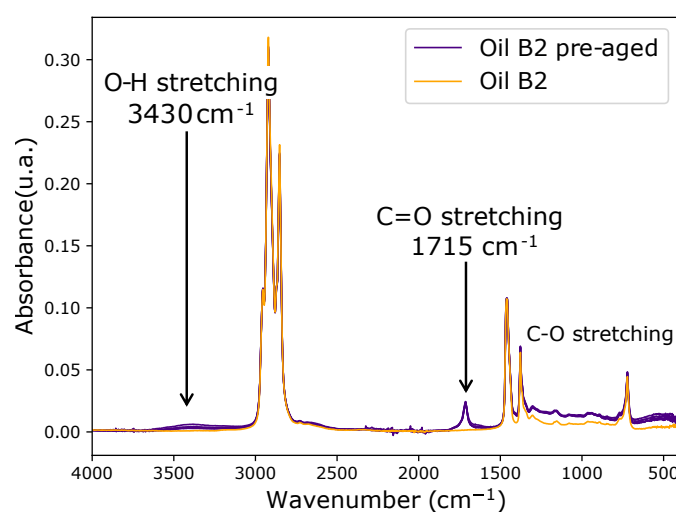


Figure 4.8: FTIR spectrum of fresh oil B2 and pre-aged oil B2 (5 samples overlaid)

4.2. EVOLUTION OF ENGINE OILS DURING ENGINE OPERATION WITH METHANE AND AMMONIA

Table 4.4: Properties of the Oil B2 after pre-aging, for 4 individual batches and the final blend

Batch	Oxygen content (%)	Nitrogen content (mg/kg)	Carbonyl peak area (A/cm)
1	2.03	114	0.91
2	1.87	118	0.85
3	2.01	117	0.87
4	1.94	127	0.86
Mean value	1.96	119	0.87
std. dev	0.08	6	0.03
rel. error (%)	4	5	3
24 Blended batches	1.99	107	0.87

The previous section described the experimental setup implemented to study the evolution of oils during engine operation with ammonia and methane as fuels, as well as the production of a pre-aged base oil and its final properties. The following paragraphs present results of various characterizations performed on oil samples collected at increasing combustion times, both at macroscopic and molecular levels. Studying the evolution of different oils directly during engine operation provides perspective on the findings from accelerated aging tests and contributes to a deeper understanding of oil degradation in engines fueled with ammonia.

2. Evolution of engine oils during engine operation with methane and ammonia

As described in Appendix C.3, oil samples were collected at increasing usage times, and macroscopically characterized as a first approach.

2.1 Evolution at the macroscopic scale

2.1.1 Elemental analysis and kinematic viscosity

Figure 4.9 a) and b) show the evolution of the total oxygen and nitrogen contents of the three oils during engine operation. "Fresh state" refers to the fresh oils. After oil drainage and filling with new oil, the pump was activated for at least 2 min to enable circulation of the new oil in the engine. As detailed in Section 4.1.1.3, a sample was collected afterwards and referred to as "t0", the realistic initial state of the oil, taking into account the contamination from the previous oil. For the commercial lubricant, "t0" state corresponds to an unknown use time (Figure 4.3).

4.2. EVOLUTION OF ENGINE OILS DURING ENGINE OPERATION WITH METHANE AND AMMONIA

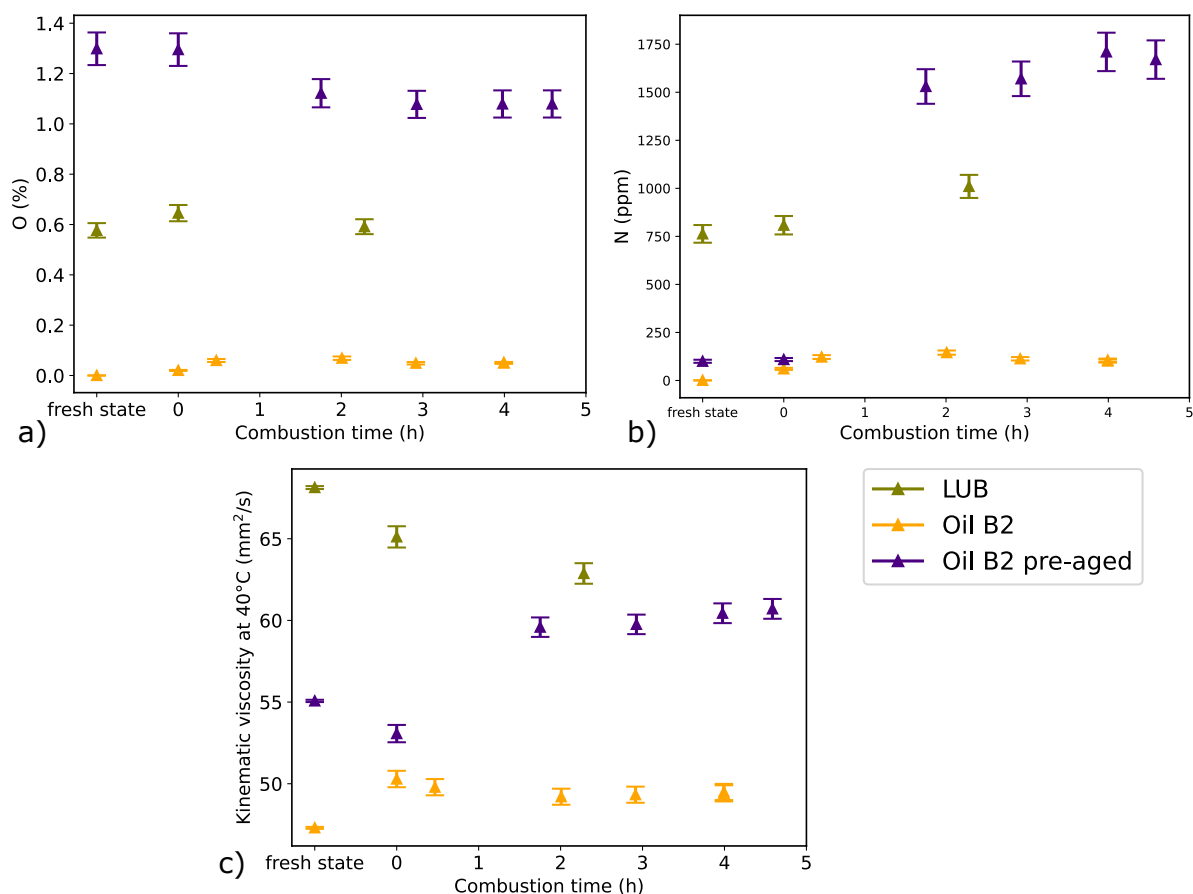


Figure 4.9: Evolution of the total oxygen (a) and nitrogen contents (b), and kinematic viscosity (c) at 40 °C during engine operation. "t0" corresponds to sampling after oil drainage and 2 min of circulation of the oil

Regarding the commercial lubricant, its oxygen content stayed constant, whereas its nitrogen content increased progressively. The initial nitrogen content was already high in this oil, as it contained aromatic amines as antioxidant additives. The kinematic viscosity at 40 °C decreased with time (Figure 4.9 c), consistent with what was observed between the fresh state and t0. The sulfur content in this oil was also measured, and showed a small decrease as it went from 0.214 ± 0.002 to 0.203 ± 0.002 %. Sulfur atoms originally came from sulfonic detergent additives. A similar decreasing trend was observed in [35,124], and was explained by the loss of volatile sulfur degradation products, such as sulfides and mercaptans.

For the base oil, the oxygen and nitrogen contents both increased between the fresh state and t0, due to the mixing with residues of commercial lubricant. Subsequently, during engine operation, the concentration in both elements continued to slightly increase. Final concentrations remained very low, respectively 0.05 % O₂ and 100 mg/kg of nitrogen, explaining why no evolution of the viscosity was measured. The small decrease in oxygen and nitrogen contents between 2 and 3 h might be explained by the fact that fresh oil had to be added to the crankcase at this stage because the remaining volume was insufficient, which led to gas bubbles being incorporated in the oil lubrication circuit.

4.2. EVOLUTION OF ENGINE OILS DURING ENGINE OPERATION WITH METHANE AND AMMONIA

The total oxygen content slightly decreased in the pre-aged base oil, especially between t_0 and the first sample. Besides, between these two sampling times, the nitrogen content dramatically increased from 100 mg/kg to more than 1500. Total nitrogen content continued to increase but at a slower rate. In parallel, the kinematic viscosity also increased significantly between t_0 and t_1 , and continued to increase progressively afterwards.

The residual amount of commercial lubricant in oil B2 after 3 oil flushing could be deduced from the nitrogen content at t_0 . The nitrogen content in oil LUB was 1010 mg/kg, and 0 in oil B2 in the fresh state. After blending, the nitrogen content reached 60 mg/kg in oil B2. By the law of conservation of matter,

$$C_{B2,t0} * (V_{LUB} + V_{B2}) = C_{LUB} * V_{LUB} + C_{B2,fresh} * V_{B2,fresh}$$

With $C_{B2,fresh}=0$.

$$\frac{V_{LUB}}{(V_{LUB} + V_{B2})} = \frac{C_{B2,t0}}{C_{LUB}}$$

The calculation gives 6 % of commercial lubricant remaining in oil B2.

Consistent with the low oxygen content in oil B2, no evolution of the infrared absorption was measured. However, the FTIR spectrum of pre-aged oil B2 at intermediate times pointed out evolution at the molecular level (Figures 4.10). In accordance with the results in Figure 4.9 showing a significant evolution of the pre-aged base oil between t_0 and the first sample, Figures 4.10 confirms the significant change at the molecular level between the first two samples. In particular, the intensity of the absorption peak of the C=O double bond was reduced, in parallel with the decrease of the oxygen content. In addition, a large absorption band centered in 1586 cm^{-1} , already present at t_0 but with a low intensity, became more intense. At longer combustion times, the evolution of the oil seemed minor, as suggested by other characterizations. Absorption in the region of 1590 cm^{-1} could be associated to [171–174]:

- C=C stretching in aromatics, alkenes $\longrightarrow$ unlikely to be newly formed
- C=N stretching in aromatics, pyridines $\longrightarrow$ unlikely to be newly formed
- N–H stretching in primary and secondary amides $\longrightarrow$ would be associated to a band at 1650 cm^{-1}
- C $\equiv$ N stretching in nitriles $\longrightarrow$ would be associated to a band at 2200 cm^{-1}
- NH₂ bending in C₂NH₂⁺...X[−] amine salts $\longrightarrow$ only very few halogens expected
- CO asymmetric stretching in COO[−]...M⁺ carboxylate, metal salts

Several hypothesis are probable but could not be unambiguously confirmed or invalidated. However, carboxylates appear as the most relevant and probable attribution. Indeed, similar ab-

4.2. EVOLUTION OF ENGINE OILS DURING ENGINE OPERATION WITH METHANE AND AMMONIA

sorption bands attributed to metal complexes, especially involving copper, calcium, manganese, cadmium, zinc, lead and iron, were observed in studies from other research fields [173, 174]. In particular, copper carboxylates showed large absorption bands centered in 1586 cm^{-1} , as on the spectra collected in this study. In the recent work by Rao *et al.* [31], a specific absorption band at 1590 cm^{-1} was also observed in a lubricant blended with 1 % ammonia solution and heated up to 80°C for 288 h. The authors attributed it either to amides, or preferably to carboxylates ammonium salts, because it was also associated to bands at 3179 cm^{-1} and 1208 cm^{-1} suggesting amines presence.

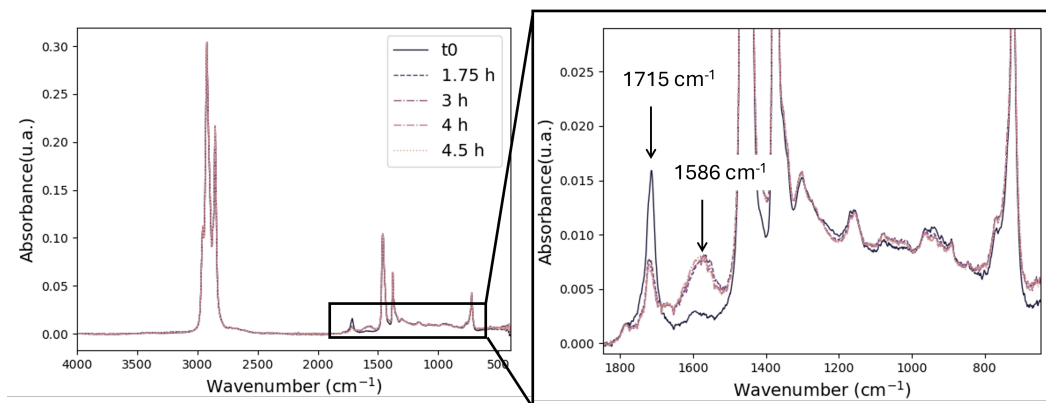


Figure 4.10: Evolution of the infrared spectrum of Oil B2 pre-aged during engine operation

No specific band suggesting the presence of nitro-oxidation products was observed in any of the three oils. This was also the case in the study from Rappo *et al.* [30] who studied lubricant degradation over 150 h in an engine operated with 90 % NH_3 and 10 % diesel.

2.1.2 Analysis of the oil fractions

As final oil samples underwent preparative distillation with a cut at 520°C (Section 2.1.3.7) to enable GC2D/MS analysis of the light fraction, light and heavy fractions were also characterized separately using elemental analysis and FTIR.

Elemental Analysis Figure 4.11 represents the mass proportion of each fraction. Their respective oxygen and nitrogen contents are reported in Table 4.5. Interestingly, the division between the two fractions did not change for fresh oil B2 after engine experiments, consistent with the stability of the kinematic viscosity (Figure 4.9). The heavy fraction still represented nearly 25 %w/w of the total mass of this oil. This division corresponded to what was expected considering simulated distillation of Oil B2, predicting that 73 % of the oil boiled above 520°C , which validated the preparative distillation methodology. However, analysis of the elemental composition of the two phases revealed that the overall mean value of 0.05 % oxygen masked a higher content in the heavy fraction (above 0.1 %) and a much lower one in the light fraction (below 0.02 %). Similarly for the nitrogen content, the heavy fraction contained proportionally more than 200 mg/kg nitrogen, but the light fraction only 40 mg/kg. Even when calculating

4.2. EVOLUTION OF ENGINE OILS DURING ENGINE OPERATION WITH METHANE AND AMMONIA

absolute quantities contained in each phase, the amount of both oxygen and nitrogen in the heavy fraction of oil B2 after engine experiments were higher than in the light fraction.

Regarding the pre-aged base oil B2, it can be noticed that the accelerated aging promoted the production of heavy products, as the heavy fraction represented 47 % after pre-aging. This can be associated to the 15 % kinematic viscosity increase during pre-aging. Meanwhile, a majority of oxygenated and nitrogenated products were found in the light fraction after the pre-aging. After use in the engine, the proportion of heavy products decreased to 37 %. The relative and absolute amounts of oxygen in the light fraction decreased but increased in the heavy fraction. However, the nitrogen content increased in both fractions, and especially in the heavy fraction.

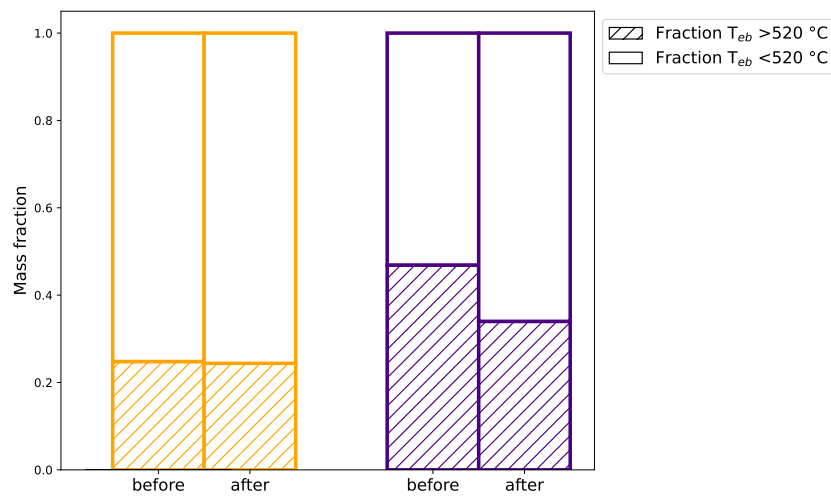


Figure 4.11: Normalized division between fractions with a boiling point higher than 520 °C (hatched) and lower than 520 °C (blank) for oil B2 fresh and pre-aged, before and after engine experiments

Table 4.5: Elemental analysis of the light and heavy fractions of the oil samples before and after engine experiments

		Oil B2		Oil B2 pre-aged	
		Before	After	Before	After
Fraction $T_{eb} < 520\text{ °C}$	% w/w	75.2	75.6	53.1	62.7
	Specific gravity	0.8452	0.8442	0.8535	0.8485
	Oxygen (%)	< 0.023	< 0.020	1.078 ± 0.05	0.639 ± 0.03
	Nitrogen (mg/kg)	< 0.63	40 ± 4	69 ± 6	520 ± 31
Fraction $T_{eb} > 520\text{ °C}$	% w/w	24.8	24.4	46.9	37.3
	Specific gravity	0.8533	0.8563	0.8579	0.8764
	Oxygen (%)	< 0.031	0.102 ± 0.005	0.454 ± 0.02	0.962 ± 0.05
	Nitrogen (mg/kg)	< 0.41	204 ± 16	43 ± 4	1950 ± 120
Total	% w/w	100	100	100	100
	Specific gravity	0.8460	0.8473	0.8601	0.8589
	Oxygen (%)	< 0.04	0.051 ± 0.003	1.658 ± 0.09	1.079 ± 0.05
	Nitrogen (mg/kg)	< 0.63	101 ± 8	119 ± 6	1670 ± 100

4.2. EVOLUTION OF ENGINE OILS DURING ENGINE OPERATION WITH METHANE AND AMMONIA

Limited evolution of the mass proportion of each fraction in the base oil B2 was consistent with the limited chemical evolution observed at the macroscopic scale. In contrast, the increase of the proportion of products with boiling points lower than 520 °C in the pre-aged base oil could be the result of thermal degradation of oxidation products produced during accelerated aging. In addition, the progressive vaporization of light oxygenated products could explain the decrease in oxygen content in the light fraction (both in mass proportion and absolute value). This decrease could be associated to the global decrease in oxygen content in the pre-aged base oil during engine operation (Figure 4.9). For both oils, engine operation seemed to promote the production of heavy functionalized products. This could also be a bias of the preparative distillation step promoting the polymerization of oxygenated products.

FTIR Infrared absorption spectra of oil samples and their fractions are presented in Figures 4.13 and 4.12. It appears clearly in Figure 4.12 that the heavy fraction was more oxidized than the light fraction for oil B2, especially because a small absorption peak could be detected in the carbonyl region, and the region between 600 and 1200 cm^{-1} had a higher intensity.

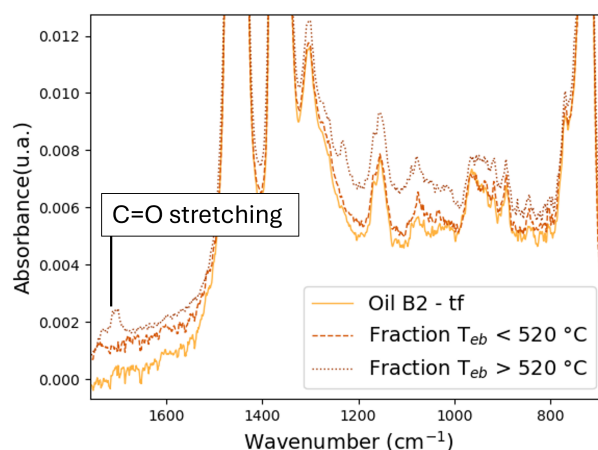


Figure 4.12: Infrared absorption spectrum of Oil B2 after engine experiments and its light and heavy fractions. Acquisition of the spectra was not performed on the same day, explaining variation of the baseline level

On the other hand, both fractions of the final sample of the pre-aged oil had very different absorption spectra, especially between 1500 and 1800 cm^{-1} . Figure 4.13 shows that the light fraction mainly contained carbonyls. This fraction also presented a small peak at 1790 cm^{-1} , which could correspond to anhydrides. The heavy fraction also contained carbonyls but had two distinct peaks centered in 1715 cm^{-1} and 1737 cm^{-1} , and the large band centered in 1586 cm^{-1} . Unfortunately, GC2D/MS could not be used to support the identification of the chemical function responsible for this large absorption band at 1586 cm^{-1} as it was only present in the heavy fraction. However, the hypothesis of metal carboxylates would be consistent with compounds with high boiling points thus only present in the heaviest fraction. The carbonyl peak centered in 1737 cm^{-1} could be associated to esters or acids.

4.2. EVOLUTION OF ENGINE OILS DURING ENGINE OPERATION WITH METHANE AND AMMONIA

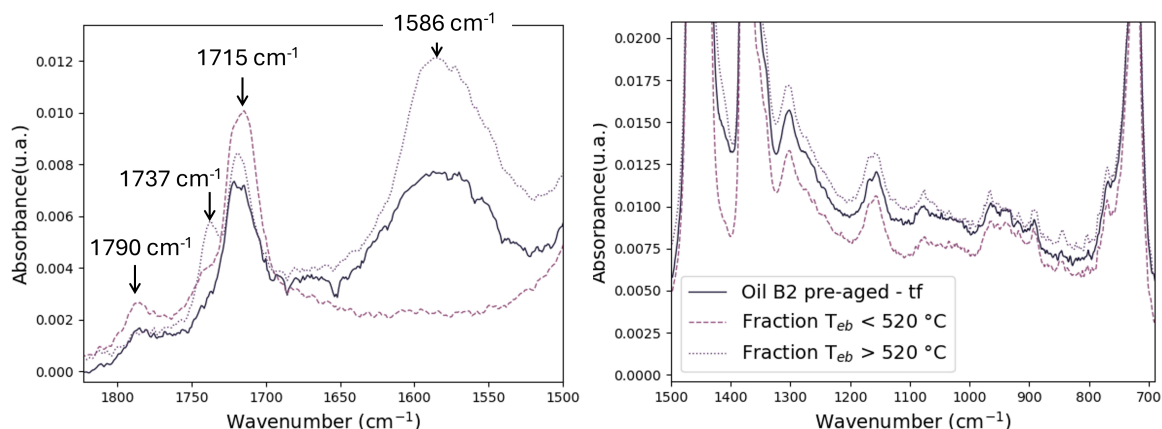


Figure 4.13: Infrared absorption spectrum of Oil B2 pre-aged after engine experiments and its light and heavy fractions

Another interesting finding of the detailed elemental analysis is that finding high nitrogen contents in the heavy fractions of the oils confirmed the presence of nitrogen in the samples, not only as a dissolved gas but as part of large molecules. Oil samples were also analyzed with GC/NCD to assess this finding.

2.1.3 GC/NCD Analysis

Figure 4.14 shows the NCD chromatograms of the three oils at intermediate sampling times. This analysis only detects nitrogen-containing molecules and does not require preparative distillation.

In its initial state, the fully formulated lubricant contained specific nitrogen compounds, as shown by the well resolved peaks with retention times of 4.5, 6.5, and 8 min (Figure 4.14 a). A broader signal at 12 min could also be observed. This corresponds to the different types of additives, as aromatic amines contained in the oil. After use in the engine, the NCD intensity of the oil showed a very high peak at short retention times, spreading out until 1.5 min. In addition, between 4.5 and 9 min, some new peaks could be observed. They might correspond to subproducts of the additives, or products of a reaction between ammonia and oil constitutive molecules. For the commercial lubricant, most of the nitrogen uptake corresponded to very short molecules, likely dissolved ammonia, but also to a lesser extent to large molecules containing nitrogen newly formed compared to the fresh oil.

On the NCD chromatogram of oil B2 (Figure 4.14 b), three peaks corresponding to residues from the oil LUB could clearly be identified. Compared to the commercial lubricant, these peaks were 10 times less intense, consistent with the dilution factors estimated using the nitrogen content. During engine operation, the intensity around 12 min decreased, meanwhile an intense peak at very short retention times appeared. After only 1 h use in the engine, the intensity of this peak reached 80 μ V.

4.2. EVOLUTION OF ENGINE OILS DURING ENGINE OPERATION WITH METHANE AND AMMONIA

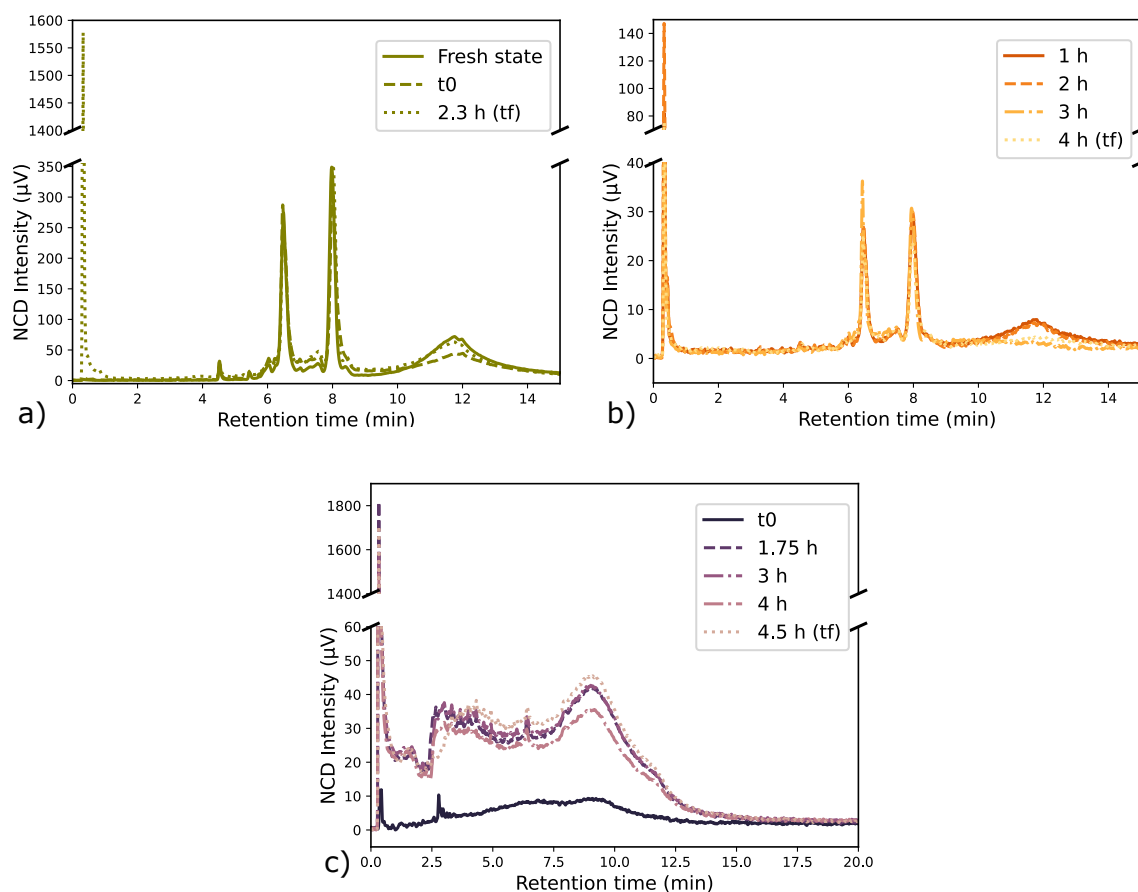


Figure 4.14: Evolution of the NCD chromatograms during engine operation. a) LUB b) Oil B2 c) Oil B2 pre-aged

The NCD chromatogram of the pre-aged base oil before use already showed the presence of multiple nitrogen-containing molecules over a wide size range (Figure 4.14 c). As found with other characterizations, the more significant evolution of the oil occurred between t_0 and t_1 . In less than 2 h of combustion time in the engine, multiple nitrogen-containing products were formed over a wide size range. In addition, large amounts of NH_3 were dissolved in the oil and the intensity at very short retention times reached $1800 \mu\text{V}$.

From these results it can be concluded that NH_3 was dissolved in all oils after very short use times in the engine. It can be noticed that the intensity of the first peak was the same order of magnitude for the oil with additives and the pre-aged one, whereas it was 10 times less intense with the base oil B2. This could indicate a higher affinity of the NH_3 for these matrices, which contain polar compounds, compared to the non polar mineral base oil. In the pre-aged base oil, already containing oxidation products and nitrogen containing molecules, the nitrogen uptake was very important, and quickly led to the production of new nitrogen-containing molecules of varied types, especially during the first operating hours.

4.2. EVOLUTION OF ENGINE OILS DURING ENGINE OPERATION WITH METHANE AND AMMONIA

2.1.4 Water content

As with ammonia, the water uptake in the formulated lubricant and the pre-aged oil were higher than in the mineral base oil B2. The water content in the latter went from 70 to 340 mg/kg, while it reached typical concentrations higher than 1000 mg/kg in the fully-formulated LUB oil and the pre-aged oil B2. Only orders of magnitude are considered for these results obtained by Karl Fischer potentiometric titration, which is associated to large errors for lubricants. However, the trend highlighted a higher affinity for oils with polar compounds, accordingly to what was observed with NH_3 . As NH_3 has a great affinity for water, a higher water uptake might promote ammonia uptake in these oils. The significant NH_3 and water uptake in the fully-formulated lubricant is one possible explanation for its decreased viscosity (Figure 4.9).

2.1.5 Metal content

The metal content in the final oil samples was also measured with ICP-OES as an indicator of the oil corrosivity towards engine parts and the potential wear occurring during engine operation, according to the method described in Section 2.1.3.6. The final contents of calcium, copper and iron and zinc are shown in Figure 4.15. Among these metals, only iron is an inherent component of moving engine parts and can therefore be used as an indicator of wear.

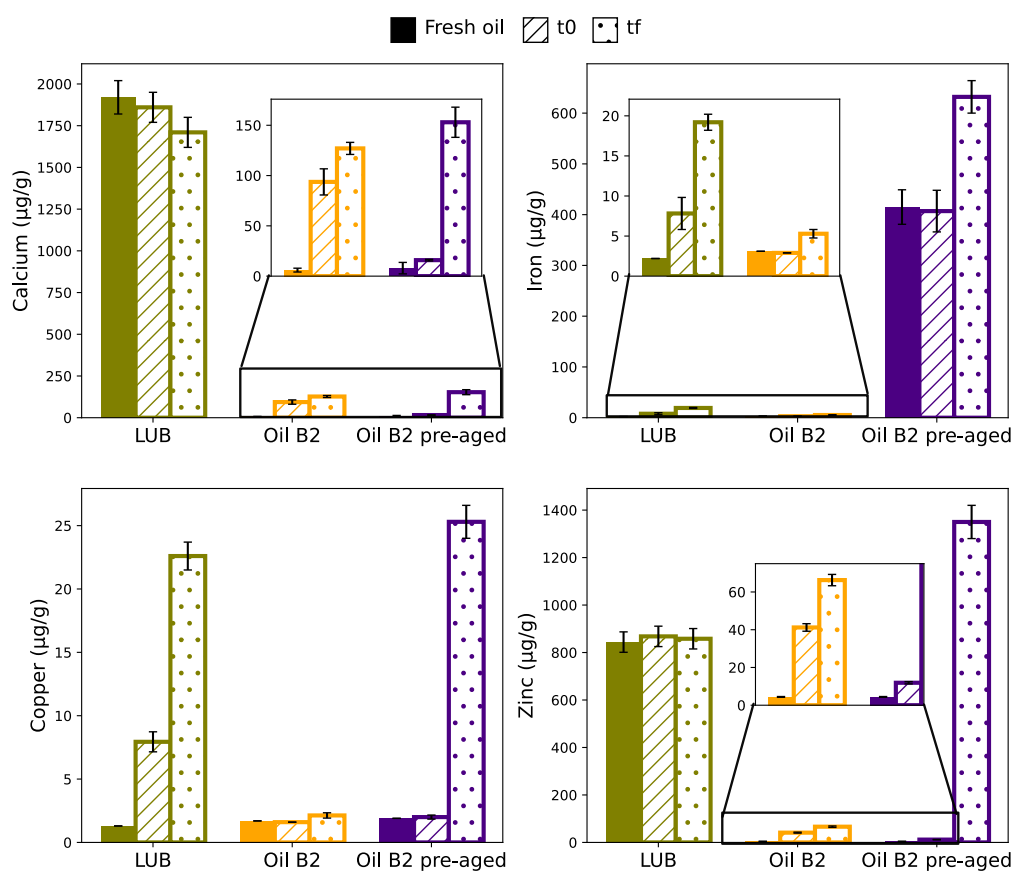


Figure 4.15: Evolution of the calcium, copper, iron and zinc contents before and after engine tests

4.2. EVOLUTION OF ENGINE OILS DURING ENGINE OPERATION WITH METHANE AND AMMONIA

The initial calcium content was already very high in the fresh fully-formulated lubricant, due to its benzenesulfonic calcium salts additives, and remained stable with time in this oil. Although fresh oil B2 contained no calcium, its concentrations reached 100 $\mu\text{g/g}$ after blending with residues of the commercial oil. Using the same calculation as in Section 4.2.1.1, but with calcium also resulted in an estimated proportion of residual LUB oil in oil B2 close to 5 %. For both base oils, fresh and pre-aged, the calcium content slightly increased after engine experiments. This was also observed in the studies [35,124] focusing on the in-field degradation of engine oils in diesel engines. The increase in the calcium content could be explained by the evaporation loss of volatile compounds increasing the calcium relative proportion. This would be consistent with the higher increase in the pre-aged oil B2, which contained a higher fraction of volatile compounds in its initial state. However, a decrease in oil volume alone would not be sufficient to account for such an increase, suggesting an additional source of calcium, possibly from additive residues in the system.

Zinc was also present in the fully-formulated lubricant due to anti-wear additives. Its concentration remained stable in this oil, however it increased in the two other oils. The increase was limited and comparable to calcium in the case of oil B2, but very important in the case of the pre-aged oil B2. Zinc is not usually employed as a constitutive metal for engine parts. However, it can be used in coatings and alloys for small parts, connections and rods in the system. The high increase in the pre-aged oil might originate from the corrosion of small parts, including parts from the crankcase system and not the engine directly. It could also originate from the scraping of the additive layer, formed during engine operation with the fully-formulated lubricant, due to poor lubrication with the pre-aged base oil.

The iron content also increased in all oils, indicating wear and/or corrosion but to significantly different extends. The original iron content in the pre-aged base oil was high due to corrosion during oil storage. All the batches were indeed kept in individual glass flasks, but all mixed together in a 2 L metal can one month before use, which exhibited visual corrosion after this time. Unlike zinc, the iron content also increased in the fully-formulated lubricant. The increase in oil B2 was very limited. The iron content especially increased in the pre-aged oil, which could be linked to higher wear due to the degraded properties of the pre-aged lubricant.

The copper content greatly increased in the commercial and the pre-aged oils, and to a lesser extend in oil B2. As ammonia is highly corrosive towards copper, this can be related to the high ammonia uptake in those oils (Figure 4.14), as opposed to the limited ammonia uptake in oil B2. This result highlighted that ammonia uptake in the oil, even though limited could lead to corrosion of metal parts in very short times.

Nickel, tin and chromium were also quantified but were only present in trace amounts. The pre-aged base oil after use was the only oil sample where nickel and chromium could be found, at respectively 2 and 1.6 $\mu\text{g/g}$, which confirmed that this oil led to more wear and corrosion. In a recent study from Rappo *et al.* [30], focusing on the evolution of lubricants over 150 h in an

4.2. EVOLUTION OF ENGINE OILS DURING ENGINE OPERATION WITH METHANE AND AMMONIA

engine operated with 90 % NH_3 and 10% diesel, they also found increasing concentrations of iron and copper due to corrosion and wear. Copper content reached 500 ppm after 150 h, and iron content reached 175 ppm over the same period of time. After 4 h copper concentration was close to 25 ppm, similarly to what we measured with the LUB fully-formulated lubricant and the pre-aged base oil. In their study, chromium and tin residues originating from wear of the liner were also found. Changing the additive package resulted in limited degradation. They also measured friction coefficients of a lubricant under air or ammonia atmosphere, highlighting that it was higher in the presence of ammonia, which led to more severe wear in a rolling-ball tribometer [30]. In addition, estimation of the tribofilm thickness revealed that it seemed to be thinner in the presence of ammonia. These findings are consistent with the findings of this study, and support the hypothesis of increased wear in addition to corrosion occurring due to ammonia environment. In our work, the base oil B2 was less affected than other oils. Therefore, from our results it appears that the increase in friction coefficient and decrease in tribofilm thickness is caused by the ammonia directly absorbed into the lubricant. The higher is the affinity of ammonia for the lubricant, the more it will affect friction, wear, and corrosion at the same time, suggesting that adapting lubricant formulation is a critical lever to mitigate these adverse effects. More specifically, even the engine oil containing additives offered poor protection here, highlighting that the main driver seems to be the polarity.

Despite the short usage times of the three oils, significant changes at the macroscopic scale could be noticed. The oxygen content increased in oil B2, especially in the heavy fraction of this oil, indicating oxidative degradation had been initiated. The nitrogen content also increased in all three oils, and especially in the pre-aged base oil. In parallel, the viscosity of both mineral oils increased, while it decreased for the fully-formulated lubricant. A major change in the chemistry of the pre-aged base oil occurred within the first usage hours, as pointed out in FTIR, elemental analysis, viscosity and GC/NCD analysis. In addition, GC/NCD analysis highlighted that NH_3 could be found in all the oil samples collected during engine operation, and especially in oils with a higher polarity, being the fully-formulated one and the pre-aged one. The accumulation of NH_3 led to corrosion, as indicated by the increasing copper, zinc and iron contents in the oils. Degradation of the chemical integrity of the base oil also affected its wear-reducing abilities and led to higher amounts of iron partly originated from wear. GC/NCD analysis and elemental analysis of the heavy fractions of oil B2 fresh and pre-aged after engine experiments also highlighted that nitrogen could be found in heavier degradation products in these oils. These results show that the pre-aging step effectively amplified and accelerated the degradation mechanisms occurring in the engine. In order to further investigate the evolution of these oils during engine operation, they were also characterized at the molecular scale.

4.2. EVOLUTION OF ENGINE OILS DURING ENGINE OPERATION WITH METHANE AND AMMONIA

2.2 Molecular evolution of the base oils

Oil B2 fresh and pre-aged were analyzed with GC2D/MS, both before and after use in the engine. Unlike oil B which could be analyzed in its entirety (Section 3.4.1), the samples of oil B2 had to undergo preparative distillation to remove products with a boiling point higher than 520 °C. This heavy fraction represented 25 % of the oil in its fresh state. This sample preparation step was required to protect the instrumentation.

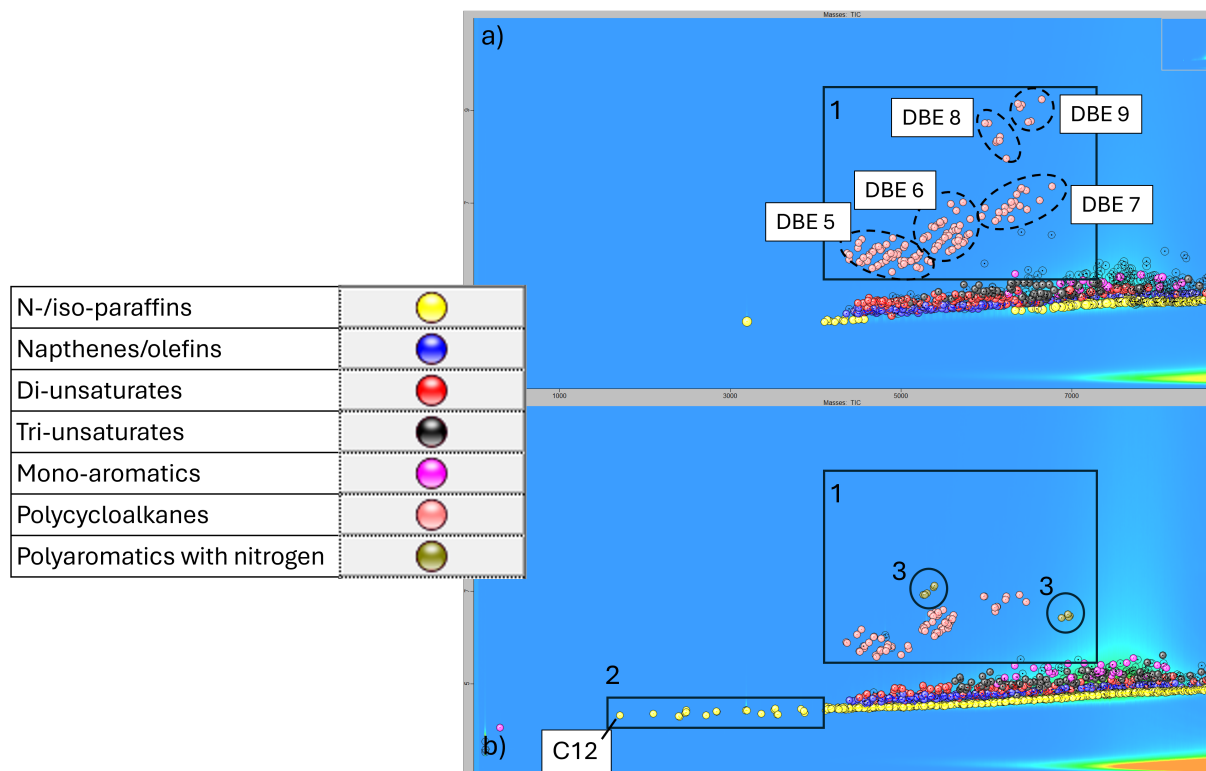


Figure 4.16: GC2D/MS Chromatogram of oil B2 in the fresh state (a) and after engine experiments (b). "DBE" stands for Double Bond Equivalent

Total ion chromatograms of oil B2 before (fresh product) and after use in the engine are shown in Figure 4.16. Despite the short use time, an evolution of the oil at the molecular level could be noticed. As observed in aging under accelerated conditions, few polycycloalkanes remained in the oil (area 1). In particular the largest compounds, with Double Bond Equivalent (DBE) 8 and 9, were no longer present in the final sample. In addition, short paraffins could be detected in the oil after engine experiments (area 2). Laboratory aging under air conditions showed that short acidic products were among the first oxidation products to be formed. This is indeed the principle of the Rancimat experiments described in Chapter 2. However, unlike the autoclave reactor, the engine crankcase is open and enables vaporization of the lightest molecules. The presence of short paraffins might suggest that short oxidation products were formed beforehand, but directly evaporated. Eventually, two clusters of heavy nitrogen-containing molecules were detected (area 3). Possible formula for these products were $C_{21}H_{29}N$ and $C_{30}H_{47}N$ which was perfectly consistent with the formula of the amine additives in the commercial lubricant, especially bis(nonylphenyl)amine. These compounds were then

4.2. EVOLUTION OF ENGINE OILS DURING ENGINE OPERATION WITH METHANE AND AMMONIA

very likely residues from the commercial lubricant, as could be seen on NCD chromatograms in Figure 4.14.

Results from elemental analysis (Table 4.5) showed that final concentrations in oxygen and nitrogen remained very low in the final sample, and especially in the light fraction analyzed using chromatography, which is consistent with the fact that no products with heteroatoms could be detected here. Even though no oxygenated compound could be detected, several elements indicated an evolution of the fresh base oil after only 4 h of combustion time at the molecular level.

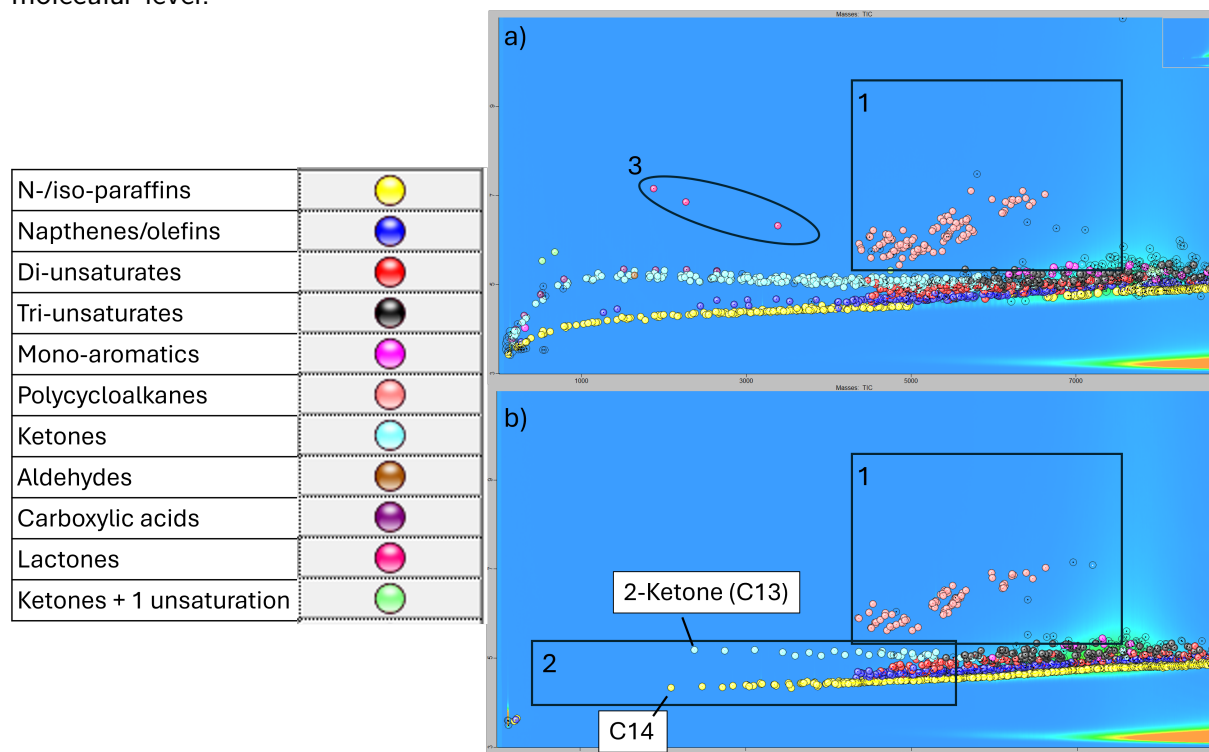


Figure 4.17: GC2D/MS Chromatogram of oil B2 pre-aged before (a) and after engine experiments (b)

Total ion chromatograms of the pre-aged oil B2 before and after engine tests are shown in Figure 4.17. As for the fresh oil, the number of polycycloalkanes (area 1), which had already significantly decreased during accelerated aging, continued to decrease during engine operation. Interestingly, using the oil in the engine resulted to a significant loss of the light oxidation products (area 2). After use in the engine, only paraffins larger than C14 remained in the oil, and 2-ketones larger than C13. Acids, lactones (area 3), and the numerous ketones isomers were no longer present. This is consistent with the FTIR spectrum of the light fraction of pre-aged oil B2 after use showing a single carbonyl peak centered in 1715 cm^{-1} in Figure 4.13. The oxygen loss (Figure 4.9) in the pre-aged oil B2, and more particularly in its light fraction (Table 4.5) could be explained by this loss of volatile oxidation products. This was probably due to the evaporation of these relatively light compounds as the oil was heated in the engine. The boiling point of the smallest molecules which can be found was 215°C for dodecane in oil B2 after use, and 250°C for tetradecane in the pre-aged oil. This indicated

4.2. EVOLUTION OF ENGINE OILS DURING ENGINE OPERATION WITH METHANE AND AMMONIA

that evaporation of the light molecules occurred in hot regions of the engine and not directly when oil was kept in the crankcase at 90 °C. These boiling temperatures can be used as an indicator of the temperatures reached by the oil in contact with hot regions of the engine. After engine experiments, no nitrogen-containing products could be unambiguously detected. This is consistent with the fact that only 500 mg/kg of nitrogen were in this analyzed fraction, among which a large contribution of dissolved ammonia.

Accelerated aging in the presence of ammonia solution had revealed that ions fragments representative of nitriles and amides could be found in the mineral oil (Section 3.5.3). The same ion fragments were also looked for in oil samples collected after engine experiments. Figure 4.18 shows that both types of molecules were potentially present in the pre-aged base oil after engine experiments. On the other hand, these fragments were not present in oil B2. Evidence of such products could not be found using FTIR.

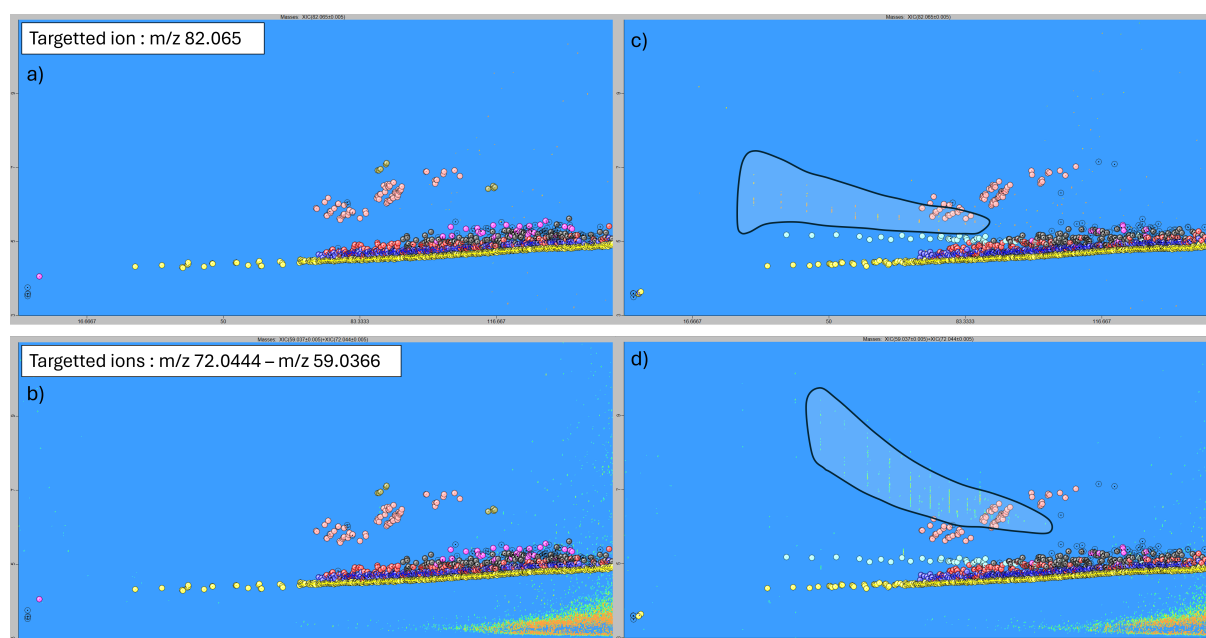


Figure 4.18: Research of target ions of nitriles in Oil B2 fresh and pre-aged after engine experiments (a) and (c), and amides (b and d)

Molecular analysis of the light fraction of oil B2 and pre-aged before and after use in the engine appeared to be highly consistent with the evolution observed at the macroscopic level, and enabled a better understanding of the degradation mechanisms that occurred over 4 h of combustion with methane and ammonia as fuels. This molecular analysis also enabled a better comparison of the pre-aging versus aging during engine operation, as will be discussed in following section. As the light fraction alone was analyzed at the molecular scale, valuable information about degradation products was lost due to the mandatory preparative distillation step. Other analytical techniques, not limited by the high boiling points of the oil should be considered as an alternative to overcome this challenge.

3. Discussion–evolution of base oils under engine conditions

Studying the evolution of different base oils under accelerated aging laboratory conditions reproducing ammonia combustion demonstrated that new degradation mechanisms involving oxygen and ammonia were taking place under such conditions. In this chapter, the evolution of a mineral base oil used directly in an engine test bench fueled with ammonia was investigated to gain a more thorough understanding of these degradation mechanisms and their consequences. As few studies focus on base oils without any additives, the evolution of a fully-formulated lubricant with a mineral base was also assessed as a reference. In addition, as combustion times were planned to be relatively short compared to lubricant aging studies which can be found in literature (Section 1.3.2), a pre-aged base oil was also produced and tested to assess the behavior of an oil with a more advanced degradation stage. Oil samples were collected over 4 h of combustion of ammonia and methane alternatively, and characterized using multiple techniques including elemental analysis (N, O), FTIR, viscosity, GC/NCD. Initial and final samples of oil B2 fresh and pre-aged were additionally characterized using ICP-OES and GC2D/MS, before and after use.

Despite the very short timescales, degradation of the three oils could be demonstrated at the molecular level and with consequences on macroscopic properties. Likely due to the antioxidant additives, the evolution of the fully-formulated lubricant was only minimal considering liquid phase oxidation. However, it accumulated some nitrogen as dissolved ammonia, which led to a viscosity decrease and corrosion of specific engine parts made of copper and iron. Even if simply dissolved, ammonia can have deleterious consequences. Xu *et al.* [24] showed that dissolved ammonia could form low energy interaction networks in lubricants, especially with acidic additives, altering their tribological properties. Besides, at longer times, dissolved ammonia might react with components of the oil, as suggested in [17] and Chapter 3 of this manuscript. The mineral base oil without additives showed signs of degradation: its oxygen and nitrogen contents both increased and evidence could be found of both oxidation and nitrogenated products in the heaviest fraction of this oil. However, the increase was only minor and did not lead to any evolution of the viscosity. Despite the non-polar nature of this oil, some NH_3 was also found in samples, to a minor extent compared to two other oils with higher polarities. This also resulted in lower corrosion compared to the two other oils. The NH_3 detected in oils using GC/NCD exhibited a non-negligible residence time in oils, as evidenced by its presence in samples collected at random intervals, including after exposure to open air for periods ranging from one night to two days. Furthermore, the intensity of the first peak attributed to NH_3 remained nearly constant with increasing combustion times for the mineral base oil B2 both fresh and pre-aged, suggesting the establishment of an equilibrium state. The pre-aged base oil degraded rapidly from the first hour of usage. Exposure to high temperature in an open environment probably led to an important loss of volatile oxidation products originated from the pre-aging step from the very beginning of the oil usage. Besides,

4.3. DISCUSSION–EVOLUTION OF BASE OILS UNDER ENGINE CONDITIONS

these oxidation products produced during accelerated aging might have polymerized resulting in large oxygenated molecules. Meanwhile, exposure to NH_3 led to high NH_3 uptake, and further reaction with oil components. Overall, the viscosity of the pre-aged base oil significantly increased from the first hour, and continued to increase at a slower rate afterwards. The pre-aged base oil appeared to be highly corrosive towards copper, but also iron. Even before use in the engine, storing the pre-aged oil in a metal container resulted in high corrosion of the iron and tin walls, and this worsened during engine operation. The high iron content might also indicate enhanced wear with this oil.

Table 4.6 summarizes the different trends in oil properties evolution during the engine test experiments. Different degradation mechanisms were observed with the fresh and pre-aged base oil, underlining the interest of the pre-aging step to study more advanced degradation mechanisms.

Table 4.6: Summary of trends in oil properties evolution during engine tests

Oil	Kin. viscosity (mm^2/s)	Oxygen content	Nitrogen content	Sulfur content	Water content	Metal content
LUB	—	=	++	—	++	++
Oil B2	=	+	+	not measured	+	+
Oil B2 pre-aged	+	—	+++	not measured	++	+++

These findings enlighten the differences between accelerated aging and aging during engine operation. One major difference here is the fact that the engine is an open environment, which led to the vaporization of the light oxidation products, as highlighted in chromatography molecular analysis. This may affect the oxidation kinetics and lead to a different distribution of oxidation products, and may slow down the oxygen accumulation in oils, as one part is directly vaporized. In this regard, the Rancimat experiment (Chapter 2) is relevant to reproduce open environments. Besides, wear and corrosion metals found in the oils may add catalytic effects influencing the reactivity. Such effects are sometimes simulated in accelerated aging via metal spiking (Section 1.3.2). Higher temperatures inside the engine may also promote thermal cracking and polymerization, resulting respectively in short and heavy molecules. Nevertheless, the degradation parameters and descriptors identified thanks to accelerated aging and preliminary work described in previous chapters appeared to be relevant to characterize degradation mechanisms occurring under complex conditions. This brings to light the dual advantage of the pre-aging methodology developed in this study: it allows faster access to advanced degradation stages, while also allowing the development of an analytical methodology to compare accelerated aging with *in-situ* aging. Two limitations can be raised regarding the findings of this study: non-negligible oil contamination occurred between the experiments despite the drain and multiple flushings, and tendencies were only studied over very short timescales which can potentially lead to interpretation errors. In the study from Obrecht *et al.* [25], the evolution of oil samples over 250 h of engine operation could indeed follow varying trends locally.

Nonetheless, one major outcome is that NH_3 can indeed partly solubilize in engine oils during engine operation, with several possible deleterious consequences. The oil polarity, determined by its additives and/or the presence of oxidation products, promotes NH_3 uptake, but NH_3 can also partly solubilize in non-polar matrices. Dissolved NH_3 can then alter the tribological properties accelerating wear and decreasing engine efficiency, make the oil corrosive towards specific engine parts, or even end up reacting with the oil components as evidenced in accelerated aging, provided sufficient residence time. This chapter points out that beyond accelerated aging under severe conditions, NH_3 can also have deleterious consequences on lubricants during engine operation. It highlights that lubricant formulations should be adapted to ammonia combustion, in particular to minimize ammonia solubilization. In addition, copper elements and alloys should really be avoided in engine fueled with ammonia. Eventually, ventilation systems could be used to reduce the residence time of ammonia, as in [175].

4. Conclusion

In this chapter, the evolution of three engines oils, a commercial reference, a mineral base oil, and the same mineral base oil after a pre-aging step, under ammonia and methane combustion was investigated in an engine test bench. The chapter first described the experimental setup implemented to conduct these engine tests, and the oil characterization workflow. Besides, the pre-aging conditions and the properties of the pre-aged base oil before use were detailed. Analysis of oil samples using varied and complementary characterization techniques enabled to gain knowledge about the consequences of ammonia combustion on lubricants. This study showed that ammonia could partly solubilize in lubricants, according to their polarity, with direct consequences on the corrosivity and the viscosity. The potential consequences of the degradation of oils on engine operation and on pollutant emissions is explored in the following chapter.

Chapter 5

Effect of the engine oil on engine operation and pollutant emissions

5.1	Experimental engine setup	154
5.1.1	Engine setup and combustion parameters	154
5.1.2	Diluter Fine Particle Sampler (FPS 4000)	155
5.1.3	Engine Exhaust Particle Sizer (EEPS)	157
5.1.4	FTIR spectroscopy	159
5.1.5	Mini Particle Sampler (MPS)	160
5.1.6	Methodology for engine test experiments and data processing	161
5.1.7	Microscopy imaging	163
5.2	Effect of the oil on engine operation and gaseous emissions	164
5.2.1	Effect of the engine oil under methane combustion	164
5.2.2	Effect of the engine oil under ammonia combustion	166
5.2.3	Effect of the engine oil under ammonia/hydrogen blends combustion	171
5.3	Investigating particulate matter emissions with methane and ammonia: in-line analysis	173
5.3.1	Particle size distributions under methane combustion	173
5.3.2	Particle size distributions under ammonia combustion	177
5.3.3	Comparison between methane and ammonia	181
5.3.4	Discussion	182
5.4	Investigating particulate matter emissions with methane and ammonia: elemental and morphological analysis	183
5.4.1	Particles obtained with the fully-formulated lubricant	183
5.4.2	Particles obtained with the mineral base oil	189
5.4.3	Particles obtained with the pre-aged mineral base oil	192
5.4.4	Particles obtained with methane	194
5.4.5	Analysis and comparison of the particles observed	200
5.4.6	Discussion–particle emissions	202
5.5	Conclusion	204

Chapter 4 focused on the evolution of a lubricant and two base oils in an engine operated with methane and ammonia. Significant changes in all the oils during engine operation were evidenced. This chapter aims at assessing the consequences of the degradation of lubricants on engine performance, as well as on the emissions of pollutants, both gaseous and particulate matter. The first section describes the experimental setup, the instruments and protocols used to measure engine parameters and exhaust emissions. Next, the following section presents the effect of the engine oil on the engine performance and associated gaseous emissions. In a third section, the emissions of particles are investigated with both methane and ammonia fuels and the three oils, thanks to in-line real-time measurements combined with particles sampling and microscope observations. Finally, the main findings of this chapter are discussed in light of previous results on the chemical evolution of the oils.

1. Experimental engine setup

1.1 Engine setup and combustion parameters

The engine was described in Section 4.1.1.1. In addition to the tailored crankcase designed to monitor the evolution of the oils during engine operation, several instruments were connected to the exhaust to monitor pollutant emissions during combustion. A gas counter with a measuring step of 5 L/min was connected to the blow-by circuit to measure its flow rate. A schematic diagram of the complete setup is shown in Figure 5.1.

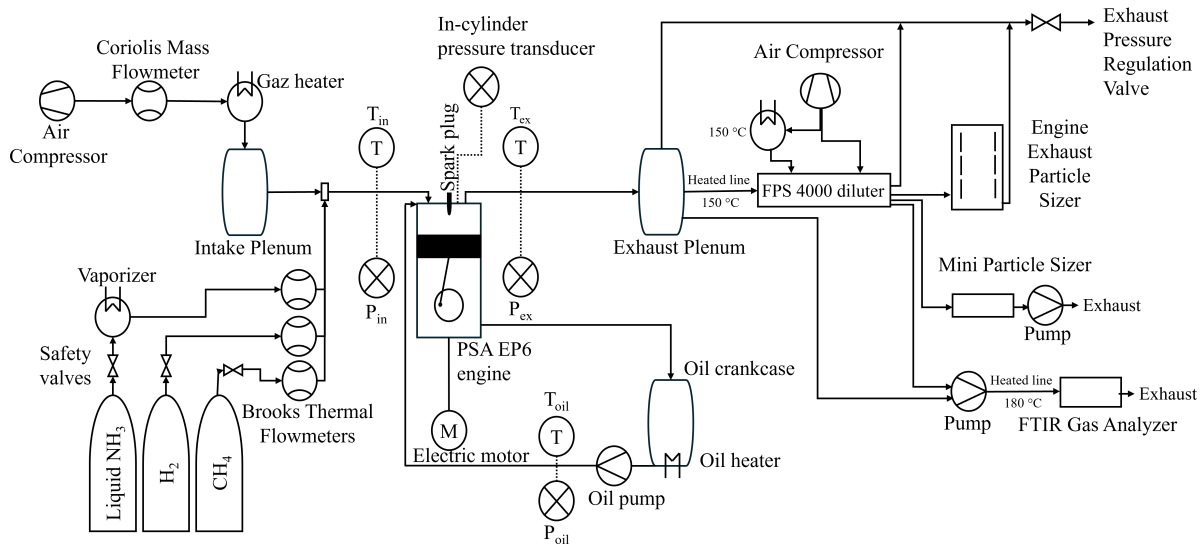


Figure 5.1: Schematic diagram of the engine setup

5.1. EXPERIMENTAL ENGINE SETUP

The Indicative Mean Effective Pressure (IMEP) was directly computed from the $P_{cylinder}$, and averaged over 100 consecutive combustion cycles:

$$IMEP = \frac{1}{V_d} \int_{\theta_{start}}^{\theta_{end}} P(\theta) \cdot \frac{dV(\theta)}{d\theta} d\theta$$

where V_d is the displacement volume, 500 cm³ here, and θ varies between 0 to 720 CAD (Table 4.1). Equivalence ratio and indicated thermal efficiency were calculated using gas flow rates, as schemed in Figure 5.2. Combustion phasing was determined by looking at the crank angle at which 50 % of the fuel mass was burned, known as the CA50 value.

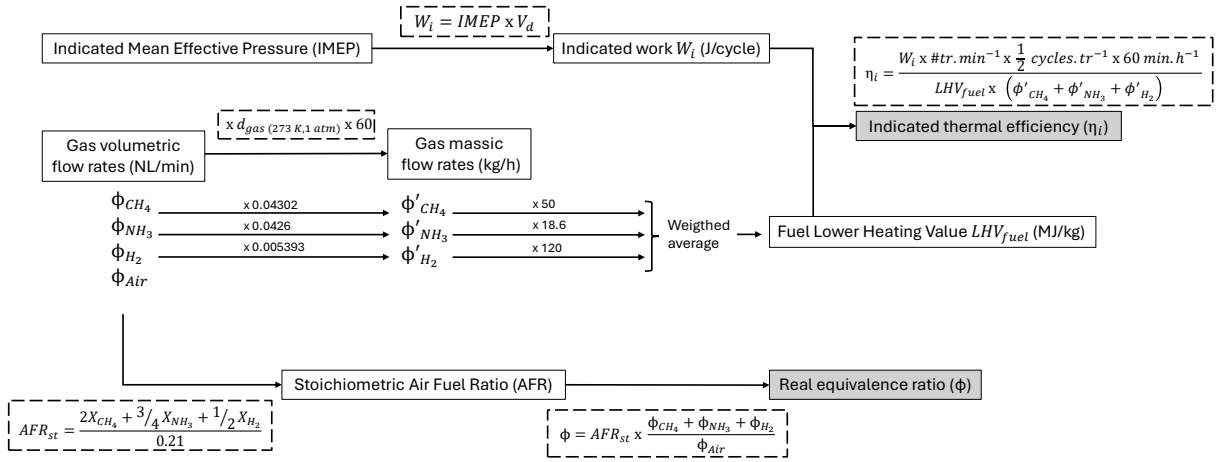


Figure 5.2: Calculation of the equivalence ratio and indicated thermal efficiency

Table 5.1 compiles the operating conditions investigated in this study. The detail of operating points can be found in Appendix C.2.

1.2 Diluter Fine Particle Sampler (FPS 4000)

In order to reduce water and ammonia contents at the exhaust to prevent condensation and corrosion in the instruments, the exhaust sample was first pre-conditioned via a two-stage dilution using a Dekati Fine Particle Sampler (FPS 4000). The principle of the instrument is schemed in Figure 5.3.

The FPS 4000 diluter involves a two-stage dilution based on a perforated tube followed by an ejector type diluter (Figure 5.3). During the first dilution step, the sample flows into the inner of a perforated tube, while diluting gas, air or nitrogen in this study, is introduced through the perforated walls. The diluting gas can be heated to temperatures up to 200 °C. The flow of dilution gas reduces particle losses on the walls. Its flow rate is determined by five valves (n° 3 to 8), and directly proportional to the inlet pressure of diluting gas which is continuously monitored and kept equal to 4500 mbar. Next, a controlled amount of sample from primary dilution is sucked due to the pressure drop generated by the high velocity flow nozzle of the

5.1. EXPERIMENTAL ENGINE SETUP

Table 5.1: Engine conditions

Fuel	P _{intake} (bar)	ϕ	Engine speed (rpm)	Spark ignition timing (°CA)
CH ₄	1	1	1000	-15
	–	–	1500	-16
	–	–	2000	-16
NH ₃	1	1	1000	-33
	–	–	1500	-39
	0.9	1	1000	-38
	0.8	1	1000	-40
	–	–	2000	-49
	0.7	1	1000	-41
NH ₃ /H ₂ –95/5 (% in vol.)	1	1	1000	-29
	0.9	1	1000	-32
	0.8	1	1000	-35
	–	–	2000	-41
	0.7	1	1000	-35
	–	–	2000	-44
	0.55	1	1000	-40
	–	–	2000	-41
NH ₃ /H ₂ –90/10 (% in vol.)	1	1	1000	-25
	0.9	1	1000	-27
	0.8	1	1000	-32
	–	–	2000	-35
	0.7	1	1000	-31
	–	–	2000	-37
	0.55	1	1000	-39
	–	–	2000	-40

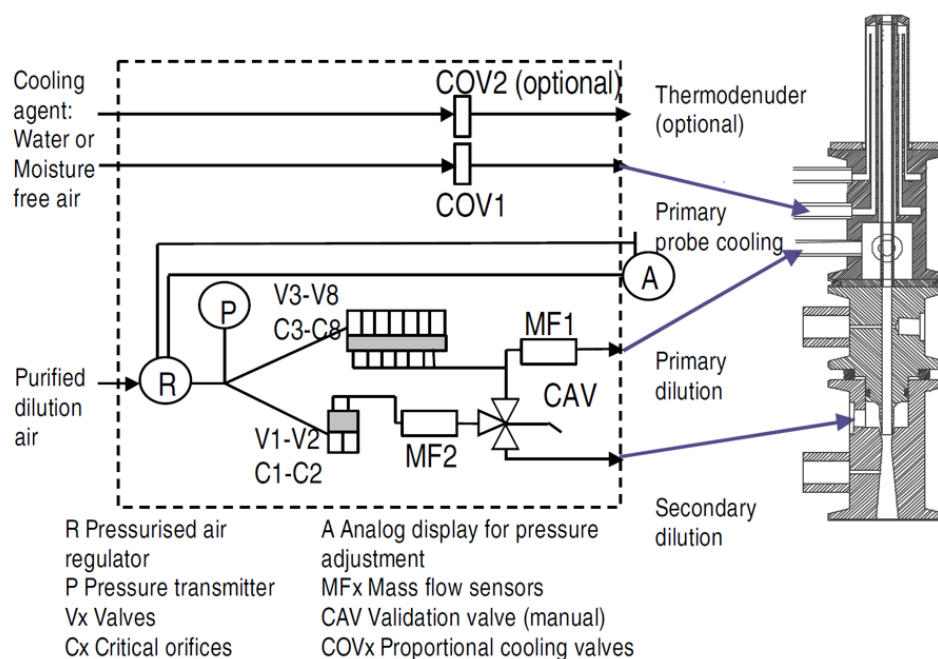


Figure 5.3: Scheme of FPS valve box and two-stage dilution [176]

ejector. The diluting gas is indeed injected at high velocity on the sides of the nozzle, creating a local low-pressure zone that entrains the sample into the flow, where it is mixed with the diluting gas. The diluting gas flow rate for the ejector is determined by two valves (n°1 and 2). Dilution ratio is determined by four parameters including diluter dimensions, dilution air flow, sample temperature and pressure drop in the ejector nozzle.

Here, the sample and the primary dilution air were heated to 150 °C. Dilution ratios associated to different valve combinations were calculated using FTIR measurements of diluted and non-diluted samples (Section 5.1.4). The diluter had several outlets, which could be connected to a FTIR gas analyzer, an Engine Exhaust Particle Sizer (EEPS), a Mini Particle Sampler (MPS), and finally connected to the exhaust.

Dilution conditions have a direct influence on the vapor pressure of each species in the exhaust. Theoretical calculation of the water content in the exhaust gases gives respectively 19.5 % and 31 % H₂O for methane and ammonia combustion at stoichiometry (Table 5.7), meaning water partial pressures close to 20 and 30 kPa at the exhaust at atmospheric pressure. Under these conditions, water condensation will occur at temperatures respectively below 60 and 70 °C [177]. Therefore, before and during the first dilution stage, the sample and dilution air must be kept at temperatures significantly higher than 70 °C, which was the case as both were heated to 150 °C. However, the second dilution occurs with air at room temperature, and the final sample temperature, measured both by a thermocouple at FPS4000 outlet and at EEPS inlet ranged between 23 and 31 °C. The water vapor saturation pressure at 23 °C, $P_{\text{sat,H}_2\text{O}}$, is 2.812 kPa [177]. Consequently, for stoichiometric ammonia combustion with a water partial pressure of 30 kPa in the exhaust, the raw exhaust must theoretically be diluted by at least a factor of 11 to prevent condensation. For methane combustion, calculation of the theoretical minimum dilution factor gives 7. In this calculation, water only was considered, but other volatile species can be found in the exhaust, such as short hydrocarbon residues, sulfates and nitrates, which can themselves nucleate, homogeneously or on pre-existing nuclei.

1.3 Engine Exhaust Particle Sizer (EEPS)

Real-time size distribution of particulate matter was monitored using a TSI Engine Exhaust Particle Sizer (EEPS). Instrument specifications are summarized in Table 5.2. As depicted in Figure 5.4, the exhaust sample is pumped into the instrument at 10 L/min and passes through an electrical diffusion charger. This charger generates ions which mix with the aerosol and electrically charge the particles contained according to a predictable charge level based on their size. Particles are then entrained via a stream of purified sheath air at 40 L/min into the sizing region, heated to 70 °C. The analyzer column consists in two concentric cylinders, the outer one being built from stacked sensing electrode rings electrically insulated from one another, while the inner is connected to a positive high voltage supply. An electric field is then generated between the two cylinders. While particles are carried along into the column by the sheath air,

5.1. EXPERIMENTAL ENGINE SETUP

they are repelled by the inner cylinder and travel towards the electrodes. They deviate and impact electrodes, according to their charge level, the latter being related to their size. Thus, the instrument measures electrical mobility diameters. As they impact an electrode, particles transfer their charge, and the generated current is amplified and digitized. This signal is then analyzed using inversion matrices as explained by the manufacturers in [178]. The SOOT inversion matrix was used here. Data is transferred to a dedicated software with a frequency of 10 acquisitions per second.

Size distributions generally follow lognormal distributions. Normalized data $\frac{dN}{d\log D_p}$, with dN the particle concentration and $d\log D_p$ the logarithmic diameter interval, are usually employed for analysis and representation, as they allow for comparison between instruments with different bin width. The Geometric Mean Diameter (GMD) can be calculated as follows:

$$\text{GMD} = \exp \left(\frac{1}{\sum_{i=1}^N n_i} * \sum_{i=1}^N n_i * \log D_{p,i} \right) \quad (5.1)$$

With:

- n ranging between 1 and 32, to calculate the global GMD of the distribution over all channels,
- n ranging between 1 and 8 (size between 5.6 and 16.5 nm), to calculate the GMD of the nucleation mode, specifically for this study

Table 5.2: Engine Exhaust Particle Sizer Specifications

Model	EEPS 3090-AK
Particle size range	5.6 to 560 nm
Particle size resolution	32 channels (16 per decade)
Charge mode of operation	dual unipolar diffusion charges
Aerosol inlet	10 L/min
Sheath flow	40 L/min
Software	EEPS 3.2.5

In this study, data were continuously acquired over time slots of 1h, and event times were recorded in parallel. Before starting a measurement sequence, acquisition of the baseline level was performed using an HEPA filter (High Efficiency Particulate Air filter standard, retaining at least 99.97 % of particles larger than 0.3 μm) for at least 5 min. In case of any residual pollution, the electrometers were cleaned using the procedure detailed by the instrument manufacturer. In total, it was cleaned three times during our experimental campaign. Subsequently, the level of the dilution air was measured before each new sequence. Once every three to six measurements in a sequence, the baseline level was measured again by placing the HEPA filter on the inlet of the instrument to ensure no pollution was accumulating.

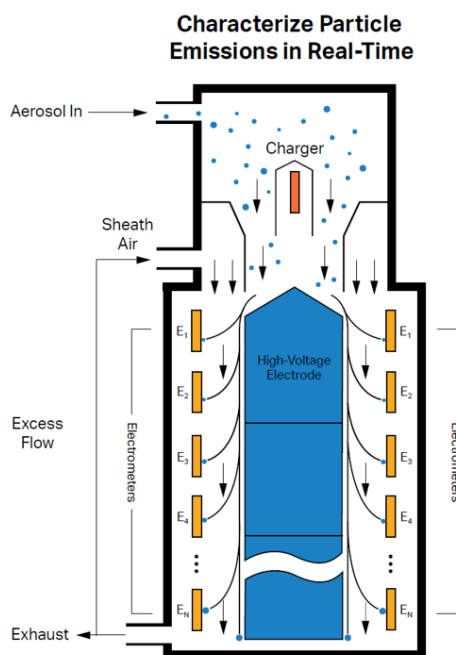


Figure 5.4: Scheme of EEPS principle [179]

1.4 FTIR spectroscopy

Gaseous emissions were measured directly at the exhaust or after dilution with a Gasmet FTIR gas analyzer. The sample was heated to 180 °C, and the pump flow rate was set to 10 L/h. Absorption spectra were recorded with a 200 cm optical path length, averaging 600 scans per sample during a 2-minute acquisition time. Spectra were collected over a wavenumber range of 594 to 4238 cm^{-1} with a spectral resolution of 7.7 cm^{-1} . The relative quantification of exhaust gases was based on spectral extrapolation using the Calcmnet database, which includes reference spectra of the target compounds across an appropriate range of standard concentrations. The wavenumber ranges used for gas quantification are summarized in Table 5.3 [180]. Cross-component interferences were indicated in the analysis settings to be taken into account by the calculation software.

Table 5.3: Analysis ranges for FTIR measurements and gas quantification

Gas	Range 1	Range 2	Range 3
H ₂ O (%)	3950–4240 cm^{-1}		
CO ₂ (%)	850–1150 cm^{-1}		
CO (ppm)	2000–2200 cm^{-1}	2540–2590 cm^{-1}	
CH ₄ (ppm)	2400–3100 cm^{-1}		
N ₂ O (ppm)	2000–2250 cm^{-1}		
NO (ppm)	1875–2138 cm^{-1}		
NO ₂ (ppm)	1250–1720 cm^{-1}	2700–2950 cm^{-1}	
NH ₃ (ppm)	1000–1240 cm^{-1}	1810–2223 cm^{-1}	2550–3450 cm^{-1}

5.1. EXPERIMENTAL ENGINE SETUP

Comparison of measurements conducted under methane combustion, directly at the exhaust and after dilution with different valve combinations was used to determine the associated Dilution Factors (DF). Dilution factors were calculated for each quantified exhaust gas to consolidate the estimation. Moreover, they were also calculated using a totally different methodology. A standard O₂ gas bottle with a concentration of 20 % and a standard CO₂ bottle with a concentration of 2000 ppm were used to calculate dilution factors independently from the engine. In that case, nitrogen was used as a diluting gas and a dedicated GenTwo Multigas V2.4 analyzer was used to measure O₂ and CO₂ resulting concentrations for different valves combinations. Dilution factors, calculated using formula (5.2) and both protocols, are summarized in Table 5.4. The measured values are only valid for dilution with a sample and primary dilution air both heated to 150 °C.

$$DF = \frac{x_{DF=1} - x_{\text{diluting gas}}}{x_{DF} - x_{\text{diluting gas}}} \quad (5.2)$$

with $x_{\text{diluting gas}}$ the molar fraction in the gas used for the dilution, $x_{DF=1}$ the molar fraction in the raw non-diluted sample, and x_{DF} in the diluted sample with an unknown dilution factor.

The two different protocols implemented to calculate dilution factors, and the different gases resulted in comparable values for each valve combination, except at high dilution factors where concentrations in the sample and the diluting gas were too close to provide accurate estimations. Overall, error on dilution factor calculation was close to the 10 % error indicated by the manufacturer Dekati.

Table 5.4: Calculation of the dilution factor for different valve combinations, based on the concentration measurements of gases at the exhaust using FTIR (H₂O, CO₂, CO, CH₄, NO) and O₂ and CO₂ analyzer with standard gas bottles

Valves	H ₂ O	CO ₂	CO	CH ₄	NO	O ₂ std.	CO ₂ std.	Dilution Factor
10100000	11	14	13	11	10	12	11	12 ± 1.5
10001000	16	20	17	16	14	18	17	17 ± 2
10000100	22	24	23	20	17	27	–	22 ± 3.3
10000010	36	39	33	25	26	43	43	35 ± 8
10110000	53	50	48	39	41	–	–	46 ± 5.9
10101000	71	–	–	77	80	–	–	76 ± 4.5

1.5 Mini Particle Sampler (MPS)

To enable further observation and characterization of particles, exhaust particles were also collected directly onto microscopy grids. Real-time size distribution measurements with the EEPs indeed detect all sorts of particles, regardless of their nature and composition. This was accomplished thanks to a Mini Particle Sampler (MPS) device from Ecomesure [181]. A scheme is displayed in Figure 5.5. This device consists of a grid holder, into which the sample is drawn by the aspiration generated by a pump. Through mechanisms such as inertial

5.1. EXPERIMENTAL ENGINE SETUP

impaction, interception, and surface diffusion, particles are collected on the grid with a size-dependent efficiency [181]. The outlet pump was a Gilian GilAir plus enabling a precise control of the sampling time and aspiration flow rate. Sampling times varied from 1 to 10 min, with a pumping flow rate between 300 to 600 cc/min. Holey Carbon on 300 gold mesh microscopy grids were used. The sampling conditions of the grids analyzed in this study are summarized in Table 5.5.

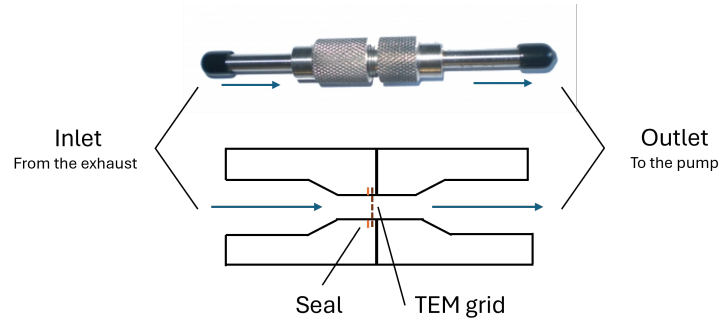


Figure 5.5: Scheme of the Mini Particle Sampler (MPS) principle

Table 5.5: Sampling conditions of the analyzed microscopy grids

Grid	Fuel	Engine speed (rpm)	DF	Sampling time (min)	Pump flow rate (cc/min)	Engine oil
1	NH ₃	1500	35	10	600	LUB
2	NH ₃	1500	35	10	600	Oil B2
3	NH ₃	1500	35	10	600	Oil B2 pre-aged
4	CH ₄	1500	22	10	600	Oil B2 pre-aged
5	Air	—	—	10	600	—

Figure 5.6 shows the microscopy grid collected after 10 min under pure dilution air. This picture enables to show the structure of the carbon membrane (dark gray) with random holes (light gray), on which particles can be deposited. Black areas on the sides delimit one square of the gold mesh. In that case, the grid was almost empty, confirming that the contribution of the air used for dilution to particles measurement was minimal.

1.6 Methodology for engine test experiments and data processing

The same sequence was repeated on each measurement day to minimize biases related to engine warm-up conditions, load ramp-up, and residual exhaust pollution between operating points. As described in Section 5.1.3, the baseline levels of the electrometers of the EEPS and the dilution air level were measured at the beginning of each measurement day. In parallel, the chemical composition of the dilution air was also measured with FTIR analysis. Next, motoring conditions at 1000 rpm were recorded. Then, the engine was warmed-up with methane combustion for a few minutes. For this operating point, FTIR analysis of the

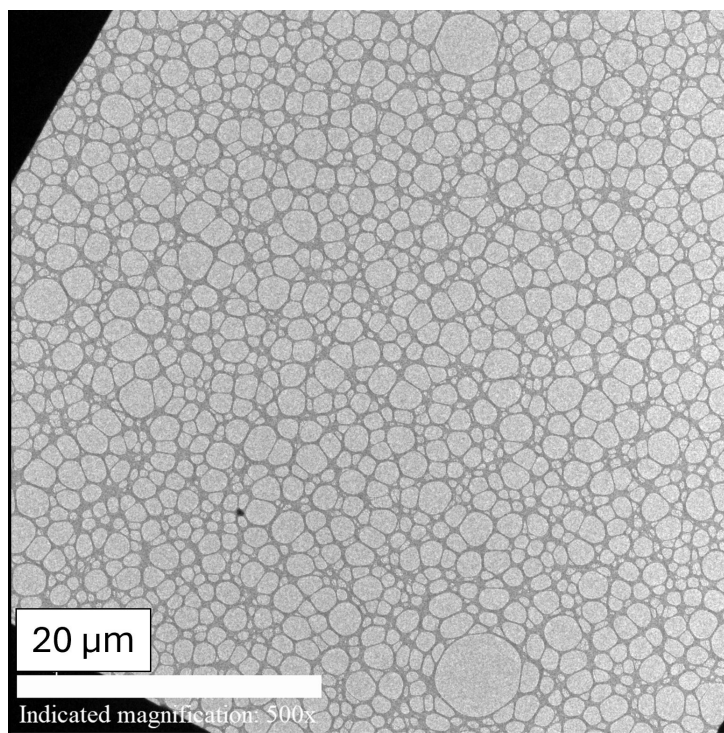


Figure 5.6: Aspect of an empty Holey carbon microscope grid, grid n°5. The gold mesh appears in black, carbon membrane in dark gray and holes in the membrane in lighter gray

combustion gases was conducted directly at the exhaust, without dilution. This procedure enabled to check the dilution factors for the following sequence. Subsequently, the engine was operated under methane and ammonia combustion separately at 1000 rpm, and alternatively at 1500 rpm and 2000 rpm. Details about the operating conditions and successive points can be found in Appendix C.2. Stability of the baseline level of the EEPS was checked by placing a HEPA filter on the inlet of the instrument after conditions resulting in high ammonia and water levels, and after three to six measurements. Engine parameters and exhaust FTIR spectra were recorded after stabilization, typically around 1 to 2 min after gas injection. For each engine condition, the engine was operated for at least 5 min, and the size distribution was averaged after stabilization.

Similar operating conditions (Table 5.1) were repeated during different sequences and on different days with each engine oil to assess between-day repeatability of the measurements. Among all the recorded conditions, fine analysis of the engine parameters enabled to select groups of points with highly similar conditions for further analysis of the exhaust emissions. Within each group, average engine parameters were calculated. The exhaust particle size distributions were also averaged by dilution factor group, and the corresponding standard deviation was calculated.

1.7 Microscopy imaging

Microscope grids were observed at three levels using: Scanning Electronic Microscopy (SEM), Scanning Transmission Electronic Microscopy (STEM), and Transmission Electronic Microscopy (TEM). The schemes in Figure 5.7 depict the principle of each of these techniques. SEM observations were conducted with a Zeiss Crossbeam 350 microscope, with tension of 25 kV, a diaphragm opening of 7.5 μm and a 3-mm working distance. It was used as a first approach to select optimal sampling conditions for TEM observations, which are more demanding. Two microscopes were used for TEM and STEM analysis, the observation conditions are summarized in Table 5.6. Energy Dispersive X-ray Spectrometer (EDS) was used to conduct element analysis of the samples in STEM mode. EDS is a technique that identifies and quantifies the elemental composition of a sample based on the detection of X-rays emitted under the electron beam. In particular, it was used to detect nitrogen. Because this element is very light, like oxygen and carbon, its quantification with EDS is uncertain. Nevertheless, absence or presence could be determined by analyzing EDX spectra of the samples showing a characteristic peak, or not, as in Figure 5.8, even if the peak area could not be further interpreted. Therefore, elemental analysis results are presented without absolute quantification in the section dedicated to microscopy observations. Microscope observations were conducted by the Analysis Department of IFPEN.

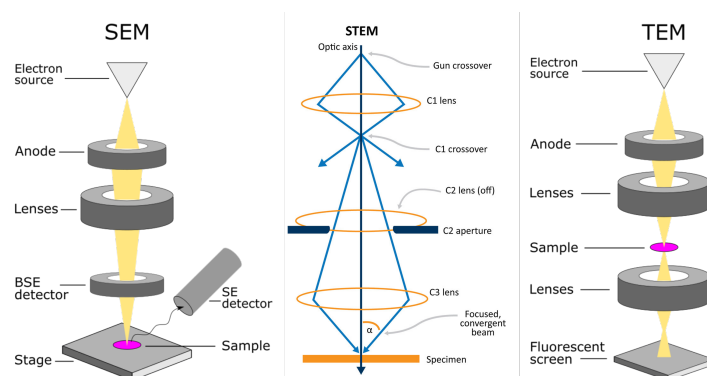


Figure 5.7: Principle of SEM, STEM and TEM microscopy. Reprinted from [182, 183], copyright AnaPath Research and Springer Science

Table 5.6: Parameters of the microscope observations

Instrument	Parameter	Conditions
JEOL 2100F and JEOL F200	Tension	200 kV
STEM HAADF	Spot	1 nm
	Image size	1024 × 1024
	Pixel time	40 μs
EDS-STEM mode	Live time (point analysis)	60 s
	Live time (map)	10 min

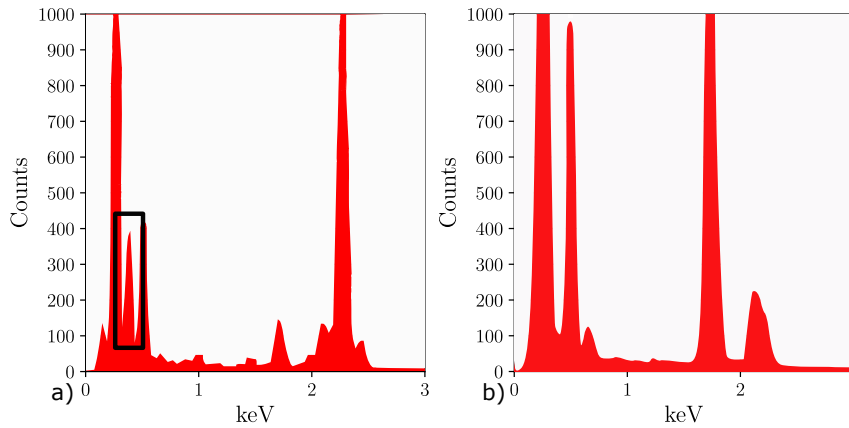


Figure 5.8: Zoom on the EDX spectra of a) an object in which nitrogen was detected, b) no nitrogen was detected

2. Effect of the oil on engine operation and gaseous emissions

2.1 Effect of the engine oil under methane combustion

The engine was alternatively operated under methane and ammonia combustion, and successively with a reference fully-formulated lubricant (LUB), a group III mineral base oil (B2), and a pre-aged base oil (pre-aged B2), as detailed in previous chapter and compiled in Appendix C.2. No influence of the engine oil on engine operation was observed during methane combustion. Figure 5.9 shows that the mean IMEP was identical with the three engine oils, for measurements conducted at 1000, 1500 and 2000 rpm. Details about operating conditions and engine parameters can be found in Appendix D.1, D.2 and D.3. The change in engine oil having no effect on the combustion of methane, it also had no effect on resulting engine exhaust composition, as shown in Figure 5.10. This figure shows the raw individual measurements of H_2O , CH_4 , CO_2 , CO , and NO concentrations in the exhaust gases, before applying dilution correction. For each gas, no significant effect of the engine oil could be observed. Measurements conducted directly at the exhaust without dilution are summarized in Table 5.7. The values measured were close to what was theoretically expected considering complete burning of methane at stoichiometry.

Table 5.7: Exhaust gas composition measured without dilution for CH_4 , $\phi=1$, $P_{in}=1$ bar, 1000 rpm, compared to theoretical values

Gas	Measured without dilution	Theoretical
H_2O (%)	18.8 ± 1	19.5
CH_4 (ppm)	1490 ± 40	
CO_2 (%)	9.6 ± 0.2	9.5
CO (ppm)	4200 ± 900	
NO (ppm)	2200 ± 140	

5.2. EFFECT OF THE OIL ON ENGINE OPERATION AND GASEOUS EMISSIONS

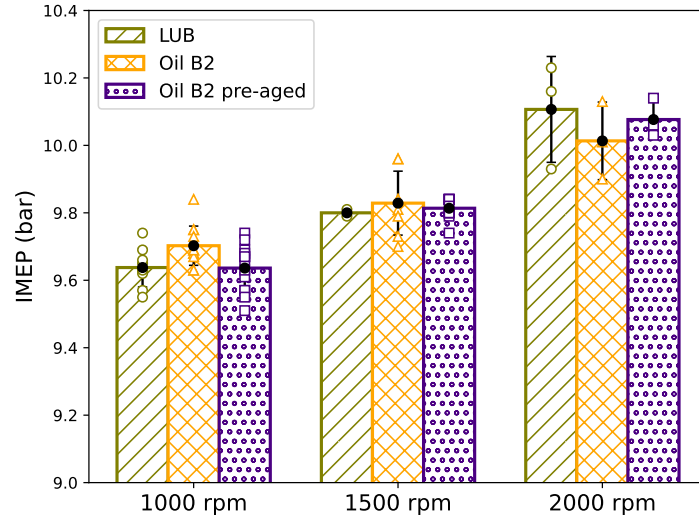


Figure 5.9: IMEP values for CH_4 , $\phi=1$, $P_{in}=1$ bar, at 1000, 1500 and 2000 rpm with three different oils

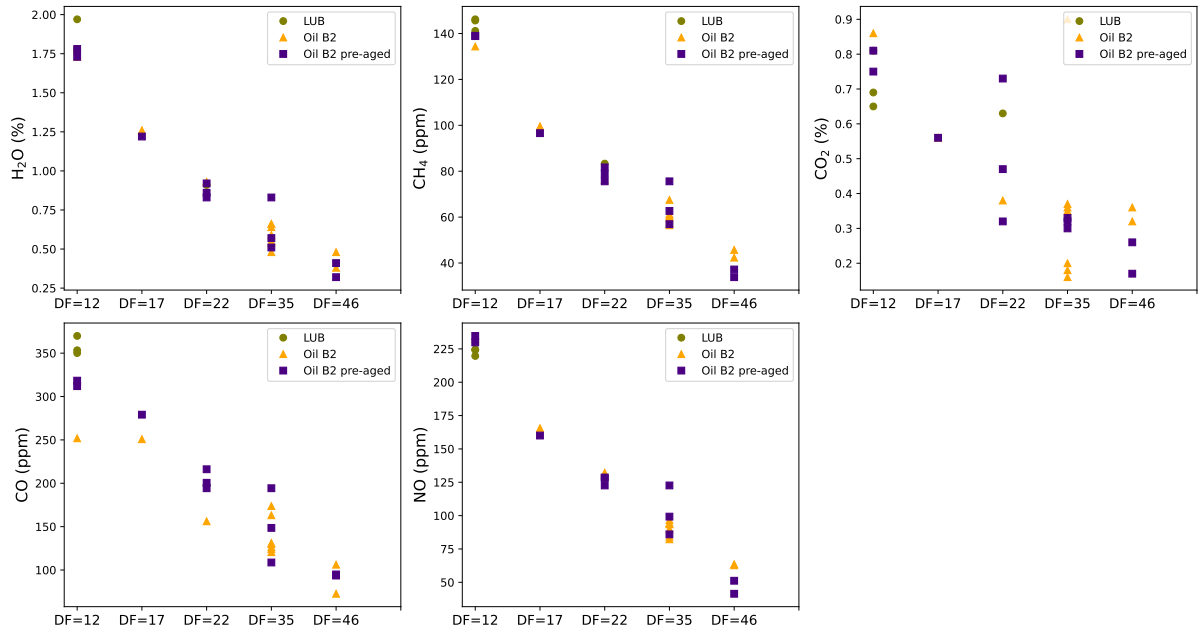


Figure 5.10: Concentrations of H_2O , CH_4 , CO_2 , CO and NO in the exhaust gases (CH_4 , $\phi=1$, $P_{in}=1$ bar, 1000 rpm). Raw diluted measurements are presented without dilution correction

2.2 Effect of the engine oil under ammonia combustion

On the contrary, engine oils seems to affect ammonia combustion. Despite consistency in the operating conditions, such as intake pressure (P_{in}), equivalence ratio (ϕ), gas flow rate and inlet temperature (Appendix D.4 and D.5), maximum in-cylinder pressure and IMEP were significantly lower with the pre-aged oil. This was both verified at 1000 and 1500 rpm (Figure 5.11). Overall, thermal efficiency was lower when the pre-aged base oil was used as the lubricant. Besides, IMEP values at stoichiometry were lower than with methane (Figure 5.9), resulting in lower indicated power, as shown in Appendix D.10.

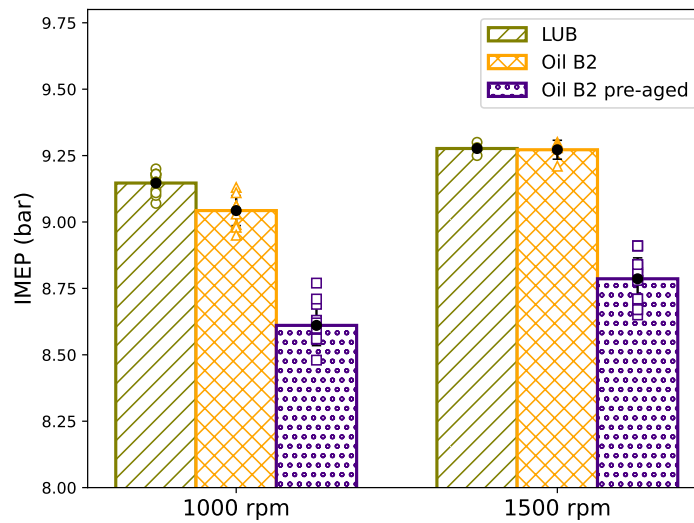


Figure 5.11: IMEP values for NH_3 , $\phi=1$, $P_{in}=1$ bar, at 1000 and 1500 rpm with three different oils

Oil B2 behaved similarly to the fully formulated lubricant, despite not containing any anti-wear, extreme-pressure, or friction-modifying additives. This indicates that the absence of additives alone does not explain the behavior of the pre-aged oil. As discussed in Chapter 4, the pre-aged oil contained a variety of oxygenated and nitrogen-containing degradation products (Figure 4.17), which likely influenced its friction coefficient, defined in Section 1.1.1. Simulated distillation also revealed that the pre-aged base oil had a higher fraction of heavy molecules with boiling points above 520°C compared to the fresh oil B2 (Figure 4.11). Furthermore, our results showed that NH_3 and H_2O exhibited greater affinity for the pre-aged base oil. This suggests that, in addition to inherent differences in friction coefficients, trapped NH_3 or H_2O vapor may have disrupted the lubricating film. Such interactions, occurring directly during combustion on the cylinder liner for instance, could locally alter lubrication, which may explain why methane combustion appeared unaffected by the engine oil. Supporting this, Rappo *et al.* [30] found that measuring the friction coefficient of a lubricant under an ammonia atmosphere led to higher values and larger wear scars, attributed to ammonia adsorption into the lubricant. Similarly, Rao *et al.* [31] reported an increased friction coefficient after exposing a lubricant to gaseous ammonia for 288 h at 80°C . Nonetheless, elemental analysis revealed high and increasing concentrations of metals such as iron, zinc, and copper in the pre-aged base

5.2. EFFECT OF THE OIL ON ENGINE OPERATION AND GASEOUS EMISSIONS

oil over time (Figure 4.15), indicating both corrosion and increased wear with this oil. This suggests that the pre-aged base oil caused higher friction between metallic engine components, increasing thermal losses and reducing engine efficiency. Lubricant formulation remains an active area of research, as it is well established that lubricants influence engine efficiency in addition to protecting engine components. It is therefore consistent that operating the engine with a degraded oil affects its efficiency. However, the fact that methane combustion was not affected points to a specific interaction between gaseous ammonia and the engine oil occurring during combustion, rather than being a general consequence of oil degradation that would impact all fuels equally.

Figure 5.12 shows the IMEP as a function of the fuel flow rate for a) methane and b) ammonia with the three engine oils. With methane combustion, all oils are grouped, whereas with ammonia distinct groups clearly appear. Due to a slight deviation of the ammonia flowmeter during engine tests with oil B2, flow rates were approximately 2 NL/min lower for these points, which was automatically taken into account on the air flow rate to maintain an equivalence ratio of 1, and the IMEP was still similar as with the fully-formulated lubricant. On the contrary, despite similar ammonia flow rates, the IMEP obtained with the engine operated with the pre-aged base oil was clearly lower than with other oils, highlighting the impact of the pre-aged base oil. Similarly, CA50 values were highly similar for the fully-formulated lubricant and pre-aged base oil, but the maximum pressures measured were significantly lower with the pre-aged base oil (Figure 5.13). This underscores the influence of engine oil, despite identical combustion phasing.

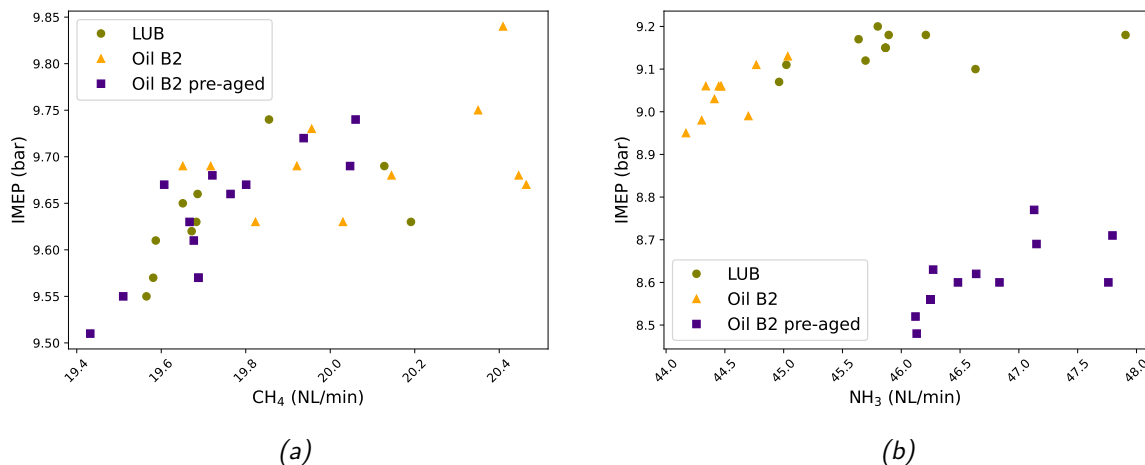


Figure 5.12: IMEP as a function of fuel flow rate for engine operation under a) CH_4 , $\phi=1$, $P_{in}=1$ bar, 1000 rpm, and b) NH_3 , $\phi=1$, $P_{in}=1$ bar, 1000 rpm

Engine oil affected the combustion, but also the resulting emissions (Figure 5.14 and Appendix D.8 for values at 1500 rpm). Figure 5.14 shows that ammonia combustion with the pre-aged base oil resulted in lower concentrations of CO, but higher NO and N_2O levels, as well as slightly lower NH_3 concentration. H_2O and CO_2 levels were comparable. Higher CO levels might indicate higher oil consumption by evaporation and burning with the fully formulated

5.2. EFFECT OF THE OIL ON ENGINE OPERATION AND GASEOUS EMISSIONS

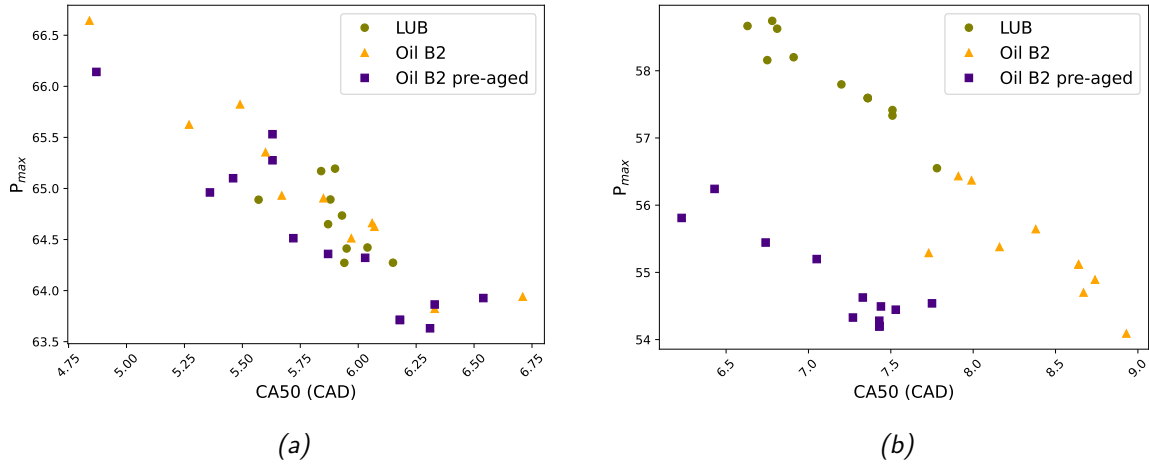


Figure 5.13: Maximum in-cylinder pressure as a function of CA50 for engine operation under a) CH_4 , $\phi=1$, $P_{in}=1$ bar, 1000 rpm, and b) NH_3 , $\phi=1$, $P_{in}=1$ bar, 1000 rpm

lubricant and the fresh mineral base oil. This could be linked to the lower viscosity of these oils compared to the pre-aged one (Table 5.8). Increased friction might have contributed to promote thermal- NO_x production by generating very high temperatures locally.

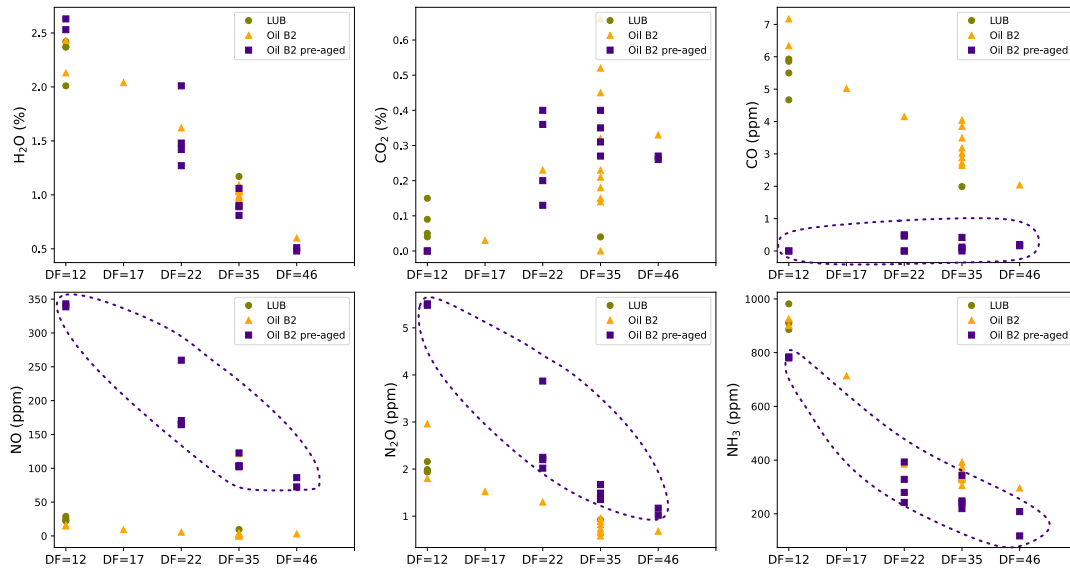


Figure 5.14: Concentrations of H_2O , CH_4 , CO_2 , CO , NO , N_2O and NH_3 in the exhaust gases (NH_3 , $\phi=1$, $P_{in}=1$ bar, 1000 rpm). Raw diluted measurements are presented without dilution correction

Table 5.8: Dynamic viscosity of the three oils at engine inlet oil temperature (60 °C) and 100 °C

Engine oil	Dyn. Viscosity at 60 °C (mPa · s)		Dyn. Viscosity at 100 °C (mPa · s)	
	t0	tf	t0	tf
LUB	27.8 ± 0.3	25.5 ± 0.3	9.4 ± 0.1	8.8 ± 0.09
Oil B2	20.0 ± 0.2	18.3 ± 0.2	6.2 ± 0.07	6.2 ± 0.07
Oil B2 pre-aged	21.5 ± 0.3	23.8 ± 0.3	6.3 ± 0.07	7.0 ± 0.07

5.2. EFFECT OF THE OIL ON ENGINE OPERATION AND GASEOUS EMISSIONS

Similar tendency for NO and N_2O levels were also observed at 1500 rpm (Figure 5.15). NO concentration, which was almost negligible at 1000 rpm for oils LUB and B2, increased but remained lower than with pre-aged oil B2 at 1500 rpm. On the contrary, CO concentration was significantly reduced for the three oils at 1500 rpm, especially for oil B2 which exhibited the highest concentrations at 1000 rpm. NH_3 level was comparable between the three oils at 1500 rpm. Normalized values, in g/kWh, can be found in Appendix D.9 and show the same trends. Normalized emission levels were comparable with values in [16], which also showed that increasing engine speed resulted in higher NO_x levels, and higher N_2O levels.

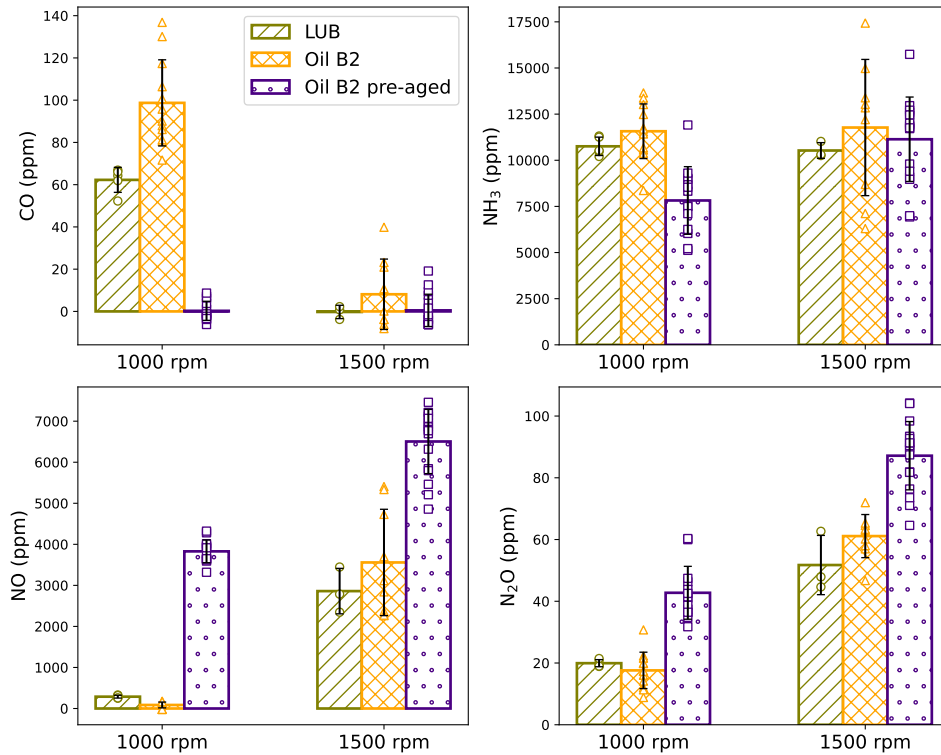


Figure 5.15: Concentrations of CO, NH_3 , NO, and N_2O in the exhaust gases (NH_3 , $\phi=1$, $P_{in}=1$ bar, 1000 and 1500 rpm), values are corrected considering dilution factors

Effect of the intake pressure The reduced thermal efficiency of the engine with the pre-aged base oil and subsequent effect on gaseous emissions was consistent at lower intake pressures, 0.9 and 0.8 bar (Figure 5.16, detailed points in Appendix D.6 and D.7). For the three oils, the IMEP decreased with the intake pressure, as several times reported in [4,16] for instance, but it remained lower with the pre-aged base oil. Exhaust gases composition did not vary in proportions with the intake pressure decrease, but retained the tendency with higher NO and N_2O , lower CO and similar NH_3 for points with the pre-aged base oil (Figure 5.17). Even after normalization, varying the intake pressure between 0.8 and 1 bar did not affect the emissions (Appendix D.11).

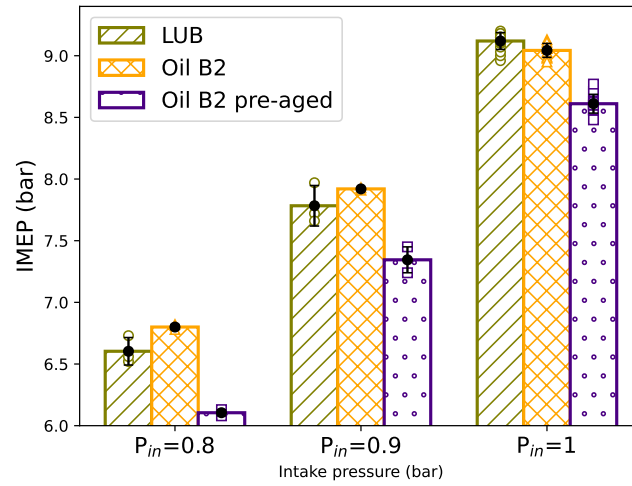


Figure 5.16: IMEP as a function of the intake pressure for the three oils (engine conditions NH_3 , $\phi=1$, $P_{in}=0.8, 0.9, 1$ bar, 1000 rpm)

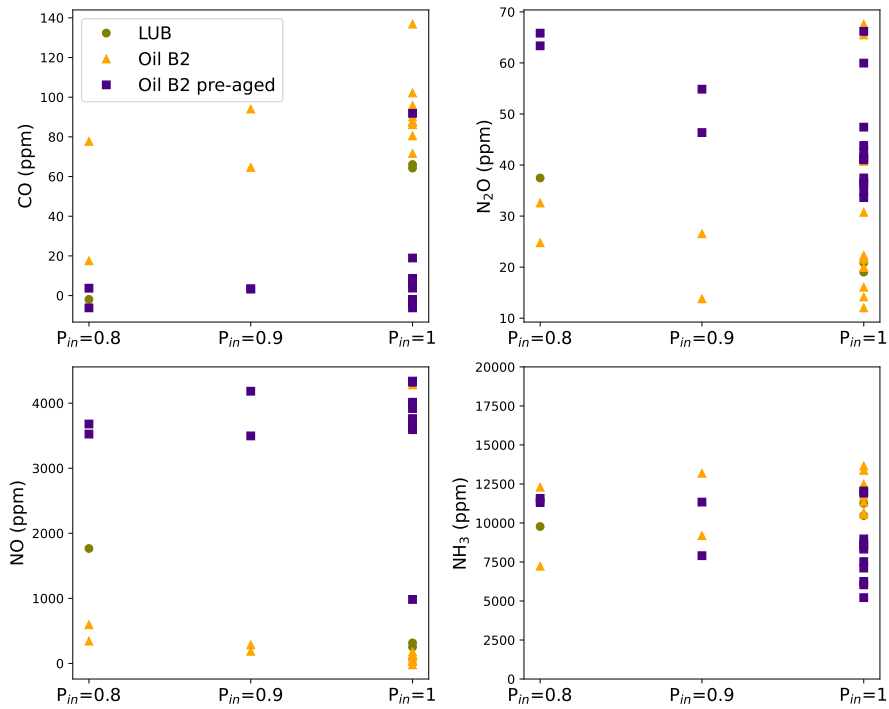


Figure 5.17: Concentrations of CO, NH_3 , NO, and N_2O in the exhaust gases (NH_3 , $\phi=1$, $P_{in}=0.8, 0.9$ and 1 bar, 1000 rpm), values are corrected considering dilution factors

Reducing the intake pressure slightly decreased the absolute gas flow rate passing into the blow-by circuit (Figure 5.18 a), consistent with the fact that the pressure difference between the combustion chamber and the crankcase was reduced. Normalizing by the total volume of injected gas (Figure 5.18 b) highlighted that the gas fraction passing into the blow-by circuit was close for experiments with P_{in} between 0.8 and 1 bar. No significant effect of the engine oil on the blow-by rate was observed.

5.2. EFFECT OF THE OIL ON ENGINE OPERATION AND GASEOUS EMISSIONS

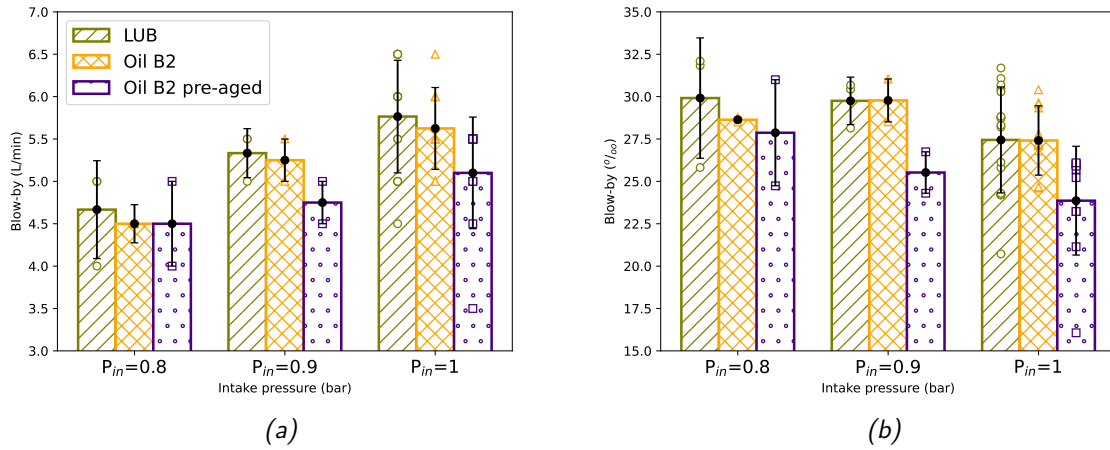


Figure 5.18: Blow-by rate a) absolute, in L/min and b) as a fraction of the total volume of gas in $\%/\text{cc}$, for NH_3 , $\phi=1$, $P_{in}=0.8, 0.9$ and 1 bar, 1000 rpm

2.3 Effect of the engine oil under ammonia/hydrogen blends combustion

Similar experiments were also conducted with ammonia/hydrogen blends, with hydrogen fraction of 5 and 10 %. Adding hydrogen enabled to stabilize the combustion over a wider range of operating conditions, for example as low as $P_{in}=0.55$ bar, still with $\phi=1$ and at 1000 rpm (Figure 5.19a). However, between 0.7 and 1 bar intake pressure, adding hydrogen up to 10 % did not affect neither the IMEP (Figure 5.19a) nor the indicated thermal efficiency, as also observed by Lhuiller *et al.* [4] and Zhang *et al.* [59] with low hydrogen fractions. Nevertheless, it helped ammonia combustion to be more stable, as shown by the lower covariance values, especially at low pressure intake in Figure 5.19b.

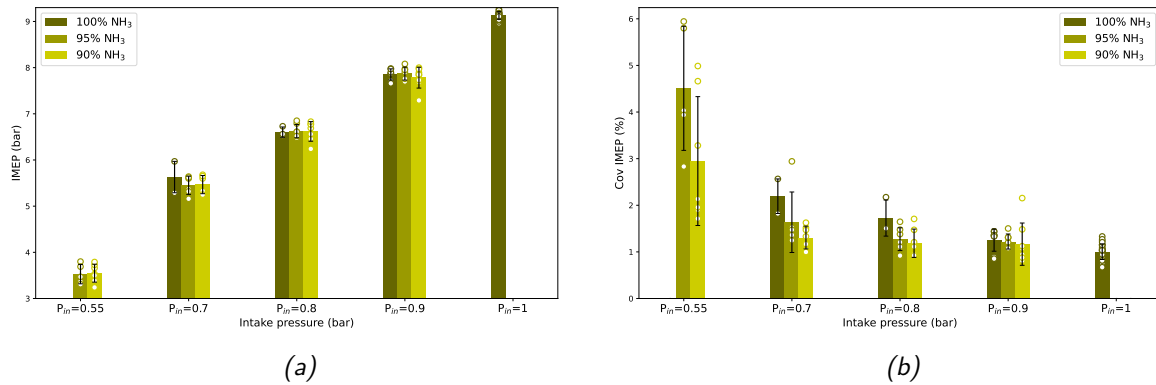


Figure 5.19: a) IMEP as a function of the intake pressure and H_2 fraction with engine oil LUB at 1000 rpm. b) Covariance of the IMEP at different intake pressures and H_2 fractions with engine oil LUB at 1000 rpm

When operated with the pre-aged base oil, the same reduction in IMEP and engine efficiency as with pure ammonia was observed with ammonia/hydrogen blends (Figure 5.20). Likewise, similar tendencies as with pure ammonia were observed regarding exhaust gases, with more NO and N_2O with the pre-aged base oil (Figure 5.21). However, for a given oil, adding 5

5.2. EFFECT OF THE OIL ON ENGINE OPERATION AND GASEOUS EMISSIONS

or 10% hydrogen had no impact on exhaust gas composition (Figure 5.21). This was also observed by Lhuillier et al. [4] who reported a clear impact on exhaust emissions starting from hydrogen fractions of 20 %.

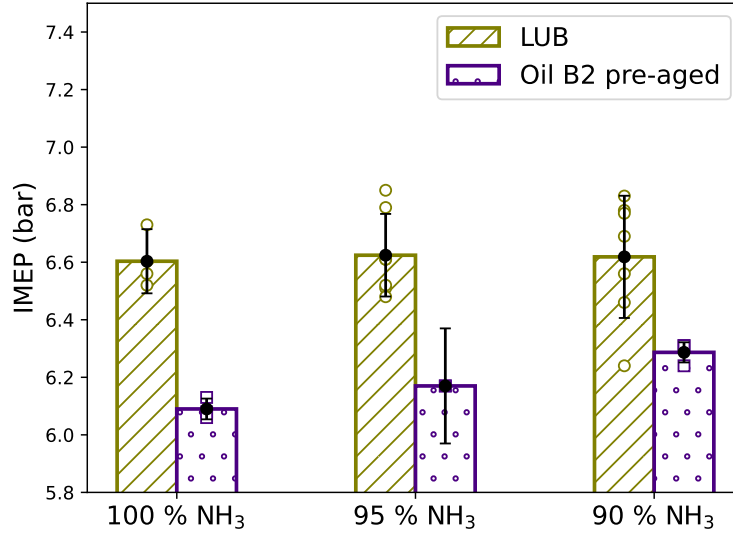


Figure 5.20: IMEP as a function of the NH_3/H_2 blend with oils LUB and B2 pre-aged ($\phi=1$, $P_{in}=0.8$ bar, 1000 rpm, 100 % NH_3 , 95 % NH_3 / 5 % H_2 and 90 % NH_3 /10 % H_2)

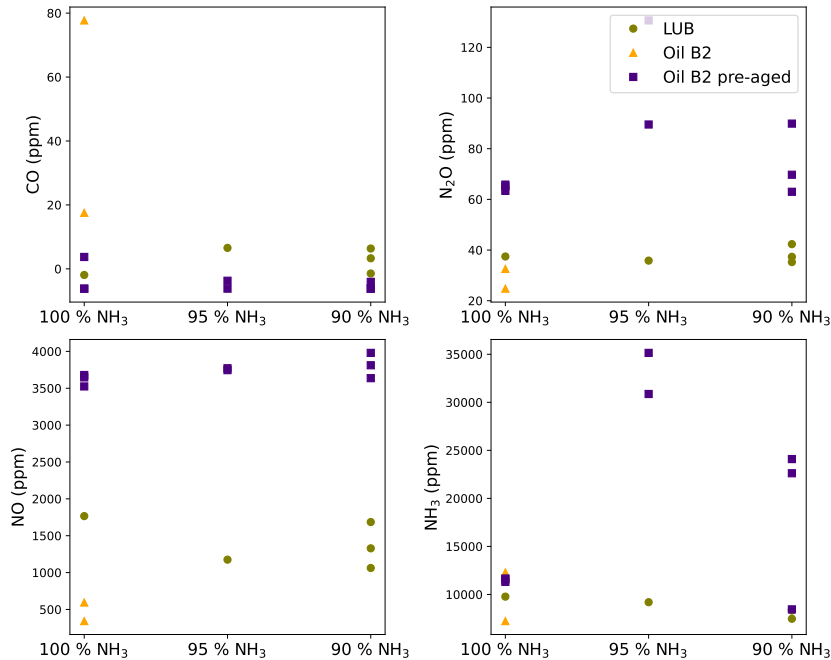


Figure 5.21: Concentrations of NO , NH_3 , N_2O , CO_2 , H_2O , and CO in the exhaust gases ($\phi=1$, $P_{in}=0.8$ bar, 1000 rpm, 100 % NH_3 , 95 % NH_3 / 5 % H_2 and 90 % NH_3 /10 % H_2), values are corrected considering dilution factors

Analysis of the engine parameters during engine tests conducted with methane, ammonia and ammonia/hydrogen blends and with three different engine oils first revealed that operating the engine with a pre-aged engine oil led to a reduced performance of the engine, with consequences on gaseous exhaust emissions. Surprisingly, this was only observed with ammonia combustion and not methane, without definitive explanation although several hypothesis were raised. Reducing the intake pressure from 1 bar to 0.8 bar did not affect the gaseous emissions in terms of relative proportions. Adding 5 and 10 % H_2 to NH_3 had no significant impact on IMEP values and exhaust gases composition. However, it enabled to stabilize NH_3 combustion for intake pressures between 0.7 and 0.9 bar, and enabled to enlarge the domain for stable combustion to intake pressures as low as 0.55 bar. The following sections investigate the particulate matter emissions generated during these same tests, focusing first on size distributions, and then on particle morphology and composition.

3. Investigating particulate matter emissions with methane and ammonia: in-line analysis

During the engine tests, real-time particle size distribution were also monitored using an EEPS under different dilution conditions. Exhaust gases may contain varied types of particles, in terms of composition, morphology and solid/volatile nature [108]. Due to its measurement principle based on aerosol charging and current sensors, the EEPS instrument does not enable to discriminate solid particles from condensed species. Therefore, dilution conditions appear as a critical parameter for the measurements, with direct influence on the vapor pressure and consequently saturation behavior of each species.

3.1 Particle size distributions under methane combustion

3.1.1 Effect of the dilution factor on the total exhaust particle concentration

Figure 5.22 shows the total particle concentration, calculated by integration of the size distribution over all the channels, obtained under methane stoichiometric combustion at different dilution factors with the LUB fully-formulated engine oil. The mean level, and error, of the dilution air is shown in black and gray dashed lines, indicating the baseline detection level in our experiments. This level was comparable to the theoretical baseline level indicated by TSI. Representation uncorrected for the dilution factor (Figure 5.22 a) highlights that dilution factors below 35 enabled to detect exhaust particles above the baseline level. After taking into account the dilution factors (Figure 5.22 b), it can be noticed that corrected total

5.3. INVESTIGATING PARTICULATE MATTER EMISSIONS WITH METHANE AND AMMONIA: IN-LINE ANALYSIS

particle numbers obtained with different dilution factors were not equal. In particular, the dilution factor of 12 resulted in a significantly higher number of particles. This might be due to enhanced homogeneous and heterogeneous nucleation of volatile species, which increased the total particle number under these conditions. A lower dilution factor indeed results in higher partial pressures of volatile species, approaching or potentially exceeding their saturation vapor pressure, thereby promoting gas-to-particle conversion and condensation on existing particles [108, 184]. As discussed in Section 5.1.2, the theoretical minimal dilution factor to prevent water condensation at the exhaust is 7 for stoichiometric methane combustion. As 12 is close to this critical value, it is likely that water and other volatile species have condensed. Higher dilution factors resulted in similar total concentrations after correction, suggesting nucleation and condensation were not specifically enhanced under these conditions. Dilution factors of 17 and 22 both enabled to measure particle level above the baseline level while limiting condensation artifacts. Besides, engine speed seemed to slightly increase the total particle numbers.

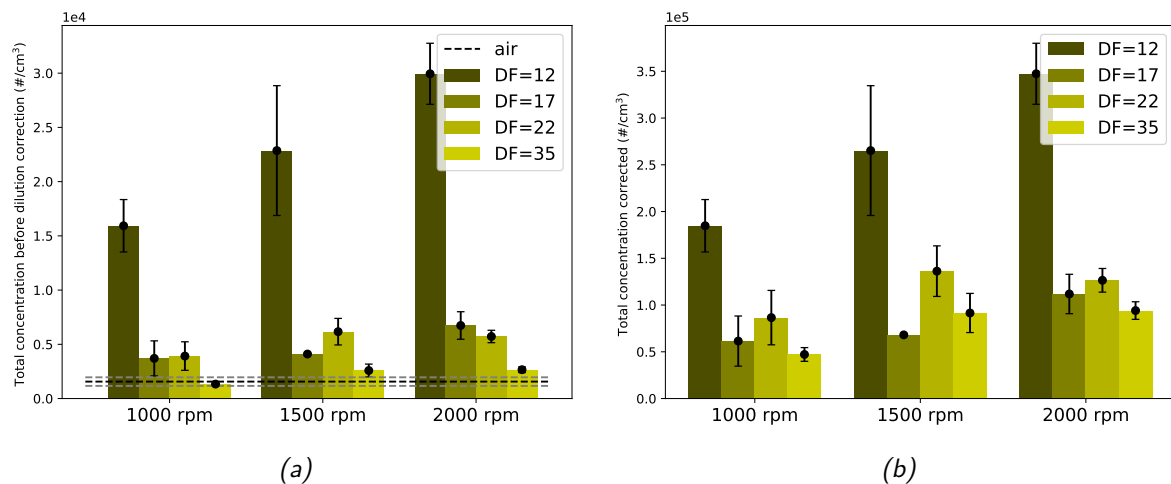


Figure 5.22: Total concentration for CH_4 , $\phi=1$, $P_{in}=1$ bar, with LUB oil at different dilution factors. a) Raw measurements b) After taking into account dilution factors

3.1.2 Effect of the dilution factor on particle size distribution

The dilution factor affects the total particle concentration, but also the aspect of the size distribution. Figure 5.23 shows the particle size distribution at different dilution factors at 1000, 1500 and 2000 rpm with the LUB fully-formulated lubricant. Particle size distribution was bimodal, as could be expected considering literature on methane exhaust emissions [108, 185, 186], with a nucleation mode, centered in 10 nm, and accumulation mode ranging between 20 and 110 nm. As detailed in Section 1.2.6, the nucleation mode corresponds to primary particles, mainly consisting of volatile organic compounds formed during exhaust dilution and cooling, and solid carbonaceous, metals or inorganic ash. The accumulation mode consists of larger particles, carbonaceous agglomerates with adsorbed condensed material. The accumulation

5.3. INVESTIGATING PARTICULATE MATTER EMISSIONS WITH METHANE AND AMMONIA: IN-LINE ANALYSIS

mode was especially visible at DF=12, and at higher speed. Increasing the dilution ratio indeed led to decrease the accumulation mode, and shift the geometrical mean diameter towards smaller values (Figure 5.24). This was also observed by Mathis *et al.* [187] who studied diesel exhaust particles, Perrier *et al.* [188] and Daoudi *et al.* [189] who studied particles directly generated by a burner. This is because lower dilution promoted condensation of volatile species on existing primary particles, increasing the number of larger particles. Similarly, the nucleation mode was specifically increased at DF=12, suggesting enhanced nucleation due to the higher partial pressures. For both accumulation and nucleation modes, dilution factors larger than 12 resulted in similar aspect of the size distribution after correction, indicating residual measurements mainly corresponded to solid particles, less affected by the dilution conditions. Higher engine speed led to both a higher nucleation mode and accumulation mode (Figure 5.23 a, b and c).

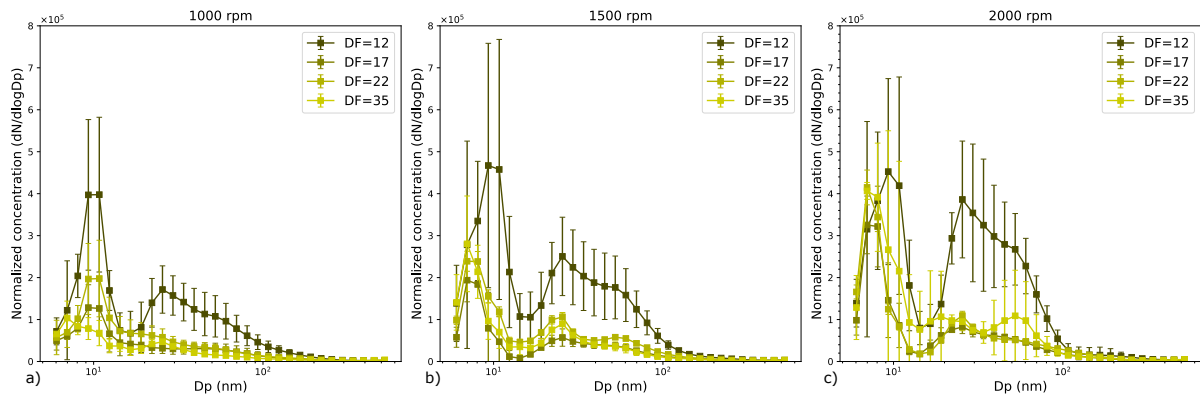


Figure 5.23: Exhaust particle size distribution at different dilution factors, for operating conditions CH_4 , $\phi=1$, $P_{in}=1$ bar, a) 1000 rpm, b) 1500 rpm, c) 2000 rpm with LUB oil. Results are presented with the dilution factor taken into account

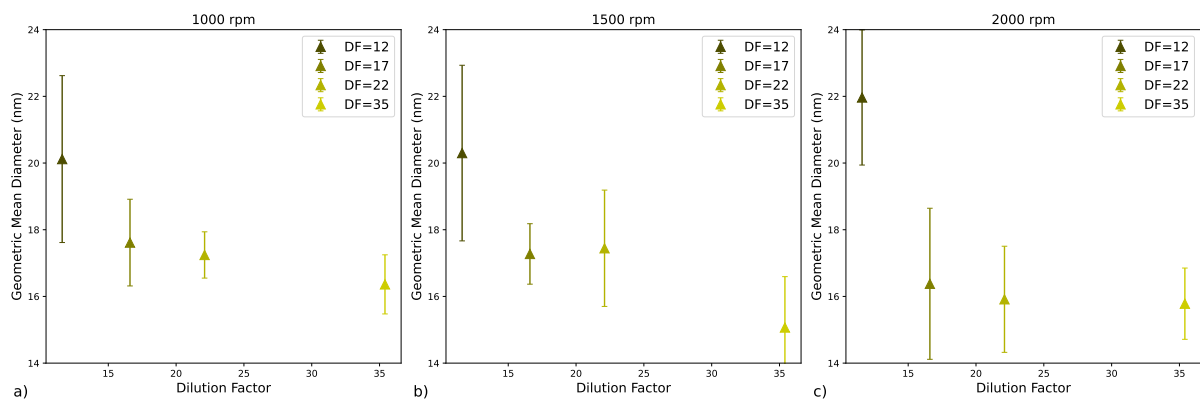


Figure 5.24: Geometric Mean Diameter as a function of the dilution factor, for operating conditions CH_4 , $\phi=1$, $P_{in}=1$ bar, a) 1000 rpm, b) 1500 rpm and c) 2000 rpm, with LUB oil

5.3. INVESTIGATING PARTICULATE MATTER EMISSIONS WITH METHANE AND AMMONIA: IN-LINE ANALYSIS

3.1.3 Effect of the engine oil

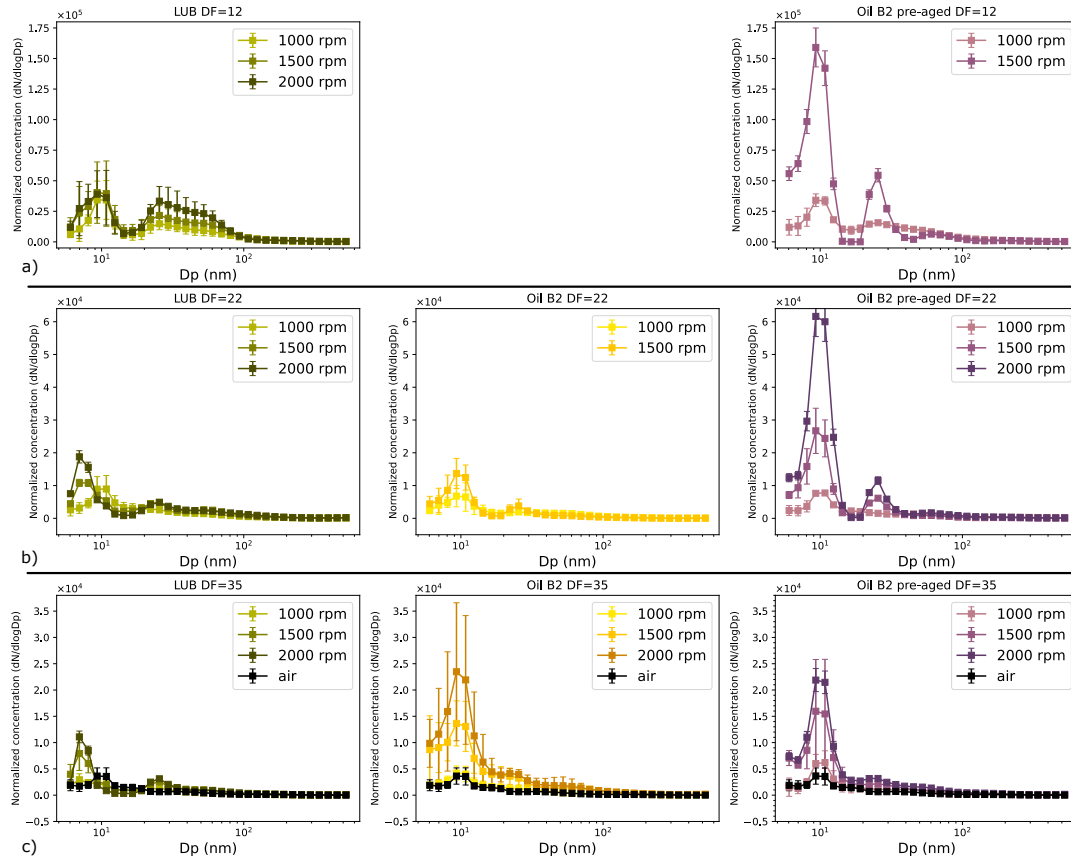


Figure 5.25: Particle size distribution with three engine oils for CH_4 , $\phi=1$, $P_{in}=1$ bar at 1000 rpm, 1500 rpm and 2000 rpm, measured at a) $DF=12$, b) $DF=22$ and c) $DF=35$ and presented without dilution correction. The black curve indicates the particle size distribution of the air used for dilution

Similar operating conditions were also tested in the same engine lubricated with the mineral base oil B2 and the pre-aged oil B2. Measurements conducted at different dilution factors and engine speeds are all summarized in Figure 5.25. At 1000 rpm, particle size distributions were similar for all the oils and dilution factors. Particle level was even at the baseline level for all oils at $DF=35$ at this low speed. The effect of the engine oil was only significant at higher engine speeds. Both oils B2 fresh and pre-aged resulted in higher numbers of particles with the increase in engine speed, and especially the pre-aged one (purple). The effect of the engine speed on particle emissions was significantly more important than for the reference lubricant. This might be due to increased engine oil consumption, considering that these oils were less viscous at high temperatures (Table 5.8). Besides, size distributions had a different aspect with a narrower accumulation mode than with the fully-formulated lubricant. This could be linked to the absence of additives in these oils, especially sulfur compounds and inorganic elements such as calcium known for contributing to particle emissions and condensed matter [106]. The higher nucleation peak measured with the pre-aged base oil at $DF=22$ could be linked to its higher proportion of heavy hydrocarbons compared to oil B2 (Figure 4.11), which reach their saturation vapor pressure more easily and tend to generate volatile nuclei [106]. This would be

5.3. INVESTIGATING PARTICULATE MATTER EMISSIONS WITH METHANE AND AMMONIA: IN-LINE ANALYSIS

consistent with the fact that similar levels were measured at higher dilution factors, limiting this phenomenon. Differences in size distributions and total number of particles were observed between the three oil even though changing the oil had no impact on the gaseous emissions (Figure 5.10).

3.2 Particle size distributions under ammonia combustion

In parallel, the engine was operated under ammonia combustion, and exhaust emissions were monitored in the same way. Unlike methane, ammonia is a carbon-free molecule, which calls into question what is established in the literature regarding engine exhaust emissions. As discussed in Section 1.2.6.3, very few studies have investigated the topic of exhaust particulate matter in an ammonia engine to date.

3.2.1 Effect of the dilution factor on the total exhaust particle concentration

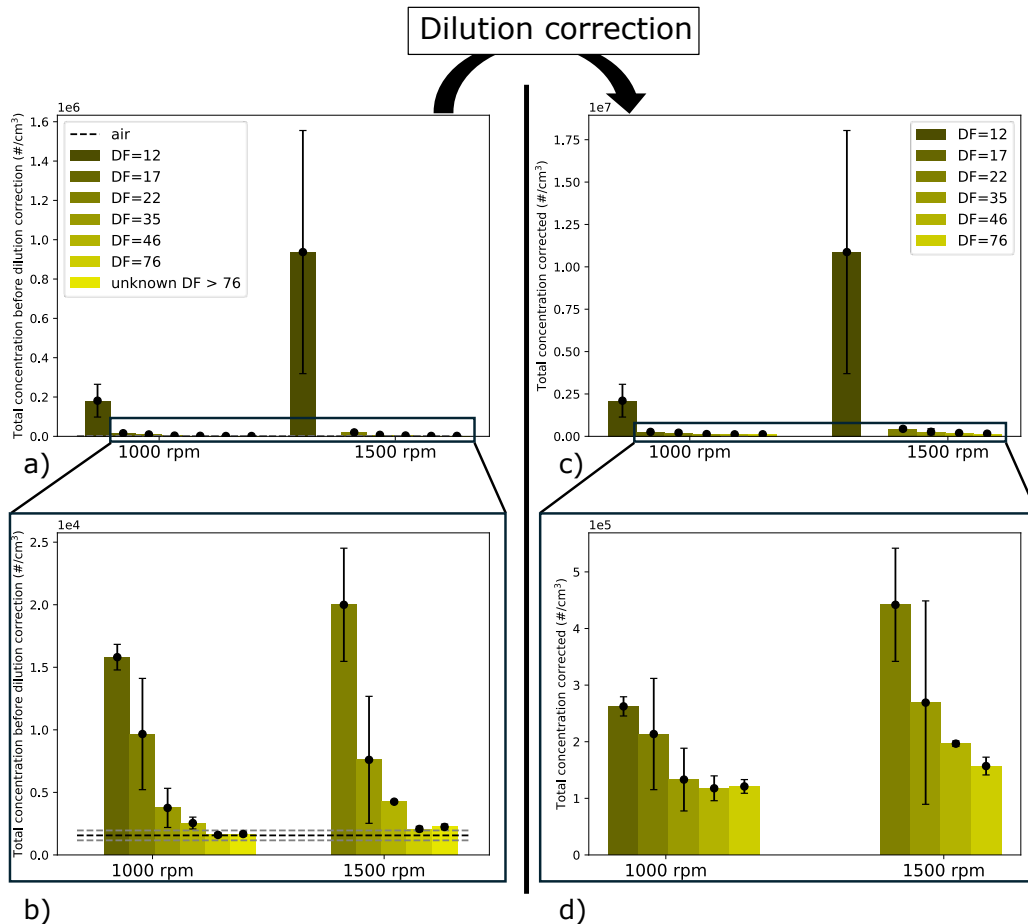


Figure 5.26: Total concentration for NH_3 , $\phi=1$, $P_{in}=1$ bar, with LUB oil at different dilution factors. a) Raw measurements, zoom in b) with DF=12 removed. c) After taking into account dilution factors, zoom in d) with DF=12 removed

As can be seen in Figure 5.26 a) and c), measurements of exhaust particles with ammonia at DF=12 resulted in a dramatic increase of the total particle concentration compared to

5.3. INVESTIGATING PARTICULATE MATTER EMISSIONS WITH METHANE AND AMMONIA: IN-LINE ANALYSIS

higher dilution factors, even after correction for the dilution factor. This is in agreement with theoretical calculations giving a required dilution factor larger than 11 to prevent water condensation at the exhaust. Here, dilution conditions at DF=12 largely promoted the nucleation of volatile species at the exhaust, resulting in a higher total number of particles compared to higher dilution conditions. With methane, diluting by 12 also resulted in a higher particle number, but to a minor extent compared to NH_3 (Figure 5.22), partly due to the lower water partial pressure in the exhaust of this fuel. On the contrary, dilution factors above 46 resulted in particle levels indistinguishable from the baseline level with the analyzer used. At 1000 rpm, total concentration was stable after correction for the dilution factor for dilution factors larger than 35 (Figure 5.26 d). However at 1500 rpm, the total concentration continued to decrease with the increase in dilution factor, and stable sampling conditions were not reached. The fact that higher dilution factors were necessary to reach stabilization compared to methane is consistent with the expected lower concentration of carbonaceous solid particles in the exhaust under ammonia combustion. This finding indicates that ammonia exhaust was mainly composed of volatile species, highly dependent on sampling conditions, and that the sampling protocol applied was not fully relevant to measure such low solid particle concentrations.

3.2.2 Effect of the dilution factor on particle size distribution

Figure 5.27 presents the corrected exhaust particle size distributions obtained under ammonia combustion and with the LUB engine oil under varying dilution conditions. At 1000 rpm (a) and dilution factors of 17 and 22, the distribution was bimodal with an accumulation mode between 15 and 100 nm. Very small particles, below the detecting minimum size of 5.6 nm, were also potentially present. Higher dilution ratios flattened the accumulation mode, almost completely at 1000 rpm, but not at 1500 rpm (b). Patil *et al.* found a mono-modal particle distribution with an engine operated on ammonia in [118] with a geometric mean diameter close to 30 nm. In their setup, the dilution factor reached 1290 which is considerably higher than here. As in this study, higher engine speed resulted in a higher number of particles.

The dilution factor directly impacted the geometric mean diameter of the nucleation mode (Figure 5.28). The GMD of the nucleation mode increased with the dilution factor, until stabilization at 10 nm above DF=35 at 1000 rpm. The GMD was probably overestimated at DF=12 because the whole nucleation peak was not included inside the measurement range of the instrument. Such a behavior was also observed by Ushakov *et al.* [184] with marine fuels with high sulfur contents. Indeed, sulfur, as well as nitrogen, were found to promote ultrafine particle nucleation.

3.2.3 Effect of the engine oil

Comparison between the engine oils (Figure 5.29) seemed to indicate that more particles were obtained with the mineral base oil B2 at both 1000 and 1500 rpm. This could be consis-

5.3. INVESTIGATING PARTICULATE MATTER EMISSIONS WITH METHANE AND AMMONIA: IN-LINE ANALYSIS

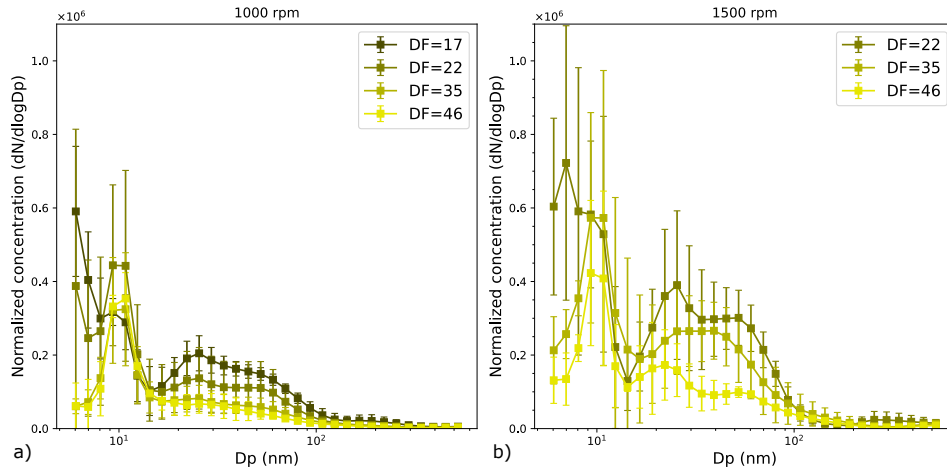


Figure 5.27: Exhaust particle size distribution at different dilution factors, for operating conditions NH_3 , $\phi=1$, $P_{in}=1$ bar, a) 1000 rpm, b) 1500 rpm with LUB oil. Results are presented with the dilution factor taken into account

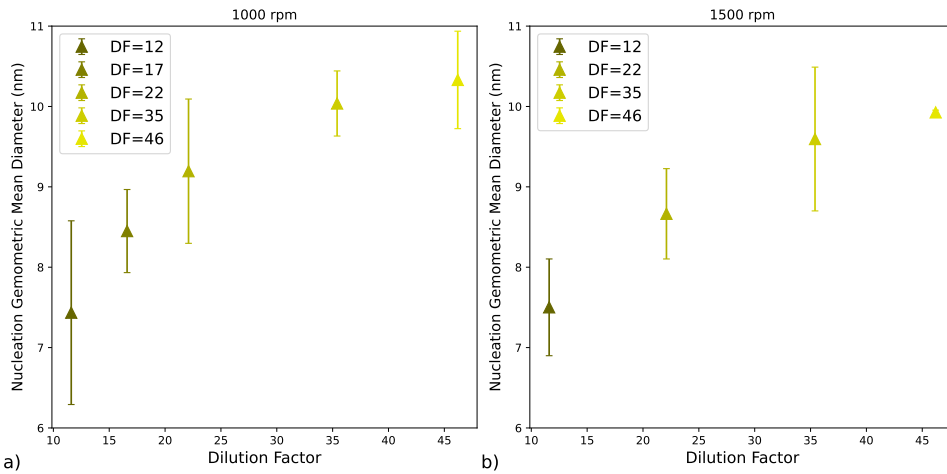


Figure 5.28: Geometric Mean Diameter of the nucleation mode as a function of the dilution factor for operating conditions NH_3 with LUB oil, $\phi=1$, $P_{in}=1$ bar 1000 rpm and 1500 rpm

tent with the higher CO emissions measured with this oil (Figure 5.14). However these values were measured with high uncertainty levels at DF=35, and a limited number of measurements at DF=46. Complementary measurements would be necessary to consolidate this finding, especially because this behavior was not observed with methane. Besides, the accumulation mode measured with this oil covered a broader size range, like a continuum rather than a well-defined mode as with the reference fully-formulated lubricant. As observed with methane, the effect of engine speed on the total particle number with the oils B2 and pre-aged B2 was more significant than with the fully-formulated lubricant.

3.2.4 Effect of the intake pressure

As shown in Figure 5.30, decreasing the intake pressure resulted in a decrease of particle emissions at 1000 rpm. Results are only shown with oil B2 because the two other oils

5.3. INVESTIGATING PARTICULATE MATTER EMISSIONS WITH METHANE AND AMMONIA: IN-LINE ANALYSIS

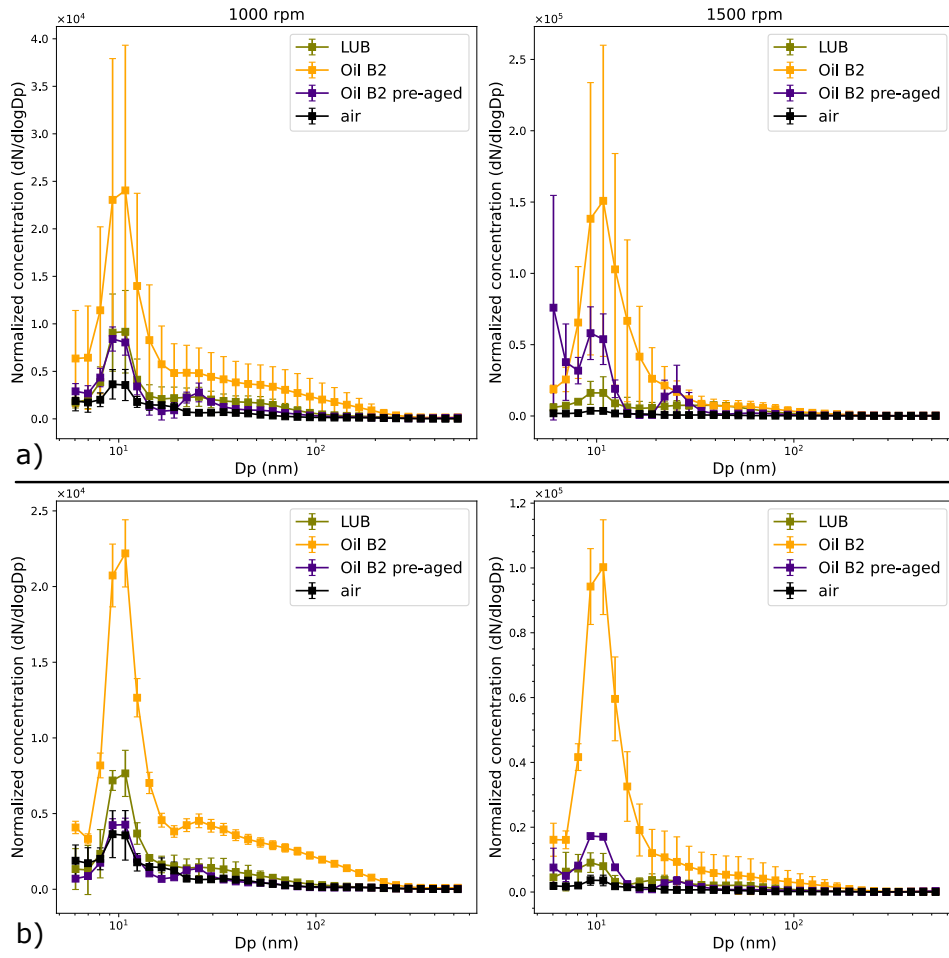


Figure 5.29: Particle size distribution with three engine oils for NH_3 , $\phi=1$, $P_{in}=1$ bar at 1000 rpm and 1500 rpm, measured at a) $DF=35$, b) $DF=46$ and presented without dilution correction. The black curve indicates the particle size distribution of the air used for dilution

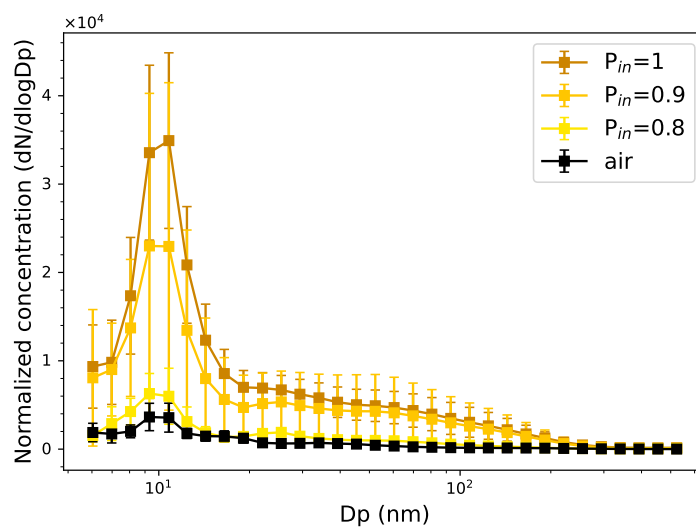


Figure 5.30: Particle size distribution with oil B2 NH_3 , $\phi=1$, $P_{in}=1$ bar at 1000 rpm, measured at $DF=35$ and presented without dilution correction. The black curve indicates the particle size distribution of the air used for dilution

5.3. INVESTIGATING PARTICULATE MATTER EMISSIONS WITH METHANE AND AMMONIA: IN-LINE ANALYSIS

resulted in very low levels, below the baseline. Reducing the intake pressure can promote oil consumption due to oil sucking by the pressure difference, thereby increasing particulate matter, as observed with hydrogen engines in [190]. Nevertheless, this was only observed when low load was combined to high engine speed up to 3000 rpm. Here, engine speed was limited to 1000 rpm, and the potential increased oil consumption was compensated by another mechanism, probably fuel consumption and power reduction, resulting in an overall decrease in particulate emissions. Similarly, experiments with hydrogen were conducted with intake pressures lower than 1, resulting in very low total particle numbers.

3.3 Comparison between methane and ammonia

Overall, under same dilution conditions, the number of particles was higher under ammonia combustion than methane despite lower indicated power (Figure 5.31). However, this observation could be an effect of the higher water contents in the exhaust of ammonia combustion. Indeed, water content was found to be correlated with the total number of particles for both gases. In Figure 5.32, similar water contents correspond to similar total particle concentrations at 1000 rpm, and the same conclusion was verified with measurements at 1500 rpm. For instance, $DF=22$ for methane and $DF=35$ for ammonia result in respectively $0.90 \pm 0.05 \%$ and $1.0 \pm 0.1 \%$ H_2O emitted, and result in similar total particle numbers. Other volatile species at the exhaust may also contribute to the increase in total particle number via nucleation and condensation even though all of them cannot be precisely monitored. No correlation could be established between the GMD of the nucleation peak, or the total GMD and the water, ammonia or methane content, and both fuels resulted in very close GMD values.

Nevertheless, dilution had different effects on the emissions of both fuels, indicating some differences in the pollutants types. In particular, a minimal plateau was reached with methane, for which particle number and distribution were independent on the dilution factor. This suggested that mainly solid particles were measured under these conditions (Figure 5.22). With ammonia on the contrary, such a plateau could not be reached and total particle number continued to decrease as the dilution increased, until the baseline level of the diluting air was reached (Figure 5.26). This suggested a principally volatile nature of the measured sample. This would be consistent with the fact that methane contains carbon atoms which can be emitted as carbonaceous particles in larger amounts than ammonia, for which the only solid particles can be derived from the lubricant or wear metals.

The effect of the engine oil was also different for both fuels, but the commercial fully-formulated lubricant resulted in lower particle concentrations in either case, and appeared to be less affected by the increase in regime.

5.3. INVESTIGATING PARTICULATE MATTER EMISSIONS WITH METHANE AND AMMONIA: IN-LINE ANALYSIS

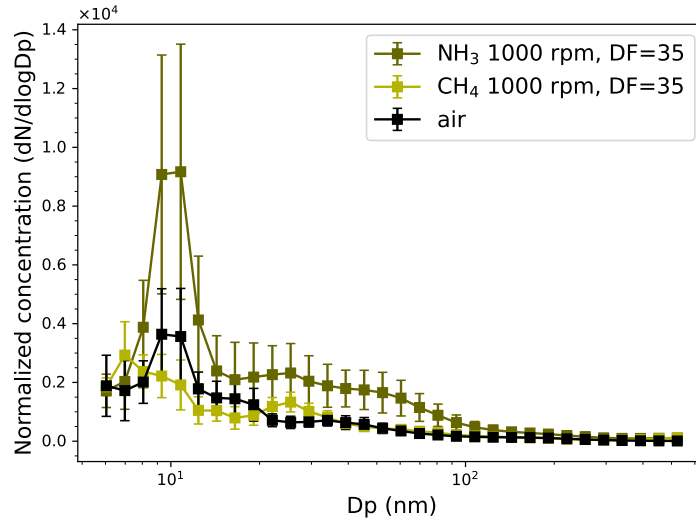


Figure 5.31: Particle size distribution with LUB oil NH₃ and CH₄, $\phi=1$, $P_{in}=1$ bar at 1000 rpm, measured at DF=35 presented without dilution correction. The black curve indicates the particle size distribution of the air used for dilution

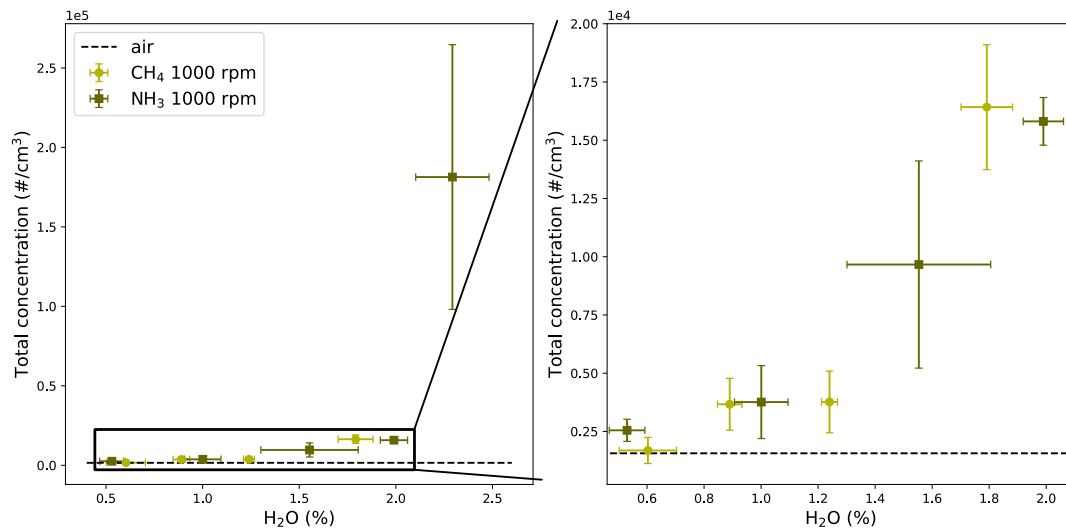


Figure 5.32: Total particle concentration as a function of the H₂O concentration in the diluted exhaust for NH₃ and CH₄, $\phi=1$, $P_{in}=1$ bar at 1000 rpm, with LUB oil

3.4 Discussion

In this section, exhaust particle size distributions obtained under methane and ammonia combustion with three different engine oils were measured and compared. The main findings highlight that sampling conditions are critical when it comes to measuring exhaust emissions of fuels producing significant amounts of volatile species. Dilution conditions directly determine the ratio between the partial pressure of volatile compounds and their saturation pressure, leading to major effects on exhaust particle measurements. The effect of dilution factors on particle size distributions, as well as total number was pointed out for both gases. Similarly, exploring the effect of primary dilution temperature would have certainly highlighted the critic-

5.4. INVESTIGATING PARTICULATE MATTER EMISSIONS WITH METHANE AND AMMONIA: ELEMENTAL AND MORPHOLOGICAL ANALYSIS

ity of this parameter. This is especially true for fuels such as ammonia or hydrogen which only produce very limited amounts of solid particles, originated from the lubricant or metals but not the combustion itself, due to their carbon-free nature. This is a major challenge for future regulations on exhaust emissions of new types of engines operated with such fuels, as conditions enabling reproducible and comparable results must be found. Changing the engine oil also seemed to affect particle emissions with both methane and ammonia, even though it had no effect on FTIR exhaust measurements for CH_4 . Base oils without friction modifier additives (B2 and pre-aged B2) had lower viscosities at high temperature, which could be the cause of increased particle emissions with these oils due to higher oil consumption, especially at high engine speed. As the total number of emitted particles was very low with these fuels, we often encountered limitations due to the trade-off between dilution conditions enabling stable and repeatable measurements while staying above the baseline level. To overcome this difficulty, a catalytic stripper could be used to remove the volatile species and focus on the residual solid fraction, having in mind that this could also involve an increase in particle losses. Besides, other particle analyzers with lower detection limits could be used, such as a Condensation Particle Counter (CPC) or a Scanning Mobility Particle Sizer (SMPS). The main findings of this section provide a strong basis for future work, repetitions and complementary experiments could further strengthen these conclusions. In order to complement these real-time particle size measurements and investigate nitrogen-related emissions, particles were also collected on microscope grids. The analysis of these grids and the main results are detailed in the following section.

4. Investigating particulate matter emissions with methane and ammonia: elemental and morphological analysis

4.1 Particles obtained with the fully-formulated lubricant

In parallel to the EEPS and FTIR analyzers, the MPS device was connected to the diluter outlet to enable particle sampling on microscope grids thanks to the activation of a dedicated pump. To determine relevant sampling conditions, several combinations of engine speeds, dilution factors, pumping flow rates and sampling times were tested with the LUB oil, and grids were rapidly screened using SEM microscopy. The grid collected after 10 min at 600 cc/min with a dilution factor of 35, from an engine operated on ammonia at 1500 rpm under $\phi=1$ and $P_{in}=1$ bar, was selected as it contained sufficient material while limited volatile deposition, which was more pronounced with lower dilution factors. Similar sampling conditions were then applied for oil B2 and the pre-aged oil.

5.4. INVESTIGATING PARTICULATE MATTER EMISSIONS WITH METHANE AND AMMONIA: ELEMENTAL AND MORPHOLOGICAL ANALYSIS

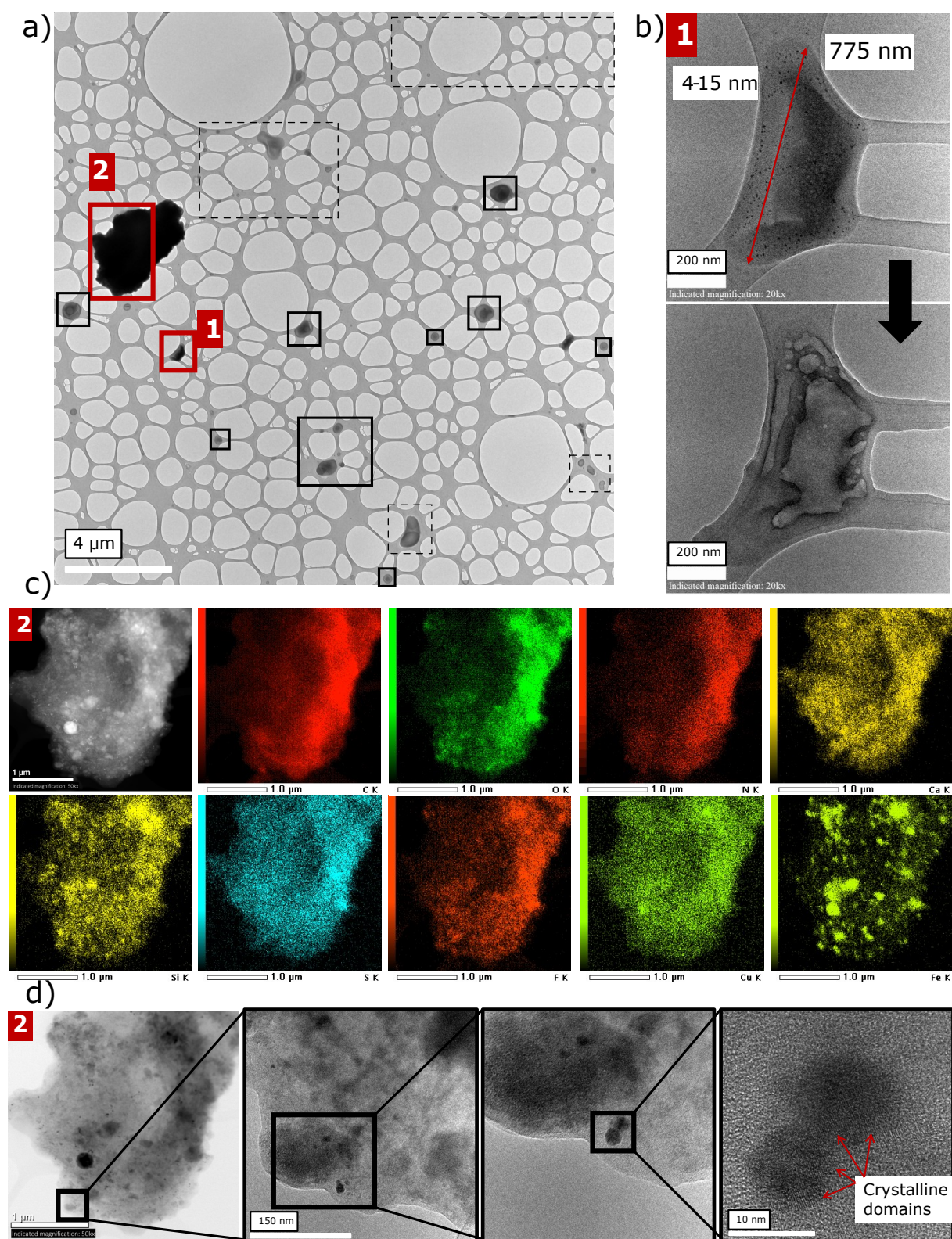


Figure 5.33: TEM observation of grid n°1 (LUB oil- NH_3). a) General aspect of grid n°1, core-shell structures (areas circled with a continuous black line) and droplet-like objects (areas circled with a dashed black line). b) Zoom on a semi-volatile structure, degraded by the electron beam in a few minutes. c) EDX mapping of a large fragment. d) Zoom on area 2, highlighting crystalline domains

5.4. INVESTIGATING PARTICULATE MATTER EMISSIONS WITH METHANE AND AMMONIA: ELEMENTAL AND MORPHOLOGICAL ANALYSIS

The general aspect of grid n°1 (Table 5.5), collected with the fully-formulated LUB oil is shown in Figure 5.33 a). It shows numerous core-shell type structures (circled in black) with a slightly denser spherical core surrounded by amorphous deposition, with a total size ranging between 70 and 150 nm for most objects, and up to 700 nm for larger ones. Other objects exhibited a droplet-like morphology without any distinguishable core (circled with a dashed line). Figure 5.33 b) is a zoom on a large agglomerate of this kind with a total length of 775 nm. This agglomerate was immediately degraded under the electron beam. As microscope observations are conducted under high vacuum, the lightest volatile species cannot be observed using this technique. However, such amorphous deposits could correspond to semi-volatile deposits composed of very large organic molecules retaining sufficient residence time on the grid, but that exhibit high sensitivity to the electron beam. Within the amorphous phase, as in many other similar objects, numerous dense spots with sizes estimated between 4 and 15 nm were observed. These spots were also degraded by the electron beam. Other examples of similar very sensitive droplet-like objects were found and are shown in Appendix D.12. Larger objects were also found and identified as metallic debris, like in Figure 5.33 c). EDX mapping of object n°2 showed that it contained many elements: carbon, oxygen, nitrogen, calcium, silicon, sulfur, fluorine, copper and iron, but also traces of magnesium, zinc, and aluminum. This agglomerate probably resulted from a mix of metal and metal oxides debris, originated from corrosion, wear, or detachment at the exhaust, mixed with lubricant residues as suggested by the presence of calcium and sulfur. Nitrogen could also be derived from aminic additives in the lubricant or other nitrogen-containing compounds formed, or directly come from exhaust gases. The microstructure of this fragment showed crystalline domains, probably corresponding to metal oxides, as shown in Figure 5.33 d). Such crystalline domains were also observed by Lagana *et al.* [117] in amorphous agglomerates rich in oxygen and metals collected at the exhaust of a hydrogen engine.

Figure 5.34 b) shows a closer view of a large core-shell type structure. As in object n°1 (Figure 5.33 b), the shell phase contained darker spots, and was degraded in only a few minutes during the observation, changing the aspect of the particle's surface. Figure 5.34 c) shows the elemental analysis of an amorphous droplet-like object. Here again, denser spots could be observed within the amorphous phase. Carbon, silicon and fluorine were mostly found in the polymer membrane of the grid, and the particle itself seemed to be rich in oxygen, sulfur, copper and nitrogen. This object could be derived from nucleated lubricants vapors. Sulfur is known for contributing to volatile particle emissions, through both independent nucleation and adsorption [106].

Examples of morphologies in which nitrogen was detected are presented in Figure 5.35. In particular, Figure 5.35 c) displays a semi-volatile object similar to object n°4 (Figure 5.34 c), with a comparable composition. In this object n°7, calcium was also detected confirming the lubricant origin. Though at low concentrations, the oil itself also contained copper (Fig-

5.4. INVESTIGATING PARTICULATE MATTER EMISSIONS WITH METHANE AND AMMONIA: ELEMENTAL AND MORPHOLOGICAL ANALYSIS

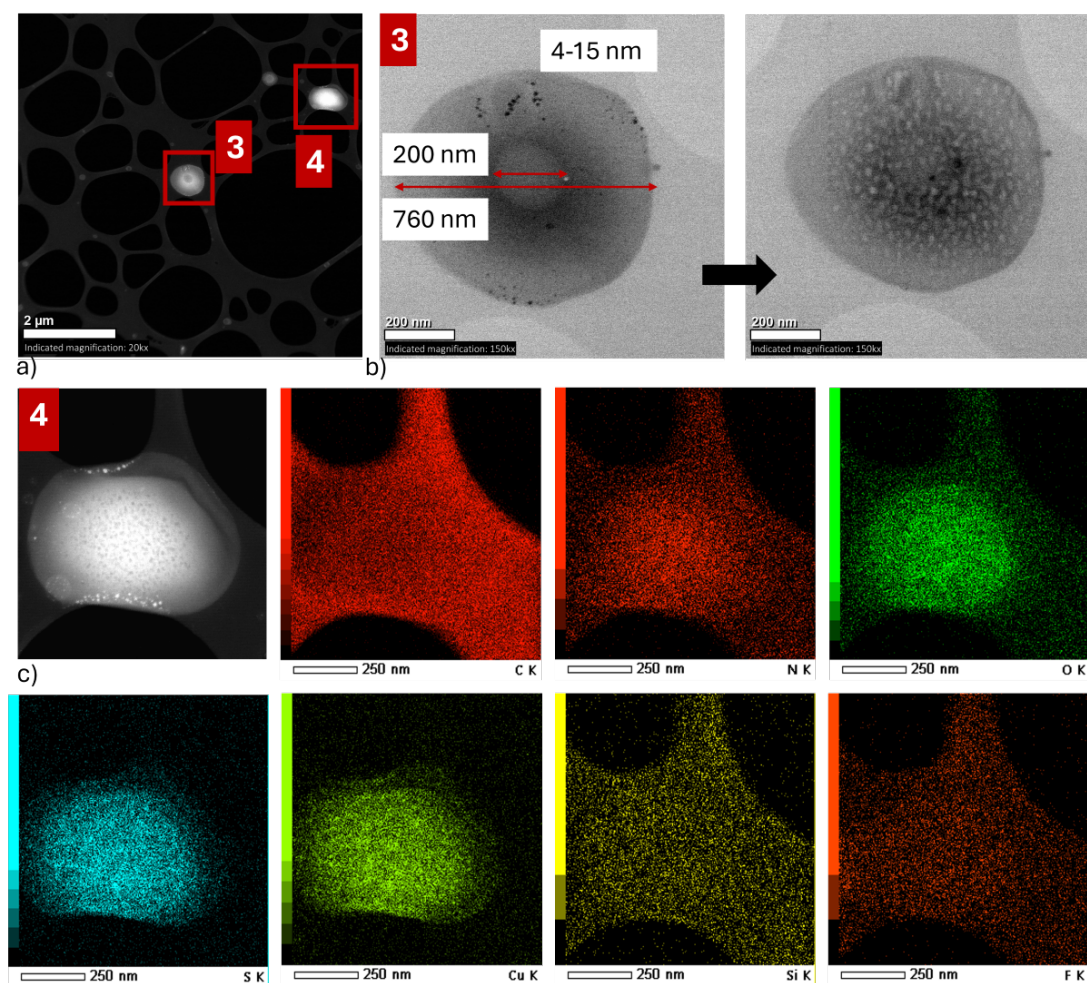


Figure 5.34: Detail of two objects on grid n°1. a) Large view with TEM. b) Detail of a core-shell type structure and degradation under the electron beam over a few minutes. c) EDX mapping of object 4

ure 4.15), which could be the origin of the copper found in the particles of Figure 5.35 and Figure 5.34 c). Figure 5.35 a) shows an amorphous agglomerate, in which iron, sodium and phosphorous were also found as traces in addition to carbon, oxygen, nitrogen and calcium. Figure 5.35 b) shows another type of mixed amorphous agglomerate with a dense particle surrounded by an amorphous deposition. The size range of all these objects was between 200 and 400 nm.

Other types of morphologies, without nitrogen atoms, were found and are presented in Figure 5.36. These objects were less affected by the electron beam. Solid amorphous agglomerates as in Figure 5.36 a) were found, but also dense spheres, as in Figure 5.36 b). These spheres were especially rich in oxygen, carbon and calcium, but other elements such as sulfur, sodium, phosphorous, copper and iron could be detected.

Agglomerates identified as soot particles were also observed, although they were rare. Two examples are shown in Figure 5.37.

5.4. INVESTIGATING PARTICULATE MATTER EMISSIONS WITH METHANE AND AMMONIA: ELEMENTAL AND MORPHOLOGICAL ANALYSIS

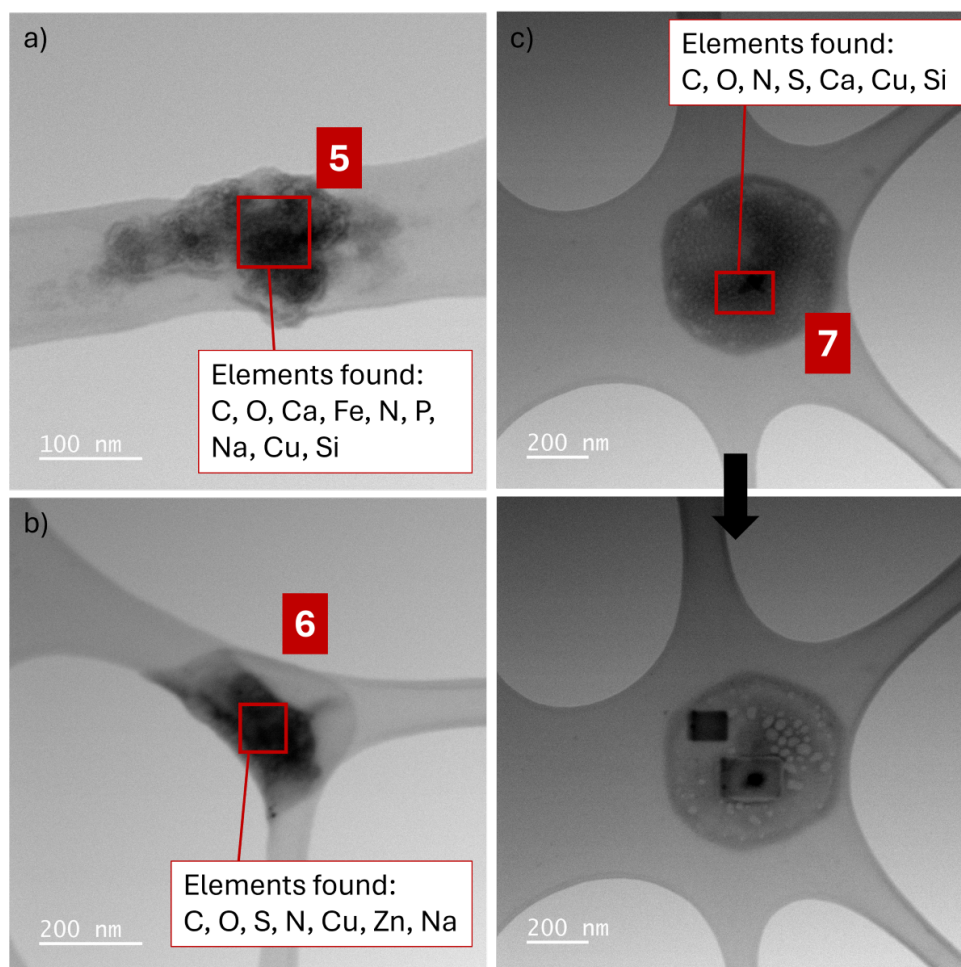


Figure 5.35: TEM observation of different morphologies and elemental analysis of objects containing nitrogen found on grid n°1

5.4. INVESTIGATING PARTICULATE MATTER EMISSIONS WITH METHANE AND AMMONIA: ELEMENTAL AND MORPHOLOGICAL ANALYSIS

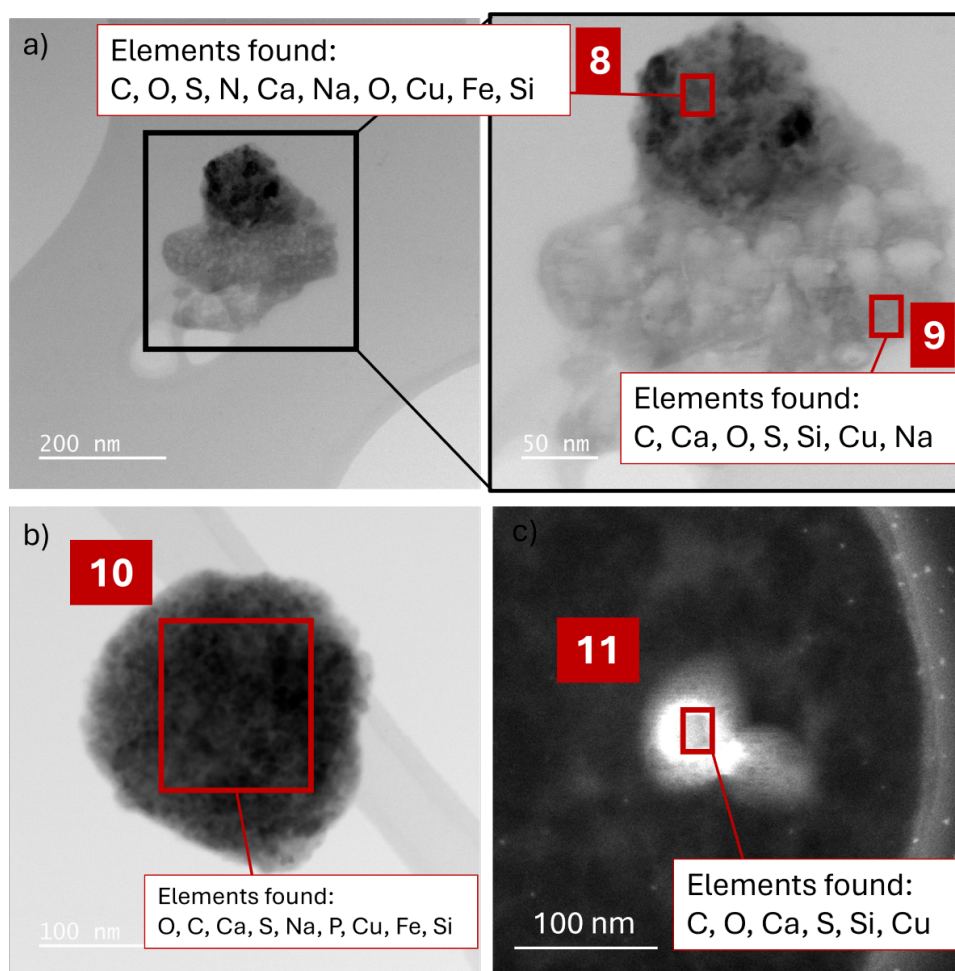


Figure 5.36: TEM observation of different morphologies and elemental analysis of objects containing few (a) or no (b, c) nitrogen found on grid n°1

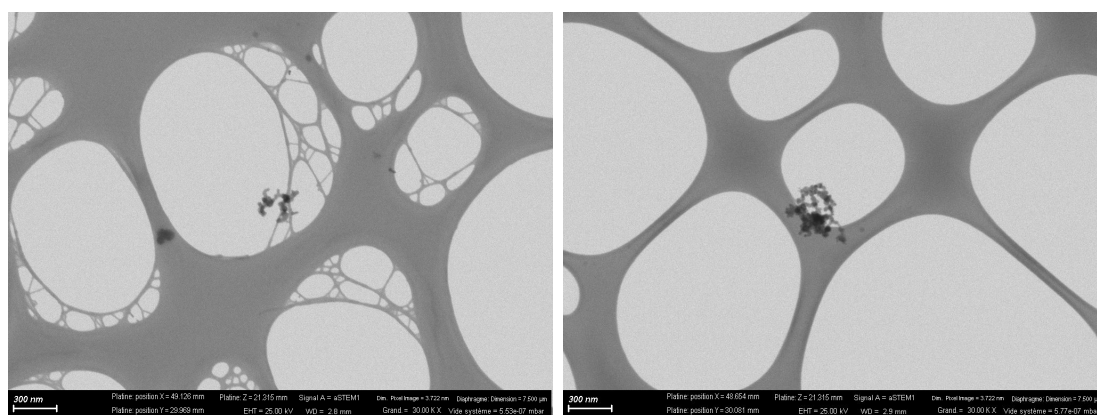


Figure 5.37: SEM observation of soot particles on a grid collected directly at the exhaust without dilution during 1 min, at 300 cc/min

5.4. INVESTIGATING PARTICULATE MATTER EMISSIONS WITH METHANE AND AMMONIA: ELEMENTAL AND MORPHOLOGICAL ANALYSIS

Overall, several types of morphologies were identified on grid n°1, including mainly droplet-like deposits and core-shell structures, as well as metal fragments, mixed amorphous agglomerates, and dense spheres. Calcium and sulfur were frequently detected in these objects, pointing to a lubricant-derived origin. Rare soot particles with primary sizes between 15 and 30 nm were also observed. Nitrogen was detected in some deposits, particularly in semi-volatile ones that exhibited high sensitivity to the electron beam. This nitrogen may originate from the lubricant, through amine additives or nitrogen-containing degradation products.

4.2 Particles obtained with the mineral base oil

Observation of grid n°2 enabled to analyze pollutant emissions obtained with the mineral base oil B2, without any additives. A general view of one grid tile, also showing varied types of morphologies, is displayed in Figure 5.38 a). A zoom on area 1 (Figure 5.38 b and c) revealed small soot particles, with overall sizes below 200 nm and primary particles ranging from 10 to 30 nm, like with LUB oil in Figure 5.37. These particles were embedded in a larger surrounding deposit resembling semi-volatile matter. Elemental analysis of two of these particles revealed high carbon and oxygen contents, as well as residual copper, nitrogen, sulfur, silicon, zinc, iron, and potassium. The presence of soot could be consistent with the higher CO emissions measured when the engine was operated with this oil (Figure 5.15), suggesting lubricant burning in the combustion chamber, and with higher numbers of emitted particles (Figure 5.29), also suggesting large oil consumption, either by burning or evaporation.

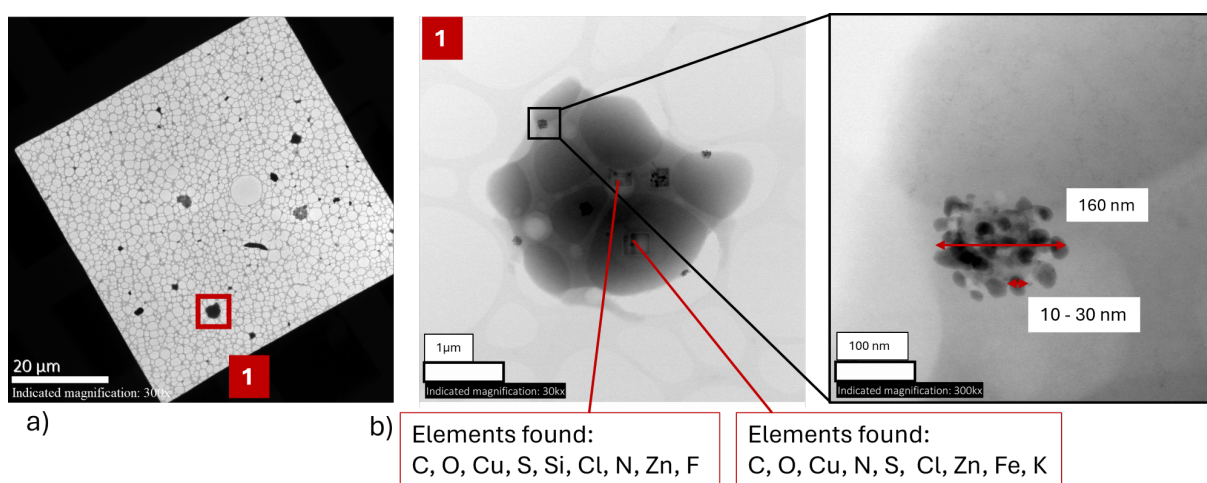


Figure 5.38: a) General aspect of grid n°2 with TEM. b) Zoom and elemental analysis of area 1

5.4. INVESTIGATING PARTICULATE MATTER EMISSIONS WITH METHANE AND AMMONIA: ELEMENTAL AND MORPHOLOGICAL ANALYSIS

Similar types of objects as with the fully-formulated lubricant were found. In particular, metal oxides fragments as in Figure 5.39, dense spheres and solid amorphous agglomerates as in Figure 5.40 a and b). The combined detection of both copper and nitrogen or metal fragments despite the low nitrogen content in this oil (Table 4.5) might indicate that nitrogen was already bound to the surface, as corrosion chemical complexes for instance. Detailed analysis of one dense sphere on grid n°2 pointed out that it was the same aspect and size (200 nm) as on grid n°1 (Figure 5.36 b), and contained common elements: both were oxygen-rich and contained metals such as a copper and iron. Calcium and sulfur were not found here, consistent with the fact that oil B2 did not contain these elements. Here, a semi-volatile layer seemed to cover the spherical particle.

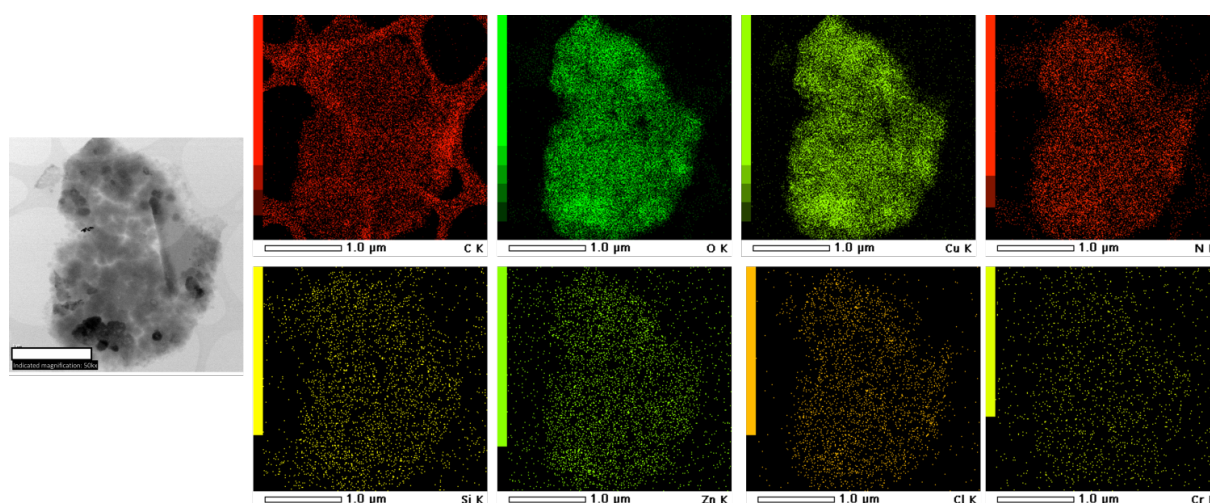


Figure 5.39: EDX mapping of a solid particle on grid n°2

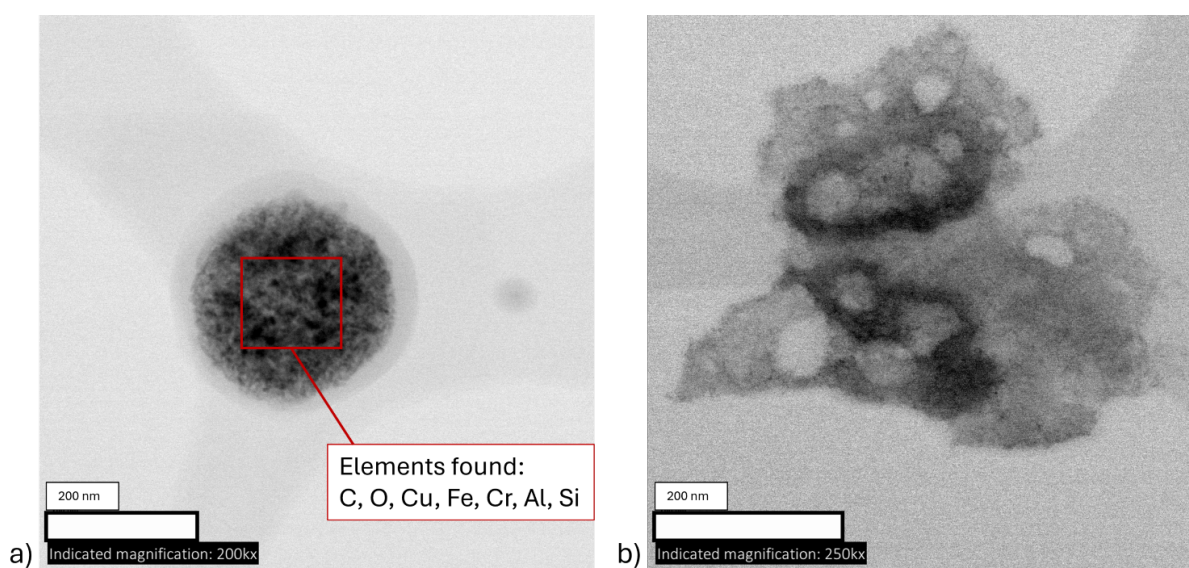


Figure 5.40: a) TEM observation and elemental analysis of a dense sphere on grid n°2. b) TEM observation of a particle on grid n°2

5.4. INVESTIGATING PARTICULATE MATTER EMISSIONS WITH METHANE AND AMMONIA: ELEMENTAL AND MORPHOLOGICAL ANALYSIS

Besides, other types of objects were observed. No core-shell structures like the one shown in Figure 5.34b were observed, nevertheless mixed structures with dense elements covered with semi-volatile matter were found (Figure 5.41). Elemental analysis of these objects showed that dense regions mainly consisted of carbon, oxygen, copper and zinc, while the surrounding layer mainly consisted of carbon and oxygen, silicon being principally found in the polymer layer of the grid itself. Unlike in the core-shell structures obtained with the fully-formulated lubricant, no nitrogen atoms were found in these mixed agglomerates. This could be consistent with the fact that only low concentrations of nitrogen were measured in this oil B2 (Table 4.5). However, sulfur was also found even though the fresh mineral oil B2 contained no sulfur atoms. This could be due to the residual pollution of the fully-formulated lubricant, calculated to reach 5 % in Section 4.2.1.

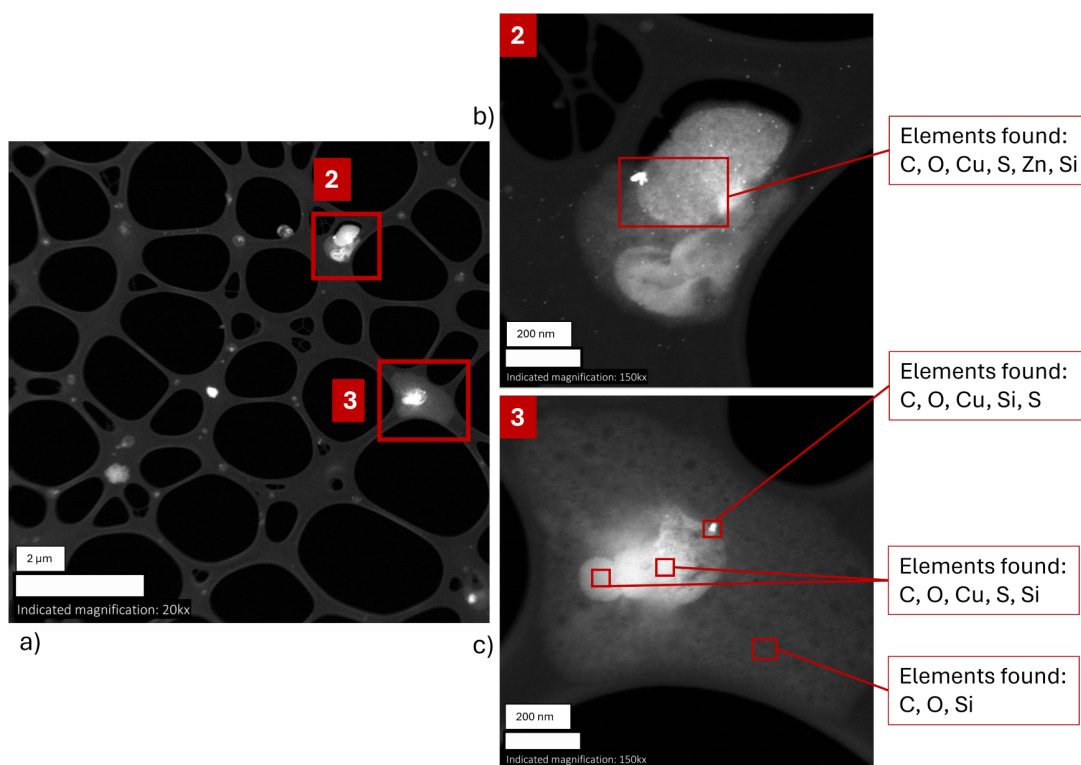


Figure 5.41: a) Large TEM view of grid n°2. b), c) Zoom and elemental analysis of areas 2 and 3

In addition, specific agglomerates with a folded aspect were observed on this grid n°2 (Figure 5.42). Elemental analysis revealed that such morphologies mostly contained carbon, oxygen and nitrogen, as well as significant amounts of copper and zinc compared to other objects. Several similar objects were found on the same grid, indicating that this object was not an isolated morphology. Nevertheless, it would be valuable to examine additional grids obtained with the same oil to verify the occurrence of this type of object and to ensure that it did not result from a localized detachment phenomenon within the oil system or in the engine.

5.4. INVESTIGATING PARTICULATE MATTER EMISSIONS WITH METHANE AND AMMONIA: ELEMENTAL AND MORPHOLOGICAL ANALYSIS

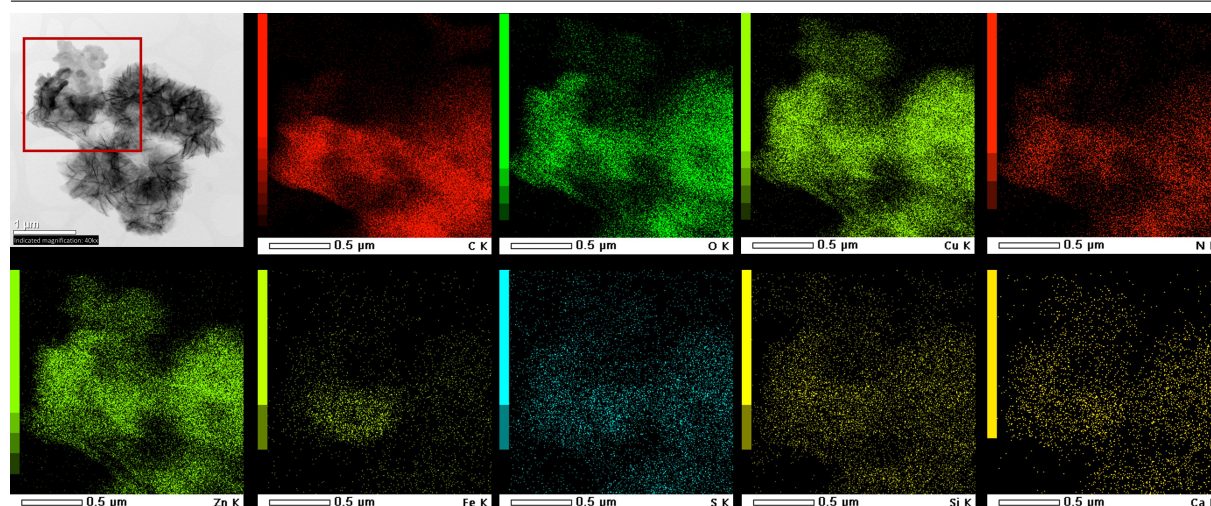


Figure 5.42: EDX mapping of a mixed agglomerate on grid n°2

4.3 Particles obtained with the pre-aged mineral base oil

Grid n°3, collected during engine operation with the pre-aged oil was especially sensitive to the electron beam and quickly degraded during the analysis, which challenged the observation. This could be linked to the higher proportion of heavy hydrocarbons in this oil (Figure 4.11), promoting the condensation of oil vapors.

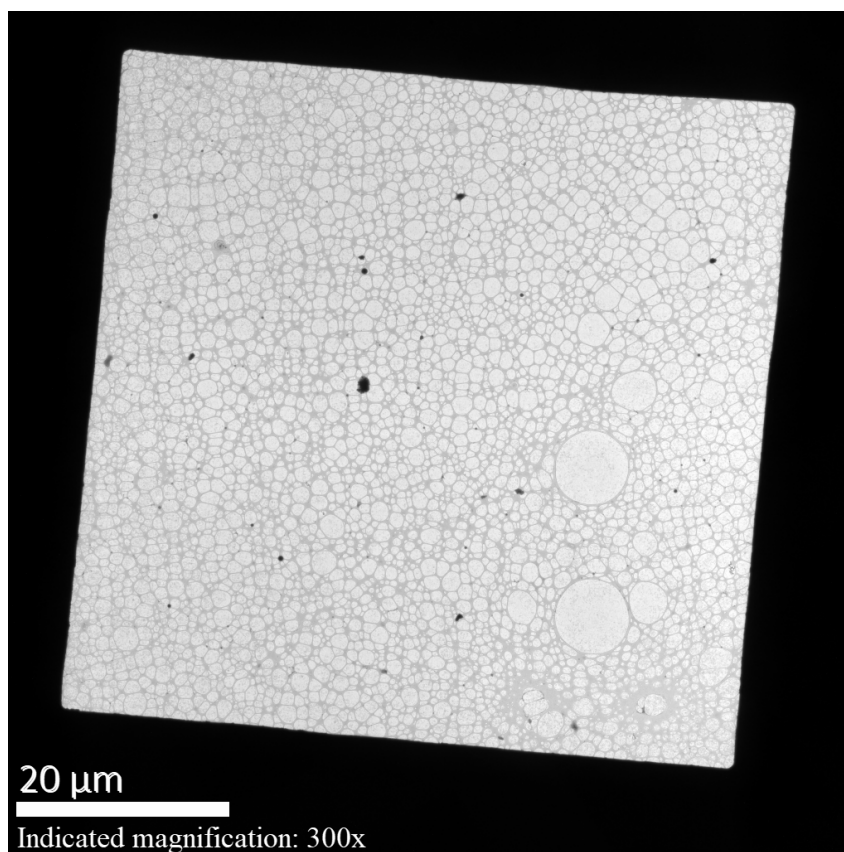


Figure 5.43: General aspect of one tile of n°3 with TEM

5.4. INVESTIGATING PARTICULATE MATTER EMISSIONS WITH METHANE AND AMMONIA: ELEMENTAL AND MORPHOLOGICAL ANALYSIS

Figure 5.43 shows the general aspect of one grid tile, on which only few particles could be observed. Figure 5.44 shows a closer view of grid n°3, highlighting the presence of different morphologies including dense spheres, soot particles and mixed semi-volatile deposits. Rare soot particles were found, as displayed in Figure 5.44 b). The size of the primary particles ranged between 40 and 60 nm, which is larger than in soot particles obtained with the fully-formulated lubricant and the mineral base oil. This could be associated to the differences of composition between the three oils, in particular the pre-aged lubricant contained high concentrations of oxygenated and nitrogenated products, and heavy hydrocarbons which can affect the primary soot structure [112]. The same kind of oxygen and calcium rich dense sphere was also observed with this oil, as with the others.

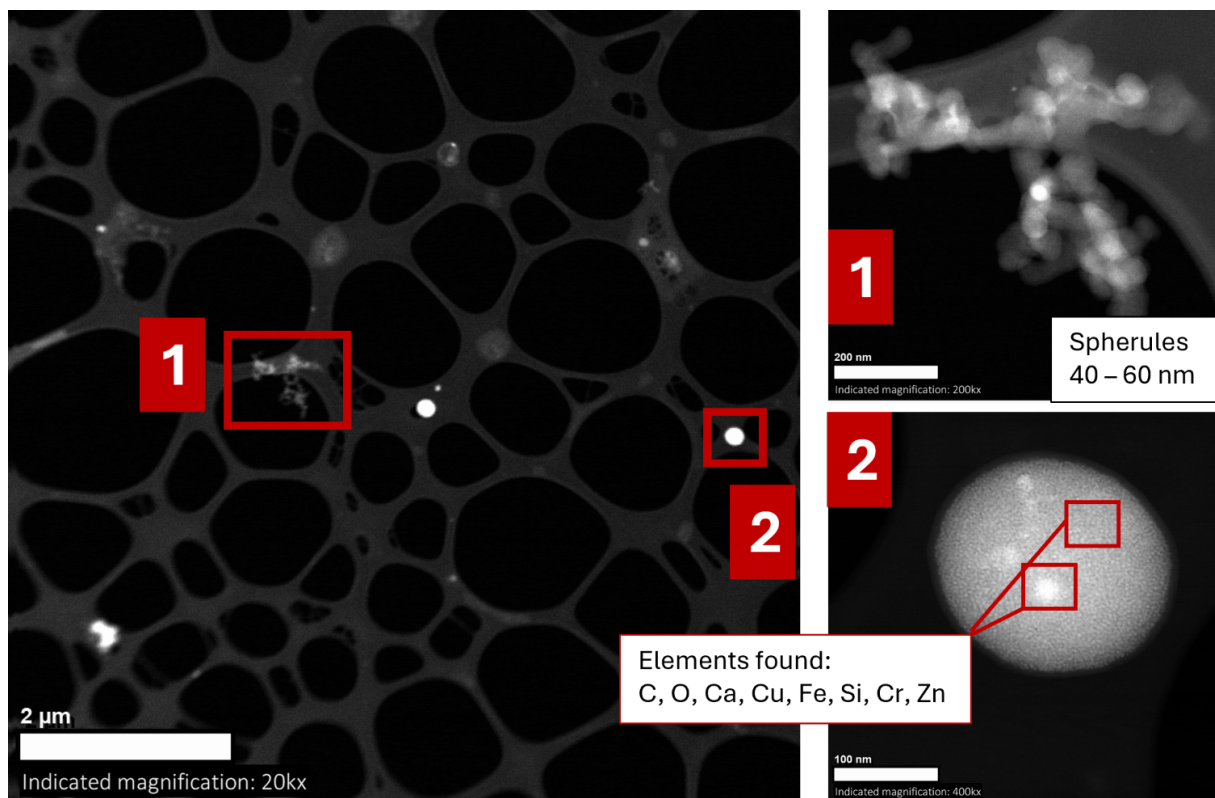


Figure 5.44: TEM observation, detail of two morphologies found on grid n°3

With the pre-aged base oil, similar mixed structures with multiple dense cores and irregular organic layer, as shown in Figure 5.41 obtained with oil B2 were found (Figure 5.45). Dense regions were also principally composed of carbon, oxygen, sulfur and copper.

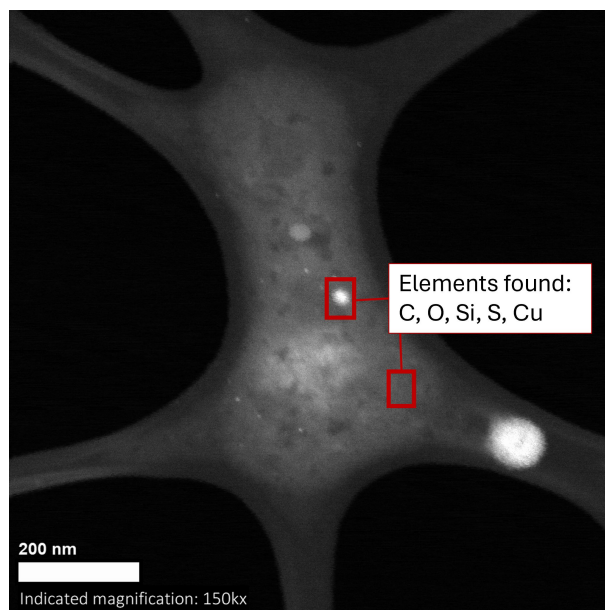


Figure 5.45: TEM observation and elemental analysis of a mixed structure on grid n°3

4.4 Particles obtained with methane

To compare the aspect and morphologies and explore the specific role and origin of nitrogen in exhaust emissions, particulate matter sample was also collected when the engine was operated on methane with the pre-aged base oil. As can be seen in Figure 5.46 a), numerous soot particles (circled in black) were found. This is consistent with the fact that contrary to ammonia, methane itself contains carbon atoms prone to generate carbonaceous particles from the combustion. Some of these soot particles seemed to be covered with amorphous deposition while other appeared to be deposited on the membrane without any surrounding phase. Here again, dense spheres with high oxygen, calcium, iron and copper contents and size close to 100 nm could be found (Figure 5.46 b). Likewise, the same kind of copper oxide metal fragment could be found on the grid (Figure 5.46 c). Soot particles seemed to be deposited on this fragment, as can be seen on the close view of object n°2. Besides, nitrogen was also detected on this metal fragment despite the absence of NH_3 at the exhaust, indicating it was originated from the oil, or directly adsorbed on the metal surface from previous operating conditions with NH_3 . The second hypothesis seems more robust because similar observation was made with the mineral oil B2 which only contained low amounts of nitrogen. Other morphologies can be seen on this picture, such as amorphous agglomerates and semi-volatile deposits.

A zoom on area 1 shows two different types of morphologies and their composition (Figure 5.47). Figure 5.47 b) presents the EDX mapping of a soot particle with surrounding traces of volatile deposition. This particle appeared to contain oxygen, sulfur and calcium. Carbon and nitrogen were also detected but could not be specifically located on the soot particle as both elements were found in large amounts in the covering phase on the particle.

5.4. INVESTIGATING PARTICULATE MATTER EMISSIONS WITH METHANE AND AMMONIA: ELEMENTAL AND MORPHOLOGICAL ANALYSIS

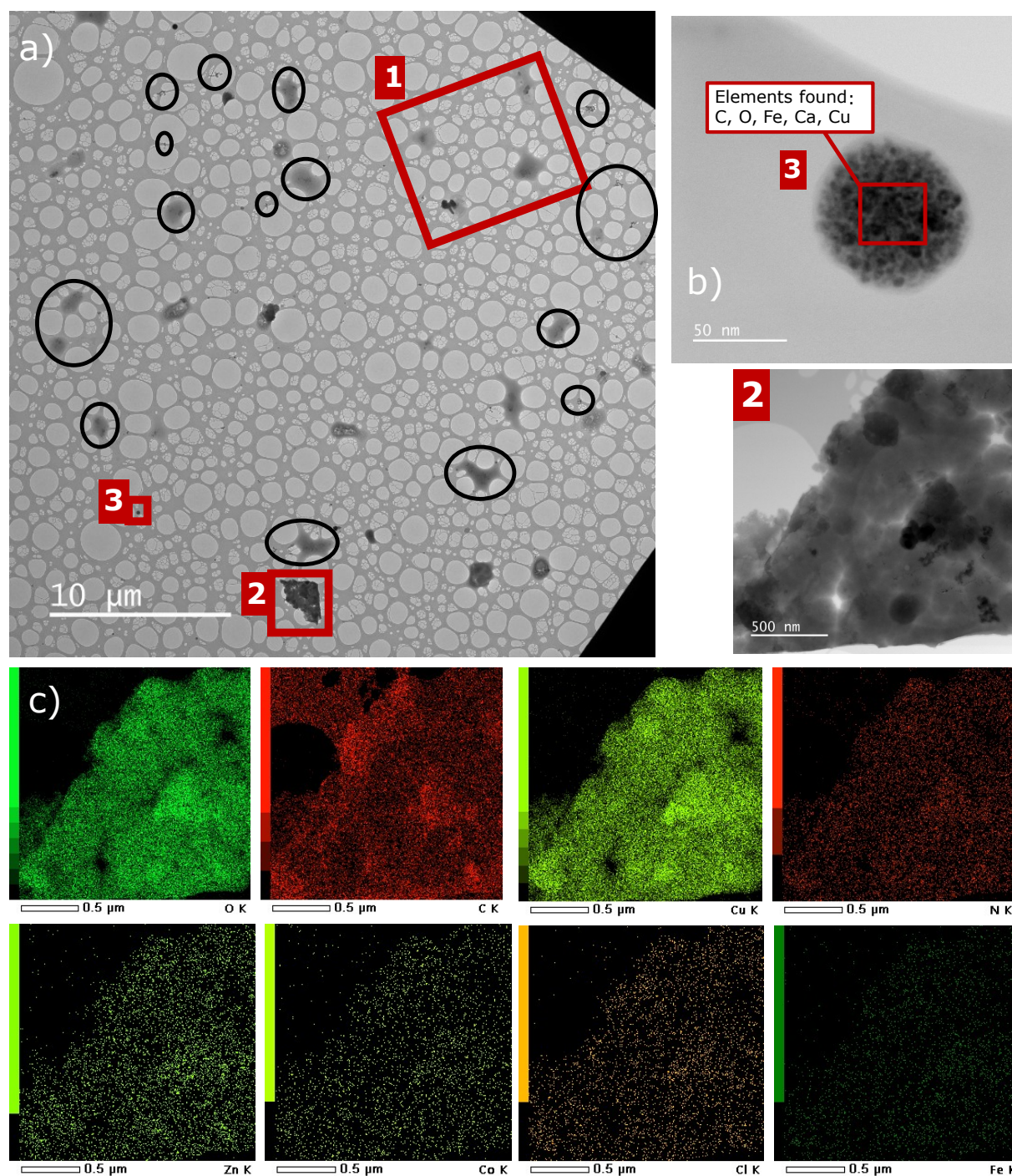


Figure 5.46: a) Large view of grid n°4, soot particles are circled in black. b) Zoom and elemental analysis of a dense sphere in area 3. c) EDX mapping of a solid particle in area 2

5.4. INVESTIGATING PARTICULATE MATTER EMISSIONS WITH METHANE AND AMMONIA: ELEMENTAL AND MORPHOLOGICAL ANALYSIS

The detection of sulfur and calcium in this particle, despite the very low concentrations of both elements in the pre-aged base oil underlines their prominent role in exhaust emissions. The presence of these elements and nitrogen in the covering layer suggests that evaporated oil vapors condensed around the pre-existing soot particle. Figure 5.47 c) shows a different morphology composed of a semi-volatile domain quickly degrading during the analysis, and an amorphous region. The amorphous region was mostly composed of carbon, nitrogen and oxygen. Interestingly, the sensitive part mainly consisted of oxygen, sulfur and calcium but only few carbon atoms were detected. This indicated that this region could not be condensed lubricant vapor, but might correspond to an inorganic salt, such as calcium carbonate found in detergent additives, or other salts involving sulfur atoms. The amorphous region might correspond to condensed lubricant vapor. A similar amorphous object, containing carbon, nitrogen and oxygen and with a length of 600 nm is shown in Figure 5.48 b).

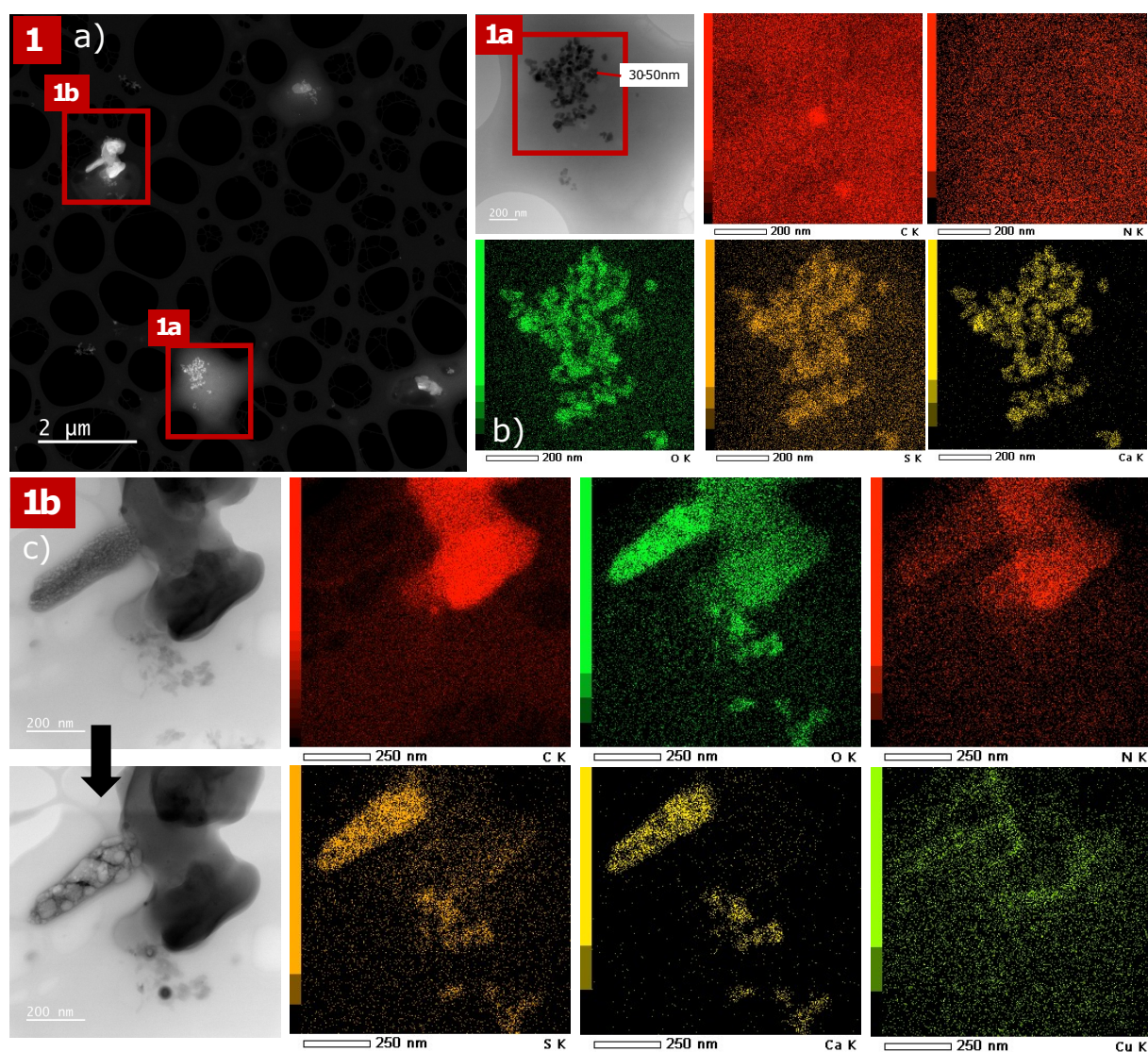


Figure 5.47: a) Zoom on area 1, large view of grid n°4. b) EDX mapping of a soot particle. c) EDX mapping of an amorphous particle

5.4. INVESTIGATING PARTICULATE MATTER EMISSIONS WITH METHANE AND AMMONIA: ELEMENTAL AND MORPHOLOGICAL ANALYSIS

Another type of soot, without surrounding phase is analyzed in Figure 5.48 a). This particle was made of slightly smaller primary particles. In this soot, no inorganic element could be detected, indicating that it was probably directly derived from CH_4 combustion. However, nitrogen atoms were detected, but might come from the condensation of lubricant vapor on the pre-existing soot.

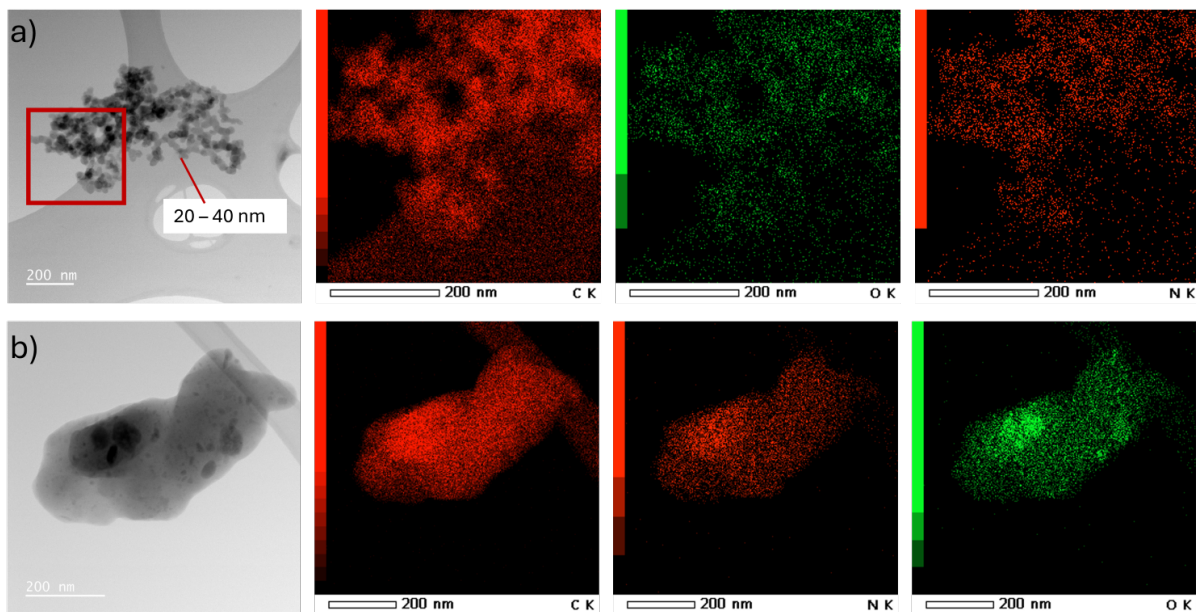


Figure 5.48: a) EDX mapping of a soot particle. b) EDX mapping of an amorphous particle

Even though soot particles were majoritarian with CH_4 combustion, other types of mixed amorphous and semi-volatile objects with denser 100-nm long cores and amorphous phase were found, and are presented in Figure 5.49.

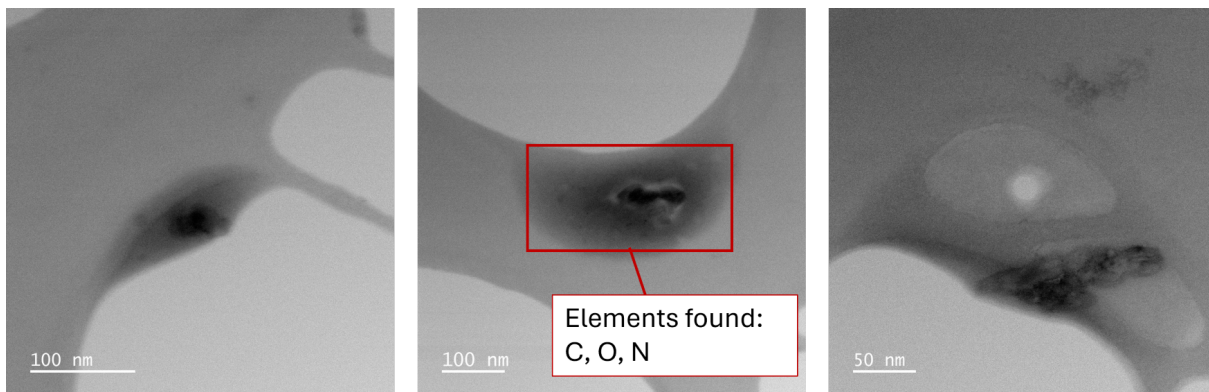


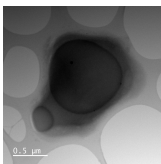
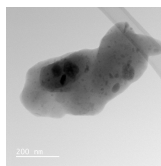
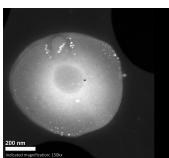
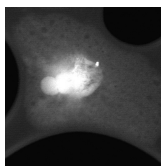
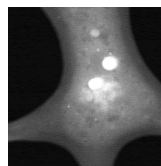
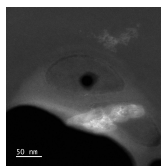
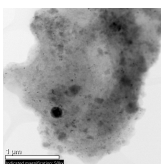
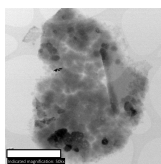
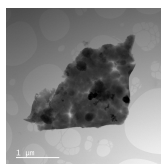
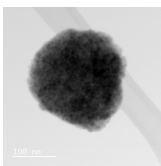
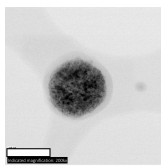
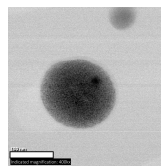
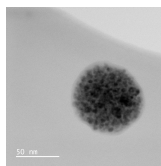
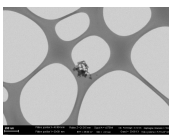
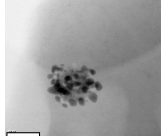
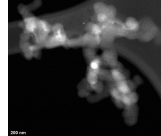
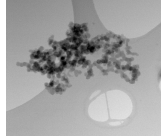
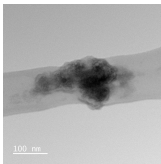
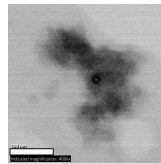
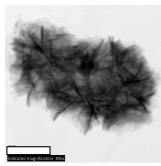
Figure 5.49: TEM observation of different amorphous particles on grid n°4

To summarize, the grid collected during methane combustion contained a markedly higher number of soot particles, along with large amorphous carbon agglomerates, dense spheres, semi-volatile deposits and metal fragments. Detecting nitrogen on metal fragments pointed out that either lubricants vapors were condensed on the fragments, or that nitrogen atoms were linked to engine parts due to the use of ammonia in the same engine, and the accumulation of ammonia and nitrogen-containing degradation products in the oil. The second hypothesis seems more likely, considering that no other elements such as sulfur or calcium were found on these fragments. The detection of nitrogen on metal fragments might indicate the presence of chemical complexes contributing to corrosion. Elements derived from the lubricant were found on some soot particles, whereas others seemed to be purely organic and derived from methane combustion. Soot particles were also larger than the ones found on grids collected with ammonia, reaching 600 nm to 1 μ m for the larger ones compared to 200 nm with ammonia. This agrees with the findings of previous section suggesting that despite apparent lower particle numbers under similar dilution conditions, methane actually generated more solid particles.

Table 5.9 summarizes the different morphologies found on the grids and provides a support for further discussion.

5.4. INVESTIGATING PARTICULATE MATTER EMISSIONS WITH METHANE AND AMMONIA: ELEMENTAL AND MORPHOLOGICAL ANALYSIS

Table 5.9: Main types of morphology types found at the exhaust of an NH_3 engine with three different engine oils

Type	Size range	Main elements	LUB- NH_3	Oil B2- NH_3	Pre-aged oil B2- NH_3	Pre-aged oil B2- CH_4
Droplet-like deposit	200 nm - 1 μm	C, N, O, Ca, Cu, S		Present but no picture	Present but no picture	Not found
Amorphous carbon particle	600 nm	C, N, O	Not found	Not found	Not found	
Spherical core-shell	Core: 10 - 100 nm Total: 70 - 200 nm	C, N, O, S, Cu, Zn		Not found	Not found	Not found
Irregular core-shell	Total 150 - 900 nm	Core: C, O, Cu, S	Not found			
Metal oxide debris	1 μm - 20 μm	C, O, Cu, Fe, Zn (+ N, Ca, S, Al)			Present but no picture	
Dense spheres	~ 200 nm	C, O, Fe, Ca, Cu (+S, Cr, Zn)				
Soot particles	Primary particles 10-60 nm	C, O, S (+ Ca, N, Cu)				
Amorphous aggregate	200 nm	C, O, Ca, Fe (+ N, S, Na, P)		Not found		Not found
Folded aggregate	1-2 μm	C, O, Cu, N, Zn	Not found		Not found	Not found

4.5 Analysis and comparison of the particles observed

Common morphologies were found on the grids obtained with different oils. Ammonia combustion resulted in purely semi-volatile deposits with droplet-like structures, resulting from homogeneous nucleation and condensation of heavy species at the exhaust. Such deposits of organic matter were found with all engine oils with ammonia, but not with methane, and were extremely sensitive to the electron beam, challenging their observation. Elements such as carbon, oxygen, nitrogen, sulfur and calcium were mainly detected in these droplet-like objects, suggesting they might be nucleated lubricant vapors. The only reference study presenting TEM observations of particles collected at the exhaust of an engine operated on ammonia, conducted by Patil *et al.* [118], also reported the detection of similar very sensitive deposits, resulting from homogeneous nucleation, and with total sizes that could exceed 1 μm , consistent with our study. Likewise, they observed a bubbly or lumpy-like aspect of these objects due to their degradation during the observations. With methane, other types of amorphous organic agglomerates originated from lubricants hydrocarbons were also found, but they seemed denser and showed less sensitivity to the electron beam. Two types of core-shell structures were also found. The fully-formulated lubricant resulted in a large number of round core-shell objects with a well defined round core of varying size between 10 and 200 nm. This indicated condensation of organic matter on a pre-existing core. However, the sensitivity of such objects challenged their more detailed analysis. The organic layer of such objects seemed to contain numerous dense nanoparticles between 4 and 15 nm, also sensitive to the electron beam, and which were not observed on grids collected with other engine oils. These could be inorganic salts such as calcium sulfate, ammonium sulfate [191] or ammonium nitrate [118] derived from the nucleation of inorganic elements from the lubricants additives and the unburned ammonia. Such salts would have a partly volatile nature, as is was the case here. With oil B2 and pre-aged oil B2, other kinds of core-shell particles were observed, with both methane and ammonia. They had more irregular shapes for the organic layer, and seemed to have multiple dense cores, with high copper content. Lagana *et al.* [117], Patil *et al.* [118] and Miller *et al.* [28] all reported the presence of core-shell particles, usually with a dense core with high metal content, depending on the main metals contained in the lubricant. All grids contained metal debris with high oxygen, copper, iron and zinc contents and crystalline regions. The size of these objects was between 1 μm and 20 μm for the largest. Nitrogen was detected on these fragments, even under methane operation. This suggested that nitrogen may have already been bound to the metal prior to combustion. This could indicate the presence of metal complexes involving ammonia and copper for instance, which may contribute to the corrosion of metal components in the system. Dense spheres with a size ranging between 100 and 200 nm were also found in every grid. They exhibited especially high carbon, oxygen, calcium, iron and copper contents. Identical objects, with similar morphology and composition, were also observed by Miller *et al.* with a hydrogen engine [28] and Patil *et al.* [118] also with

5.4. INVESTIGATING PARTICULATE MATTER EMISSIONS WITH METHANE AND AMMONIA: ELEMENTAL AND MORPHOLOGICAL ANALYSIS

ammonia. These particles would come from the pyrolysis of oil droplets, only leaving the inorganic core. Additionally, some soot particles were found at the exhaust. The grid collected with methane showed a markedly higher amount of soot particles compared to those collected with ammonia, as the latter could only result from direct combustion of the engine oil. Under ammonia combustion, no significant differences could be observed between the three oils for soot particles, as the analysis performed here does not allow for a quantitative assessment. Nevertheless, the contrast with methane was unambiguous, confirming that soot production was substantially higher with methane. Organized carbon particles were also observed by Patil *et al.* [118] and Miller *et al.* [28], but not Lagana *et al.* [117], with high carbon, oxygen, nitrogen, magnesium, and sulfur contents. Other amorphous structures with fewer occurrence were observed. In particular, several folded-like objects with high nitrogen, copper, and zinc contents were found on the grid collected with oil B2. Examination of additional grids obtained with the same oil would be required to assess whether this morphology is reproducible or if it resulted from a singular event.

Some differences between the engine oils could be noticed. Only few objects found on grid n°2, with the mineral oil B2, contained nitrogen. This is consistent with the low nitrogen content of the oil itself, thereby indicating that nitrogen atoms found in the particles mostly directly come from the lubricant. On the other hand, calcium and sulfur were detected in different types of morphologies obtained with the oil without additives, though to a lesser extend. It means that even small concentration of these species, here as residues from oil drains, still contribute to pollutants emissions.

Only few references are available in the literature to compare these findings. Direct observation of the particles collected at the exhaust of an ammonia engine was only performed by Patil *et al.* [118]. Similarities were already pointed out, however they also observed different types of morphologies. In particular, their study aims at demonstrating the identification of ammonium nitrate salts, via multiple characterizations including FTIR, Raman, XPS, and TEM coupled to EDS. They identified volatile particles as salts, supported by nitrogen and oxygen overlaid presence, and characteristic absorption bands detected at the scale of the microscope grid. In parallel, gas exhaust measurements showed the simultaneous presence of NH_3 and NO_2 , allowing for ammonium nitrate formation as described in Section 1.2.6.3. Cores of core-shell particles were also identified as ammonium nitrate salts, with overlaying condensed organic and inorganic matter. Such salts did not seem to be present here. This can be linked to the differences in experimental conditions: different engines were used, and theirs was operated at $\phi=0.7$, changing the exhaust composition and temperature. This also highlights the difficulty of identifying semi-volatile particles, which quickly degrade or sublime under the electron beam, preventing precise analysis of their morphology.

Future studies could build on these findings to improve knowledge about the emissions associated to ammonia combustion. Collecting condensable matter and conducting in-depth

5.4. INVESTIGATING PARTICULATE MATTER EMISSIONS WITH METHANE AND AMMONIA: ELEMENTAL AND MORPHOLOGICAL ANALYSIS

analysis, as performed by Apicella *et al.* [29,190] with hydrogen engines, would certainly bring new insights about the exhaust emissions of ammonia engines. Lowering the tension of the electron beam could also enable to limit the degradation of the sample during the observation, but it would be a limitation for the resolution of the observations. Mass spectrometers connected directly on the exhaust could also enable a more precise identification of the exhaust species.

4.6 Discussion—particle emissions

In this chapter, the effects of running an engine on methane and ammonia with different engine oils including a pre-aged oil, degraded in the laboratory under conditions reproducing ammonia combustion were studied. Consequences on engine operation as well as on gaseous and particulate matter emissions were investigated. A decrease in engine efficiency was observed with ammonia, which could partly be attributed to the adsorption of ammonia in the oil film locally in the engine, disrupting the oil film and increasing its friction coefficient. Other mechanisms might contribute to this decreased efficiency. This had consequences on gaseous emissions measured with ammonia combustion, leading in particular to lower NH_3 and CO but higher NO and N_2O levels. Meanwhile, methane combustion and associated gaseous emissions appeared unaffected by the change in engine oil.

Regarding particulate matter, as only very few studies investigated this issue with ammonia engines, the purpose of this work was to provide an initial exploration of the topic, by assessing different parameters and provide useful insights for future research. Methane was used as a reference fuel, for which more data can be found. Real-time measurements of the particle size distributions showed bimodal or monomodal distributions depending on dilution conditions. At 1000 rpm and with a dilution factor of 35, the nucleation peak was centered in 8.6 ± 1.2 nm for ammonia and 8.2 ± 0.5 nm for methane. At low dilution factors, an accumulation mode was observed between 20 and 100 nm with methane, and 15 and 100 nm with ammonia. Increasing the dilution factor led to decrease the peak heights of both nucleation and accumulation modes, for both fuels. Diluting only by 12 led to an important increase in total particle number, especially for ammonia, which was attributed to conditions enhancing the nucleation of volatile species, including exhaust water. Under methane combustion, it was possible to find a dilution factor above which total particle numbers and distributions remained stable, but not with ammonia. These results highlighted that dilution conditions had a critical influence on the measurements and confirmed the mostly volatile nature of the measured exhaust aerosol samples. The effect of changing the engine oil seemed limited at 1000 rpm for both fuels, but the mineral base oil and the pre-aged mineral base oil both generated more particles than the fully-formulated one at higher engine speeds. Changing the oil also affected the aspect of the size distribution and especially the accumulation mode which was narrower with the pre-aged base oil. Decreasing the intake pressure led to decrease the IMEP and subsequently

5.4. INVESTIGATING PARTICULATE MATTER EMISSIONS WITH METHANE AND AMMONIA: ELEMENTAL AND MORPHOLOGICAL ANALYSIS

the total number of emitted particles. However, the slightly lower IMEP values measured with the pre-aged base oil did not result in lower emission levels.

Combining this analysis with microscope observations greatly improved the understanding and level of detail on pollutant emissions generated by methane and ammonia combustion. One important thing to notice is that the observed particles did not enter the size range of in-line measurements. The observed objects were between 50 nm and several microns, largely exceeding the 100 nm maximum found with the EEPs instrument. This was also the case in the study by Lagana *et al.* [117], in which they measured size distributions of particles generated in a hydrogen engine with a DMS500 instrument and performed microscope observations. This is partly due to the fact that mainly volatile particles are counted using the EEPs, while these cannot be retained on microscope grids, or are desorbed when introduced in high vacuum chamber. This could also be linked to the sampling time, 10 min here, promoting the aggregation of small objects into larger ones, as opposed to real-time measurements. The grid collected with methane contained more solid material, and especially exhibited numerous soot particles. In contrast, the majoritarian morphology was round semi-volatile core-shell structures with ammonia and the fully-formulated lubricant, and other types of amorphous agglomerates with the mineral base oil and the pre-aged base oil. Grids collected with ammonia contained numerous objects that were highly sensitive to the electron beam. In addition to semi-volatile deposits, rare soot agglomerates, metal particle and other amorphous agglomerates were also observed on the grids collected under ammonia combustion. Although nitrogen atoms were detected in several types of objects, no nitrogen-based particle was identified in this study, unlike in the work of Patil *et al.* [118] supporting the hypothesis of ammonium nitrate formation under their experimental conditions. Nevertheless, nitrogen atoms were detected in certain types of morphologies, mostly derived from the different engine oils themselves containing dissolved ammonia and molecular nitrogen, as studied in Chapter 4. Furthermore, nitrogen atoms were detected in metal and metals oxides particles collected with methane, and with oil B2 with a low nitrogen content, suggesting that some nitrogen might be bound to metal surfaces in the system. This could be linked to the corrosion phenomenon, which was evidenced by the increasing copper, iron, and zinc contents in the engine oils in Chapter 4. The high proportion of organic matter at the exhaust is also consistent with the increasing calcium content in oil B2 and the pre-aged base oil, suggesting evaporation of an organic fraction of these oils. As only few material was collected and few grids were analyzed, the microscope observations conducted did not enable a quantitative comparison between the engine oils. However, particle types and compositions could be qualitatively compared, pointing out the role of sulfur and calcium additives in both semi-volatile deposits and inorganic ashes.

These findings highlight the challenge of evaluating ammonia exhaust emissions, especially in a regulatory context or when comparing results from different experiments. In Europe, current standards regulating particle emissions from on-road vehicles focus mainly on solid

particles with diameters larger than 23 nm, with limits expressed in terms of particulate mass. Volatile components such as sulfates, unburned fuel, and lubricant residues are not included in the regulated fraction. The forthcoming Euro 7 regulation, which is expected to be progressively implemented, will extend the scope to particles as small as 10 nm and regulate particle number [192]. For marine engines, the current framework defined by the IMO in Annex VI of the MARPOL Convention regulates sulfur content in marine fuels, nitrogen oxides NO_x , Volatile Organic Compounds (VOCs), and greenhouse gas emissions [193]. However, no direct limits are imposed on particulate matter, either in terms of mass or total particle number, although this could be implemented in future regulations.

5. Conclusion

After examining the effects of combustion on engine oil properties during ammonia and methane operation with three different engine oils, this chapter focused on the reciprocal influence of lubricants on engine performance and pollutant emissions. First, the experimental setup implemented to monitor engine parameters, gaseous species, and particulate matter emissions was described. Then, results indicating a reduction in engine efficiency with the pre-aged mineral base oil under ammonia combustion and its consequences on resulting gaseous emissions were presented. Several hypotheses were proposed to explain this phenomenon, including a specific interaction between ammonia and the oil film on the cylinder liner that could modify friction properties. Particle emissions were successfully investigated through a dual approach, combining in-line real-time measurements with particle sampling for microscopic observations. An overview of the types of morphologies observed with methane and ammonia and the different engine oils was provided. It was shown that particle emissions mainly consisted of volatile species derived from the lubricant in the case of ammonia operation, and the influence of sampling conditions was also highlighted. This study paves the way for future work focusing on adapting lubricant formulations to ensure maximized engine efficiency while minimizing pollutant emissions.

General conclusion and perspectives

In the context of the development of alternative fuels such as ammonia, characterized by combustion properties and chemical behavior markedly different from conventional fuels, the main objective of this work was to investigate the potential challenges posed to lubricants, as well as the reciprocal effects of lubricants aging on combustion and pollutant emissions.

To address this objective, the study was structured around the following stages:

1. Identifying the specific challenges associated with ammonia combustion thanks to a thorough literature review.
2. Investigating the oxidation behavior of base oils under reference conditions; developing an experimental workflow for accelerated aging and subsequent characterization; and establishing a portfolio of analytical techniques relevant to monitoring base oil degradation.
3. Studying the evolution of base oils under modified accelerated aging conditions, in particular assessing the effects of nitrogen oxides and ammonia.
4. Evaluating the evolution of the same base oils directly during engine operation.
5. In the mean time, evaluating the reciprocal influence of lubricants on engine operation and pollutant emissions, gaseous and particulate matter.

These objectives were pursued in four main phases, each corresponding to one chapter on this manuscript. Chapter 1 established the central role of lubricants in internal combustion engines and how they could potentially be affected by the specific combustion characteristics of ammonia and its blends, in addition to conventional aging mechanisms. A review of state-of-the-art characterization techniques for lubricant degradation analysis was also provided. Reactivity with nitrogen oxides, unburned ammonia, and water were identified as the main potential issues for lubricants in ammonia engines, requiring further investigation. The contribution of lubricants to particle emissions, depending on their properties, was also identified as a critical issue for the development of clean engines.

Chapter 2 focused on the oxidation behavior of selected base oils through a multitechnique and innovative approach. Combining *operando* oxidation in a headspace autosampler and Rancimat method enabled a comprehensive understanding of the oxidation behavior of eight base oil, mineral and synthetic. The degradation pathways of two base oils, one min-

eral and one complex polyester, were further investigated using a pressurized reactor under oxygen atmosphere. This study enabled the development of a comprehensive portfolio of analytical techniques—including infrared spectroscopy, viscosity, elemental analysis and molecular analysis—to assess the evolution of key properties of base oils under reference conditions.

Building on this groundwork, Chapter 3 investigated the same two selected base oils under unconventional accelerated aging conditions involving NO_x , gaseous NH_3 , and aqueous NH_3 in addition to O_2 . NO_2 was shown to significantly increase the rate of the oxidation reaction, especially its initiation, without being involved in termination products. On the contrary, NH_3 was shown to progressively dissolve in hydrocarbon matrices and react with oxidation products as they start to be formed, moderating the oxidation rate and leading to nitrogen-containing products. New degradation pathways involving ammonia, oxygen, and mineral base oils were then evidenced under accelerated conditions.

To compare accelerated aging with real operation, Chapter 4 examined the evolution of three different engine oils during ammonia and methane combustion, using the same characterization workflow as throughout the thesis. The oils included a fully-formulated commercial lubricant, the group III mineral base oil studied previously in the fresh state, and in a pre-aged state. The pre-aging step consisted in exposing the mineral oil to oxygen and ammonia in a pressurized reactor under heating to simulate a moderately severe degradation state while limiting running hours on the engine. The engine was operated with the three oils successively and oil samples were collected at increasing use times. Despite short combustion times, degradation at the molecular level could be demonstrated during the engine tests, with measurable consequences on macroscopic properties of all three oils, such as infrared spectroscopy, viscosity and elemental analysis. Nitrogen incorporation was identified in all oils, mainly as dissolved ammonia, but also as large degradation products in the pre-aged base oil. This accumulation was shown to depend on oil polarity and correlated with the presence of corrosion metals.

Finally, Chapter 5 addressed the reciprocal effects of lubricants on engine performance and emissions. The pre-aged base oil was found to reduce engine efficiency under ammonia combustion, though no impact was observed with methane. This was attributed to specific interactions between the pre-aged oil and ammonia happening directly in the engine. Particle emissions were investigated through a dual approach combining real-time in-line monitoring and *a posteriori* microscopic observation and elemental analysis of sampled particles. Results showed that, under ammonia operation, particle emissions were dominated by volatile species originating from the lubricant and greatly influenced by dilution conditions. An overview of the types of morphologies observed with methane and ammonia and the different engine oils was provided.

This study is one of the first to investigate this topic of ammonia/engine oil compatibility. The implementation of a multiscale methodology combining accelerated aging with engine test bench experiments, bridged by the use of common characterization techniques provided new

insights into the understanding of the interaction between ammonia and engine oils and paves the way for future studies in several directions. Major results indicating deleterious interactions between ammonia and engine oils were evidenced, and call for future studies to better understand these degradation mechanisms. In particular, the antioxidant effect of gaseous ammonia and its reactivity with engine oil components could be further explored under accelerated aging conditions. For instance, analysis of the gas phase in closed-stirred reactor such as the one used in this study could help further understanding of the detailed interaction between ammonia, oxygen and base oils. Other characterization techniques such as hydroperoxides titration could also improve the understanding of the reactivity in the liquid phase. As nitrogen oxides and ammonia appeared to have antagonist effects, their combined effect could also be explored. Furthermore, the identification of nitrogen-containing degradation products was not definitive in this study and could be further investigated with an in-depth analytical approach. The consequences of these chemical changes on the tribological properties were not directly explored in this study but would bring valuable information about the consequences of such degradation mechanisms. Experiments conducted directly in the engine showed that the affinity of ammonia for the engine oil was a critical issue, because it could modify the friction properties, the corrosivity of the oil, and initiate further reactivity between dissolved ammonia and oil components. Research on oil formulations and additive packages, with a specific attention to lubricant polarity, then appears as necessary to minimize these effects. In addition, other studies focusing on particle emissions could help consolidating the findings of this thesis regarding exhaust emissions generated by the combustion of ammonia. The main outcomes of this thesis highlight the critical need to consider this fuel/engine oil compatibility issue for the safe and durable operation of forthcoming ammonia engines.

Appendices

Appendix A—Chapter 2

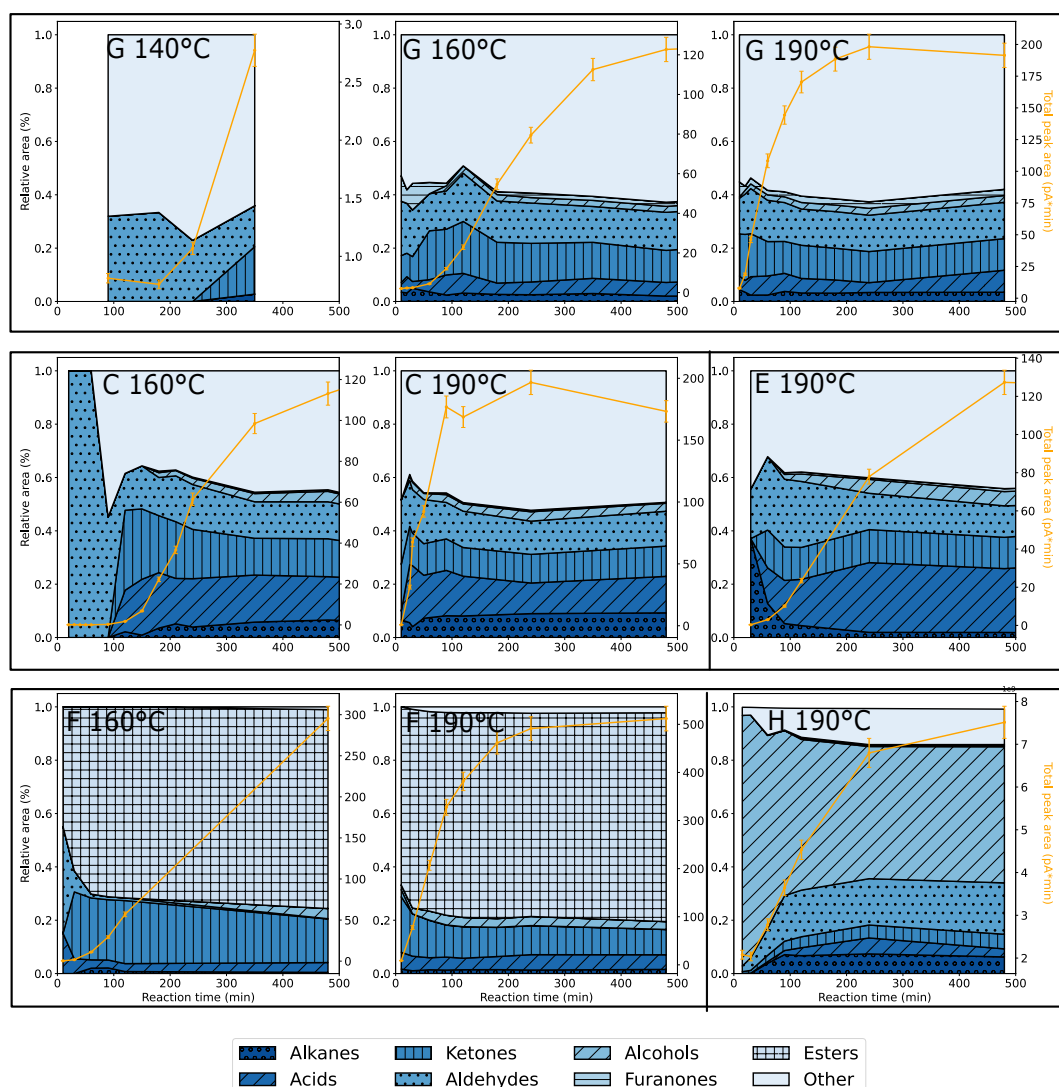


Figure A.1: Relative contribution of each category of product to the total peak area at different temperatures and increasing times—oils C, E, F, G, H

APPENDIX A

Table A.1: Summary of the products identified via headspace chromatography. " t_{r1} " is the retention time with GC/MS experiments, and " t_{r2} " the corresponding retention times in GC/FID.

Molecule	Type	t_{r1}	t_{r2}	A	B	C	F	G	H	D	E
Formic acid	acid	1.69							X		
Acetic acid	acid	2.48-2.57	5.32	X	X	X		X	X	X	X
1-Butanol	alcohol	2.59	6.50	X	X				X		
2-Pentanone	ketone	2.85	6.99	X	X	X		X	X	X	X
Pentanal	aldehyde	2.98	7.26	X	X	X		X		X	X
Propanoic acid	acid	3.37-5.02	5.48	X	X	X		X	X	X	X
1-Pentanol	alcohol	4.90	9.90	X	X			X	X		
2-Hexanone	ketone	5.53	10.59	X	X	X		X	X	X	X
Hexanal	aldehyde	6.00	10.95	X	X	X		X	X	X	X
Butanoic acid	acid	6.44-8.74	11.58	X	X	X		X	X	X	X
1-Hexanol	alcohol	8.89	13.63	X	X	X		X	X		X
3-Heptanone	ketone	9.47	14.25		X				X		
2-Heptanone	ketone	9.70	14.39	X	X	X		X	X	X	X
Nonane	alkane	9.97	14.708	X	X	X		X	X	X	X
Heptanal	aldehyde	10.12	14.77		X	X		X	X	X	
Pentanoic acid	acid	10.21-12.18	14.91	X	X	X		X		X	X
2(3H)-Furanone, dihydro-5-methyl-	furanone	12.09	16.59	X	X	X		X		X	X
1-Heptanol	alcohol	12.90	17.19	X	X	X		X	X	X	
2-Octanone	ketone	13.55	17.89	X	X	X	X	X	X	X	X
Hexanoic acid	acid	13.68-15.28	18.05		X	X		X		X	X
Decane	alkane	13.86	18.18	X	X	X		X		X	
Octanal	aldehyde	13.97	18.29	X	X	X			X		X
2(3H)-Furanone, dihydro-5-ethyl	furanone	15.71		X	X			X			X
1-Octanol	alcohol	16.42	19.95	X	X	X		X		X	X
Heptanoic acid	acid	16.85-18.22	20.91			X			X	X	X
3-Nonanone	ketone	16.93									
2-Nonanone	ketone	17.08	21.12	X	X	X	X	X		X	X
Undecane	alkane	17.32	21.35	X	X	X		X	X	X	
Nonanal	aldehyde	17.47	21.35		X	X			X		X
2(3H)-Furanone, dihydro-5-propyl-	furanone	19.05	22.10					X			
1-Nonanol	alcohol	19.68	22.99			X		X	X		
Octanoic acid	acid	19.80-20.82	23.61	X	X	X		X	X	X	
Naphthalene	alkane	19.84	23.95							X	
2-Decanone	ketone	20.31	24.09	X	X	X		X	X		
Dodecane	alkane	20.52	24.28	X	X	X		X		X	
Decanal	aldehyde	20.62	24.46		X	X			X	X	
2(3H)-Furanone, 5-butyl-dihydro-	furanone	22.37	25.97			X		X			X

See next page

APPENDIX A

Molecule	Type	t_{r1}	t_{r2}	A	B	C	F	G	H	D	E
Nonanoic acid	acid	22.64-23.44	26.20	X	X	X		X	X		X
1-Decanol	alcohol	22.83									
2-Undecanone	ketone	23.32	26.87	X	X	X			X		
Tridecane	alkane	23.52	27.02	X	X	X				X	
Undecanal	aldehyde	23.70									
n-Decanoic acid	acid	25.29-25.85	28.73			X		X	X	X	X
2(3H)-Furanone, dihydro-5-pentyl-	furanone	25.30							X		
2-Dodecanone	ketone	26.15									X
Undecanoic acid	acid	27.98	31.40					X		X	X
2(3H)-Furanone, 5-hexyldihydro-	furanone	28.15									
2-Tridecanone	ketone	28.83						X			

APPENDIX A

Table A.2: Summary of the products identified via headspace chromatography specific to different samples. " t_{r1} " is the retention time with GC/MS experiments, and " t_{r2} " the corresponding retention times in GC/FID.

Oil	Molecule	t_{r1}	t_{r2}
Oil A 140 °C–90 min	Butanoic acid, 3-methyl	8.27	
	Ethanone, 1-cyclopentyl-	11.17	
	Cyclohexanone, 3-methyl-	11.85	
	2-Heptanone, 6-methyl-	12.24	
	Pentanoic acid, 4-methyl-	12.41	
	Cyclopentylcarboxylic acid	14.69	
	2-Hexanone, 6-methyl-	16.06	
Oil F 190 °C–60 min	2-Butanone, 3,3-dimethyl-	3.33	7.71
	tert-Butyl hydroperoxide	3.52	
	2-Pentanone, 4,4-dimethyl-	5.36	10.247
	3-Pentanone, 2,2-dimethyl-	6.06	10.898
	2-Pentanol, 4,4-dimethyl-	6.47	11.112
	Propanoic acid, 2,2-dimethyl-	9.39	
	Hexanal, 3,5,5-trimethyl-	12.85	17.297
	3,5-Heptanedione	13.07	
	3,6-Heptanedione	14.85	19.015
	2,4,4-Trimethyl-1-pentanol	15.18	
	Hexanoic acid, 2-ethyl-, methyl ester	15.48	19.606
	2-Heptanone, 6-methyl	15.71	19.837
	Methyl 3,5,5-trimethylhexanoate	16.7	20.723
	Hexanoic acid, 2-ethyl-	18.73	
	Hexanoic acid, 3,5,5,5-trimethyl-	20,58	22.94
Oil G 190 °C–60 min	2-Ethylhexyl 2-ethylhexanoate	31.55	
	Hexanoic acid, 3,5,5-trimethyl-, 2-ethylhexyl ester	32.36	22.589
	Octanoic acid, methyl ester	18.2	
	1,3-Propanediol, 2-ethyl-2-(hydroxymethyl)-	22.49	
	2H-Pyran-2-one, tetrahydro-6-propyl-	23.15	
	Decanoic acid, methyl ester	24.23	
	2H-Pyran-2-one, tetrahydro-6-pentyl-	28.87	
	Caprylic anhydride	29.94	
	Heptadecane	33.76	
	d-Dodecalactone	33.98	
Oil H 160 °C–90 min	Decanoic anhydride	34.66	
	Hexanal, 2-ethyl-	12.16	
	1-Hexanol, 2-ethyl	15.16	
	Acetic acid, 2-ethylhexyl ester	19.04	
	n-Butyric acid 2-ethylhexyl ester	24.2	
	Pentanoic acid, 2-ethylhexyl ester	26.79	
	Hexanoic acid, 2-ethylhexyl ester	29.29	

APPENDIX A

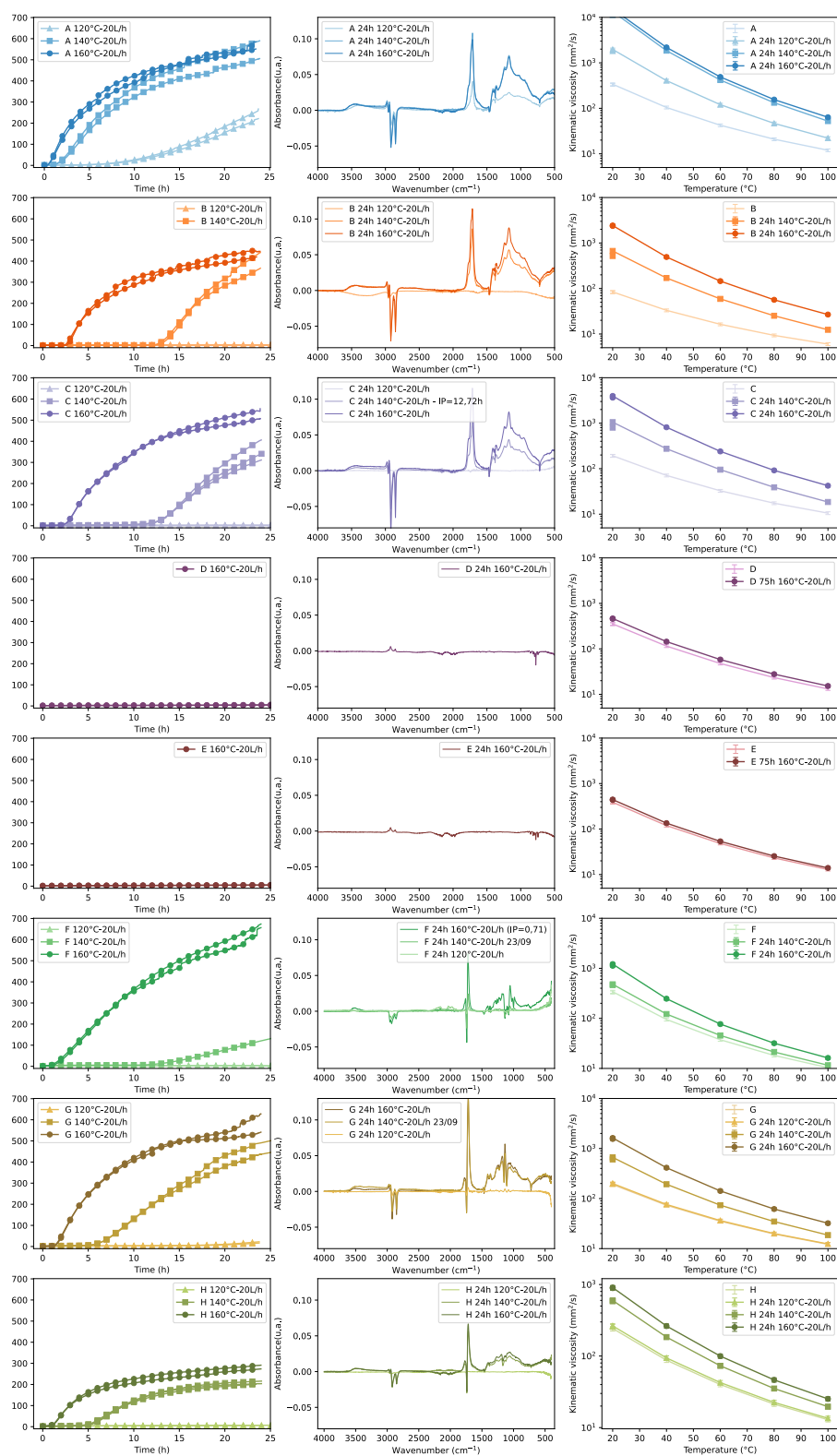


Figure A.2: Conductivity curves, IR Spectra and kinematic viscosity of the 8 base oils after 24 h experiments in Rancimat at different temperatures

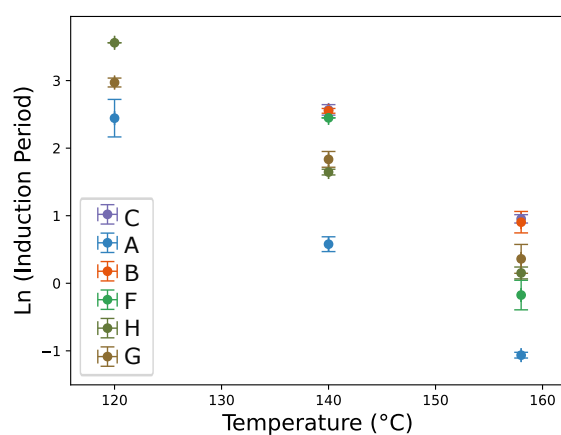


Figure A.3: Logarithm of the induction periods measured with Rancimat

Appendix B—Chapter 3

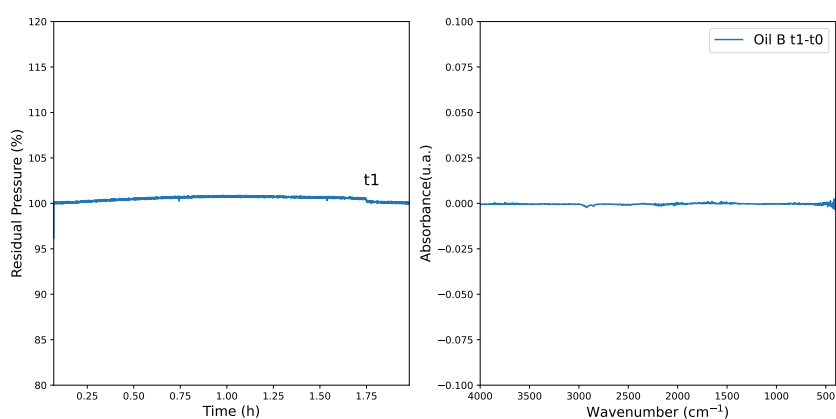


Figure B.1: Oil B —NO in N_2 at 10 bar—135 °C. Left: residual pressure with time. Right: Difference between infrared absorption spectrum before the gas injection, and after 2 h

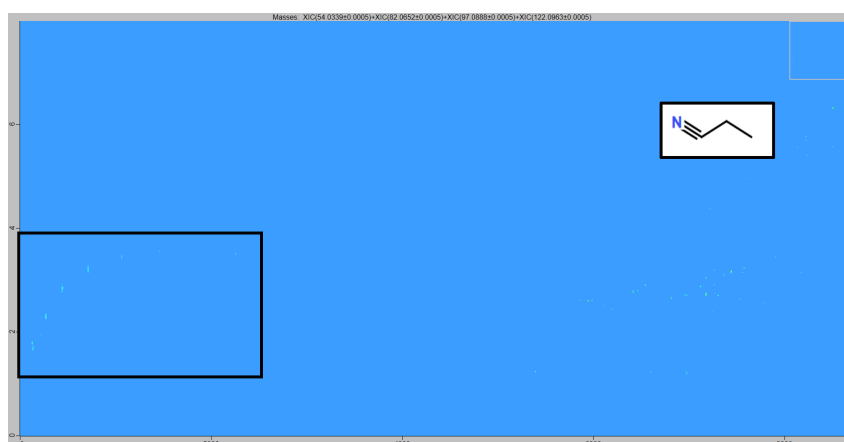


Figure B.2: GC2D/MS chromatogram of oil B after exposure to air + NH_3 at 135 °C 10 bar. Research of ions specific to the nitrile family. Based on the study from Ozel et al. [159], the researched ions 54.0339, 82.0652, 97.0888 and 122.0963 correspond to nitrile fragments.

Appendix C—Chapter 4

Table C.1: Dynamic viscosity, kinematic viscosity and specific gravity of oil B2 after pre-aging

Sample	Dyn. Viscosity (mPa.s)	Kin. viscosity (mm ² /s)	Specific gravity
1	45.102	53.486	0.8433
2	45.325	53.730	0.8436
3	44.800	53.050	0.8438
4	46.423	54.981	0.8444
5	45.576	54.057	0.8431
6	44.960	53.233	0.8446
7	47.501	56.177	0.8456
8	47.284	55.895	0.8459
9	46.118	54.588	0.8448
10	46.259	54.747	0.8450
11	46.976	55.541	0.8458
12	46.756	55.341	0.8449
13	46.450	55.022	0.8442
14	46.603	55.164	0.8448
15	46.190	54.676	0.8448
16	47.242	55.945	0.8444
17	46.440	55.182	0.8416
Mean value	46.23	54.75	0.8444
std. dev	0.83	0.95	0.001
rel. error (%)	1.8	1.7	0.12

Table C.2: Summary of the engine operating conditions. "LUB1" refers to experiments conducted with the regular 20 L crankcase. "Oil B2 pa" refers to pre-aged oil B2. SI = Spark Ignition timing.

Date	xNH ₃	xCH ₄	xH ₂	P _{intake} (bar)	ϕ	Speed (rpm)	SI (°CA)	Oil	FTIR	EEPS	MPS
241217	1.00	0.00	0.00	1.00	0.9	999	-40	LUB1		X	
241217	0.00	1.00	0.00	1.00	1.0	999	-14	LUB1		X	
241217	0.00	1.00	0.00	0.70	1.0	999	-17	LUB1		X	
241217	0.00	1.00	0.00	0.61	1.0	999	-18	LUB1		X	
241217	0.00	1.00	0.00	0.50	1.0	999	-20	LUB1		X	
241217	0.00	1.00	0.00	0.70	1.0	999	-16	LUB1		X	
241217	0.00	1.00	0.00	0.99	1.0	998	-16	LUB1		X	
241217	0.00	1.00	0.00	1.00	1.0	999	-15	LUB1		X	
241217	1.00	0.00	0.00	1.00	0.9	1000	-28	LUB1		X	
241217	1.00	0.00	0.00	1.00	0.9	999	-32	LUB1		X	
241217	1.00	0.00	0.00	0.80	0.8	1006	-40	LUB1		X	

See next page

APPENDIX C

Date	xNH ₃	xCH ₄	xH ₂	P _{intake} (bar)	ϕ	Speed (rpm)	SI (°CA)	Oil	FTIR	EEPS	MPS
241217	1.00	0.00	0.00	0.90	0.8	998	-40	LUB1		X	
241217	1.00	0.00	0.00	0.99	0.8	1000	-40	LUB1		X	
241217	0.00	1.00	0.00	1.00	1.0	999	-15	LUB1		X	
241217	0.00	1.00	0.00	0.85	1.0	999	-18	LUB1		X	
241217	0.00	1.00	0.00	0.85	0.9	999	-20	LUB1		X	
241217	1.00	0.00	0.00	1.00	1.0	999	-35	LUB1		X	
241217	1.00	0.00	0.00	0.85	1.0	1001	-48	LUB1		X	
241217	1.00	0.00	0.00	1.00	1.0	1000	-38	LUB1		X	
241217	1.00	0.00	0.00	1.00	1.0	1499	-38	LUB1		X	
241217	1.00	0.00	0.00	1.00	1.0	1499	-38	LUB1		X	
241217	1.00	0.00	0.00	1.00	1.0	1999	-44	LUB1		X	
241217	1.00	0.00	0.00	1.00	1.0	1999	-44	LUB1		X	
241217	1.00	0.00	0.00	1.00	1.0	999	-38	LUB1		X	
241217	0.90	0.00	0.10	0.85	1.1	999	-40	LUB1		X	
250108	0.00	1.00	0.00	1.03	1.0	1499	-16	LUB1		X	
250108	0.00	1.00	0.00	1.05	0.9	1999	-16	LUB1		X	
250108	0.00	1.00	0.00	1.01	1.0	999	-16	LUB1		X	
250108	0.00	1.00	0.00	1.02	1.0	1499	-16	LUB1		X	
250108	0.00	1.00	0.00	1.05	0.9	1998	-16	LUB1		X	
250108	0.00	1.00	0.00	1.01	1.0	999	-16	LUB1		X	
250108	1.00	0.00	0.00	1.00	1.0	999	-35	LUB1		X	
250108	1.00	0.00	0.00	1.00	1.0	998	-35	LUB1		X	
250108	1.00	0.00	0.00	1.00	1.0	999	-35	LUB1		X	
250108	0.00	1.00	0.00	1.00	1.0	998	-16	LUB1		X	
250108	0.00	1.00	0.00	1.00	1.0	999	-16	LUB1		X	
250108	0.00	1.00	0.00	1.00	1.0	999	-16	LUB1		X	
250114	0.00	1.00	0.00	1.01	1.0	999	-16	LUB1		X	
250114	0.00	1.00	0.00	1.00	1.0	999	-16	LUB1		X	
250114	1.00	0.00	0.00	1.00	1.0	999	-35	LUB1		X	
250114	1.00	0.00	0.00	1.00	1.0	998	-35	LUB1		X	X
250114	1.00	0.00	0.00	1.00	1.0	999	-35	LUB1		X	X
250114	1.00	0.00	0.00	1.00	1.0	999	-35	LUB1		X	X
250116	0.00	1.00	0.00	1.02	1.0	999	-16	LUB1		X	
250116	0.00	1.00	0.00	1.03	0.8	1498	-16	LUB1		X	
250116	0.00	1.00	0.00	1.00	1.0	1499	-16	LUB1		X	
250116	0.00	1.00	0.00	1.04	1.0	1998	-16	LUB1		X	
250116	0.00	1.00	0.00	1.01	1.0	999	-16	LUB1		X	
250116	0.00	1.00	0.00	1.02	1.0	1998	-16	LUB1		X	
250116	0.00	1.00	0.00	1.00	1.0	1998	-16	LUB1		X	
250116	0.00	1.00	0.00	1.03	1.0	1498	-16	LUB1		X	
250116	0.00	1.00	0.00	1.00	1.0	1499	-16	LUB1		X	
250116	1.00	0.00	0.00	1.00	1.0	999	-35	LUB1		X	
250116	1.00	0.00	0.00	1.00	1.0	999	-35	LUB1		X	X
250116	0.00	1.00	0.00	1.01	1.0	1499	-16	LUB1		X	
250116	1.00	0.00	0.00	1.04	1.0	1499	-35	LUB1		X	
250116	0.00	1.00	0.00	1.02	1.0	1998	-16	LUB1		X	
250116	0.00	1.00	0.00	1.00	1.0	999	-16	LUB1		X	
250116	1.00	0.00	0.00	1.00	1.0	998	-35	LUB1		X	X
250116	1.00	0.00	0.00	1.00	1.0	999	-35	LUB1		X	X
250116	1.00	0.00	0.00	1.00	0.9	998	-32	LUB1		X	
250116	1.00	0.00	0.00	1.00	0.9	996	-32	LUB1		X	
250116	1.00	0.00	0.00	0.85	1.0	999	-40	LUB1		X	
250116	1.00	0.00	0.00	0.85	1.0	1000	-40	LUB1		X	
250116	1.00	0.00	0.00	0.85	1.0	999	-40	LUB1		X	
250116	0.00	1.00	0.00	0.86	0.9	999	-18	LUB1		X	
250124	0.00	1.00	0.00	1.00	1.0	999	-15	LUB1		X	

See next page

APPENDIX C

Date	xNH ₃	xCH ₄	xH ₂	P_{intake} (bar)	ϕ	Speed (rpm)	SI (°CA)	Oil	FTIR	EEPS	MPS
250124	0.00	1.00	0.00	0.99	1.0	1499	-15	LUB1		X	
250124	0.00	1.00	0.00	0.99	1.0	1749	-15	LUB1		X	
250124	0.00	1.00	0.00	1.00	1.0	1998	-15	LUB1		X	
250124	0.00	1.00	0.00	1.01	1.0	999	-15	LUB1		X	
250124	0.00	1.00	0.00	1.00	1.0	999	-15	LUB1		X	
250124	0.00	1.00	0.00	1.01	1.0	999	-15	LUB1		X	
250124	0.00	1.00	0.00	1.00	1.0	999	-15	LUB1		X	
250124	0.00	1.00	0.00	1.00	1.0	1499	-15	LUB1		X	
250124	0.00	1.00	0.00	1.03	1.0	1999	-15	LUB1		X	
250124	1.00	0.00	0.00	1.01	1.0	999	-35	LUB1		X	
250124	1.00	0.00	0.00	1.00	1.0	999	-33	LUB1		X	X
250124	1.00	0.00	0.00	1.00	1.0	999	-33	LUB1		X	X
250124	1.00	0.00	0.00	1.00	1.0	999	-33	LUB1		X	X
250124	1.00	0.00	0.00	1.04	0.9	1499	-38	LUB1		X	X
250124	1.00	0.00	0.00	1.05	0.6	1498	-40	LUB1		X	X
250124	1.00	0.00	0.00	1.02	1.0	999	-35	LUB1		X	
250127	0.00	1.00	0.00	1.00	1.0	999	-15	LUB1		X	
250127	0.00	0.00	0.00	1.00		999		LUB1		X	X
250127	1.00	0.00	0.00	1.00	1.0	999	-35	LUB1		X	X
250127	1.00	0.00	0.00	1.00	1.0	999	-33	LUB1		X	
250127	0.00	1.00	0.00	1.03	0.8	1498	-15	LUB1		X	X
250127	1.00	0.00	0.00	1.04	0.9	1497	-38	LUB1		X	
250127	0.00	1.00	0.00	1.02	0.9	999	-15	LUB1		X	
250127	1.00	0.00	0.00	1.02	1.0	999	-33	LUB1		X	X
250127	0.00	1.00	0.00	1.02	1.0	1499	-15	LUB1		X	
250205	0.00	1.00	0.00	1.01	1.0	999	-15	LUB1		X	
250205	0.00	1.00	0.00	1.03	1.0	1499	-15	LUB1		X	
250205	0.00	1.00	0.00	1.03	1.0	1749	-15	LUB1		X	
250205	0.00	1.00	0.00	1.01	1.0	1748	-15	LUB1		X	
250205	0.00	1.00	0.00	1.04	1.0	1998	-15	LUB1		X	
250205	0.00	1.00	0.00	1.00	1.0	999	-15	LUB1		X	
250205	0.00	1.00	0.00	1.00	1.0	999	-15	LUB1		X	
250205	1.00	0.00	0.00	1.00	1.0	999	-33	LUB1		X	
250205	1.00	0.00	0.00	1.00	1.0	999	-33	LUB1		X	
250205	0.00	1.00	0.00	1.02	1.0	1499	-15	LUB1		X	
250205	0.00	1.00	0.00	1.02	1.0	999	-15	LUB1		X	
250205	1.00	0.00	0.00	1.00	1.0	999	-33	LUB1		X	
250205	1.00	0.00	0.00	1.00	1.0	999	-33	LUB1		X	
250205	0.00	1.00	0.00	1.02	1.0	1498	-15	LUB1		X	
250205	0.00	1.00	0.00	1.00	1.0	1499	-15	LUB1		X	
250205	1.00	0.00	0.00	1.02	1.0	1497	-37	LUB1		X	
250205	0.00	1.00	0.00	1.03	1.0	1747	-15	LUB1		X	
250205	1.00	0.00	0.00	1.03	1.0	999	-33	LUB1		X	
250205	0.00	1.00	0.00	1.03	0.9	1499	-15	LUB1		X	
250205	0.00	1.00	0.00	1.00	1.0	1498	-15	LUB1		X	
250205	1.00	0.00	0.00	1.03	0.9	1498	-37	LUB1		X	
250205	0.00	1.00	0.00	1.04	1.0	1748	-15	LUB1		X	
250205	1.00	0.00	0.00	1.01	1.0	1500	-37	LUB1		X	
250205	1.00	0.00	0.00	1.01	1.0	999	-33	LUB1		X	
250205	1.00	0.00	0.00	1.00	1.0	999	-33	LUB1		X	
250205	0.00	1.00	0.00	1.01	1.0	999	-15	LUB1		X	
250205	0.00	1.00	0.00	1.03	0.8	1499	-15	LUB1		X	
250205	0.00	1.00	0.00	1.00	1.0	1498	-15	LUB1		X	
250205	0.00	1.00	0.00	1.04	1.0	1748	-15	LUB1		X	
250205	0.00	1.00	0.00	1.02	0.6	1998	-15	LUB1		X	
250205	1.00	0.00	0.00	1.00	1.0	1249	-37	LUB1		X	

See next page

APPENDIX C

Date	xNH ₃	xCH ₄	xH ₂	P _{intake} (bar)	ϕ	Speed (rpm)	SI (°CA)	Oil	FTIR	EEPS	MPS
250207	0.00	0.00	0.00	1.00		999		LUB1		X	
250207	1.00	0.00	0.00	1.01	1.0	1499	-38	LUB1		X	
250207	0.00	1.00	0.00	1.01	1.0	1498	-16	LUB1		X	
250207	0.00	1.00	0.00	1.00	1.0	999	-15	LUB1		X	
250207	1.00	0.00	0.00	1.04	0.9	1499	-37	LUB1		X	
250207	1.00	0.00	0.00	1.01	1.0	1499	-37	LUB1		X	
250207	1.00	0.00	0.00	1.03	1.0	999	-33	LUB1		X	
250210	0.00	0.00	0.00	1.00		999		LUB1		X	
250210	0.90	0.00	0.10	0.92	1.0	999	-27	LUB1		X	
250210	0.90	0.00	0.10	0.90	1.0	999	-27	LUB1		X	
250210	0.90	0.00	0.10	0.80	1.0	999	-32	LUB1		X	
250210	0.90	0.00	0.10	0.71	1.0	999	-35	LUB1		X	
250210	0.90	0.00	0.10	0.56	1.0	999	-39	LUB1		X	
250210	0.95	0.00	0.05	0.90	1.0	999	-32	LUB1		X	
250210	0.95	0.00	0.05	0.81	1.0	999	-35	LUB1		X	
250210	0.95	0.00	0.05	0.81	1.0	999	-35	LUB1		X	
250210	0.95	0.00	0.05	0.70	1.0	998	-35	LUB1		X	
250210	0.95	0.00	0.05	0.55	1.0	1000	-40	LUB1		X	
250210	0.95	0.00	0.05	0.81	1.0	998	-35	LUB1		X	
250210	0.95	0.00	0.05	0.84	1.0	999	-33	LUB1		X	
250210	0.95	0.00	0.05	0.88	1.0	999	-32	LUB1		X	
250210	0.95	0.00	0.05	0.90	1.0	999	-32	LUB1		X	
250210	0.95	0.00	0.05	0.92	1.0	999	-27	LUB1		X	
250210	0.95	0.00	0.05	0.85	1.0	999	-31	LUB1		X	
250210	0.95	0.00	0.05	0.82	1.0	999	-32	LUB1		X	
250210	0.95	0.00	0.05	0.71	1.0	999	-35	LUB1		X	
250210	0.95	0.00	0.05	0.56	1.0	999	-39	LUB1		X	
250210	1.00	0.00	0.00	1.03	1.0	999	-33	LUB1		X	
250210	1.00	0.00	0.00	1.00	1.0	999	-33	LUB1		X	
250210	1.00	0.00	0.00	0.91	1.0	999	-38	LUB1		X	
250210	1.00	0.00	0.00	0.81	1.0	999	-40	LUB1		X	
250210	1.00	0.00	0.00	0.71	1.0	999	-41	LUB1		X	
250210	0.90	0.00	0.10	0.71	1.0	1996	-37	LUB1		X	
250210	0.90	0.00	0.10	0.71	1.0	1998	-41	LUB1		X	
250210	0.90	0.00	0.10	0.57	1.0	1999	-41	LUB1		X	
250210	0.90	0.00	0.10	0.55	1.0	1998	-40	LUB1		X	
250211	0.90	0.00	0.10	0.90	1.0	999	-27	LUB1		X	
250211	0.90	0.00	0.10	0.80	1.0	999	-28	LUB1		X	
250211	0.90	0.00	0.10	0.70	1.0	999	-32	LUB1		X	
250211	0.89	0.00	0.11	0.55	1.0	999	-39	LUB1		X	
250211	0.90	0.00	0.10	0.92	1.0	999	-27	LUB1		X	
250211	0.90	0.00	0.10	0.90	1.0	1000	-27	LUB1		X	
250211	0.90	0.00	0.10	0.90	1.0	998	-27	LUB1		X	
250211	0.94	0.00	0.06	0.92	1.0	1000	-32	LUB1		X	
250211	0.95	0.00	0.05	0.82	1.0	999	-35	LUB1		X	
250211	0.95	0.00	0.05	0.55	1.0	1000	-41	LUB1		X	
250211	0.95	0.00	0.05	0.70	1.0	999	-35	LUB1		X	
250211	1.00	0.00	0.00	1.03	1.0	999	-34	LUB1		X	
250211	1.00	0.00	0.00	0.90	1.0	999	-38	LUB1		X	
250211	1.00	0.00	0.00	0.80	1.0	999	-40	LUB1		X	
250211	1.00	0.00	0.00	0.75	1.0	999	-41	LUB1		X	
250211	0.90	0.00	0.10	0.83	1.0	1997	-36	LUB1		X	
250211	0.95	0.00	0.05	0.81	1.0	1996	-41	LUB1		X	
250211	0.95	0.00	0.05	0.55	1.0	2000	-42	LUB1		X	
250212	0.00	1.00	0.00	1.00	1.0	999	-15	LUB1		X	
250212	1.00	0.00	0.00	1.03	1.0	999	-33	LUB1		X	

See next page

APPENDIX C

Date	xNH ₃	xCH ₄	xH ₂	P _{intake} (bar)	ϕ	Speed (rpm)	SI (°CA)	Oil	FTIR	EEPS	MPS
250212	0.00	1.00	0.00	1.02	1.0	1498	-15	LUB1		X	
250212	1.00	0.00	0.00	1.02	1.0	1498	-37	LUB1		X	
250212	0.90	0.00	0.10	0.70	1.0	1998	-38	LUB1		X	
250212	0.90	0.00	0.10	0.58	1.0	1998	-40	LUB1		X	
250212	0.95	0.00	0.05	0.55	1.0	1999	-43	LUB1		X	
250212	0.95	0.00	0.05	0.84	0.9	1999	-40	LUB1		X	
250212	0.98	0.00	0.02	0.84	0.9	1998	-48	LUB1		X	
250212	0.98	0.00	0.02	0.81	0.9	1998	-48	LUB1		X	
250212	1.00	0.00	0.00	0.80	0.9	1998	-49	LUB1		X	
250212	0.95	0.00	0.05	0.65	1.0	999	-37	LUB1		X	
250212	0.95	0.00	0.05	0.55	1.0	998	-39	LUB1		X	
250212	0.00	1.00	0.00	1.03	1.0	1499	-15	LUB1		X	
250212	0.00	1.00	0.00	1.00	1.0	1499	-15	LUB1		X	
250212	1.00	0.00	0.00	1.02	1.0	1498	-37	LUB1		X	X
250213	0.00	1.00	0.00	1.01	1.0	999	-15	LUB		X	
250213	1.00	0.00	0.00	1.03	1.0	999	-33	LUB		X	
250213	0.00	1.00	0.00	1.03	1.0	1499	-15	LUB		X	
250213	0.00	1.00	0.00	1.00	1.0	999	-15	LUB		X	
250213	1.00	0.00	0.00	1.03	1.0	999	-33	LUB		X	
250213	1.00	0.00	0.00	1.01	1.0	999	-33	LUB		X	
250213	1.00	0.00	0.00	0.90	0.9	999	-30	LUB		X	
250225	0.00	0.00	0.00	1.00		999		LUB	X	X	
250225	0.00	1.00	0.00	1.01	1.0	999	-15	LUB	X		
250225	0.00	1.00	0.00	1.00	1.0	999	-15	LUB	X		
250225	1.00	0.00	0.00	1.03	0.9	999	-33	LUB	X		
250225	1.00	0.00	0.00	0.92	1.0	999	-38	LUB	X		
250225	1.00	0.00	0.00	0.80	1.0	999	-40	LUB	X		
250225	0.99	0.00	0.01	0.90	1.0	999	-32	LUB	X		
250225	1.00	0.00	0.00	0.80	1.0	999	-35	LUB	X		
250225	0.99	0.00	0.01	0.70	1.0	1000	-37	LUB	X		
250225	0.00	1.00	0.00	1.00	1.0	999	-15	LUB	X		
250225	1.00	0.00	0.00	0.90	0.8	999	-28	LUB	X		
250225	0.90	0.00	0.10	0.82	0.9	999	-29	LUB	X		
250225	0.90	0.00	0.10	0.90	0.9	999	-28	LUB	X		
250225	0.90	0.00	0.10	0.55	0.9	1000	-38	LUB	X		
250225	0.95	0.00	0.05	0.55	1.0	1001	-40	LUB	X		
250225	1.00	0.00	0.00	1.00	1.0	999	-33	LUB	X		
250225	1.00	0.00	0.00	1.00	1.0	999	-33	LUB	X		
250225	1.00	0.00	0.00	1.00	1.0	999	-33	LUB	X		
250225	1.00	0.00	0.00	1.02	1.0	999	-33	LUB	X		
250225	1.00	0.00	0.00	1.00	1.0	999	-33	LUB	X		
250225	0.00	1.00	1.00	1.02	1.0	1498	-16	LUB	X		
250225	0.00	1.00	1.00	1.00	1.0	1498	-16	LUB	X		
250225	1.00	0.00	0.00	1.02	0.9	1499	-37	LUB	X		
250225	0.89	0.00	0.11	0.85	0.9	1998	-35	LUB	X		
250225	0.90	0.00	0.10	0.70	1.0	1998	-37	LUB	X		
250225	0.90	0.00	0.10	0.57	1.0	1996	-40	LUB	X		
250225	0.90	0.00	0.10	0.70	1.0	1999	-38	LUB	X		
250225	0.95	0.00	0.05	0.82	0.9	1998	-41	LUB	X		
250225	0.95	0.00	0.05	0.73	1.0	1999	-43	LUB	X		
250225	0.95	0.00	0.05	0.70	1.0	1999	-44	LUB	X		
250225	0.89	0.00	0.11	0.83	0.9	1997	-35	LUB	X		
250225	0.95	0.00	0.05	0.72	1.0	999	-37	LUB	X		
250225	0.95	0.00	0.05	0.55	1.0	999	-40	LUB	X		
250226	0.00	1.00	0.00	1.01	1.0	999	-15	LUB	X	X	
250226	0.00	1.00	0.00	1.00	1.0	999	-15	LUB	X	X	

See next page

APPENDIX C

Date	xNH ₃	xCH ₄	xH ₂	P _{intake} (bar)	ϕ	Speed (rpm)	SI (°CA)	Oil	FTIR	EEPS	MPS
250226	0.00	1.00	0.00	1.00	1.0	999	-15	LUB	X	X	
250226	0.00	1.00	0.00	1.00	1.0	999	-15	LUB	X	X	
250226	1.00	0.00	0.00	1.00	1.0	999	-33	LUB	X	X	
250226	1.00	0.00	0.00	0.80	1.0	999	-40	LUB	X	X	
250226	0.95	0.00	0.05	0.91	1.0	999	-32	LUB	X	X	
250226	0.95	0.00	0.05	0.82	1.0	999	-35	LUB	X	X	
250226	0.95	0.00	0.05	0.70	1.0	999	-37	LUB	X	X	
250226	0.95	0.00	0.05	0.55	1.0	999	-40	LUB	X	X	
250226	0.95	0.00	0.05	0.90	1.0	999	-32	LUB	X	X	
250226	0.90	0.00	0.10	0.93	1.0	999	-27	LUB	X	X	
250226	0.90	0.00	0.10	0.83	1.0	999	-29	LUB	X	X	
250226	0.90	0.00	0.10	0.70	1.0	999	-31	LUB	X	X	
250226	0.89	0.00	0.11	0.57	1.0	999	-39	LUB	X	X	
250226	0.90	0.00	0.10	0.70	1.0	999	-31	LUB	X	X	
250226	0.90	0.00	0.10	0.80	1.0	999	-29	LUB	X	X	
250226	1.00	0.00	0.00	0.90	1.0	999	-37	LUB	X	X	
250226	1.00	0.00	0.00	0.90	1.0	999	-37	LUB	X	X	
250226	1.00	0.00	0.00	0.90	1.0	999	-37	LUB	X	X	
250226	0.95	0.00	0.05	0.90	1.0	999	-32	LUB	X	X	
250226	0.94	0.00	0.06	0.84	1.0	999	-35	LUB	X	X	
250226	0.95	0.00	0.05	0.74	1.0	999	-37	LUB	X	X	
250226	0.90	0.00	0.10	0.92	0.8	998	-27	LUB	X	X	
250226	0.90	0.00	0.10	0.82	1.0	999	-29	LUB	X	X	
250226	0.90	0.00	0.10	0.74	1.0	999	-31	LUB	X	X	
250226	0.90	0.00	0.10	0.55	1.0	999	-38	LUB	X	X	
250226	0.89	0.00	0.11	0.85	0.8	1998	-35	LUB	X	X	
250226	0.90	0.00	0.10	0.70	1.0	1998	-39	LUB	X	X	
250226	0.90	0.00	0.10	0.55	1.0	1997	-41	LUB	X	X	
250226	0.95	0.00	0.05	0.77	1.0	1998	-44	LUB	X	X	
250226	0.00	1.00	0.00	1.00	1.0	999	-15	LUB	X	X	
250226	1.00	0.00	0.00	1.05	0.8	1498	-37	LUB	X	X	
250226	1.00	0.00	0.00	1.00	0.9	1498	-37	LUB		X	
250226	1.00	0.00	0.00	1.00	1.0	1499	-37	LUB	X	X	
250226	1.00	0.00	0.00	0.80	0.9	1995	-49	LUB	X	X	
250228	0.00	0.00	0.00	1.00		999		Oil B2	X	X	
250228	0.00	1.00	0.00	1.01	1.0	999	-15	Oil B2	X	X	
250228	0.00	1.00	0.00	1.00	1.0	999	-15	Oil B2	X	X	
250228	0.00	1.00	0.00	1.01	1.0	999	-15	Oil B2	X	X	
250228	1.00	0.00	0.00	1.00	1.0	999	-33	Oil B2	X	X	
250228	1.00	0.00	0.00	0.90	1.0	999	-37	Oil B2	X	X	
250228	1.00	0.00	0.00	0.82	1.0	999	-40	Oil B2	X	X	
250228	0.00	1.00	0.00	1.03	1.0	1498	-16	Oil B2		X	
250228	0.00	1.00	0.00	1.00	1.0	1498	-16	Oil B2	X	X	
250228	0.00	1.00	0.00	1.04	0.9	1998	-16	Oil B2	X	X	
250228	1.00	0.00	0.00	1.02	0.9	1498	-37	Oil B2	X	X	
250228	0.94	0.00	0.06	0.81	0.9	1999	-41	Oil B2	X	X	
250228	1.00	0.00	0.00	1.00	1.0	1000	-33	Oil B2	X	X	
250228	1.00	0.00	0.00	1.00	1.0	999	-33	Oil B2		X	
250228	1.00	0.00	0.00	1.00	1.0	999	-33	Oil B2	X	X	
250228	1.00	0.00	0.00	1.00	1.0	999	-33	Oil B2	X	X	
250228	1.00	0.00	0.00	1.00	1.0	999	-33	Oil B2	X	X	
250228	1.00	0.00	0.00	1.00	1.0	999	-33	Oil B2	X	X	
250228	1.00	0.00	0.00	1.00	1.0	999	-33	Oil B2	X	X	
250228	1.00	0.00	0.00	1.03	0.8	1499	-37	Oil B2	X	X	
250228	1.00	0.00	0.00	1.00	0.9	1498	-37	Oil B2	X	X	
250228	1.00	0.00	0.00	1.00	1.0	999	-33	Oil B2		X	
250228	1.00	0.00	0.00	1.00	1.0	999	-33	Oil B2	X	X	

See next page

APPENDIX C

Date	xNH ₃	xCH ₄	xH ₂	P _{intake} (bar)	ϕ	Speed (rpm)	SI (°CA)	Oil	FTIR	EEPS	MPS
250228	1.00	0.00	0.00	0.90	1.0	999	-35	Oil B2	X	X	
250228	1.00	0.00	0.00	0.82	1.0	998	-36	Oil B2	X	X	
250228	1.00	0.00	0.00	1.00	1.0	998	-33	Oil B2	X	X	
250228	0.90	0.00	0.10	0.81	0.9	1999	-35	Oil B2	X	X	
250228	0.89	0.00	0.11	0.83	0.9	1998	-40	Oil B2		X	
250228	1.00	0.00	0.00	0.80	0.9	1998	-38	Oil B2	X	X	
250228	0.94	0.00	0.06	0.82	0.9	1999	-40	Oil B2	X	X	
250228	0.94	0.00	0.06	0.82	0.9	1998	-15	Oil B2	X	X	
250228	0.00	1.00	0.00	1.00	1.0	999	-33	Oil B2	X	X	
250228	1.00	0.00	0.00	1.00	1.0	999	-27	Oil B2	X	X	
250306	0.90	0.00	0.10	0.90	1.0	999	-27	Oil B2	X	X	
250306	0.90	0.00	0.10	0.90	1.0	999	-33	Oil B2	X	X	
250306	1.00	0.00	0.00	1.00	0.9	999	-33	Oil B2	X	X	
250306	1.00	0.00	0.00	1.03	0.9	999	-37	Oil B2	X	X	
250306	1.00	0.00	0.00	0.92	0.9	999	-39	Oil B2	X	X	
250306	1.00	0.00	0.00	0.80	0.9	999	-39	Oil B2	X	X	
250306	1.00	0.00	0.00	0.92	0.9	999	-40	Oil B2	X	X	
250306	1.00	0.00	0.00	0.80	0.9	999	-34	Oil B2	X	X	
250306	1.00	0.00	0.00	1.00	0.9	999	-37	Oil B2	X	X	
250306	1.00	0.00	0.00	0.92	0.9	999	-39	Oil B2	X	X	
250306	1.00	0.00	0.00	1.02	0.8	1499	-39	Oil B2	X	X	
250306	1.00	0.00	0.00	1.00	0.9	1499	-39	Oil B2	X	X	
250306	1.00	0.00	0.00	1.00	0.8	1497	-39	Oil B2	X	X	
250306	1.00	0.00	0.00	1.00	0.8	1497	-42	Oil B2	X	X	
250306	0.94	0.00	0.06	0.85	0.7	1997	-42	Oil B2	X	X	
250306	0.92	0.00	0.08	0.85	0.5	1998	-49	Oil B2	X	X	
250306	1.00	0.00	0.00	0.80	0.8	1998	-42	Oil B2	X	X	
250306	0.95	0.00	0.05	0.80	0.8	1998	-29	Oil B2	X	X	
250306	0.90	0.00	0.10	0.90	1.0	999	-34	Oil B2	X	X	
250306	1.00	0.00	0.00	1.00	1.0	999	-15	Oil B2	X	X	
250307	0.00	1.00	0.00	1.00	1.0	999	-15	Oil B2	X	X	
250307	0.00	0.00	0.00	1.00		1000		Oil B2	X	X	
250307	0.00	1.00	0.00	1.02	1.2	999	-15	Oil B2	X	X	
250307	0.00	1.00	0.00	1.00	1.0	999	-15	Oil B2	X	X	
250307	0.00	1.00	0.00	1.01	1.0	1499	-16	Oil B2	X	X	X
250307	0.00	1.00	0.00	0.99	0.9	1998	-15	Oil B2	X	X	
250310	0.00	0.00	0.00	1.00		0		Oil B2	X	X	
250310	0.00	1.00	0.00	1.01	1.0	999	-15	Oil B2	X	X	
250310	0.00	1.00	0.00	1.01	1.0	999	-33	Oil B2	X	X	
250310	1.00	0.00	0.00	1.01	1.0	999	-33	Oil B2	X	X	
250310	1.00	0.00	0.00	1.00	1.0	997	-16	Oil B2	X	X	
250310	0.00	1.00	0.00	1.00	1.0	999	-16	Oil B2	X	X	
250310	0.00	1.00	0.00	1.03	0.9	1499	-34	Oil B2	X	X	
250310	1.00	0.00	0.00	1.00	1.0	999	-16	Oil B2	X	X	
250310	0.00	1.00	0.00	1.00	0.9	1998	-16	Oil B2		X	
250310	0.00	1.00	0.00	1.01	1.0	1998	-16	Oil B2	X	X	
250310	0.00	1.00	0.00	1.01	1.0	1998	-16	Oil B2	X	X	
250310	0.00	1.00	0.00	1.01	1.0	1499	-33	Oil B2		X	
250312	1.00	0.00	0.00	1.02	1.0	999	-33	Oil B2	X	X	
250312	1.00	0.00	0.00	1.00	1.0	998	-16	Oil B2	X	X	
250312	0.00	1.00	0.00	1.03	1.0	1499	-16	Oil B2	X	X	
250312	0.00	1.00	0.00	1.02	1.0	1498	-16	Oil B2	X	X	X
250312	0.00	1.00	0.00	1.00	1.0	1498	-16	Oil B2	X	X	X
250312	0.00	1.00	0.00	1.02	0.8	1998	-41	Oil B2	X	X	
250312	1.00	0.00	0.00	0.85	0.8	1999	-41	Oil B2	X	X	
250312	0.95	0.00	0.05	0.81	1.0	1998	-15	Oil B2	X	X	

See next page

APPENDIX C

Date	xNH ₃	xCH ₄	xH ₂	P _{intake} (bar)	ϕ	Speed (rpm)	SI (°CA)	Oil	FTIR	EEPS	MPS
250312	0.00	1.00	0.00	1.01	1.0	999	-16	Oil B2	X	X	
250312	0.00	1.00	0.00	1.02	1.0	1498	-16	Oil B2	X	X	
250312	0.00	1.00	0.00	1.01	1.0	999	-49	Oil B2	X	X	
250312	1.00	0.00	0.00	0.80	1.0	2000	-39	Oil B2	X	X	
250312	1.00	0.00	0.00	1.00	1.0	1498	-39	Oil B2	X	X	X
250312	1.00	0.00	0.00	1.02	1.0	1498	-39	Oil B2	X	X	X
250313	0.00	0.00	0.00	1.00		999		Oil B2 pa	X	X	
250313	0.00	1.00	0.00	1.00	1.0	999	-15	Oil B2 pa	X	X	
250313	0.00	1.00	0.00	1.01	1.0	999	-15	Oil B2 pa	X	X	
250313	0.00	1.00	0.00	1.01	1.0	999	-33	Oil B2 pa	X	X	
250313	1.00	0.00	0.00	1.00	1.0	1000	-16	Oil B2 pa	X	X	
250313	0.00	1.00	0.00	1.01	1.0	1499	-39	Oil B2 pa	X	X	
250313	1.00	0.00	0.00	1.01	1.0	1499	-39	Oil B2 pa	X	X	X
250313	1.00	0.00	0.00	1.00	1.0	1500	-16	Oil B2 pa	X	X	X
250313	0.00	1.00	0.00	1.00	1.0	1498	-15	Oil B2 pa	X	X	X
250313	0.00	1.00	0.00	1.00	1.0	999	-15	Oil B2 pa	X	X	
250313	0.00	0.00	0.00	1.00		994		Oil B2 pa	X	X	
250313	0.00	1.00	0.00	1.00	1.0	999	-15	Oil B2 pa	X	X	
250313	0.00	1.00	0.00	1.00	1.0	999	-33	Oil B2 pa	X	X	
250313	1.00	0.00	0.00	1.01	1.0	999	-39	Oil B2 pa	X	X	
250313	1.00	0.00	0.00	1.04	1.0	1498	-39	Oil B2 pa	X	X	
250313	1.00	0.00	0.00	1.00	1.0	1498	-39	Oil B2 pa	X	X	
250313	1.00	0.00	0.00	1.03	1.0	1499	-39	Oil B2 pa	X	X	
250313	0.00	1.00	0.00	1.02	1.0	1998	-39	Oil B2 pa	X	X	
250313	1.00	0.00	0.00	1.00	1.0	1498	-15	Oil B2 pa	X	X	
250313	0.00	1.00	0.00	1.01	1.0	999	-39	Oil B2 pa	X	X	
250313	1.00	0.00	0.00	1.01	1.0	1499	-33	Oil B2 pa		X	X
250313	1.00	0.00	0.00	1.00	1.0	999	-15	Oil B2 pa	X	X	
250313	0.00	1.00	0.00	1.00	1.0	999	-15	Oil B2 pa	X	X	X
250313	0.00	1.00	0.00	1.00	1.0	999	-33	Oil B2 pa		X	X
250313	1.00	0.00	0.00	1.00	1.0	999	-16	Oil B2 pa	X	X	
250313	0.00	1.00	0.00	1.00	1.0	999	-33	Oil B2 pa	X	X	
250313	1.00	0.00	0.00	1.02	1.0	1000	-15	Oil B2 pa	X	X	
250318	0.00	0.00	0.00	1.00		999		Oil B2 pa	X	X	
250318	0.00	1.00	0.00	1.01	1.0	999	-15	Oil B2 pa	X	X	
250318	0.00	1.00	0.00	1.01	1.0	999	-15	Oil B2 pa	X	X	
250318	0.00	1.00	0.00	1.01	0.9	999	-15	Oil B2 pa	X	X	
250318	1.00	0.00	0.00	1.03	1.0	999	-15	Oil B2 pa	X	X	
250318	0.00	1.00	0.00	1.00	1.0	999	-33	Oil B2 pa	X	X	
250318	1.00	0.00	0.00	1.00	1.0	1000	-15	Oil B2 pa	X	X	
250318	0.00	1.00	0.00	1.01	1.2	999	-33	Oil B2 pa	X	X	
250318	1.00	0.00	0.00	1.01	1.0	998	-33	Oil B2 pa		X	
250318	1.00	0.00	0.00	1.00	1.0	999	-35	Oil B2 pa	X	X	
250318	1.00	0.00	0.00	0.90	1.0	999	-39	Oil B2 pa	X	X	
250318	1.00	0.00	0.00	0.80	1.0	999	-15	Oil B2 pa	X	X	
250318	0.00	1.00	0.00	0.90	1.0	999	-39	Oil B2 pa	X	X	
250318	1.00	0.00	0.00	0.83	1.0	1000	-16	Oil B2 pa	X	X	
250318	0.00	1.00	0.00	1.02	1.0	1499	-16	Oil B2 pa	X	X	
250318	1.00	0.00	0.00	1.03	1.0	1498	-39	Oil B2 pa	X	X	
250318	1.00	0.00	0.00	1.00	1.0	1499	-15	Oil B2 pa	X	X	
250318	0.00	1.00	0.00	1.00	1.0	999	-16	Oil B2 pa	X	X	
250318	0.00	1.00	0.00	1.01	1.0	1499	-16	Oil B2 pa	X	X	
250318	1.00	0.00	0.00	1.00	1.0	1499	-38	Oil B2 pa	X	X	
250318	1.00	0.00	0.00	1.00	1.0	1498	-33	Oil B2 pa	X	X	
250318	1.00	0.00	0.00	1.00	1.0	998	-39	Oil B2 pa	X	X	
250318	1.00	0.00	0.00	1.00	1.0	1499	-16	Oil B2 pa	X	X	

See next page

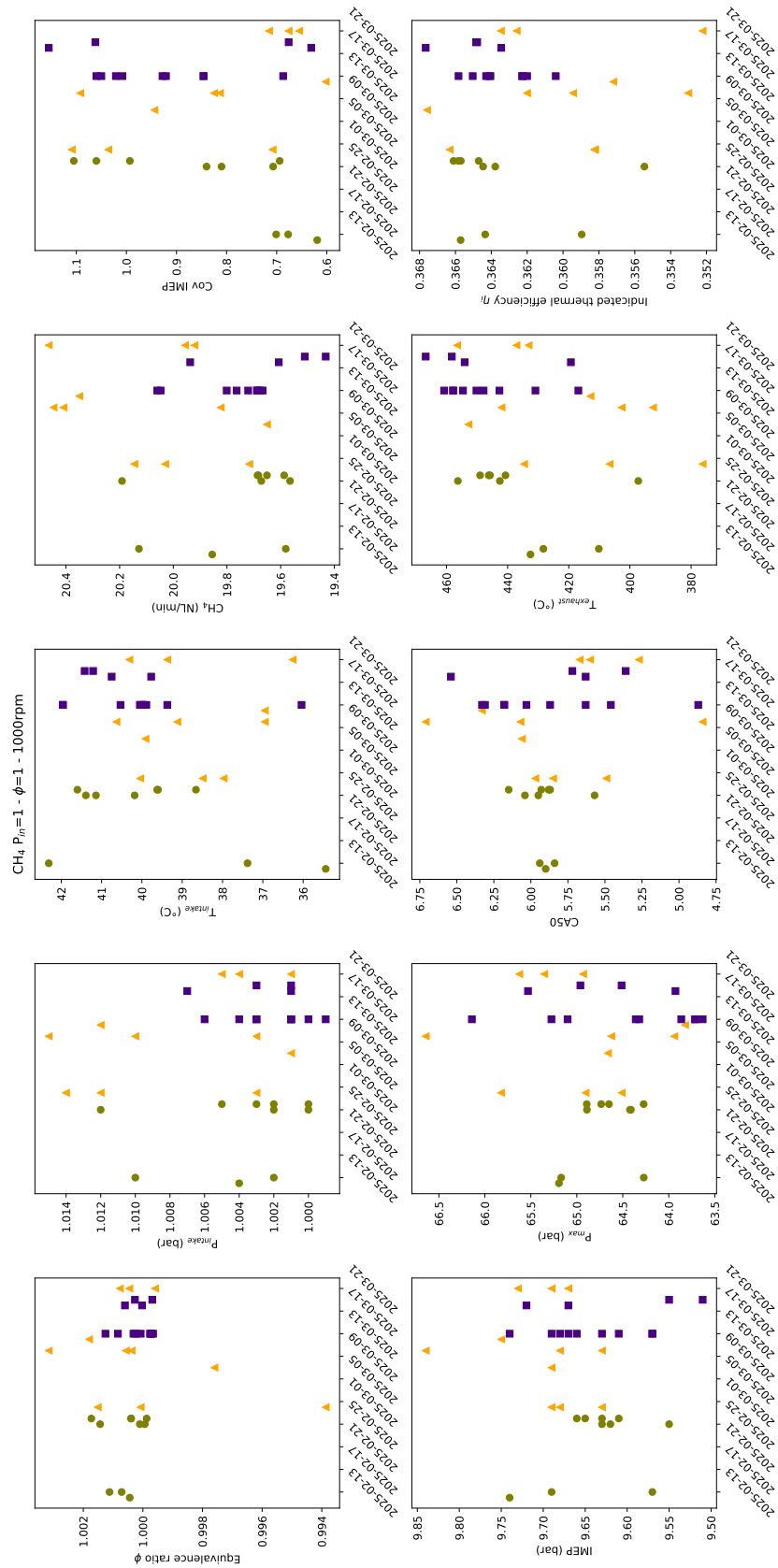
APPENDIX C

Date	xNH ₃	xCH ₄	xH ₂	P_{intake} (bar)	ϕ	Speed (rpm)	SI (°CA)	Oil	FTIR	EEPS	MPS
250318	0.00	1.00	0.00	1.03	1.0	1998	-34	Oil B2 pa	X	X	
250318	0.90	0.00	0.10	0.81	1.0	1997	-42	Oil B2 pa	X	X	
250318	0.95	0.00	0.05	0.80	1.0	1998	-49	Oil B2 pa	X	X	
250318	1.00	0.00	0.00	0.80	1.0	1999	-16	Oil B2 pa	X	X	
250318	0.00	1.00	0.00	0.85	1.0	1998	-34	Oil B2 pa	X	X	
250318	0.90	0.00	0.10	0.88	1.0	1998	-41	Oil B2 pa	X	X	
250318	0.93	0.00	0.07	0.82	1.0	1998	-49	Oil B2 pa	X	X	
250318	1.00	0.00	0.00	0.82	1.0	2000	-16	Oil B2 pa	X	X	
250318	0.00	1.00	0.00	1.05	1.0	1998	-39	Oil B2 pa	X	X	
250318	1.00	0.00	0.00	1.04	1.0	1500	-39	Oil B2 pa	X	X	
250318	0.90	0.00	0.10	1.00	1.0	999	-29	Oil B2 pa	X	X	
250318	0.95	0.00	0.05	1.00	1.0	999	-33	Oil B2 pa	X	X	
250318	1.00	0.00	0.00	1.00	1.0	999	-33	Oil B2 pa	X	X	
250318	1.00	0.00	0.00	1.02	1.0	999	-29	Oil B2 pa	X	X	
250318	0.96	0.00	0.04	1.00	1.0	999	-25	Oil B2 pa	X	X	
250318	0.90	0.00	0.10	1.03	1.0	999	-25	Oil B2 pa	X	X	
250318	0.90	0.00	0.10	1.02	1.0	999	-25	Oil B2 pa	X	X	
250318	0.90	0.00	0.10	0.80	1.0	999	-29	Oil B2 pa	X	X	
250318	0.95	0.00	0.05	0.80	1.0	998	-35	Oil B2 pa	X	X	
250318	1.00	0.00	0.00	0.80	1.0	998	-30	Oil B2 pa	X	X	
250318	0.95	0.00	0.05	0.80	1.0	998	-30	Oil B2 pa	X	X	
250318	0.90	0.00	0.10	0.80	1.0	999	-15	Oil B2 pa	X	X	
250318	0.00	1.00	0.00	0.81	1.0	999	-15	Oil B2 pa	X	X	
250318	0.00	1.00	0.00	0.79	0.4	711	-35	Oil B2 pa	X	X	
250318	1.00	0.00	0.00	0.91	1.0	999	-15	Oil B2 pa	X	X	
250319	0.00	1.00	0.00	0.80	1.0	999	-15	Oil B2 pa	X	X	
250319	0.00	1.00	0.00	0.91	1.0	1000	-15	Oil B2 pa	X	X	
250319	0.00	1.00	0.00	1.01	0.9	999	-16	Oil B2 pa	X	X	
250319	0.00	1.00	0.00	1.01	1.0	1499	-16	Oil B2 pa	X	X	
250319	0.00	1.00	0.00	1.00	1.0	1499	-39	Oil B2 pa	X	X	
250319	1.00	0.00	0.00	1.00	1.0	1498	-39	Oil B2 pa	X	X	
250319	1.00	0.00	0.00	1.00	1.0	1499	-33	Oil B2 pa	X	X	
250319	1.00	0.00	0.00	1.00	1.0	998	-15	Oil B2 pa	X	X	
250319	0.00	1.00	0.00	1.00	1.0	999	-15	Oil B2 pa	X	X	
250319	0.00	1.00	0.00	1.00	1.0	999	-15	Oil B2 pa		X	
250321	0.00	1.00	0.00	1.00	1.0	999	-16	Oil B2	X		
250321	0.00	1.00	0.00	0.98	0.7	1499	-16	Oil B2	X	X	
250321	0.00	1.00	0.00	1.02	1.0	1499	-16	Oil B2	X	X	
250321	0.00	1.00	0.00	0.98	1.0	1998	-34	Oil B2	X	X	
250321	0.90	0.00	0.10	0.83	1.0	1998	-41	Oil B2	X	X	
250321	0.95	0.00	0.05	0.80	1.0	1998	-39	Oil B2	X	X	
250321	1.00	0.00	0.00	1.04	1.0	1498	-15	Oil B2		X	
250321	0.00	1.00	0.00	1.00	1.0	999	-16	Oil B2	X		
250321	0.00	1.00	0.00	0.97	0.9	1499	-15	Oil B2		X	
250321	0.00	1.00	0.00	1.00	1.0	999	-15	Oil B2			
250321	0.00	1.00	0.00	1.00	1.0	999	-15	Oil B2			
250321	0.00	1.00	0.00	1.00	1.0	999	-33	Oil B2			
250321	1.00	0.00	0.00	1.00	1.0	998	-15	Oil B2			
250321	0.00	1.00	0.00	1.02	1.0	999	-33	Oil B2			
250321	1.00	0.00	0.00	1.01	1.0	999	-33	Oil B2			
250321	1.00	0.00	0.00	1.00	1.0	999	-16	Oil B2			

Table C.3: Summary of the oil samples and characterizations conducted

Oil	Sample	Total time (h)	Vol. (mL)	IR	Kin. visco. (mm ² /s)	O (%)	N (mg/kg)	S (%)	H ₂ O (mg/kg)	GC/NCD	GC2D/MS	ICP
LUB	Fresh	0	50	X	68.13	0.577	763	0.214	1480-960	X		X
	t0	unknown	25	X	65.11	0.645	808			X		X
	tf	t0+2.29	1500	X	62.87	0.591	1010	0.203	840	X		X
Oil B2	Fresh	0	50	X	47.3	<0.04	<0.6	<0.001	70			X
	Fresh < 520°C	0				< 0.02	<0.6				X	
	t0	0	50	X	51.06	0.020	60.5					X
	t1	0.47	4	X	49.79	0.057	122					
	t3	2.01	4	X	49.21	0.069	145			X		
	t4	2.91	5	X	49.33	0.049	113			X		
	t5	3.99	4	X	49.41	<0.049	105			X		
	tf	3.99	1500	X	49.50	0.051	101		340	X		X
	tf < 520°C	3.99		X		< 0.02	40				X	
	tf > 520°C	3.99		X		0.1024	204					
Pre-aged Oil B2	Fresh	0.00	15	X	55.07	1.299	99.2		1170	X		X
	Fresh < 520°C	0.00				1.078	68				X	
	t0	0.00	15	X	53.07	1.295	109					X
	t1	1.75	5	X	59.59	1.122	1530			X		
	t2	2.93	5	X	59.76	1.078	1570			X		
	t3	3.98	5	X	60.44	1.079	1710			X		
	tf	4.59	1500	X	60.71	1.079	1670		850	X		X
	tf < 520°C	4.59		X		0.639	520				X	
	tf > 520°C	4.59		X		0.962	1950					

Appendix D—Chapter 5

Figure D.1: Summary- CH_4 , $\phi=1$, $P_{in}=1$ bar, 1000 rpm

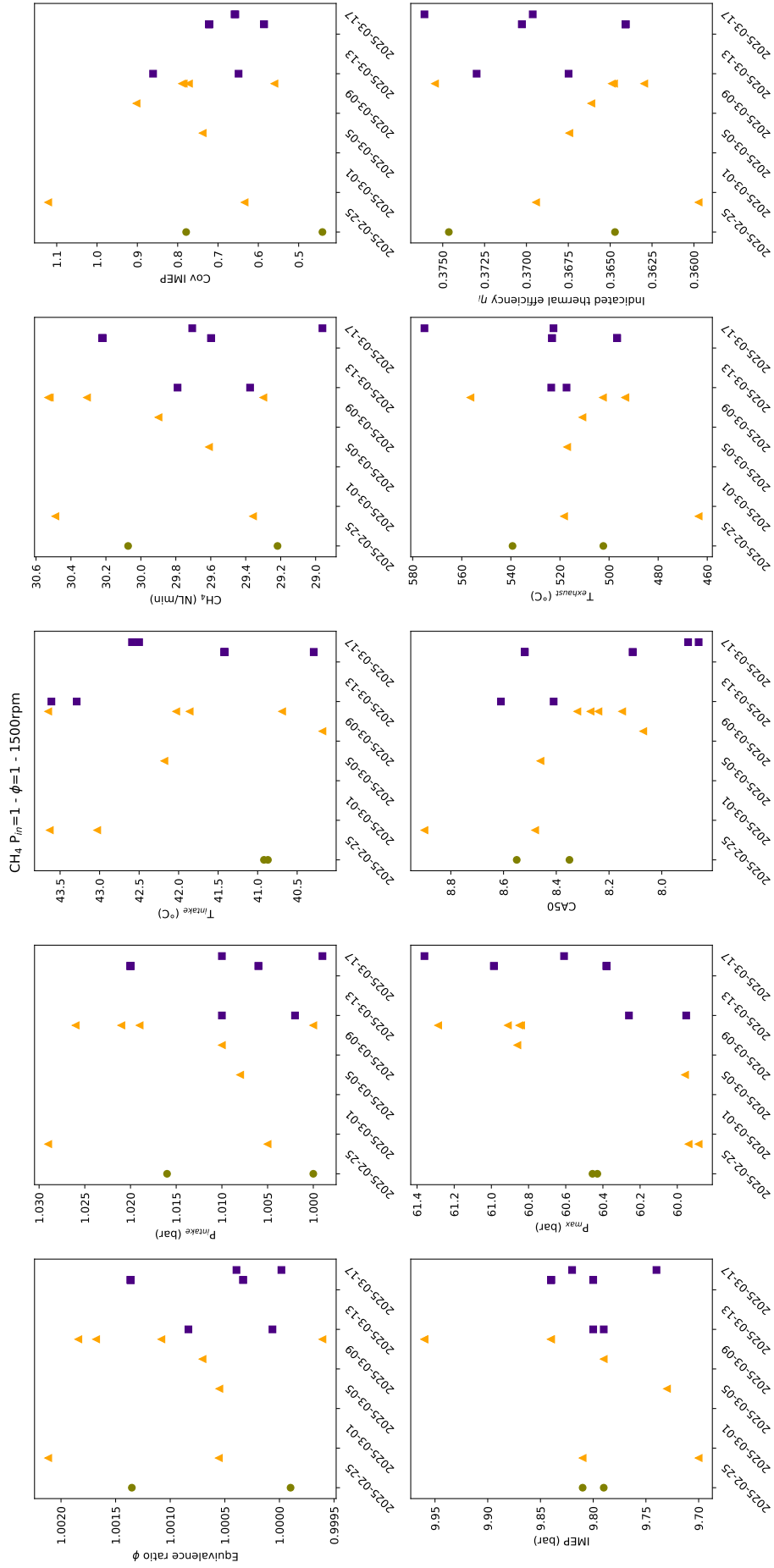


Figure D.2: Summary-CH₄, $\phi=1$, $P_{in}=1$ bar, 1500 rpm

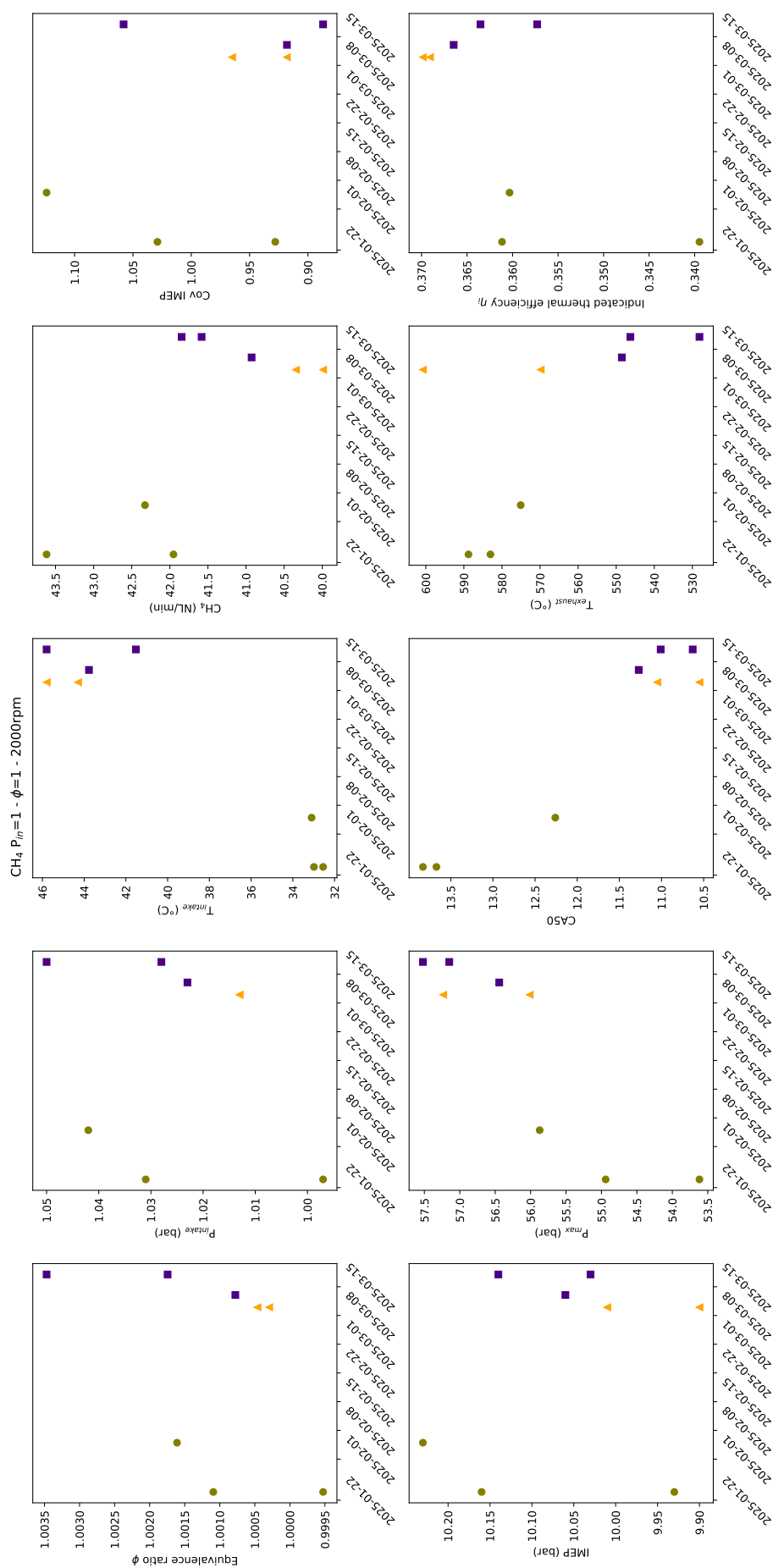
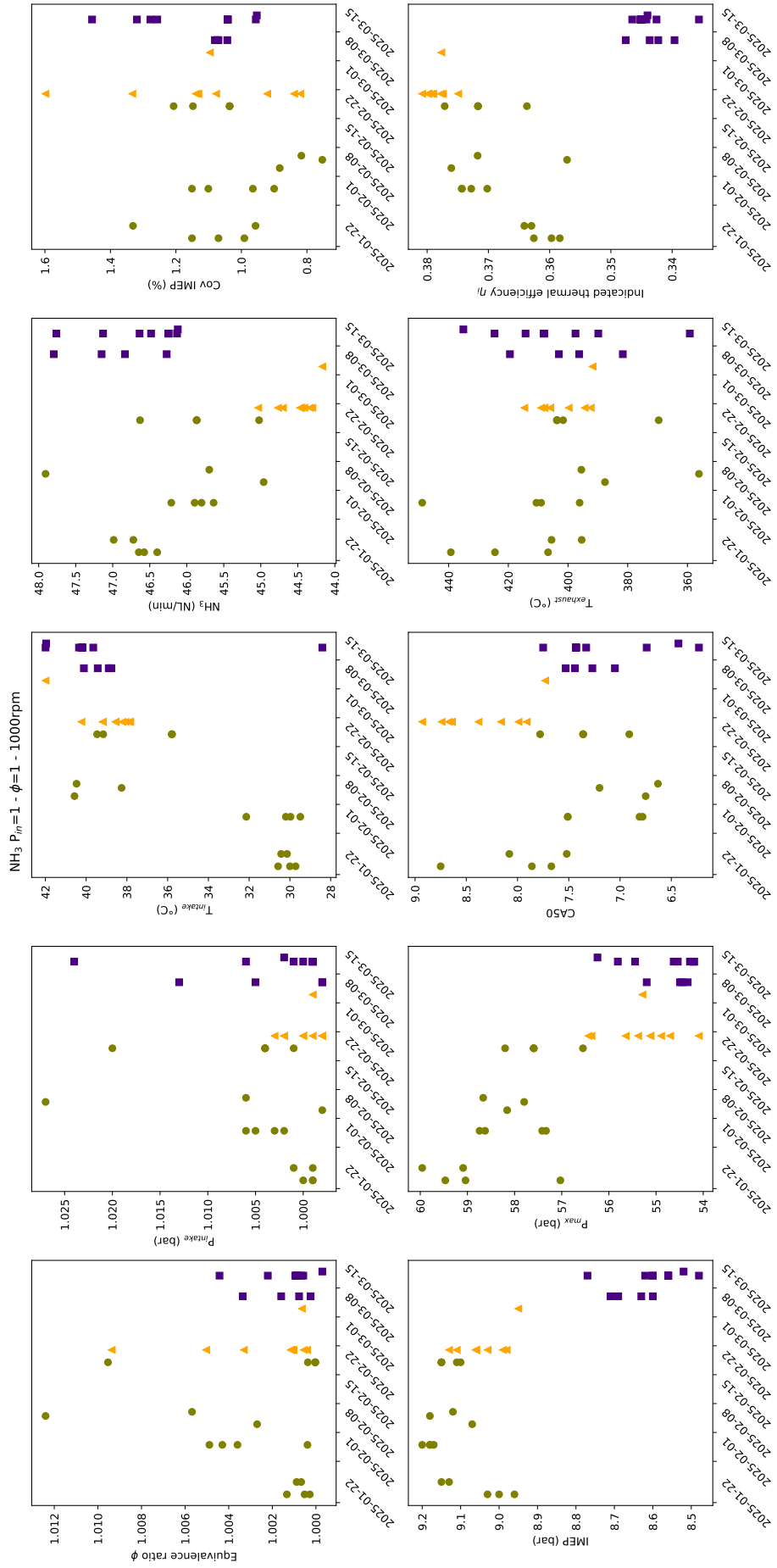
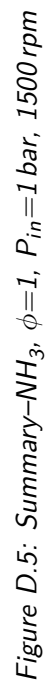


Figure D.3: Summary-CH₄, $\phi=1$, P_{in}=1 bar, 2000 rpm

Figure D.4: Summary- NH_3 , $\phi=1$, $P_{in}=1$ bar, 1000 rpm



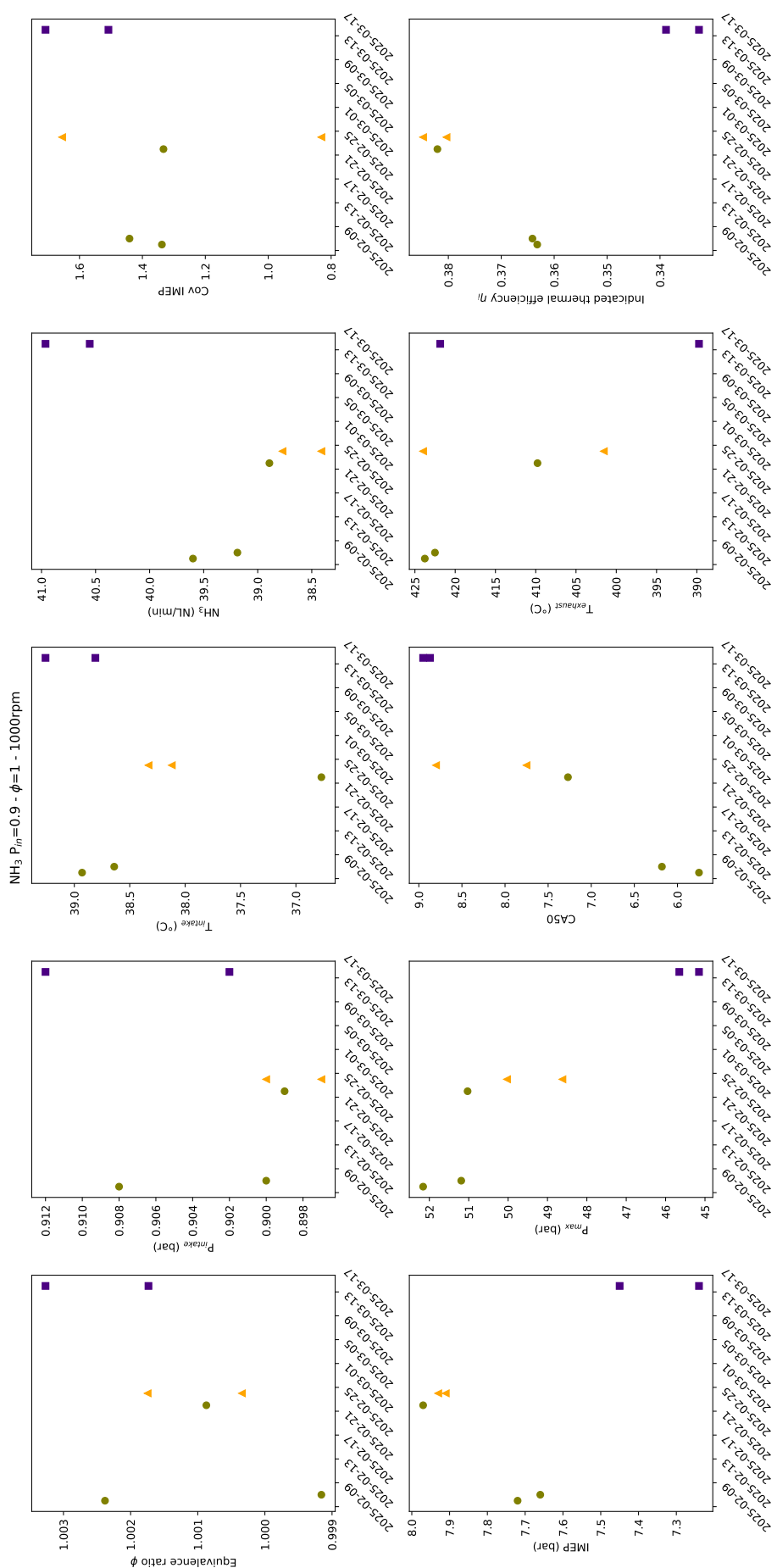
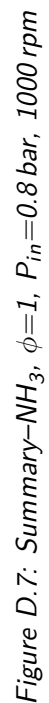


Figure D.6: Summary- NH_3 , $\phi=1$, $P_{\text{in}}=0.9$ bar, 1000 rpm



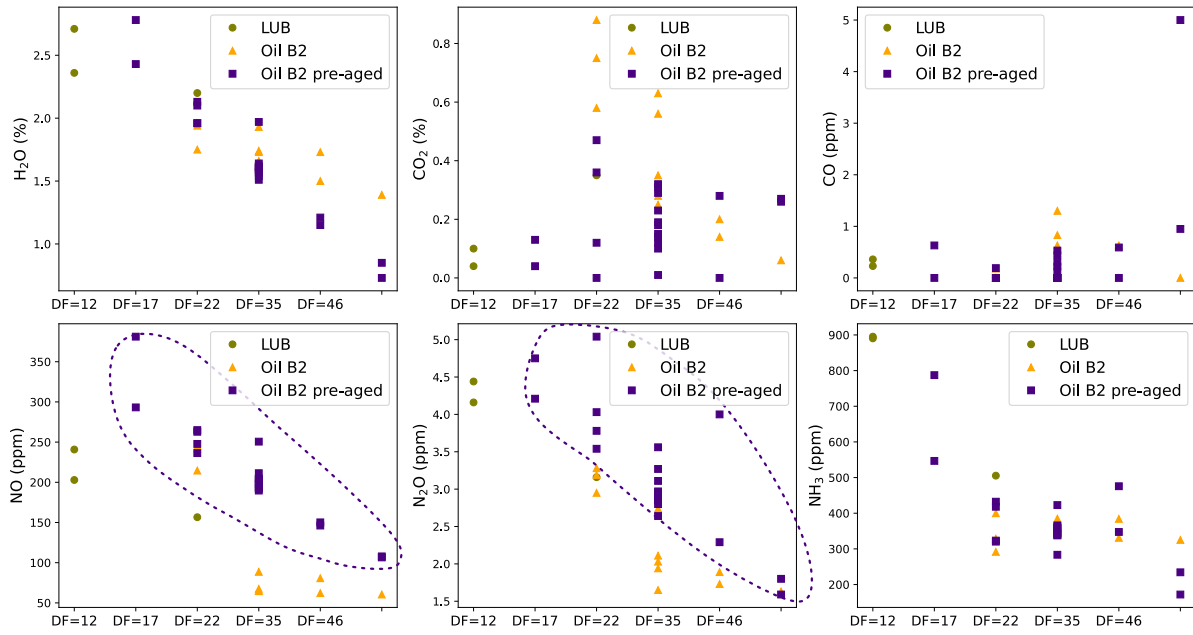


Figure D.8: Concentrations of H_2O , CH_4 , CO_2 , CO , NO , N_2O and NH_3 in the exhaust gases (NH_3 , $\phi=1$, $P_{in}=1$ bar, 1500 rpm). Raw diluted measurements are presented without dilution correction

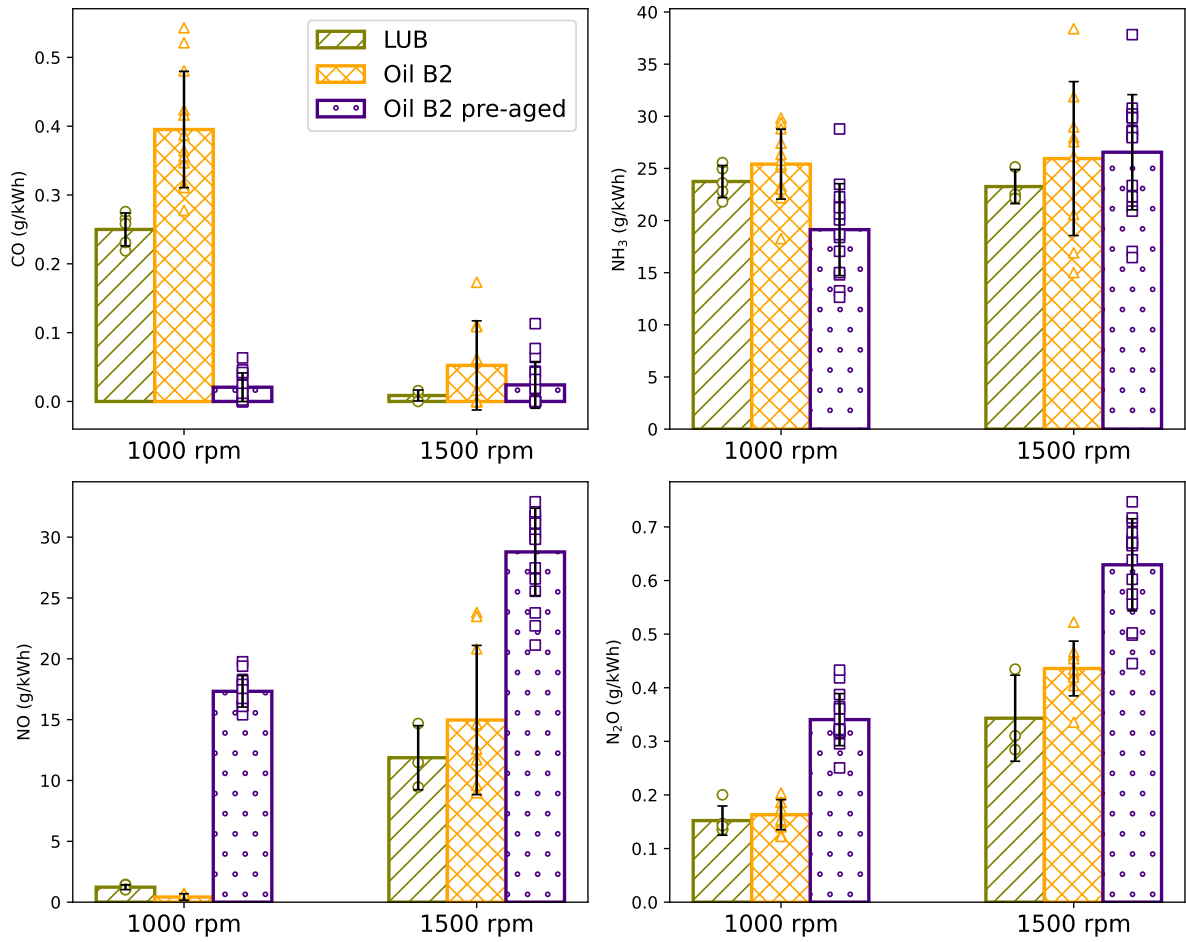


Figure D.9: Normalized emissions of CO, NH₃, NO, and N₂O in the exhaust gases (NH₃, $\phi=1$, $P_{in}=1$ bar, 1000 and 1500 rpm), values are corrected considering dilution factors

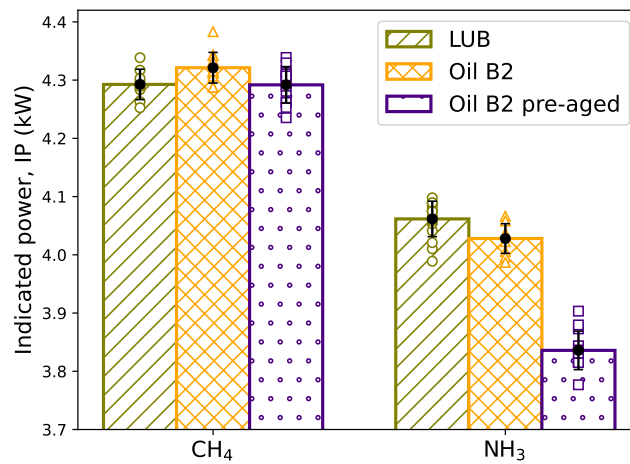


Figure D.10: Indicated power for CH₄ and NH₃, $\phi=1$, $P_{in}=1$ bar, 1000 rpm, with three engine oils

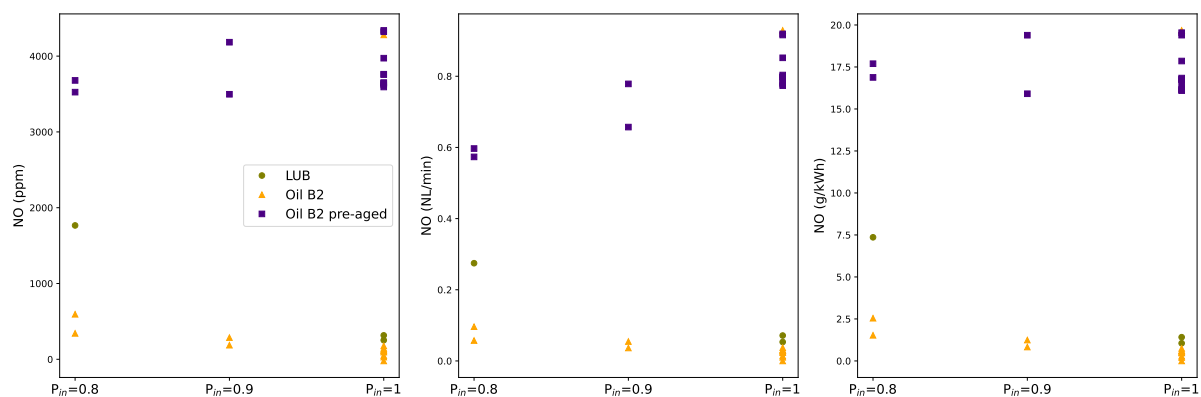


Figure D.11: Concentration, corresponding exhaust flow rate and normalized emission of NO in the exhaust gases (NH_3 , $\phi=1$, $P_{in}=0.8, 0.9$ and 1 bar, 1000 rpm), values are corrected considering dilution factors

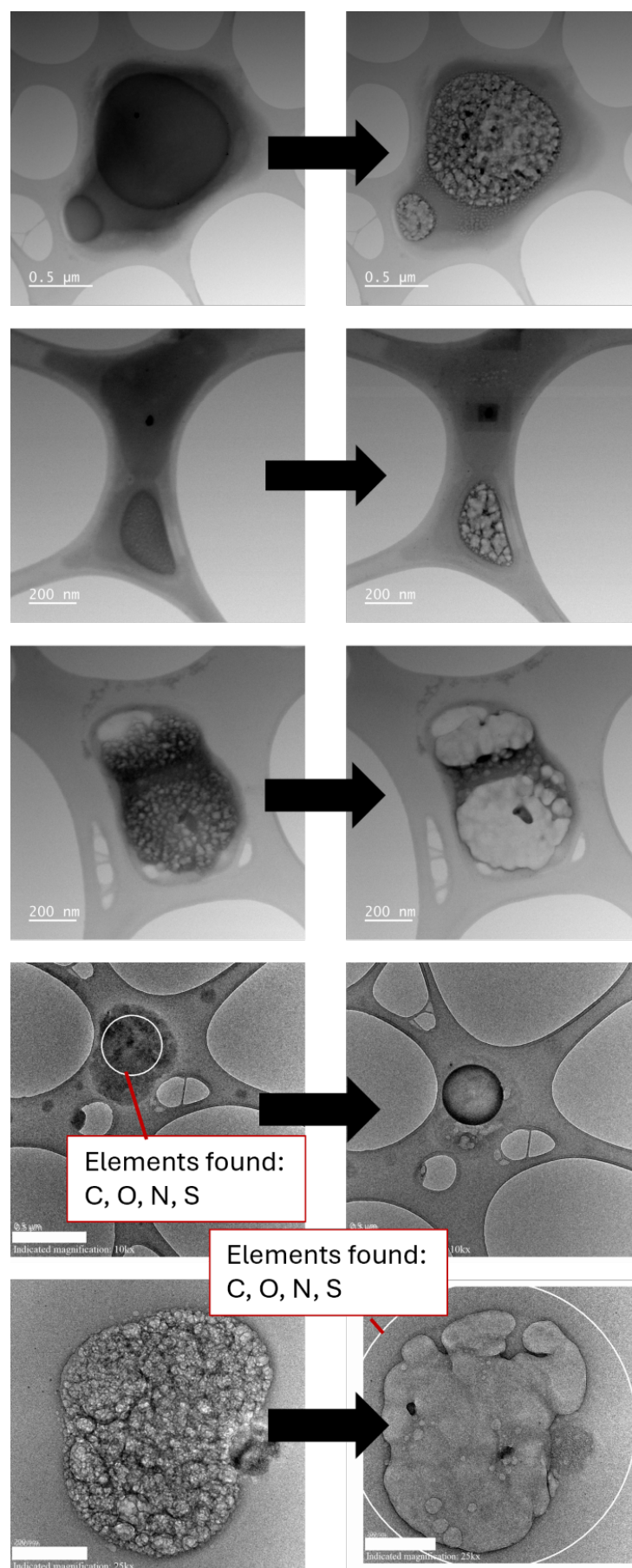


Figure D.12: TEM observations of volatile structures, immediately degrading during the analysis

Acronyms

API American Petroleum Institute.

ATR Attenuated Total Reflectance.

CIMAC Conseil International des Machines à Combustion.

DBE Double Bond Equivalent.

DSC Differential Scanning Calorimetry.

EA Elemental Analysis.

EDS Energy Dispersive X-ray Spectrometer.

EDX Energy Dispersive X-ray Spectroscopy.

EEPS Engine Exhaust Particle Sizer.

FID Flame Ionization Detector.

FPS 4000 Fine Particle Sampler.

FTIR Fourier Transform Infrared.

GC Gas Chromatography.

GC2D two dimensional Gas Chromatography.

GMD Geometric Mean Diameter.

HAADF High Angle Annular Dark Field.

HPLC High Performance Liquid Chromatography.

ICP-OES Induced Coupled Plasma Optical Emission Spectrometry.

IEA International Energy Agency.

IFPEN IFP Energies nouvelles.

IMEP Indicative Mean Effective Pressure.

IMO International Maritime Organization.

IP Induction Period.

LC Liquid Chromatography.

MoDTC molybdenum dithiocarbamate.

MPS Mini Particle Sampler.

MS Mass Spectrometry.

NCD Nitrogen Chemiluminescence Detector.

PAHs Poly-Aromatic Hydrocarbons.

PAO polyalphaolefins.

SEM Scanning Electronic Microscopy.

SOF Soluble Organic Fraction.

STEM Scanning Transmission Electronic Microscopy.

TAN Total Acid Number.

TBN Total Base Number.

TEM Transmission Electronic Microscopy.

TGA Thermo-Gravimetric Analysis.

ToF Time-of-Flight.

UV Ultra-Violet.

VOC Volatile Organic Compounds.

XPS X-ray Photoelectronic Spectroscopy.

ZnDTP zinc dithiophosphate.

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