The Oxidative Stability of FAME in the Model Crankcase Environment

by

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Abstract
The use of biodiesel has increased in recent years due to the implementation of governmental policies driven by environmental, economic and political reasons. Biodiesel is composed of fatty acid methyl esters (FAME), which can be derived from plant, marine and animal sources. There have been reports of some potential problems associated with biodiesel use in modern diesel engines, with lubricant dilution by blended biodiesel fuels leading to accumulation of FAME in the oil sump in the crankcase.

This project focuses on the design and implementation of an experimental model based on the Rancimat apparatus that can simulate certain aspects of the FAME degradation chemistry occurring in the crankcase and oil sump. An analysis procedure to compliment the experimental model is applied to carry out product distribution analysis on a series of (C18) model FAME, identifying and quantifying the oxidation products formed under the experimental conditions, where epoxides are the major monomeric degradation.

Some oxidation kinetic parameters have been investigated using biodiesel samples, with noticeable differences in oxidation rates found when FAME are oxidised individually and when in mixtures. Kinetic factors of FAME and model base oil in single and multi-component systems have also been investigated, with the base oil displaying good oxidative stability in mixtures as well as on its own.

The influence of antioxidants on stabilising various model systems has shown synergistic effects. Combinations of primary and secondary antioxidants have displayed good synergy, with the suppression of the rate of hydroperoxide formation by primary antioxidants enhancing the effectiveness of the secondary antioxidant. Primary antioxidants have been observed to affect the onset of oxidation, whilst secondary antioxidants decrease the hydroperoxide and epoxide, but increase the alcohol yields as a result of autoxidation.
Acknowledgments
First and foremost I would like to thank Infineum U.K. Ltd for the funding of the project, without which none of the following research would have taken place. Particular praise must go to Steve Marsh who has been a fountain of knowledge on the subject of the project and has proved to have the patience of a saint during the completion of this thesis. I also thank Matt Irving, Joe Hartley, and Stuart McTavish for their contributions to my understanding of the research topic, thank you for sharing your wisdom with me.

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JHE
**List of Abbreviations**

<table>
<thead>
<tr>
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<th>Description</th>
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<tbody>
<tr>
<td>[x]</td>
<td>Concentration (of x)</td>
</tr>
<tr>
<td>18:0</td>
<td>Methyl stearate</td>
</tr>
<tr>
<td>18:1</td>
<td>Methyl oleate</td>
</tr>
<tr>
<td>18:2</td>
<td>Methyl linoleate</td>
</tr>
<tr>
<td>18:3</td>
<td>Methyl linolenate</td>
</tr>
<tr>
<td>4-HNE</td>
<td>4-Hydroxynonenal</td>
</tr>
<tr>
<td>acac</td>
<td>Acetylacetonate</td>
</tr>
<tr>
<td>ADPA</td>
<td>Alkylated diphenylamine</td>
</tr>
<tr>
<td>AO</td>
<td>Antioxidant</td>
</tr>
<tr>
<td>API</td>
<td>American petroleum institute</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated total reflection</td>
</tr>
<tr>
<td>BDE</td>
<td>Bond dissociation enthalpy</td>
</tr>
<tr>
<td>BHA</td>
<td>Butylated hydroxyanisole</td>
</tr>
<tr>
<td>BHT</td>
<td>Butylated hydroxytoluene</td>
</tr>
<tr>
<td>C</td>
<td>Carbon</td>
</tr>
<tr>
<td>°C</td>
<td>Degrees centigrade</td>
</tr>
<tr>
<td>CAS</td>
<td>Chemical abstracts service</td>
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<tr>
<td>cf.</td>
<td><em>Confer</em> (compare)</td>
</tr>
<tr>
<td>CFPP</td>
<td>Cold filter plugging point</td>
</tr>
<tr>
<td>cm</td>
<td>Centimetres</td>
</tr>
<tr>
<td>CN</td>
<td>Cetane number</td>
</tr>
<tr>
<td>Cor</td>
<td>Methyl coronarate</td>
</tr>
<tr>
<td>CP</td>
<td>Cloud point</td>
</tr>
<tr>
<td>DAGs</td>
<td>Diacylglycerides</td>
</tr>
<tr>
<td>DNA</td>
<td>Deoxyribonucleic acid</td>
</tr>
<tr>
<td>DPF</td>
<td>Diesel particulate filter</td>
</tr>
<tr>
<td>ECN</td>
<td>Effective carbon number</td>
</tr>
<tr>
<td>EDTA</td>
<td>Ethylenediaminetetraacetic acid</td>
</tr>
<tr>
<td>EtOH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>FA</td>
<td>Fatty acid</td>
</tr>
<tr>
<td>FAME</td>
<td>Fatty acid methyl esters</td>
</tr>
<tr>
<td>g</td>
<td>Grams</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatography</td>
</tr>
<tr>
<td>GC-MS</td>
<td>Gas chromatography-mass spectrometry</td>
</tr>
<tr>
<td>GHG</td>
<td>Greenhouse gas</td>
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<tr>
<td>GLC</td>
<td>Gas-liquid chromatography</td>
</tr>
<tr>
<td>h</td>
<td>Hours</td>
</tr>
<tr>
<td>HMN</td>
<td>Heptamethylnonane</td>
</tr>
<tr>
<td>HPh</td>
<td>Synthetic Phenol</td>
</tr>
<tr>
<td>HTCBT</td>
<td>High temperature corrosion bench test</td>
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Initiator
Internal diameter
Induction Period
iso-Propanol
Infrared
Iodine Value
J-coupling constant
Kelvin
Rate constant
kilocalories
Inhibition rate constant
Kilojoules
Relative rate constant
Litres
Natural logarithm
Limited
Metres
Molar
Mass/charge ratio
Monoacylglycerides
Molybdenum dialkylthiocarbamates
Methyl
Milliequivalents
Megahertz
Minutes
Millilitres
Microlitres
Millimetres
Micrometres
Millimoles
Moles
Mole percentage
Microsiemens
Mass spectrometry
Monounsaturated fatty acids
Monounsaturated fatty acid methyl esters
Normal
Not applicable
Not determined
Nuclear magnetic resonance spectroscopy
Oxides of nitrogen
OAc  Acetate
OS   Organic Sulphur
PAO  Polyalphaolefins
PDSC Pressure differential scanning calorimetry
PG   Propyl gallate
PH   Partially hydrogenated
pK_a Logarithmic acid dissociation constant
PP   Pour point
ppm  Parts per million
PUFA Polyunsaturated fatty acids
PUFAME Polyunsaturated fatty acid methyl esters
PV   Peroxide value
PY   Pyrogallol
R    Alkyl group
R'   Alkyl radical
Rel % Relative percentage
RME  Rapeseed methyl esters
RSD  Relative standard deviation
s    Seconds
SD   Standard deviation
Sen  Photosensitizer
SME  Soybean methyl esters
SME/PAO Binary mixture of SME and PAO
t    Time
T    Temperature
TAGs Triacylglycerides
TBHQ Tertiary-butyl hydroxyquinone
TLC  Thin layer chromatography
Toco \( \alpha \)-Tocopherol
vs. Versus
wt-% Weight percentage
ZDDP Zinc \( OO' \)-dialkyldithiophosphates and Zinc \( OO' \)-diisopropylidithiophosphate
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1. Introduction
1.1. Preface

The purpose of this work is to investigate the impact that everyday biodiesel use may have upon the lubricating oil in diesel engines. Rather than carrying out expensive bench engine and field tests, the approach to achieving the project objectives revolves around lab based experiments which are designed to simulate biofuel and lubricant aging in the oil under crankcase conditions. Once a suitable model is developed, a number of studies can be undertaken to assess the behaviour of FAMEs and the possible interactions with lubricating oils. These include the following:

- Review and understand FAME oxidation pathways under crankcase conditions by analysing degradation product formation.
- Assessing oxidative stability and degradation kinetics of FAMEs and model base oils under the setup.
- Investigate the effects of FAME and its oxidation products upon model base oils.
- Study the influence of additives upon oxidative stability and the degradation product distribution of FAME.
- Screening of effective antioxidant combinations in search of beneficial effects.

Overall, the individual objectives will work towards two goals, which are the improved understanding of the oxidative degradation of FAMEs and its impact on base oil stability. This should lead towards new advances to help improve the compatibility of biodiesel and lubricating oil in modern diesel engines.

In Chapter 1 the necessary information that is required for understanding the scope of the project is provided. The background material on alternative energy, biofuels, existing literature knowledge on biodiesel oxidative degradation pathways, and the crankcase conditions found in diesel engines is reported.
1.2. Alternative Energy, Biodiesel and FAMEs

1.2.1. Alternative Energy
The need for alternative energy sources has been highlighted in recent decades, with evidence linking increases in atmospheric CO$_2$ levels to increasing global temperatures now being widely accepted.\textsuperscript{1} The consequences of this global warming have been documented as potentially catastrophic\textsuperscript{2} and great efforts from the developed world are being made to reduce the CO$_2$ emissions being released into the atmosphere by man. Since the start of the industrial revolution, fossil fuels have been the primary source of man’s energy needs. As populations have grown and industrialisation has developed globally, the demand for fossil fuels has increased and subsequently CO$_2$ emissions and its atmospheric concentration have increased. The combustion of fossil fuels is the major contributor to anthropogenic greenhouse gas (GHG) emissions, as this fuel is the source of the majority of the energy that we consume. Attempts to lower GHG levels in the atmosphere require us to move away from our centuries of dependence on fossil fuels and use cleaner, renewable energies.

Besides the need to lower GHG emissions, in the Western world there are economic and supply incentives to explore and embrace alternative energy sources. The demand from developing countries, as well as depleting supplies of fossil fuels and the political unrest in and around the oil producing countries in the Middle East, mean that prices of crude oils have recently fluctuated around an upwards trend. Energy security is required to reduce the dependence of supply from oil producing nations, and can be achieved by the use of several alternative energies.

The main technologies and areas of research that are considered the most plausible to generate sufficient energy with the lowest environmental impact are: bioenergy, solar energy, geothermal energy, hydropower, ocean energy and wind energy. From this list above, bioenergy is highlighted as an important alternative energy owing to the possibility of it providing a fuel in a liquid form. Whilst the other technologies ultimately focus on producing clean and renewable electricity that can be used to power our domestic and industrial needs, bioenergy allows for the production of natural and synthetic liquid fuels that can be used to power automotive, marine and aeronautic engines, the modes of transport that we have become dependent on in this modern age.
Bioenergy is energy derived from biomass and recently dead biological materials, as opposed to long dead biological materials that are the source of fossil fuels. Sources of bioenergy can include plants and trees, animal products and waste, marine organisms and organic waste streams. The energy can be stored as gas, liquid or solid fuels and used for a number of different applications. Of particular interest are liquid biofuels and their application as automotive fuels. Mainly sourced from plant, animal and marine products, biofuels are substitute fuels for petroleum fuels such as gasoline and diesel and are considered by many as carbon neutral as the CO$_2$ released from their combustion is sequestered by crops grown as a fuel source.$^3$ Whilst fossil fuel supplies are in decline, biofuels are from renewable sources so theoretically are inexhaustible. The most commonly used biofuels used today are bioethanol, mainly for use in gasoline engines and biodiesel, which is only used in diesel engines.

The idea of using biofuels to power automotive engines is not a new one. When Rudolph Diesel created his eponymous engine at the end of the nineteenth century, he envisaged an engine that could run on a variety of fuels, including whale oil, hemp oil and coal dust. Diesel himself opted to run his engine on kerosene due to its low cost. It was at the 1900 Paris World Fair that the use of biofuels in a diesel engine was first demonstrated. The French company Otto manufactured a diesel engine and exhibited it running on peanut oil. The engine was slightly smaller than normal and had been built to run on mineral oil but worked perfectly without modification when run on vegetable oils. It seems that this initiative was encouraged by the French government, who at the time had colonies in Africa where peanuts were in abundance. It was their intention for the colonial countries to be able to be self sufficient in supplying themselves with a fuel, from which they could power their own industries without dependence on imported fuels. Rudolph Diesel later carried out similar tests with vegetable oils and insightfully remarked:

“The use of vegetable oils for engine fuels may seem insignificant today, but such oils may become, in the course of time, as important as petroleum and the coal-tar products of the present time.”$^4$

There has been a renaissance in the use of biofuels recently due to political concerns such as the increasing atmospheric CO$_2$ levels and the depletion of fossil fuel sources. This has lead
to an increased awareness of the potential benefits that biofuels could provide and their role in the energy economy of the future.

Since 2003 European directives have been introduced outlining the need for the increased use of biofuels for domestic road transport fuels by blending biofuels with fossil fuels, stating at the time that the current technology would allow for low biofuel blends (up to 10 %) without any problems for vehicles. In 2009 the Official Journal of the European Union published its ongoing drive to increase the use of renewable energies in a bid to reduce GHG emissions. They used the example of biodiesel use in Germany accounting for 6 % of the diesel market, prompting predictions that by 2020 biofuels could make up 14 % of all transport fuels in the EU, though a minimum target of 10 % had been set for that date. In the UK similar legislation is in place to keep in line with the EU, with the Renewable Transport Fuel Obligations dictating the percentage of biofuels that are to make up the domestic transport fuels in Britain.

Currently, standard European pump diesel (EN 590) is B7 and can contain up to 7 % biodiesel. Similar limits exist in other regions. Some fleet vehicles do run on higher biodiesel blends such as B20 or even B100. Vehicle manufactures remain cautious over the use of higher biodiesel blends due to concerns over the effects of fuel dilution of lubricants by FAME.

### 1.2.2. Biodiesel and FAMEs

By definition, biodiesel is the mono alkyl esters of fatty acids. Commonly methyl esters are used due to the lower cost of methanol over other alcohols. This leads to the term Fatty Acid Methyl Esters (FAMEs), being used as a synonym for biodiesel. Figure 1.1 shows the structure of methyl oleate, a C18 FAME.

![Figure 1.1 Methyl Oleate](methyl_oleate.png)
FAMEs can be used as a neat fuel (B100) or as a diesel fuel extender, whereby it is blended with petro-diesel to make up a certain proportion of the fuel and is represented by the moniker B5 or B20 etc, indicating biodiesel blends of 5 % and 20 % respectively.

1.2.3. Biodiesel Production
Sources of biodiesel include virgin vegetable and plant oils, oils from algae, animal fats and recycled cooking oils. Oils produced by plants tend to be located in the seeds and act as a nutritional reserve to provide sustenance to seedlings as they germinate. It is this oil that is extracted and converted to biodiesel. Biodiesel is produced globally and the source of the oils depends on where it is made. In Europe, the most common biodiesel feedstock is rapeseed oil, whilst in North America soybean is the main source. In Asia palm oil is grown as it has a high oil yield. In Africa and India, hardier oil producing plants that are resistant to pests and drought and can grow on rough, non-arable land such as Jatropha and Karanja are used. Ultimately the source of biodiesel will be dictated by the geographic and economic factors that surround the producer and customer. The EU leads the way in biodiesel production accounting for nearly 93% of the global production, making rapeseed oil the most common biodiesel source, accounting for approximately 37% of global biodiesel production (Figure 1.2).  

![Figure 1.2 Biodiesel production sources (UCO = used cooking oil)](image)

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8
The source from which biodiesel is produced has a great influence upon the properties of the fuel, owing to the variation in the relative abundance of the fatty acids in the oil or fat used (Table 1.1). Each biodiesel feedstock has a different fatty acid profile; the composition also varies within different varieties of the same crop. For instance, rapeseed oil from Europe can have a significantly different fatty acid profile to that of oil obtained from rapeseed in North America. The fatty acid content of the starting material will be reflected in the final biodiesel product and physical properties of the fuel, so the quality of the oil is an important consideration when selecting a source of biodiesel.

<table>
<thead>
<tr>
<th>Fatty Acid</th>
<th>Soybean</th>
<th>PH Soybean</th>
<th>Corn</th>
<th>Sunflower</th>
<th>Rapeseed</th>
</tr>
</thead>
<tbody>
<tr>
<td>14:0</td>
<td>0.1</td>
<td>&lt; 0.1</td>
<td>0.0</td>
<td>&lt; 0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>16:0</td>
<td>10.9</td>
<td>11.9</td>
<td>12.0</td>
<td>6.2</td>
<td>5.1</td>
</tr>
<tr>
<td>16:1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.0</td>
<td>0.3</td>
</tr>
<tr>
<td>18:0</td>
<td>4.2</td>
<td>4.0</td>
<td>2.3</td>
<td>4.8</td>
<td>2.3</td>
</tr>
<tr>
<td>18:1</td>
<td>26.5</td>
<td>35.8</td>
<td>28.5</td>
<td>25.1</td>
<td>54.4</td>
</tr>
<tr>
<td>18:2</td>
<td>46.1</td>
<td>39.1</td>
<td>52.0</td>
<td>58.0</td>
<td>21.5</td>
</tr>
<tr>
<td>18:3</td>
<td>8.2</td>
<td>4.0</td>
<td>1.9</td>
<td>1.6</td>
<td>10.1</td>
</tr>
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<td>2.4</td>
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</tr>
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<td>1.4</td>
<td>3.1</td>
</tr>
<tr>
<td>22:0</td>
<td>0.2</td>
<td>0.3</td>
<td>0.0</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>MUFA/PUFA ratio</td>
<td>0.5:1</td>
<td>0.9:1</td>
<td>0.6:1</td>
<td>0.4:1</td>
<td>1.8:1</td>
</tr>
</tbody>
</table>

Table 1.1 Fatty acid composition (wt-%) in conventional vegetable oils. Reproduced from Merrill et al.13 (PH = partially hydrogenated)

1.2.4. Transesterification
The industrial process by which biodiesel is produced is called transesterification. The fatty acids in natural oils and fats exist as esters of glycerol (propane-1,2,3-triol) called triacylglycerides (TAGs). When fatty acids are bound in this way, the TAGs are high in molecular weight and as a consequence have a high viscosity. Transesterification is necessary to convert the TAGs into mono alkyl esters, such as FAMES, and in doing so lower the viscosity of the biofuel closer to that of conventional petro-diesel. This improves the fuel injection process and makes for better combustion when the fuel enters the engine.
cylinder. Some older diesel engines were able to run on raw vegetable oil, but it is not suitable for modern diesel engines with precision fuel injection systems.

The transesterification process involves reaction between TAGs and an alcohol, usually methanol, and a catalyst. The catalyst can be homogenous (acid or base) or heterogeneous (acid, base, or enzymatic).

The most common method used commercially has been with a homogenous base catalyst such as sodium or potassium hydroxide or methoxide (Figure 1.3). Base catalysed transesterification are generally preferred over acid catalysts for kinetic reasons, it is reported that base catalysed transesterification proceeds between 1000 – 4000 times the rate of an acid catalysed reaction with the same amounts of catalyst.

![Figure 1.3 Homogenous base catalysed transesterification scheme](image)

In the homogenous base catalysed transesterification, the mechanism is thought to proceed by a number of consecutive, reversible reactions (Figure 1.4). In the first step TAGs react with an alkoxide anion (in this case methoxide) to give a FAME and diacylglyceride (DAG) anions, which deprotonate the alcohol used in the reaction to give DAG. This mechanism continues, converting DAGs into monoacylglycerides (MAGs), which in turn are converted to glycerol. In each step a FAME molecule is generated for every glyceride conversion.
A major drawback to the alkali catalysed transesterification arises through unwanted side reactions when fatty acids (un-esterified) and water are present in the feedstock at high levels. At fatty acid levels above 2% the base catalyst reacts with the acids to form soaps and water by saponification and salification reactions. Water can go on to hydrolyse FAMEs to give fatty acids (Figure 1.5). In these cases with lower quality starting materials, acid catalysed transesterification is a better option than base catalysed reactions.\textsuperscript{18,19}

Separation of the product from side products and catalyst are major issues when using homogenous catalysts. The treatment process involves the use of mineral acids and solvents to separate the components of the reaction. When sodium hydroxide or methoxide are used, the sodium is recovered as sodium glycerate, sodium methylate, and sodium soaps which require conversion back to hydroxide or methoxide, all of which is costly and time consuming. Heterogeneous catalysts make the separation process simpler, as the catalyst can be easily removed from the product mixture, and as fewer unwanted side reactions occur. The reaction conditions used for heterogeneous catalysts often are harsher than those used in homogenous processes, with higher temperatures and pressures used.
1.3. Structure and Physical Properties of Fatty Acids and FAMEs

1.3.1. Structure and Associated Terminology

Fatty acids are long chain carboxylic acids that can exist as “free” acids (Figure 1.6 a and b) or as esters with glycerol as TAGs (Figure 1.6 c) or as mono alkyl esters (Figure 1.6 d and e). The main variables of the fatty acid moiety structure are carbon chain length and degree of unsaturation. Chain length can vary from 6-24 carbon atoms long and are usually composed of an even number of carbon atoms, as the biological mechanism employed to create fatty acids adds two carbon atoms at a time. The smallest carboxylic acid considered to be classed as a fatty acid is caproic acid (C₆), as this is the smallest acid that is separated from animal and vegetable fats.

![Figure 1.6 Examples of a - b) fatty acids, c) TAGs, and d - e) FAMEs structures with varying carbon chain lengths](image)

The degree of unsaturation in fatty acids can range from totally saturated to monounsaturated and polyunsaturated (Figure 1.7). The double bonds in the majority of naturally occurring unsaturated fatty acids adopts cis geometry. Some trans isomers do form in nature but only in very minor amounts. The double bonds in polyunsaturated species are methylene interrupted meaning that they are non-conjugated. The methylene groups directly adjacent (allylic) to the double bonds in unsaturated molecules have lower C-H bond dissociation enthalpies than those adjacent to saturated sites. The methylene groups between two double bonds (bis-allylic) in polyunsaturated species posses even more labile C-H bonds than those in allylic positions. This feature is significant as it is an important factor in determining a chemical property of a fatty acid or FAME called oxidative stability. The oxidative stability is a measure of how readily a species reacts with oxygen, i.e. how easily a compound oxidises. FAME oxidation is discussed in greater detail in section 1.4.
Figure 1.7 Structures of C18 FAMEs with varying degrees of unsaturation: a) methyl stearate; b) methyl oleate; c) methyl linoleate; d) methyl linolenate

Given the variation in carbon chain length and degree of unsaturation there are many possible fatty acids and FAME structures. Systematic names can be quite long and unwieldy, whilst remembering all the seemingly arbitrary trivial names is difficult. As a result shorthand notations have been developed to help easily distinguish between fatty acid and FAME structures. A numerical notation that gives the number of carbon atoms (n) and double bonds (x) in the fatty acid chain is given as n:x; so for example 16:0 is palmitic acid and 18:1 is oleic acid. There are limitations to this nomenclature as it does not specify where the positions of the double bonds are located in unsaturated species. There are a couple of different methods to overcome this drawback. The chemist’s method is to label the carbonyl site as C1 (the ∆ terminal) and count the carbon atoms down towards the methyl terminal. In this case, the position at which the first double bond appears will be labelled ∆⁹, so methyl oleate becomes ∆⁹. The biochemist’s approach is to label the double bond closest to the methyl terminal (the ω terminal) with the symbol ω−x. Oleic acid becomes ω-9, whilst linolenic acid is ω-3. This terminology is often associated with dietary and nutritional information of oils in foods. Double bond geometries can be described using standard IUPAC terms Z and E for cis and trans respectively, whilst “Greek” letter prefixes help to distinguish between positional isomers of unsaturated molecules. Together, using the different nomenclatures, details of the structure of fatty acids and FAMEs can easily be conveyed in a shorthand notation (Table 1.2).
<table>
<thead>
<tr>
<th>Trivial Name</th>
<th>n:x</th>
<th>Systematic Name</th>
<th>Δ</th>
<th>ω-x</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lauric acid</td>
<td>12:0</td>
<td>Dodecanoic acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Myristic acid</td>
<td>14:0</td>
<td>Tetradecanoic acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Palmitic acid</td>
<td>16:0</td>
<td>Hexadecanoic acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Palmitoleic acid</td>
<td>16:1</td>
<td>9Z-Hexadecenoic acid</td>
<td>Δ⁹</td>
<td>ω-7</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>18:0</td>
<td>Octadecanoic acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oleic acid</td>
<td>18:1</td>
<td>9Z-Octadecenoic acid</td>
<td>Δ⁹</td>
<td>ω-9</td>
</tr>
<tr>
<td>Linoleic acid</td>
<td>18:2</td>
<td>9Z,12Z-Octadecadienoic acid</td>
<td>Δ⁹,¹²</td>
<td>ω-6</td>
</tr>
<tr>
<td>α-Linolenic acid</td>
<td>18:3</td>
<td>9Z,12Z,15Z-Octadecatrienoic acid</td>
<td>Δ⁹,¹²,¹⁵</td>
<td>ω-3</td>
</tr>
<tr>
<td>γ-Linolenic acid</td>
<td>18:3</td>
<td>6Z,9Z,12Z-Octadecatrienoic acid</td>
<td>Δ⁶,⁹,¹²</td>
<td>ω-6</td>
</tr>
<tr>
<td>Arachidic acid</td>
<td>20:0</td>
<td>Icosanoic acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arachidonic acid</td>
<td>20:4</td>
<td>5Z,8Z,11Z,14Z-Icosatetraenoic acid</td>
<td>Δ⁵,⁸,¹¹,¹⁴</td>
<td>ω-6</td>
</tr>
</tbody>
</table>

Table 1.2: Nomenclature for selected fatty acids

A minor variation of fatty acid structure is through chain branching, though most naturally occurring fatty acids are unbranched due to the biosynthetic pathways that produce them. Studies have reported that chain branching of both the alcohol and fatty acid moiety can have significant effects on the physical properties of a FAME, with properties such as melting point, cetane number (CN), pour point (PP) and cloud point (CP) affected.²²⁻²⁸

1.3.2. EN 14214

Physical and chemical properties are important to FAMEs as they influence how effectively the fuel will perform. EN 14214 is a regulation set by the European Committee for Standardisation, consisting of a list of test methods and the limits for the physical and chemical properties of B100 biodiesel that must be satisfied if it is to be used as fuel in the EU (Table 1.3).²⁹ Contaminates from the raw materials or manufacturing processes can remain in the biodiesel product and affect the properties of the fuel. These specifications are set in place to limit the level of impurities found in biodiesel, ensuring it is compatible with petrodiesel and performs to an acceptable standard. This compatibility is demonstrated by the equivalent standards for petrodiesel (EN 590), which are similar to those required of FAMEs, with respective values for density and viscosity (820 – 845 vs. 860 – 900 Kg/m³ at 15°C and 2.0 – 4.5 vs. 3.5 – 5.0 mm²/s at 40°C respectively) being comparable.
<table>
<thead>
<tr>
<th>Property</th>
<th>Test method</th>
<th>Unit</th>
<th>Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester content</td>
<td>EN 14103</td>
<td>[wt-%]</td>
<td>≥ 96.5</td>
</tr>
<tr>
<td>Density at 15°C</td>
<td>ISO 3675</td>
<td>[kg/m³]</td>
<td>860-900</td>
</tr>
<tr>
<td>Viscosity at 40°C</td>
<td>ISO 3104</td>
<td>[mm²/s]</td>
<td>3.5-5.0</td>
</tr>
<tr>
<td>Flashpoint</td>
<td>DIN EN 22719</td>
<td>[°C]</td>
<td>≥ 120</td>
</tr>
<tr>
<td>Sulphur content</td>
<td>EN ISO 20846</td>
<td>[mg/kg]</td>
<td>≤ 10.0</td>
</tr>
<tr>
<td>Carbon residue of 100%</td>
<td>EN ISO 10370</td>
<td>[wt-%]</td>
<td>≤ 0.03</td>
</tr>
<tr>
<td>Cold filter plugging point</td>
<td>EN 116</td>
<td>[°C]</td>
<td>+5/-20</td>
</tr>
<tr>
<td>Sulphated ash content</td>
<td>ISO 3987</td>
<td>[wt-%]</td>
<td>≤ 0.02</td>
</tr>
<tr>
<td>Water content</td>
<td>EN ISO 12937</td>
<td>[mg/kg]</td>
<td>≤ 500</td>
</tr>
<tr>
<td>Total contamination</td>
<td>EN 12662</td>
<td>[mg/kg]</td>
<td>≤ 24</td>
</tr>
<tr>
<td>Acid value</td>
<td>EN 14104</td>
<td>[mg KOH/g]</td>
<td>≤ 0.50</td>
</tr>
<tr>
<td>Oxidative stability</td>
<td>EN 14112</td>
<td>[h]</td>
<td>≥ 6.0</td>
</tr>
<tr>
<td>Methanol content</td>
<td>EN 14110</td>
<td>[wt-%]</td>
<td>≤ 0.20</td>
</tr>
<tr>
<td>Iodine value</td>
<td>EN 14111</td>
<td>[g I₂/100 g]</td>
<td>≤ 120</td>
</tr>
<tr>
<td>Monoglyceride content</td>
<td>EN 14105</td>
<td>[wt-%]</td>
<td>≤ 0.80</td>
</tr>
<tr>
<td>Diglyceride content</td>
<td>EN 14105</td>
<td>[wt-%]</td>
<td>≤ 0.20</td>
</tr>
<tr>
<td>Triglyceride content</td>
<td>EN 14105</td>
<td>[wt-%]</td>
<td>≤ 0.20</td>
</tr>
<tr>
<td>Free glycerol</td>
<td>EN 14105</td>
<td>[wt-%]</td>
<td>≤ 0.02</td>
</tr>
<tr>
<td>Total glycerol</td>
<td>EN 14105</td>
<td>[wt-%]</td>
<td>≤ 0.25</td>
</tr>
<tr>
<td>Phosphorus content</td>
<td>EN 14107</td>
<td>[mg/kg]</td>
<td>≤ 10.0</td>
</tr>
<tr>
<td>Group I metals: Na</td>
<td>EN 14108</td>
<td>[mg/kg]</td>
<td>≤ 5.0</td>
</tr>
<tr>
<td>Group I metals: K</td>
<td>EN 14109</td>
<td>[mg/kg]</td>
<td>≤ 5.0</td>
</tr>
<tr>
<td>Group II metals: (Ca + Mg)</td>
<td>EN 14538</td>
<td>[mg/kg]</td>
<td>≤ 5.0</td>
</tr>
</tbody>
</table>

Table 1.3 Specification of physical and chemical properties of FAMEs according to EN 14214.²⁹

1.3.3. Oxidative Stability

Oxidative stability decreases with increasing degree of unsaturation of FAMEs. This is due to the increasing number of allylic and bis-allylic sites, the reactive positions where oxidation occurs. Biodiesel made from oils high in polyunsaturated fatty acids (PUFAs) have lower
oxidative stabilities than those with more saturated or monounsaturated fatty acid (MUFA) content. Sometimes those oils with high PUFA content are treated by partial hydrogenation to lower the level of unsaturation, and improve its oxidative stability. Though saturated species have better oxidative stability, as discussed earlier they have poorer cold weather performance properties, so saturating feedstock does not necessarily make FAMEs suitable for use as biodiesel.

To measure the oxidative stability of FAMEs the standardised test method EN 14112 – also known as the Rancimat test – has been developed. This accelerated oxidation requires any biodiesel to be used in the EU to have an induction period of at least 6 hours at 110°C. This value has been determined to provide biodiesel with a shelf life of 1 year when stored under ambient conditions. The induction period represents the time during which FAME oxidation is being suppressed, the period after this the oxidation is rapid and self propagating. Further details of the Rancimat test method are discussed in section 2.2.1.

1.3.4. Iodine Value
Another term that is related to oxidative stability is the Iodine Value (IV). This property is a measure of the unsaturation in a biodiesel sample, determined by an idiometric titration whereby iodine is added across the double bonds on unsaturated FAMEs and is expressed by grams of I₂ per 100 grams of material (g I₂/100 g). The higher the IV of a biodiesel sample, the poorer the oxidative stability of the fuel, resulting in a greater propensity of the biodiesel to oxidise and form polymers and engine deposits. There is some debate to the relevance of the IV given that mixtures of different FAMEs can have the same IV. Increasing carbon chain length also lowers the IV though not necessarily lowering the oxidative stability. Although specified in EN 14214, in the American equivalent (ASTM D6751) IV is not listed as a required specification.

1.3.5. Cetane Number
As with the effect of chain branching, the chain length and level of unsaturation affect the physical properties of FAMEs, with cetane number (CN), oxidative stability and cold filter plugging point (CFPP) amongst the most important. CN is an indicator of the ignition quality of a diesel fuel relative to hexadecane (the systematic name of cetane), which has a CN
equal to 100. At the other end of the scale, α-methylnaphthalene has a CN of 0. Mixtures of cetane and α-methylnaphthalene are used to give reference values for a fuel, which is given as a percentage of cetane in α-methylnaphthalene.\textsuperscript{34} The compound 2,2,4,4,6,8,8-heptamethylnonane (HMN) is a low CN standard with a value of 15. Cetane and HMN are structural isomers of one another but are at opposite ends of the CN scale, as the relationship between structure and CN follows the trend of the more linear a hydrocarbon the higher the CN, and the more branched a compound the lower the CN. This is the opposite of the petroleum equivalent – the octane rating – in which the more branched a hydrocarbon is, the greater the ignition quality. Other structural features to affect the CN are the carbon chain length and degree of unsaturation. The greater the molecular mass of a FAME or fatty acid, the higher the CN. However, the CN is significantly lowered by increasing degrees of unsaturation (Figure 1.8). The CN of FAMEs are comparable or sometimes even better than those of petrodiesel, making biodiesel a suitable fuel for use in diesel engines.

![Figure 1.8](image-url)  
**Figure 1.8** Effect of molecular mass of FAMEs on CN. Taken from Gopintha et al.\textsuperscript{35}

### 1.3.6 Cold Weather Performance Properties

The cold weather performance properties of biodiesel are important in regions of biodiesel use that are subjected to low temperatures, as the FAMEs in the biodiesel have the potential to solidify at low temperatures. This can affect the performance of the fuel due to fuel line and filter blocking. Cold filter plugging point (CFPP) is a cold weather performance property, which is related to the pour point (PP) and cloud point (CP).\textsuperscript{24} CP is the
temperature at which FAMEs start to become cloudy due to the crystallisation and solidification of saturates present. A study has shown that it is the high melting point saturated FAME content that determines CP, regardless of the unsaturated content.\textsuperscript{36} At lower temperatures the PP is met, this is the point at which FAMEs no longer flow as a liquid.\textsuperscript{37} For unsaturated fatty acids and FAMEs the double bond geometry also influences the melting point, with lower melting points observed for cis isomers compared to their trans equivalents.\textsuperscript{20} Cold weather properties of FAMEs are improved with increasing carbon chain length and branching, as well as increasing the degree of unsaturation.

### 1.3.7. Boiling Point

FAMEs tend to have a higher boiling point and narrower boiling point range than many of the hydrocarbon components of diesel. This can cause the separation of the two fuels when biodiesel blends are exposed to the high temperatures found in the crankcase. FAME therefore also has a greater tendency to accumulate in the engine oil sump than petrodiesel. This is potentially problematic due to changes in the viscosity of the lubricant and the propensity of FAME molecules to undergo oxidative degradation in the sump environment, which may affect the performance of the engine. Petrodiesel either evaporates from the sump more readily or the stability of the molecule is more similar to that of lubricating base oil.\textsuperscript{38}

### 1.4. FAME Oxidation

FAME oxidation can occur by two different mechanisms – photo-oxidation and autoxidation – by reactions with singlet oxygen and triplet oxygen respectively. The reaction mechanisms are very different, proceeding at different rates and can lead to the formation of different products. To understand FAME oxidation it is first important to discuss molecular oxygen and the many roles that it can play.

#### 1.4.1. Oxygen

Molecular oxygen exists in its ground state as triplet oxygen, but also has two low lying excited states with the following term symbols: $^1\Delta_g$ and $^1\Sigma_g^+$, which lay 95 kJ mol\textsuperscript{-1} and 158 kJ
respectively above the ground state of triplet oxygen. The electronic configurations of these states of oxygen differ only in their $2p\pi$ antibonding orbitals (Figure 1.9). Triplet oxygen has unpaired electrons of the same spin occupying two $\pi^*$ orbitals, as dictated by Hund’s rule. In the first excited state, $^1\Delta_g$ has paired electrons of opposite spin in one of the $\pi^*$ orbitals, while in the second excited state, $^1\Sigma_g^+$ two electrons of opposite spin occupy two different $\pi^*$ orbitals. With two unpaired electrons each with the same spin, oxygen in its ground state has a total spin quantum number of 1, giving a spin multiplicity of 3 (from $2S + 1$) and hence is termed triplet oxygen. Singlet oxygen having two unpaired electrons of opposite spin, has a total spin number of 0 and therefore a spin multiplicity of 1, leading to the term singlet oxygen.

<table>
<thead>
<tr>
<th>Term Symbol</th>
<th>Orbital Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1\Sigma_g^+$</td>
<td>$\pi^*$</td>
</tr>
<tr>
<td>$^1\Delta_g$</td>
<td>$\pi^*$</td>
</tr>
<tr>
<td>$^3\Sigma_g^-$</td>
<td>$\pi^*$</td>
</tr>
</tbody>
</table>

Figure 1.9 Frontier orbital electron distributions in $O_2$ states. Adapted from Crutchley et al.\textsuperscript{39}

Oxygen in its triplet ground state is relatively unreactive as it has two unpaired parallel spin electrons, making it diradical and only reactive towards other radical species. As most stable compounds are non-radical, there is not much for triplet oxygen to react with and can be considered stable and relatively inert without a significant energy input.

Singlet oxygen is less abundant, less stable and more reactive than triplet oxygen. The $^1\Delta_g$ state has a relatively long gas-phase lifetime, reported as 45 – 64 mins\textsuperscript{40-42} due to the transition to the triplet ground state being spin-forbidden. This relatively long lifetime allows singlet oxygen in the lowest excited state to react rapidly with electron rich, non-radical, singlet state molecules. Owing to the pairing of anti-parallel electrons and an empty $\pi^*$ orbital, singlet oxygen is electrophilic and often participates in reactions with olefins\textsuperscript{43} and other neutral nucleophiles such as sulphides and amines. An extensive study by
Wilkinson et al. listed the reaction kinetics of singlet oxygen with over 1900 compounds in 145 solvents or solvent mixtures, with reaction rate constants varying from the order of $10^{10} - 10^2$ L mol$^{-1}$ s$^{-1}$. The gas-phase lifetime of the higher energy state of singlet oxygen, $^{1}\Sigma_g^+$, is much shorter than that of $^1\Delta_g$ and thought to be in the region of 7 -12 s. The shorter lifetime can be explained by the spin-allowed transition to the triplet ground state. Interactions with solvents reduce the lifetime of singlet oxygen drastically, with the type of solvent deemed integral to the lifetime. In the case of water the $^1\text{O}_2$ lifetime is shortened to just a few microseconds, while in CCl$_4$ it exists for hundreds of milliseconds.

### 1.4.2. Photo-oxidation

Photo-oxidation is an oxidation pathway that involves a reaction between a substrate and singlet oxygen. Unsaturated FAMEs are susceptible to photo-oxidation if exposed to light for prolonged periods in the presence of compounds capable of generating singlet oxygen. Generation of singlet oxygen can occur by chemical, enzymatic, and physical routes (Figure 1.10) but most common examples of fatty acid and FAME photo-oxidation utilise photosensitizers such as chlorophyll, porphyrins, pheophytins, riboflavins, or myoglobin. In order to be a photosensitizer, a molecule must have a high absorption coefficient in the visible region of the electromagnetic spectrum, a triplet state equal to or greater than that of singlet oxygen (95 kJ mol$^{-1}$), a triplet state lifetime greater than 1 µs and high photostability.
Chapter 1

Figure 1.10 Routes to singlet oxygen formation

The mechanism for the photochemical formation of singlet oxygen proceeds by a photosensitizer being able to absorb light in its singlet ground state ($^1$Sen) and reach an excited singlet state ($^1$Sen*). The excited singlet sensitizer has a short lifetime and will follow one of three processes: return to its ground state, whilst in doing so fluorescing; undergo internal conversion to a lower energy level and emit heat; or intersystem crossing, whereby the sensitizer loses some energy and falls to an excited triplet state ($^3$Sen*). The lifetime of the sensitizer in its excited triplet state is longer than that of the sensitizer in its excited singlet state ($\mu$s vs. ns respectively), allowing $^3$Sen* to act in a number ways (Figure 1.11).

Figure 1.11 Photoexcitation of a sensitizer and subsequent reaction pathways
The type I mechanism involves the excited triplet sensitizer reacting directly with a substrate by hydrogen or electron transfer, in doing so generating free radicals or free radical ions. In these cases the photosensitizer is acting as an initiator for autoxidation (see section 1.3.1.). Another possibility in the Type I mechanism comes about from a reaction between \(^3\text{Sen}^*\) and \(^3\text{O}_2\) to form a superoxide anion, \(\text{O}_2^-\). This outcome only accounts for less than 1% of the reaction between a triplet sensitizer and triplet oxygen,\(^49\) as the most common product of that reaction is the formation of singlet oxygen, and is known as the Type II mechanism. However, if the \(^3\text{Sen}^*\) does not react with a substrate or oxygen it can return to its singlet ground state, phosphorescing in the process. In the Type II mechanism the \(^3\text{Sen}^*\) reacts with \(^3\text{O}_2\) by a triplet-triplet annihilation reaction, in which energy is transferred from the excited triplet sensitizer to the ground state triplet oxygen to give the excited state singlet oxygen, with the sensitizer returning to its singlet ground state. A photosensitizer can typically generate \(10^3 - 10^5\) molecules of singlet oxygen before becoming exhausted through photobleaching or other degradation processes.\(^48\)

Singlet oxygen reacts readily with electron rich groups such as olefins. Unsaturated compounds will react with singlet oxygen in three different ways (See Figure 1.12): 1,4-cycloadditions (a); 1,2-cycloadditions (b); and “ene” reactions (c). In the 1,4-cycloaddition reaction \(^1\text{O}_2\) acts as a dienophile and undergoes a cycloaddition to form an endoperoxide, whilst in the 1,2-cycloaddition singlet oxygen reacts with an olefin to yield a dioxetane. In the “ene” reaction \(^1\text{O}_2\) reacts with olefins with allylic hydrogen atoms to form an allylic hydroperoxide (Figure 1.12).\(^50\)

![Diagram of reactions](image)

**Figure 1.12** Reactions of singlet oxygen with alkenes by a) 1,4-cycloaddition, b) 1,2-cycloaddition, and c) "ene" reaction\(^50\)
For unsaturated FAME the “ene” reaction applies due to the presence of the allylic hydrogen sites. This reaction yields non-conjugated hydroperoxides which cannot be observed from the reaction of triplet oxygen with the same FAME. The non-conjugated hydroperoxides formed in the reaction of methyl linolenate with singlet oxygen at the C10 and C15 positions are shown in Figure 1.13 a and b respectively.

**Figure 1.13** Oxidation of methyl linoleate by singlet oxygen at the a) C10 and b) C15 positions

Singlet oxygen is reported to react with unsaturated fatty acids and FAMEs very quickly, with reaction rates in the order of $10^4 - 10^5$ L mol$^{-1}$ s$^{-1}$ (Table 1.4). The general trend shows that the greater the degree of unsaturation of the fatty acid or FAME, the faster the reaction with singlet oxygen. However, the effect of the unsaturation upon the rate of oxidation in photo-oxidation is not as significant as it is in autoxidation.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>18:1 H</th>
<th>18:1 Me</th>
<th>18:2 H</th>
<th>18:2 Me</th>
<th>18:3 H</th>
<th>18:3 Me</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_6$D$_6$</td>
<td>$5.3 \times 10^4$</td>
<td>$7.3 \times 10^4$</td>
<td>$1.0 \times 10^5$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>$1.7 \times 10^4$</td>
<td>$4.2 \times 10^4$</td>
<td>$8 \times 10^4$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CD$_3$OD</td>
<td></td>
<td>$7.9 \times 10^4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$CN</td>
<td>$1.6 \times 10^5$</td>
<td>$2.8 \times 10^5$</td>
<td>$6.4 \times 10^5$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_5$H$_5$N</td>
<td>$7.4 \times 10^4$</td>
<td></td>
<td>$1.3 \times 10^5$</td>
<td></td>
<td>$1.6 - 1.9 \times 10^5$</td>
<td></td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>$2.4 \times 10^4$</td>
<td></td>
<td>$3.8 \times 10^4$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 1.4** Rate constants (L mol$^{-1}$ s$^{-1}$) for reactions of C18 fatty acids (H) and FAMEs (Me) with singlet oxygen in selected solvents. Data from Wilkinson *et al.*

41
1.5. Autoxidation

Autoxidation is the reaction of hydrocarbons with molecular oxygen under mild conditions. It is a mechanism by which organic substances undergo atmospheric degradation over prolonged periods by reacting with oxygen in its triplet state. Triplet oxygen, with its two parallel spin electrons in two different $\pi^*$ orbitals is diradical and reacts with other radical species. Given that most stable compounds are non-radical by nature, oxidation by triplet oxygen does not happen spontaneously but instead requires activation. Autoxidation proceeds by three distinct stages: Initiation, propagation, and termination.

1.5.1. Initiation

Initiation can occur due to external influences, such as trace metals, organic species such as acids, heat, light (UV radiation), abstracting a hydrogen atom from the FAME to yield a FAME radical (Eq 1.1). Reactions of FAME with oxygen at elevated temperatures are also thought to initiate autoxidation (Eq 1.2 and 1.3). Photo-oxidation has been theorised as playing a role as an initiator for the autoxidation of fatty acids given its fast reaction rate relative to autoxidation, whilst excited triplet state photosensitizers are thought to be capable of generating radicals through hydrogen or electron transfer processes. The following equations describe the initiation stage.

\[
\text{FAME-H} + \text{I} \rightarrow \text{FAME}^- + \text{H}^+ + \text{I}^- \quad [\text{Eq 1.1}]
\]

\[
\text{FAME-H} + \text{O}_2 \rightarrow \text{FAME}^- + \text{HO}_2^-. \quad [\text{Eq 1.2}]
\]

\[
2 \text{FAME-H} + \text{O}_2 \rightarrow 2 \text{FAME}^- + \text{H}_2\text{O}_2 \quad [\text{Eq 1.3}]
\]

The site of the hydrogen abstraction depends on the type of FAME being oxidised and the minimum energy required to activate the removal of the hydrogen radical. Saturated sites require approximately 98 kcal mol$^{-1}$ to initiate hydrogen abstraction from secondary C-H bonds, whilst allylic or bis-allylic positions require around 83 – 87 or 73 kcal mol$^{-1}$ respectively. In polyunsaturated fatty acid methyl esters (PUFAME) the bis-allylic positions is where the initial abstraction takes place, whilst in monounsaturated fatty acid methyl esters (MUFAME) studies have shown that abstraction occurs with approximately equal probability at the two allylic positions. The trend showing a lowering of activation...
energy of the active hydrogen sites from fully saturated to bis-allylic positions can be explained by the relative stability of FAME radicals generated. The resonance structures of a PUFAME radical allow for the radical to be spread over a pentadienyl system, which also gives rise to a conjugated diene affording extra stability to be gained (Figure 1.14). In MUFAME there is no possibility of conjugation, resulting in higher activation energy than for PUFAME, however the delocalised nature of the allyl radical system does allow for some extra stability and therefore lower activation energy is required than for saturated hydrogen abstraction.

![Figure 1.14](image)

Figure 1.14 Hydrogen abstraction by an initiator (I) of a polyunsaturated molecule and stabilisation by delocalisation of the radical over a pentadienyl system

1.5.2. Propagation
The first step of the propagation stages of autoxidation involves the reaction between the FAME radical and triplet oxygen to yield a peroxy radical (Equation 1.4). There are various types of subsequent reactions that can happen after this step including hydrogen atom transfer (Equation 1.5), β-fragmentation (Equation 1.6), rearrangement/cyclization, reactions with external olefins (cross linking), disproportionation (Equation 1.7), recombination, and electron transfer (FAME-OO’ + e⁻ → FAME-OO’). The simplest description of the propagation steps usually describes it as the hydrogen atom transfer reaction of hydrogen abstraction from a FAME by a peroxy radical to generate the primary oxidation product and another FAME radical (Equation 1.5). The FAME radical then continues the propagation cycle and in turn generates more radical species.
The addition of oxygen to a carbon centred FAME radical (Equation 1.4) is a rapid reaction that is reported to occur at the diffusion-controlled rate at oxygen pressure above 100 mmHg. Equation 1.5 is the rate limiting step of the propagation stage and can be relatively slow as it depends on many factors such as the type of solvent that the reaction is carried out in, as well as the bond dissociation energy (BDE) of the FAME C-H bond that is being broken. In order for this reaction to occur rapidly the strength of the bond being formed must be at least as strong as the bond being broken. In the case of FAMEs the O-H bond of the hydroperoxide is approximately 88 – 90 kcal mol\(^{-1}\), whilst the allylic C-H bonds are in the region of 84 kcal mol\(^{-1}\), and primary saturated C-H bonds about 98 kcal mol\(^{-1}\). This explains the relative inertness of saturated FAME towards autoxidation under ambient conditions. The reverse reaction of Equation 1.4 is known as $\beta$-fragmentation (Equation 1.6) and is also a significant factor in the kinetic and thermodynamic effects of FAME oxidation product distribution. Owing to the relatively slow propagation reaction shown in Equation 1.5, equation 1.6 is in competition with it, thus allowing thermodynamically favourable isomers to form.

In linoleate (18:2) oxidation, hydrogen abstraction occurs at the bis-allylic position on C11 leading to the formation of a pentadienyl radical system, to which addition of O\(_2\) gives 9- and 13-trans-cis-peroxy radical intermediates (Figure 1.15). In the presence of a good hydrogen donor such as $\alpha$-tocopherol, the kinetic hydroperoxide products are formed in the greatest yields. However in the absence of a good hydrogen donor the peroxy radicals can undergo $\beta$-fragmentation (loss of O\(_2\)) to reform the pentadienyl radical system, allowing for isomerisation of the molecule. The rate constants of $\beta$-fragmentation ($k\beta$) vary according to the configuration of the resulting FAME radical formed. The values of $k\beta$ for reactions resulting in transoid centred pentadienyl radical systems is much higher than those for cisoid centred products (625 s\(^{-1}\) vs. 70 s\(^{-1}\)). This means that if the rate of propagation is slow...
relative to equation 1.5, then the possibility of the formation of the thermodynamic products (the lower energy configuration 9- and 13-trans-trans-peroxy radicals) is greater.

Figure 1.15 Formation of kinetic (trans-cis) and thermodynamic (trans-trans) hydroperoxides from linoleate autoxidation

A stereochemical study by Frankel et al. reported the formation of four isomers from linoleate autoxidation with the following distribution at various temperatures (Table 1.5). The 9- and 13 hydroperoxides are formed at roughly equal concentrations, though at lower temperatures the cis-trans kinetic products are formed in greater proportion than the trans-trans thermodynamic products. An increase the temperature of the autoxidation conditions resulted in higher proportions of the thermodynamic product formation.
Table 1.5 Relative proportions (%) of hydroperoxide isomers of linoleate formed during autoxidation at various temperatures

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>13-OOH cis,trans</th>
<th>13-OOH trans,trans</th>
<th>9-OOH cis,trans</th>
<th>9-OOH trans,trans</th>
<th>Total 9-OOH</th>
<th>Total 13-OOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>31.0</td>
<td>20.1</td>
<td>29.7</td>
<td>19.2</td>
<td>51.2</td>
<td>48.9</td>
</tr>
<tr>
<td>50</td>
<td>19.5</td>
<td>28.0</td>
<td>22.9</td>
<td>29.6</td>
<td>47.5</td>
<td>52.5</td>
</tr>
<tr>
<td>65</td>
<td>18.6</td>
<td>33.5</td>
<td>17.5</td>
<td>30.4</td>
<td>52.1</td>
<td>47.9</td>
</tr>
</tbody>
</table>

The detection of the 11-hydroperoxide of linoleate was reported in a kinetically controlled autoxidation by the use of tocopherol by Brash.\(^{68}\) Previously the 11-hydroperoxide of linoleate was unreported, though electron spin resonance studies had determined spin density ratios of 0.98:1.11:0.98 at carbons 9:11:13 in the pentadienyl system of linoleate.\(^{69}\) This suggests that oxygen addition is more likely to occur at the 11- position rather than at the 9- or 13- positions. However, as discussed above, due to the possibility of \(\beta\)-fragmentation the thermodynamic products of reactions between linoleate pentadienyl systems and \(O_2\) are the 9- and 13- peroxy radical. The kinetic product when the reaction is carried out in the presence of \(\alpha\)-tocopherol as a hydrogen donor able to trap the kinetic product, resulted in the formation of the 11-hydroperoxide. Further studies by Porter and co-workers demonstrated the linear relationship between \(\alpha\)-tocopherol concentration and 11-hydroperoxide product formation,\(^{61}\) as well as the influence of diene geometry and substituent effects on regioselectivity of oxygen addition to pentadienyl systems.\(^{70,71}\)

Peroxy radical cyclizations are observed during the propagation stages of linolenate autoxidation, with the internal 12- and 13-peroxy radicals readily undergoing intramolecular rearrangement due to the presence of \(\beta-\gamma\) olefins. These cyclization reactions form epidioxides with adjacent carbon centred radicals that are susceptible to further propagation reactions, which usually result in the formation of FAME hydroperoxide epidioxides.\(^{72,73}\) This cyclization reaction accounts for the relatively low yields of internal hydroperoxides detected from linolenate autoxidation (see section 1.6.2, Figure 1.24).
1.5.3. Termination

The termination stage of autoxidation is the period when the formation of non-radical products from recombination reactions of radicals outweighs the formation of new radicals through autocatalysis. The reactions that produce non-radical products from radicals are called termination reactions and many have been described in the literature.\textsuperscript{74,75}

\[ 2 \text{FAME-OO}^- \rightarrow \text{FAME-OO-FAME} + \text{O}_2 \quad \text{[Eq 1.8]} \]

\[ \text{FAME-O}^- + \text{FAME}^- \rightarrow \text{FAME-O-FAME} \quad \text{[Eq 1.9]} \]

\[ 2 \text{FAME}^\cdot \rightarrow \text{FAME- FAME} \quad \text{[Eq 1.10]} \]

\[ 2 \text{FAME-OO}^- \rightarrow \text{FAME=O FAME-OH} + \text{O}_2 \quad \text{[Eq 1.11]} \]

At low temperature termination reactions between two peroxy radicals can result in the formation of peroxide linked dimers by the elimination of oxygen (Equation 1.8),\textsuperscript{74} whilst at low oxygen pressures and elevated temperatures, termination reactions involving alkoxy and carbon centred radicals yield ether and carbon linked dimers (Equations 1.9 and 1.10). The formation of dimers, oligomers and polymers is discussed in greater detail in section 1.4.3.

Equation 1.11 shows the Russell mechanism, a long established termination reaction that proceeds by the combination of two peroxy radicals to reversibly form an unstable tetroxide intermediate.\textsuperscript{75} This intermediate decomposes irreversibly to form an alcohol, a ketone and molecular oxygen (Figure 1.16). Ingold later went on to prove that the singlet oxygen is released in the reaction in order not to violate the Wigner spin conservation rule.\textsuperscript{76}

\begin{center}
\textbf{Figure 1.16} The Russell mechanism: a termination reaction of two peroxy radicals via a tetroxide intermediate
\end{center}

Other important termination reactions are those involving antioxidants. These molecules act as hydrogen donors to interrupt the free radical chain, in turn yielding stable radicals that do
not propagate the oxidation further (Equations 1.11 – 1.13). Antioxidants are discussed in greater detail in section 1.6.1.

FAME-OO' + AH $\rightarrow$ FAME-OOH + A' \hspace{1cm} \text{[Eq 1.11]}

2 A' $\rightarrow$ A-A \hspace{1cm} \text{[Eq 1.12]}

FAME' + A' $\rightarrow$ FAME-A \hspace{1cm} \text{[Eq 1.13]}

1.6. Oxidative Degradation Products
The hydroperoxides formed through primary oxidation are unstable species containing a weak O-O bond (45 – 50 kcal mol$^{-1}$)\textsuperscript{77} that readily decompose thermally to form alkoxy and hydroxyl radicals. Alkoxy and hydroxyl radicals are extremely reactive and are able to abstract hydrogen from allylic and bis-allylic sites and can undergo a number of reactions depending on conditions, to form volatile, monomeric, and polymeric degradation products.

1.6.1. Volatile Degradation Products
Volatile degradation products arise through the $\beta$-scission of alkoxy radicals.\textsuperscript{78} The fragments of the homolytic cleavage form aldehydes, alkyl and olefinic radicals which are then subject to further reactions (Figure 1.17). Alkyl radicals can undergo termination reactions to form hydrocarbons by hydrogen abstraction, or alcohols from reactions with hydroxyl radicals. Reactions between alkyl radicals and O$_2$ produce primary hydroperoxides which can follow further $\beta$-scission mechanisms to yield formaldehyde and small alkyl chain radicals with one less carbon atom. Olefinic radicals can react with hydrogen radicals to form alkenes or terminate with hydroxyl radicals to give 1-enols, which tautomerise into saturated aldehydes.\textsuperscript{79}
Formation of volatile degradation products via the homolytic cleavage of a monoene hydroperoxide

The Hock cleavage is a non-radical heterolytic decomposition mechanism that proceeds via a cationic intermediate. The rearrangement reaction is Lewis acid-promoted, though is known to also proceed thermally even at temperatures below room temperature. In the reaction an allylic hydroperoxide undergoes oxygen insertion between the \( \alpha-\beta \) C-C bond to yield an oxycarbonium intermediate which is subject to nucleophilic attack by water. The end result is C-C bond cleavage and the formation of two carbonyl compounds. This mechanism does not account for the formation of alcohols, saturated hydrocarbons and lower order FAME.

Figure 1.17 Formation of volatile degradation products via the homolytic cleavage of a monoene hydroperoxide

Figure 1.18 Hock cleavage of an allylic hydroperoxide
There is some opposition to the idea of the homolytic $\beta$-scission mechanism occurring exclusively, owing to the formation of unstable vinyl radicals in the reaction mechanism. One proposed mechanism incorporates a mix of both homolytic and heterolytic cleavage of the O-O bond. Homolytic cleavage (indicated as $\Delta$ in Figure 1.19) still occurs on the alkyl side of the hydroperoxides to form 2-alkenals and alkyl radicals, whilst Hock-like heterolytic cleavage (indicated by $H^+$ in Figure 1.19) is observed on the unsaturated side of the hydroperoxides to give saturated aldehydes (Figure 1.19). This mechanism allows for the formation of saturated hydrocarbons, alcohols, carbonyls, and lower order FAME, whilst avoiding vinyl radical intermediates.\(^81\)

![Figure 1.19 Homolytic/heterolytic mechanism of hydroperoxide decomposition ($\Delta$ indicates homolytic cleavage and $H^+$ indicates heterolytic cleavage of the O-O bond)](image)

In a study by Frankel et al. pure linolenate hydroperoxides were decomposed thermally at 150°C and catalytically by FeCl$_2$/ascorbic acid to yield 7.4% and 2.1% volatile degradation products respectively.\(^82\) Of the volatile products detected, thermal degradation favoured the formation of 2,4-heptadienal, while more methyl octanoate was formed from the catalytic method, though both compounds were major products in both methods. Other significant degradation products include 2,4,7-decatrienal and methyl 9-oxo-nonanoate. The mechanism for the formation of the major volatile products is attributed to homolytic
scission of the hydroperoxides, whilst the minor products appear to be the result of the heterolytic decomposition mechanism, adding further evidence towards the mixed mechanism proposed by Frankel et al. previously.\textsuperscript{81}

Many volatiles can form as a result of further oxidation of secondary oxidation products. Volatile compounds such as unsaturated aldehydes and ketones are prone to further oxidation reactions, as are some monomeric and polymeric compounds. Oxidation of unsaturated aldehydes produces a range of other volatile degradation products such as alkanals, dialdehydes, $\alpha$-keto aldehydes, peracids and volatile fatty acids (VFAs).

VFAs are formed as a result of the scission of $\alpha$-hydroperoxy aldehydes, formed from aldehyde peroxidation. Loury suggested that an equilibrium exists between two carbonyl free radical tautomers (Figure 1.20). On reactions with oxygen, one isomer forms a peracid radical and subsequent peracid, while the other isomer yields an $\alpha$-peroxy aldehyde and the corresponding $\alpha$-hydroperoxy aldehyde. The $\alpha$-hydroperoxy aldehyde degrades to give formic acid and a lower aldehyde (one carbon less) from C-C and O-O bond scissions.\textsuperscript{83}

\begin{center}
\textbf{Figure 1.20} Formic acid formation via $\alpha$-hydroperoxy aldehyde decomposition
\end{center}

In mixtures, unsaturated aldehydes oxidise faster than polyunsaturated FAME such as methyl linoleate and methyl linolenate, which in turn oxidise faster than saturated aldehydes. As a result there tends to be a build-up of saturated aldehydes at the more advanced stages of oxidation, with unsaturated aldehydes being oxidised to small aldehydes and dialdehydes. Saturated aldehydes oxidise at higher temperatures to form acids.
Malonaldehyde is a significant volatile product formed from the oxidation of polyunsaturated FAME.\textsuperscript{84-87} Thermal degradation of bicycloendoperoxides and hydroperoxy epidioxides – monomeric products formed from PUFAME oxidation – results in scission around the cyclic peroxide yielding malonaldehyde and other volatile degradation products (Figure 1.21).

\textbf{Figure 1.21} Formation of malonaldehyde from hydroperoxy epidioxides (red) and hydroperoxy bicycloendoperoxides (blue). Figure adapted from Pryor \textit{et al.}\textsuperscript{85}

\textbf{1.6.2. Monomeric Degradation Products}

Rather than follow homolytic and heterolytic decomposition mechanisms to form volatile products, alkoxy radicals can undergo simple termination steps to form monomeric degradation products. Methyl oleate oxidation results in the simplest range of monomeric product formation, with epoxy-stearates and epoxy-oleates forming from cyclisation of allylic alkoxy radicals followed by termination with hydrogen radicals (Figure 1.22). Allylic alcohols, dihydroxy-oleates and di-hydroxy-stearates have also been reported from methyl oleate oxidation.\textsuperscript{57} Allylic ketones are also detected form methyl oleate oxidation, possibly from dehydration of the hydroperoxides. Owing to the four isomeric hydroperoxides that form as a result of oleate autoxidation there are a number of positional isomers of the monomeric degradation products that can be observed. Epoxides can occupy the 8,9- 9,10-
and 10,11-positions, with the 9,10-isomers forming from both the 9- and 10-hydroperoxides. Alcohols and ketones can be found at the 8-, 9-, 10-, and 11-positions, and dihydroxy-species tend to be vicinal occupying the 9,10-position, though 8,9- and 10,11-isomers are also reported as minor products.\textsuperscript{88}

![Figure 1.22 Formation of epoxy and hydroperoxy products from alkoxy radicals](image)

Similar products are formed from linoleate oxidation as those found from oleate oxidation, though with an extra degree of unsaturation, linoleate is able to add more oxygen across the carbon backbone. As a result there is a high proportion of polyoxygenated species such as 9-,13-dihydroxy-, trihydroxy- and epoxyhydroxy-species. The trihydroxy-species are composed of either the 9,10- or 12,13-vicinal diol group with the other hydroxy group at the 13-, or 9- position respectively. Epoxyhydroxy-compounds are reported as both allylic species with the olefin separating the epoxide and alcohol, or as isomers where the epoxide and alcohol are adjacent to one another.\textsuperscript{88} These can be formed from cyclisation of an alkoxy radical followed by termination with a hydroxyl radical or further reactions with molecular oxygen to yield an epoxyperoxy-species which is subject to further reactions. Mono epoxides are also reported\textsuperscript{88} as are allylic hydroxy- and keto-dienes in the 9-and 13-positions.\textsuperscript{89} Routes to these products were proposed by Gardner \textit{et al.} who decomposed linoleic acid hydroperoxides catalytically by Fe(II)/cysteine to produce an alkoxy radical, from which the products mentioned above were formed through a series of subsequent reactions (Figure 1.23).\textsuperscript{90}
Figure 1.23 Formation of monomeric degradation products from linoleic acid hydroperoxide decomposition

The major monomeric degradation product of linolenate oxidation is reported to be the hydroperoxy epidioxides, which are formed as a result of cyclisation of 12- and 13-peroxy linolenates to give five-membered rings containing O-O bonds. The internal 12- and 13-hydroperoxides of linolenate had been reported to form in lower concentrations than the external 9- and 16-isomers, initially it was proposed that the internal hydroperoxides decomposed easily or that steric factors dictated the preference for external hydroperoxides. Dahle who later realised that the internal peroxy compounds readily cyclised due to an unsaturated site β–γ to the peroxy radical to form the epidioxides and subsequent hydroperoxy epidioxides. Pryor et al. reported the formation of prostaglandin like bicycloendoperoxides as a result of the intramolecular cyclisation of an epidioxide radical (Figure 1.24), and from the findings suggested that it may be possible that some prostaglandin molecules may be formed by non-enzymatic pathways.
During the oxidation of linolenate the large excess of linolenate present prevents the isomerisation of the internal (12- and 13-) hydroperoxides to the external (9- and 16-) isomers, and as a result the rapid cyclisation of the internal hydroperoxides upon formation prevails. When pure linolenate hydroperoxides are oxidised in the absence of excess linolenate, isomerisation occurs and thermodynamics dictates that internal hydroperoxides like to isomerise to external hydroperoxides. As there is a competing route for external hydroperoxides to take – the formation of dihydroperoxides – there is less isomerisation of external hydroperoxides to internal hydroperoxides and therefore lower yields of hydroperoxy epidioxides. Dihydroperoxides still form in lower yields than cyclic peroxides. Other monomeric products formed from linolenate oxidation include epoxy-hydroxydienes and epoxy-hydroperoxydienes.

1.6.3. Oligomeric Degradation Products
FAME hydroperoxide decomposition can result in the formation of high molecular weight species such as oligomers and polymers. Oligomeric compounds of linoleate and linolenate are formed under mild autoxidation conditions. Dimers form through peroxide, ether or carbon linkages and can contain other functional groups such as hydroperoxy-, hydroxy-, or oxo-groups. Peroxy-linked dimers tend to be the major product when polymerisation conditions are at lower temperatures and with a reliable source of oxygen. Under harsher conditions, carbon-linked dimers are more prevalent. A mechanism for the formation of
carbon and ether linked dimers was proposed by Lercker et al.\textsuperscript{94} When a carbon linked dimer is formed through the reaction between two hydroperoxides, molecular oxygen and hydrogen peroxide are produced. Ether linked dimers form along with molecular oxygen and water, through a bimolecular reaction of two hydroperoxides (Figure 1.25).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure125.png}
\caption{Mechanism for the formation of a) carbon linked and b) ether linked dimers proposed by Lerker et al.\textsuperscript{94}}
\end{figure}

Neff et al. polymerised pure linolenate mono-hydroperoxides by three different methods: oxidatively by bubbling O\textsubscript{2} through 100 – 1000 mg of the substrate kept at 40\textdegree C; thermally by heating the substrate at 150\textdegree C under oxygen; and catalytically with FeCl\textsubscript{2} and ascorbic acid at room temperature. The authors found that the oxidative method had a higher conversion to dimeric/oligomeric products and the highest selectivity towards peroxide linkages. The thermal method had the lowest conversion to dimeric/oligomeric products and also produced the most volatile products. Of the dimeric/oligomeric products formed by the thermal method, a higher proportion of them were oligomeric than seen by other polymerisation methods and no peroxide linkages were observed, only carbon linked. The catalytic oxidation showed a greater selectivity towards forming dimers over oligomerisation, the products of which were approximately 43.3\% peroxide linked.\textsuperscript{95}
Miyashita et al. reported the detection of linoleate dimers during the early stages of autoxidation. Methyl linoleate was oxidised at 30°C with dry air bubbled through it for 192 hours. Regular sampling and TLC/GPC analysis throughout the oxidation revealed the detection of dimers at relatively high concentrations in the early stages of linoleate autoxidation, whilst monohydroperoxides were still being formed. In other papers by Miyashita et al. dimers of linoleate autoxidation were characterised as being peroxide linked through the 9- or 13-positions of mono-, di-, and tri-hydroperoxy linoleate monomeric units.

In a study by Wheeler et al. cyclic dimers were reported from the Diels-Alder coupling of normal and thermally induced conjugated methyl linoleate, along with bicyclic dimers derived from conjugated linoleate. Figure 1.27 shows the coupling of conjugated linoleate and normal linoleate monomers by thermally induced Diels-Alder cyclisation. Thermal isomerisation of normal linoleate produces conjugated linoleate which can act as a diene, whilst one of the olefinic sites of normal linolenate acts as a dienophile and the two can undergo a Diels-Alder cyclisation. When two linoleate monomers form a dehydro-dimer through autoxidation, the resulting molecule can undergo rapid intramolecular cyclisation to form a bicyclic dimer. The formation of a number of cyclic- and bicyclic-dimer isomers is possible due to the positions of the olefins used for the cyclization.
Tolvanen et al. oligomerised technical grade linoleic acid to yield dimers, trimers and unsaturated cyclic-species and cyclic aromatics under anaerobic and aerobic conditions at temperatures above 260°C. Trimers were observed only when temperatures of 280°C or higher were used, whilst the detection of unsaturated cyclic-dimers and cyclic aromatics indicated that Diels-Alder cyclisation was occurring. The presence of water was reported to inhibit the initial stages of oligomerisation of the starting material, but over a prolonged period of reaction the effect of water was less significant.

The decomposition products of dimeric species formed through FAME oxidation is reported throughout the literature. Miyashita et al. isolated and characterised a number of monomeric and volatile degradation products from the decomposition of linoleate dimers. The monomeric products included hydroxy-dienes, epoxyhydroxy-monoenes as the major products, and dihydroxy- and trihydroxy-monoenes as minor products. Major volatile products detected were 4-hydroxynonenal (4-HNE), 4-hydroxynonanal, methyl 8-hydroxyoctanoate, whilst the minor volatile products were methyl 11-oxo-9-undecenoate, methyl 12-oxo-9-hydroxydodecanoate and methyl 12-oxo-9-hydroxy-10-dodecenoate. At

Figure 1.27 Formation of a) cyclic dimer and b) bicyclic dimers from methyl linoleate by Diels-Alder cyclisations from Wheeler et al.99
the time of publication no direct routes to the formation of 4-HNE from linoleate autoxidation were known, which lead the authors to concluded that dimers are important intermediates in linoleate autoxidation. Frankel et al. thermally decomposed monohydroperoxy-, dihydroperoxy-, and epidioxide-dimers of linolenate autoxidation and was able to compare the degradation products to those derived from the thermal degradation of the corresponding monomers. A range of volatile degradation products were characterised (Figure 1.28), with the major degradation product from each of the dimers being methyl 9-oxononanoate. It too was the major volatile product formed from the corresponding monomers, except for monohydroperoxy linoleate where it was formed in the second highest yield to 2,4,7-decatrienal.\textsuperscript{102}

![Figure 1.28 Major volatile products formed from the thermal decomposition of methyl linolenate dimers from Frankel et al.\textsuperscript{102}]

\textbf{1.7. The Crankcase and Lubricants}

\textbf{1.7.1. The Crankcase}
The crankcase is a large cavity in the engine positioned beneath the cylinder block which houses the crankshaft and oil sump. The crankshaft is connected to the pistons and translates the linear motion from the pistons into rotation. The oil sump is an area at the bottom of the crankcase that stores oil for distribution around the engine. The oil reservoir is not in direct contact with crankshaft or cylinder block. Oil from the sump, is pressurised by
the oil pump, passed through the oil filter and circulated to the crankshaft, cylinder walls and valve train regions of the engine.

![Diagram of Diesel engine crankcase schematic](Image provided by Infineum UK Ltd)

Given its proximity to the piston zone, under operating conditions the crankcase reaches temperatures between $100 - 150^\circ C$.\textsuperscript{103} Under these temperatures the oil in the sump is exposed to an environment capable of facilitating chemical reactions. The oil is also exposed to higher temperatures ($274 - 366^\circ C$)\textsuperscript{104} for short periods of time as it circulates through the piston ring zone.

1.7.2. Engine Lubricating Oil

Engine lubricating oil consists of base oil and a chemical additive package. The base oil can be derived from a mineral oil source or made synthetically. The primary role of the oil is to provide a lubricating fluid layer which separates the moving parts of the engine and ultimately increases the engine lifetime. It does this by reducing the friction between the moving parts, but also acts as a solvent to deliver the chemical additives to the critical areas where they are needed, whilst helping to remove heat, chemical contaminates and debris from the moving parts. Suitable base oils are required to maintain optimal viscosity and solubility under operating conditions of high temperature and high pressure.

Chemically, base oils are composed of a complex mixture of hydrocarbons. The hydrocarbons commonly found in base oils can be classed as the following: paraffins,
olefins, naphthenes, aromatics, and heteroaromatics. The chemical composition of the base oil is known to affect the lubricant performance and stability, which varies depending on the source of the crude oil and the processing technology used to refine it. The American Petroleum Institute (API) classifies oils depending on the viscosity index (VI) and the saturated hydrocarbon and sulphur content of the oil (Table 1.6). The viscosity index is a scale used to describe the changes in viscosity of a substance in response to changes in temperature. Oils with a higher VI exhibit less of a decrease in viscosity on increasing temperature than those with a lower VI. The type of oil used impacts oil quality and performance.

<table>
<thead>
<tr>
<th>Group</th>
<th>Saturates</th>
<th>Sulphur</th>
<th>Viscosity Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>&lt; 90%</td>
<td>&gt; 0.03</td>
<td>≥ 80 to &lt; 120</td>
</tr>
<tr>
<td>II</td>
<td>≥ 90%</td>
<td>≤ 0.03</td>
<td>≥ 80 to &lt; 120</td>
</tr>
<tr>
<td>III</td>
<td>≥ 90%</td>
<td>≤ 0.03</td>
<td>≥ 120</td>
</tr>
<tr>
<td>IV</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1.6 Oil classifications according to the API

Engine lubricants come into contact with a number of contaminants due to its proximity to the cylinders and pistons where many combustion products form. The types of contaminants include unburned or partly oxidised fuel components, water, soot and acids. Contaminants can enter the engine oil through contact with the oil layer on the cylinder wall or by being transported along with blow-by-gases past the piston rings and contacting the sump oil in the crankcase.

The accumulation of fuel in the lubricant is known as fuel dilution. The increasing use of biodiesel is leading to FAME and FAME degradation products contaminants being found in engine oils, potentially causing the deterioration of the lubricant at an even quicker rate than the cases without biodiesel use. Without lubricants with the necessary additive reserves for biodiesel use, more frequent oil changes are required, otherwise the function of the lubricant may be compromised, leading to increased wear of the engine and decreased engine life times. Modern diesel engines are often equipped with a diesel particulate filter (DPF). Some engines use in-cylinder post-injection to regenerate the DPF.
This may lead to increased levels of fuel dilution due to fuel contacting the cylinder walls and running down into the oil sump. While for most vehicles the levels of biodiesel fuel dilution are relatively low, biodiesel fuel dilution of 5 – 10% has been reported for engines equipped with in-cylinder post-injection DPF regeneration.\(^{106}\)

### 1.8. Additives

Biodiesel, petro-diesel and engine lubricants all contain additives, which are a blend of components that are incorporated to improve the properties of the fuel or lubricant and to ensure that it also meets the regulated standards. Given the relative ease at which FAME oxidises, the primary additives used in biodiesel are antioxidants. Many biodiesel feedstocks contain significant amounts of natural antioxidants though the concentrations of these can decrease through the processes carried out to yield FAMEs. Other additives important to biodiesel use are cold flow improvers. Petro-diesel has a wider range of additives which serve to improve fuel performance, reliability and comfort, whilst also lowering emissions to meet standards. Engine lubricants contain many additives, some of which can be physical property modifiers of base oil, such as viscosity, oxidative stability and demulsibility. Other additives are used to affect metal surfaces by modifying their physiochemical properties such as reducing, friction, wear and corrosion.

#### 1.8.1. Antioxidants

Antioxidants are a class of compounds that inhibit the oxidation of other molecules. Some antioxidants are naturally occurring species that can be found in biological systems as a means to prevent the oxidation of important biological molecules such as lipids, proteins and DNA, thus maintaining the structural integrity and function of cells. Plant seeds and nuts contain oils as a nutritional source for the seed whilst it germinates. Present in those oils are natural antioxidants such as tocopherol (vitamin E) which help to protect the oils from oxidising. Other natural antioxidants such as ascorbic acid (vitamin C) are found in plant tissues and once more its role is to protect the plant from oxidative stress.

Vitamin E is the most widely distributed antioxidant in nature, found in many vegetable oils, nuts, seeds, grain, and green leafy vegetables. It is fat soluble and stored in the membranes
of its sources. Vitamin E consists of a class of related compounds called tocopherols and tocotrienols. The basic structure of tocopherol and tocotrienol is shown in Figure 1.30. Each has four different homologues - α, β, γ, δ - defined by the R groups attached to the chromanol ring (Table 1.8). The structural relationship between tocopherol and tocotrienol varies only by the degree of unsaturation of the C₁₆ side chain. For tocopherol this consist of a saturated isoprenoid side chain, whilst for tocotrienol the side chain is triply unsaturated in the α–β position relative to the branched methyl groups. Tocotrienol also has the same α, β, γ, δ forms as tocopherol.

![Figure 1.30 Structures of tocopherol and tocotrienol](image)

<table>
<thead>
<tr>
<th>Homologue</th>
<th>R₁</th>
<th>R₂</th>
<th>R₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>Me</td>
<td>Me</td>
<td>Me</td>
</tr>
<tr>
<td>β</td>
<td>Me</td>
<td>H</td>
<td>Me</td>
</tr>
<tr>
<td>γ</td>
<td>Me</td>
<td>Me</td>
<td>H</td>
</tr>
<tr>
<td>δ</td>
<td>Me</td>
<td>H</td>
<td>H</td>
</tr>
</tbody>
</table>

Table 1.7 R groups of tocopherol and tocotrienol homologues

A modern research theme has been the development of synthetic antioxidants that are better inhibitors of oxidation than natural antioxidants. Many compounds have been trialed and screened for their antioxidant performance in various mediums. In a study on the stability of biodiesel storage over a year long period by Bondioli et al., synthetic antioxidants were shown to be more stable than tocopherol. One advantage of using
synthetic antioxidants allows for markedly increased oxidative stabilities whilst using lower concentration of additives.

Antioxidants have many mechanisms by which they may inhibit oxidation, classes include: radical chain breakers, hydroperoxide decomposers, metal chelators, singlet oxygen quenchers. Radical chain breaking species are referred to as primary antioxidants, whilst hydroperoxide decomposers are called secondary antioxidants. Metal chelators such as EDTA help prevent oxidation by binding to metals which can act as initiators of the autoxidation process, whilst singlet oxygen quenchers can quench chemically or physically to either form an oxidised product (of the quencher) or return singlet oxygen to its triplet ground state, respectively.

The radical chain breaking action of an antioxidant arises from the hydrogen donating ability of phenols and amines to intercept some propagating radicals during autoxidation. The reaction between a FAME radical and molecular oxygen is diffusion controlled and therefore too rapid for any other bimolecular reaction to compete with. The hydrogen transfer reaction between a peroxy radical and a FAME molecule is much slower and can be affected by the presence of other species with greater hydrogen donating abilities than the FAME substrate. By transferring the hydrogen atoms of low BDE of functionalised compounds such as hindered phenols or aromatic amines to a peroxy radical, an antioxidant interrupts the propagation cycle of autoxidation by forming the hydroperoxide and a stable antioxidant radical (Figure 1.31 a). The antioxidants radicals formed are stabilised usually by resonance and steric factors which prevent the radicals reacting quickly with un-oxidised substrates. By delocalisation of the radical over the antioxidant molecule, the radical can reside in positions that allow for subsequent termination reactions with other peroxy radicals (Figure 1.31 b), thereby quenching more propagating radicals and increasing the stoichiometric factor of the antioxidant.\textsuperscript{114}
Whilst most radical chain breaking antioxidants work by a hydrogen donating mechanism, a novel application of a species of lactone radicals formed from their dimers as radical chain breaking antioxidants has been reported by Frenette et al.\textsuperscript{112} The group reported that through the thermal dissociation of the dimers two carbon centred radicals are formed, which rather than react with molecular oxygen to form peroxy radicals, undergo termination reactions with peroxy radicals thus trapping propagating radicals and serving as effective antioxidants (Figure 1.32).

In radical chain breaking antioxidants one of the important properties of the compound is the X-H BDE (X = O, N, etc), as this is the bond that is broken during the hydrogen atom transfer from the antioxidant to the peroxy radical. For an antioxidant to act as a good oxidation inhibitor the BDE of X-H must be significantly lower than that of the new bond being formed, in the case of FAME hydroperoxides this value ranges from 88 – 90 kcal mol\textsuperscript{-1}, in order for the reaction to be thermodynamically favourable. Though most effective
antioxidants are phenolic in nature, phenol itself is not a good antioxidant. This can be attributed to the O-H BDE of phenol being approximately 87 kcal mol$^{-1}$, making the hydrogen transfer reaction between phenol and a peroxy radical reversible. Substituted phenols containing electron-donating groups in the ortho and para positions, significantly lowers the O-H BDE.$^{115-117}$ A major drawback of substituting electron-donating groups into a compound results in a lowering of the ionisation potential and subsequent decreases in the air stability of the molecule. It was predicted by Porter et al. that substitution of nitrogen atoms into the 3- and 5- positions into a phenolic structure would improve the ionisation potential whilst also slightly lowering the O-H BDE.$^{110}$ These predictions were confirmed by experimental results, when a 5-pyrimidinol (Figure 1.33) was shown to be air stable whilst also having an inhibition rate constant twice that of $\alpha$-tocopherol.$^{118}$

![Figure 1.33 2-(dimethylamino)-4,6-dimethylpyrimidin-5-ol](image)

The kinetic parameter affecting antioxidant performance is the rate constant of the hydrogen transfer reaction, which for antioxidants is known as the inhibition rate constant, $k_{inh}$. Many studies have been carried out using various techniques to measure the kinetics of these antioxidant reactions by a number of groups.$^{65,108,119,120}$ The rate constant of the hydrogen transfer reaction dictates the effectiveness of an antioxidant, with $k_{inh} > 10^5$ M$^{-1}$ s$^{-1}$ (at 21$^\circ$C) being sufficient to offer complete inhibition against autoxidation, but antioxidants with $k_{inh} < 10^5$ M$^{-1}$ s$^{-1}$ (at 21$^\circ$C) only able to retard autoxidation. Table 1.9 shows the rate constants for hydrogen transfer reactions between various radicals (peroxy, alkoxy and hydroxy) and fatty acid substrates and antioxidants. The reactions between the radicals and antioxidants have greater rate constants than those between the same radicals and fatty acids, demonstrating that the antioxidants will react quicker than the FA substrates and in doing so disrupting the chain branching and propagation reactions of the autoxidation. Also the antioxidants can react faster with alkoxy and hydroxy radicals than the fatty acids, which
is beneficial as alkoxy and hydroxy radicals are both very reactive species capable of abstracting hydrogen from saturated FAs at room temperature.

<table>
<thead>
<tr>
<th>Substrate, S</th>
<th>( k(R^\cdot + S) ), ( \text{M}^{-1}\text{s}^{-1} ) (at 21°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stearic Acid</td>
<td>( 10^{-4} ) ( \sim 10^9 )</td>
</tr>
<tr>
<td>Oleic Acid</td>
<td>( 0.1 \sim 1 ) ( 8.8 \times 10^6 ) ( 9.0 \times 10^9 )</td>
</tr>
<tr>
<td>Linoleic Acid</td>
<td>( 120 ) ( 1.3 \times 10^7 ) ( 7.3 \times 10^9 )</td>
</tr>
<tr>
<td>Linolenic Acid</td>
<td>( 1 \times 10^6 ) ( 4 \times 10^7 ) ( 10^{10} )</td>
</tr>
<tr>
<td>BHT</td>
<td>( 5.7 \times 10^6 ) ( \text{N/D} ) ( 10^{10} )</td>
</tr>
<tr>
<td>( \alpha )-Tocopherol</td>
<td>( 10^4 ) ( 4 \times 10^7 ) ( 10^{10} )</td>
</tr>
</tbody>
</table>

**Table 1.8** Reaction rate constants for oxyl radicals with fatty acids and selected antioxidants in solution at room temperature. Adapted from Simic et al.\(^{121}\)

Secondary antioxidants are a class of compounds that can decompose hydroperoxides. These antioxidants tend to contain sulphur, phosphorus or both elements, and work by reducing hydroperoxides to alcohols with the sulphur or phosphorus atoms being oxidised. Many organosulphur and organophosphorus compounds are able to reduce hydroperoxides to non-radical products such as alcohols and carbonyls. Often compounds containing sulphur and phosphorus are incorporated as ligands to metal complexes to form species such as Zinc dialkyldithiophosphates (ZDDP) and Molybdenum dialkyldithiocarbamates (MDDC) (Figure 1.34). These species have dual functionality as they act as antioxidants as well as having anti-wear and anti-friction properties. ZDDP has been used as an anti-wear agent in engine oils since the 1930’s and has been a common additive in lubricant formulations since, due to its relatively low production cost and multifunctional component action.\(^{122}\)

\[\begin{align*}
\text{RO} & \quad \text{S} & \quad \text{Zn} & \quad \text{S} & \quad \text{P} & \quad \text{OR} \\
\text{RO} & \quad \text{S} & \quad \text{Zn} & \quad \text{S} & \quad \text{P} & \quad \text{OR} \\
\text{R} & \quad \text{S} & \quad \text{Mo} & \quad \text{X} & \quad \text{X} & \quad \text{Mo} & \quad \text{N} & \quad \text{R} \quad \text{X} = \text{S or O} \end{align*}\]

**Figure 1.34** Zinc dialkyldithiophosphate and Molybdenum dialkyldithiocarbamate
The use of transition metal containing compounds such as MDDC in lubricating oils as antioxidants offers an interesting dichotomy. On one hand, transition metals can act as radical scavengers by reducing peroxy radicals and oxidising alkyl radicals to non-radical products (Equations 1.14 and 1.15), whilst on the other hand, they are also quite capable of acting as pro-oxidants by complexing with hydroperoxides and then subsequently decomposing them to form chain propagating peroxy, alkoxy and hydroxy radicals (Equations 1.16 and 1.17).

\[
\text{ROO}^\cdot + \text{M}^{n+} \rightarrow \text{M}^{(n+1)+} + \text{Non-Radical Products} \quad [\text{Eq 1.14}]
\]

\[
\text{R}^\cdot + \text{M}^{(n+1)+} \rightarrow \text{M}^{n+} + \text{Non-Radical Products} \quad [\text{Eq 1.15}]
\]

\[
\text{ROOH} + \text{M}^{n+} \rightarrow (\text{ROOHM})^{n+} \rightarrow \text{M}^{n+} + \text{RO}^\cdot + \text{HO}^\cdot \quad [\text{Eq 1.16}]
\]

\[
\text{ROOH} + \text{M}^{n+} \rightarrow (\text{ROOHM})^{n+} \rightarrow \text{M}^{(n+1)+} + \text{ROO}^\cdot + \text{H}^+ \quad [\text{Eq 1.17}]
\]

Molybdenum dialkyldithiocarbamates have two modes of antioxidant activity, the radical scavenging action of the molybdenum and the hydroperoxide decomposing action of the dialkyldithiocarbamate ligand. Trinuclear MDDC structures with [Mo$_3$S$_4$]$^{4+}$ or [Mo$_3$S$_7$]$^{4+}$ cores with four coordinating dialkyldithiocarbamate ligands have been reported as more effective hydroperoxide decomposers than their binuclear analogues, and are most effective as antioxidants when used in combination with good radical chain breaking antioxidants.

1.8.2. Detergents and Dispersants
Detergents and dispersants are used as diesel fuel and engine lubricant additives with the primary goal of keeping engine surfaces clean and clear of contaminates by neutralising acids, removing sludge and deposit formations. The general structure of a detergents and dispersants consist of a non-polar tail and a polar head group. In the case of dispersants there is a connecting unit between the tail and the head. The polar head group is attracted towards contaminating particles and envelope them to form micelles. The non-polar tail serves to keep the molecule in solution within the base oil or diesel fuel. This mode of action prevents soot particles from aggregating and away from surfaces, thus keeping surfaces clean.
Detergents that are commonly found in diesel fuel range from amines and amides to succinimides, imidazolines, polyetheramines and polyalkyl succinimides. In lubrication formulations metal salts of salicylates, phenates, thiophosphonates, and sulfonates are typically used as detergents. The metals used in detergents tend to be calcium and magnesium. Though barium was once commonly employed, it is rarely these days due to toxicological concerns. Detergents such as salicylates, phenates and sulphonates can also be “over-based” by using an excess of a metal carbonate or hydroxide and carbon dioxide during manufacture, as described by Roman et al. This process results in the formation of a colloid having a metal carbonate core with many detergent molecules surrounding it. Over-based detergents have a metal to surfactant ratio above 1, making this highly basic type of detergent very effective at neutralising the acidic contaminants that form in lubricants as a result of blow-by-gases getting into the crankcase. The general structural features of typical detergents used in lubrication formulations are shown in Figure 1.35.

\[
a) \quad \text{neutral salicylate, } b) \quad \text{basic sulphonate, } c) \quad \text{over-based phenate}
\]

Ashless dispersants differ from detergents as they are metal-free, and whereas detergents neutralise acids, dispersants have the primary role of suspending soot, oxidation and nitration particles. Ashless dispersant are commonly composed of a poly-isobutyl chains, succinic acid connecting units and poly-ethylene amine heads. These compounds are most effective at removing soot, oxidation and nitration particles.

\section{Cold Flow Additives}

Biodiesel, diesel and engine lubricants contain cold weather performance enhancing additives to overcome the issues regarding the crystallisation of FAME and paraffinic components. The main properties of a fuel or lubricant that can be measured to assess the cold flow performance are: cloud point (CP), pour point (PP) and cold filter plugging point.
(CFPP). The cloud point is the temperature at which the fuel starts to visibly precipitate, becoming cloudy and turbid. The pour point is the temperature at which a fluid ceases to flow by becoming a semi-solid. The cold filter plugging point is the temperature where a diesel fuel is unable to pass through a metal sieve filter during a specified period of time. Each of these characteristics can be measured by standard test methods which have been defined by the American Society for Testing Materials or the European Committee for Standardisation.

There are different classes of cold flow additives: Flow improvers, wax anti-settling additives, cloud point depressants and pour point depressants. Each type of additive has different mechanisms by which they work. Flow improvers work by two mechanisms: Firstly the additive creates many nucleation sites for crystallisation at the cloud point, to which wax crystals become adsorbed. Secondly, the additive is adsorbed to the growing crystal which slows the speed at which the crystal grows. These effects result in the formation of many smaller wax crystals rather than the formation of few larger crystals which would form a precipitate. Wax anti-settling additives work by keeping wax crystals in suspension so that they do not form layers of wax. Working in a similar way to flow improvers, wax anti-settling additives slow crystal growth, keeping the crystals small so that they stay suspended for longer, reducing the sedimentation and subsequent formation of wax layers. Cloud point depressants work by shifting the thermodynamic equilibrium to irreversibly reduce the crystallisation temperature. Whilst in lubricants pour point depressants affect the crystal morphology, with smaller, rounder crystals forming rather than needle-like crystals. These small round crystals have less effect on the flow properties of a substance than the needle-like crystals which tend to cause paraffin gelation.

In biodiesel saturated FAMEs tend to be present due to their good oxidative stability relative to their unsaturated analogues. However, the saturated FAMEs have poorer cold performance properties due to the higher melting points when compared to unsaturated FAMEs. The use of smaller carbon chain FAMEs and branched alcohols for forming fatty acid esters with improved cold flow properties has been reported. Whilst the use of other cold flow additives has been shown to improve CFPP properties of FAMEs from various biodiesel feedstocks. Diesel fuel cold flow additives are formed of polymers of vinyl
acetate, unsaturated esters, imides or olefins. Lubricant cold flow additives are polymers such as poly-alkyl methacrylates and poly-alkyl naphthalenes.

1.9. Chemistry in the Crankcase
In the crankcase of an engine fuelled by biodiesel there is an array of different chemicals coming into contact with one another. The various FAMEs and their oxidation products described in section 1.6 encounter hydrocarbon feedstock of diesel fuel and the lubricating engine oils, as well as combustion gases and the performance additives of both the fuel and the oil, in an environment exposed to elevated temperatures. The combination of all these factors results in the potential for a series of complicated chemical reactions and interactions between the components.

1.9.1. FAME and Oxidation Products
The introduction of biodiesel blends into diesel engines is laden with technical issues. Given that the FAMEs used in biodiesel are primarily unsaturated, the oxidative stability of biodiesel tends to be relatively poor, resulting in the formation of a multitude of degradation products (section 1.4). Some of the more problematic FAME oxidative degradation products are the VFAs and the oligomeric/polymeric products.

Studies have shown that the VFAs formed in the greatest concentrations from biodiesel oxidation are formic acid, followed by acetic acid and propionic acid. The strength of linear carboxylic acids decreases with increasing carbon chain length, an effect that can be explained by the electron donating nature of alkyl groups. With increasing chain length there is greater electron density on the carboxylate group, making it harder for the acidic proton to dissociate, as reflected in the $pK_a$ values of the acids in Table 1.9. The acid strength correlates directly to the corrosive properties of organic acids, with the order of acid strength and corrosiveness applying to the following acids: Formic > Acetic > Propionic.
<table>
<thead>
<tr>
<th>Acid</th>
<th>C atoms</th>
<th>pKₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formic</td>
<td>1</td>
<td>3.77</td>
</tr>
<tr>
<td>Acetic</td>
<td>2</td>
<td>4.76</td>
</tr>
<tr>
<td>Propionic</td>
<td>3</td>
<td>4.88</td>
</tr>
</tbody>
</table>

Table 1.9 Structural relationships between selected VFAs and their pKₐ values

It has been shown that the presence of PUFAMEs increases the copper and lead corrosion in laboratory bench tests and lead corrosion in operating diesel engines, though formulations solutions can be found.\textsuperscript{136}

Not only are VFAs from FAME oxidation capable of corroding the metal surfaces of an engine that they come into contact with, but they also can catalyse hydrocarbon oxidation.\textsuperscript{137}

The lubricating oil in the sump, although more stable than FAME owing to its primarily saturated make up, is also prone to oxidation as a result of interactions with acidic degradation products.\textsuperscript{137} The increased concentration of acids in lubricating oils as a result of FAME oxidation has been reported to lower the total base number (a measure of a lubricants alkalinity) of the oil due to reactions with the detergents present.\textsuperscript{138}

Oligomeric and polymeric degradation products pose a different problem in the context of the diesel engine and crankcase. Whereas the presence of acids coming into contact with metal surfaces and lubricating oil causes chemical reactions, the oligomeric and polymeric compounds have more of a physical effect upon surfaces and the lubricant. The high molecular mass compounds that remain in solution in lubricating oil can cause an increase in viscosity of the oil, which compromises its function if the oil becomes too viscous to pump.

As a result of using biodiesel blends the quantity of solid deposits and sludge residues found in the fuel and the lubricating oil has been reported to increase in some cases. As FAMEs are relatively polar compared to petrodiesel, the polar oxidation products formed have the ability to remain in solution in neat FAMEs. However, one set of authors found that when biodiesel blends are prepared within the concentration range of B20 – B30, the formation of solid deposits in the fuel system increases vastly owing to the low polarity of the petrodiesel and its inability to solubilise such polar compounds.\textsuperscript{139} Another group claimed that after 75 hours of an engine test on lubricating oil that had been diluted by a B30 fuel by 15%,
resulting analysis showed that 5% of the oil was composed of FAME derived polymers. The precipitation of oligomeric and polymeric products from fuel and lubricants has the potential to cause blockages of fuel lines and injectors, piston ring sticking, and increased friction between moving parts, all of which may contribute to a decrease in the engine performance and lifetime.

When lubricating oil is diluted by petro-diesel, the diesel will more readily evaporate from the sump under operating temperatures. In the case of oil dilution by FAME, greater accumulation of the fuel in the sump tends to occur due to the narrow, high boiling point range of the FAME molecules. As FAMEs are less viscous than lubricating oil this will tend to reduce the viscosity of the lubricant. The accumulated FAME then has the potential to oxidise in the lubricant.

1.9.2. Blow-by-Gases
The incorporation of exhaust gas recirculation systems into modern engines has led to an increase in the volume of blow-by-gases that are able to enter the crankcase. Blow-by-gases contain a number of reactive species such as oxides of nitrogen (NO\textsubscript{x}) and sulphur dioxide SO\textsubscript{2}, which can react with water to form inorganic acids such as HNO\textsubscript{3} and H\textsubscript{2}SO\textsubscript{4}. These strong acids are capable of catalysing the oxidation of the hydrocarbon base oil, which in turn generates organic acids further propagating the oxidation. Direct reactions between NO\textsubscript{2} and methyl linoleate have also been reported. Formulated engine oils contain basic additives that neutralise organic and inorganic acids. As mentioned in 1.5.3., organic and inorganic acids are corrosive and will degrade the metals surfaces of the engine, leading to increased friction between moving parts, and ultimately reduced engine lifetimes.
2. Experimental
2.1. Introduction
In this chapter, an experimental model is designed to simulate aspects of fuel dilution of the engine oil in the sump by biodiesel under diesel engine crankcase conditions. The development of the model was carried out by a series of trial experiments related to conditions found in the crankcase. The aging of FAME and combinations of base oil and FAME can be carried out by modification of the Rancimat test procedure, EN 14112. Subsequently, an analysis procedure is implemented, whereby aliquots of test samples are removed over the course of the aging experiments and analysed by GC and GC-MS. This process enables the evaluation of the FAME and base oil oxidation by Rancimat induction period measurements, and by identification and quantification of the degradation products formed under the experimental conditions. Literature relevant to the methodology and experimental procedures in this thesis are reviewed. This covers experimental designs, corrosion performance, lubricant dilution by FAMEs (fuel dilution) and crankcase chemistry.

2.1.1. Crankcase Chemistry Literature
Historically, there has been little published work on simulating the impact of FAME on engine oil in the crankcase sump. However, as this project has progressed more studies have emerged related to aspects of this topic. Shaffer and Jette described a laboratory experiment designed to mimic crankcase conditions in order to investigate the effects of diesel engine lubricating oil contaminated by sunflower oil. Their crankcase simulation involved the oxidation of a mixture of 5% sunflower oil in a lubricant with a strip of copper foil as a catalyst, carried out in a resin flask with oxygen or nitrogen percolated through a glass frit at a flow rate of 120 ml/min. The reactions were carried out at 150°C by submerging the flask in an oil bath.

Richard and McTavish investigated the influence of biodiesel upon lubricant corrosion performance. In high temperature corrosion bench tests (HTCBT) on oils diluted by 10% with biodiesels from various sources, those containing biodiesel with higher unsaturated FAME content showed greater copper corrosion than those with greater saturated FAME content. It was shown that the copper corrosion could be significantly lowered by the formulation of the lubricant with an additive booster.
The issue of fuel dilution is discussed in Section 1.7.2. The increasing use of biodiesel is introducing FAME and FAME degradation products into lubricating oils through fuel dilution. The literature reflects this with many reports on the effect of fuel dilution upon lubricating oil stability, and the various methodologies used to study this issue.\textsuperscript{38,142-144}

In 2000 Perez carried out experiments to investigate the effects of fuel dilution on lubricating oil.\textsuperscript{142} In these experiments a method called the crankcase contamination simulation was employed whereby a 1:4 mixture of fuel and lubricant were shaken in a sealed flask for three, one hour periods a day, for seven days after which the fractions were isolated and analysed. Three different fractions were reported, the first being the lubricant layer, the second layer containing the fuel, and the third an emulsion which was rich in additives.

More recently a study by Bannister \textit{et al.} investigated the degradation of biodiesel under simulated oil sump conditions.\textsuperscript{38} In the experiments dodecane was used as a model lubricating oil and was mixed with a model FAME (18:1 or 18:2) in a 50:50 or 75:25 ratio. The sample was placed in a sealed three-neck flask and heated between 90°C and 140°C (citing 140°C as an extreme operating temperature) on an oil bath. A constant air flow was bubbled into the model FAME/oil mixture at 25 L/h with constant stirring. A condenser was connected to the flask in order to condense, collect and monitor by pH the volatile degradation products that formed as a result of the oxidation. The result of the study suggested that the oxidation of FAMEs in the sump could be reduced by lower operating temperatures and aeration in the sump, but acknowledged that this would not be realistically feasible. They suggested as an alternative that more antioxidants could be introduced to the sump instead.

Other investigations on the effects of the contamination of lubricating oil by FAMEs or neat vegetable oils have been reported. Seikmann \textit{et al.} diluted a lubricant with SME at levels of 5%, 10%, and 20% and carried out laboratory, bench and driven engine tests.\textsuperscript{143} The laboratory test involved the use of a MacCoull apparatus which simulates engine bearing working conditions at 150 and 170°C. After 8 hours testing the viscosity of the lubricant had increased whilst the total base number had decreased. Interestingly, the bench engine tests
results were not as extreme as the laboratory tests and the driven engine test were less harsh than the bench tests.

Kowalski reported the influence of lubricant dilution by pure rapeseed oil on the oxidative stability of the lubricant. The experiments were carried out using pressure differential scanning calorimetry (PDSC) to determine the onset of oxidation for lubricants that had been contaminated by rapeseed oil of amounts between 2 – 10%. The results of the testing led to the conclusion that the rapeseed oil dramatically decreased the oxidative stability of the lubricant.

2.2. Methodology
The increasing use of biodiesel as a diesel fuel extender requires research into the effects of introducing FAME and their oxidation products into direct contact with engine lubricants and the components within. There is potential for interactions between FAMEs, oxidation products and automotive lubricants in the crankcase under elevated temperatures (100 – 150°C), which can possibly lead to lubricant contamination and shorter oil drain intervals for oils which do not have the necessary additive reserves. Given the reports outlined in Sections 2.1.1 and 2.1.2, the most important factors in crankcase simulation under the conditions most related to biodiesel degradation are temperature, air/oxygen flow and fuel dilution. Control of these variables can be implemented by use of the Rancimat apparatus.

2.2.1. Rancimat Oxidations
The majority of the experiments carried out in this thesis are standardised oxidations using the Metrohm Biodiesel Rancimat apparatus, ensuring consistent experimental procedures are applied. The Standard method for measuring the oxidative stability of a FAME outlined in EN 14112, requires an operating temperature of 110°C with an air flow rate of 10 L/h. The tests should be carried out on a 3 g sample of the test material and the measuring vessel must contain 60 ml of water. Though the standard method requires a 3 g FAME sample, in this series of experiments a 4 g sample is used to compensate for the removal of aliquots for analysis during the course of the oxidations.
A schematic of the Metrohm Biodiesel Rancimat apparatus is shown in Figure 2.1 and describes the operation of the equipment. The apparatus consists of two heating blocks, each with 4 individual positions for reaction vessels, allowing for a total of 8 simultaneous oxidations to be carried out. A reaction vessel is loaded with 4 g of a sample to be oxidised and placed into a heating block position. On heating, with the passing of air at a constant flow rate through the sample, oxidation occurs. Oxidation of FAME gives rise to formation of volatile fatty acids (VFAs) such as formic and acetic acid. The VFAs pass from the reaction vessel to the measuring vessel where they dissolve in the water present and cause an increase in the conductivity of the cell. The change in conductivity is detected by a probe and is recorded at regular time intervals.

![Figure 2.1 Rancimat schematic (From Metrohm Biodiesel Rancimat user manual)](image)

Plotting the conductivity of the measuring vessel solution over time gives graphs like that shown in Figure 2.2. The most important feature of the generated graphs is the inflection of plot, which represents induction period (IP) of the sample being tested. The IP can be defined by the point at which the gradients of the curve (either side of the inflection) cross, which can then be read against the x (time) axis to give a value equal to the IP. The IP is automatically recorded and determined by the Rancimat apparatus, though can also be manually determined.
The induction period is the measure of oxidative stability of a substance and is given a value with the specified unit of time in hours. The specifications in EN 14214 require a biodiesel to have a minimum IP of 6 hours under the conditions outlined in EN 14112. An IP of 6 hours ensures a shelf life of about 1 year under ambient conditions.

2.2.2. Sampling Procedure
Aliquot samples were taken from the Rancimat oxidation apparatus periodically with a heavy emphasis on the first six hours of the oxidation. Unless otherwise stated, the sampling periods were as follows: 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 9, 12, 15, 18, 21, 24, 27, 30, 33, 36, 39, 42, 45, and 48 hours (± 1 min). To overcome the issue of availability for sample taking, a 12 hour staggering of the oxidation reactions was applied. Utilising the twin heating block feature of the Rancimat, the first set of sample oxidations were started at t = 0 h, whilst a duplicate set of sample oxidations were started when t = 12 h for the first set of samples. This allowed a continual sampling period whereby the data set was recorded at the desired intervals.

Aliquots (20 µl) were removed directly from the reaction vessel by a calibrated pipette and prepared for quantitative GC analysis by mixing with a stock solution of ethyl acetate (400
μl) containing an internal standard (nonadecane, ca. 1.5 mol %). The samples were stored at -20°C in the absence of light until ready for analysis by GC. Before running the GC the samples were allowed to warm to room temperature and shaken to dissolve any precipitate. In order to evaluate the hydroperoxide concentration of the samples, after GC analysis of each sample an excess of PPh₃ (a micro spatula tip) was added to reduce hydroperoxides to the corresponding alcohol (Figure 2.3).

![Figure 2.3 Hydroperoxide reduction by triphenylphosphine](image)

The samples were then analysed again by GC and the difference between the alcohol yields before and after PPh₃ treatment was used to calculate the hydroperoxide content. A more detailed review of hydroperoxide detection and quantification is discussed in Section 3.3.2.

2.2.3. Repeatability
In order to assess the repeatability of the experimental system, multiple oxidative degradation reactions using methyl oleate as the substrate were carried out using the test method outlined in Section 2.2.1. Four separate reactions were undertaken and evaluated by measuring the change in concentration by GC during the decomposition of methyl oleate and the formation of a major degradation product over the first 6 hours of oxidation (Figure 2.4).
Figure 2.4 Plots of concentration vs. time for a) methyl oleate degradation and b) monomeric degradation product formation during oxidation of methyl oleate.

Table 2.1 shows the data values plotted in Figure 2.4 a, the induction period and the calculated statistical analysis (mean, standard deviation (SD), and relative standard deviation (RSD)) for the degradation of methyl oleate in each of the individual oxidations. Though the largest RSD for the concentration measurements is approximately 8% the averaged RSD is 2.87 %, which reflects good repeatability for this experimental system. The induction periods show a greater degree of variation than the concentration measurements, though this is likely to be due to the difficulty in quantifying the very short induction periods that methyl oleate exhibits.
<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
<th>Run 4</th>
<th>Mean</th>
<th>SD</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>2.81</td>
<td>2.75</td>
<td>2.70</td>
<td>2.70</td>
<td>2.74</td>
<td>0.05</td>
<td>1.87</td>
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<tr>
<td>1</td>
<td>2.69</td>
<td>2.68</td>
<td>2.48</td>
<td>2.50</td>
<td>2.58</td>
<td>0.11</td>
<td>4.44</td>
</tr>
<tr>
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<td>2.50</td>
<td>2.33</td>
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<td>2.64</td>
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<td>2.28</td>
<td>2.45</td>
<td>0.20</td>
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<tr>
<td>2.5</td>
<td>2.17</td>
<td>2.18</td>
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<td>2.21</td>
<td>2.19</td>
<td>0.02</td>
<td>0.82</td>
</tr>
<tr>
<td>3</td>
<td>2.15</td>
<td>2.16</td>
<td>2.10</td>
<td>2.08</td>
<td>2.12</td>
<td>0.04</td>
<td>1.83</td>
</tr>
<tr>
<td>3.5</td>
<td>2.18</td>
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<td>1.94</td>
<td>1.94</td>
<td>2.00</td>
<td>0.12</td>
<td>6.03</td>
</tr>
<tr>
<td>4</td>
<td>1.99</td>
<td>1.96</td>
<td>1.85</td>
<td>1.86</td>
<td>1.92</td>
<td>0.07</td>
<td>3.58</td>
</tr>
<tr>
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<td>1.73</td>
<td>1.75</td>
<td>1.76</td>
<td>1.77</td>
<td>1.75</td>
<td>0.02</td>
<td>0.87</td>
</tr>
<tr>
<td>5</td>
<td>1.64</td>
<td>1.62</td>
<td>1.61</td>
<td>1.61</td>
<td>1.62</td>
<td>0.01</td>
<td>0.83</td>
</tr>
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<td>5.5</td>
<td>1.57</td>
<td>1.56</td>
<td>1.56</td>
<td>1.56</td>
<td>1.56</td>
<td>0.01</td>
<td>0.45</td>
</tr>
<tr>
<td>6</td>
<td>1.42</td>
<td>1.43</td>
<td>1.47</td>
<td>1.47</td>
<td>1.45</td>
<td>0.03</td>
<td>1.80</td>
</tr>
<tr>
<td>IP (h)</td>
<td>0.48</td>
<td>0.43</td>
<td>0.51</td>
<td>0.60</td>
<td>0.51</td>
<td>0.07</td>
<td>14.1</td>
</tr>
</tbody>
</table>

Table 2.1 Measurements of methyl oleate concentration (M) and induction period (IP) in four separate oxidations to demonstrate repeatability of experimental system.

Table 2.2 shows the data values plotted in Figure 2.4 b and the calculated statistical values related to the formation of a degradation product of methyl oleate. Again, the highest RSD is approximately 8 % which can be attributed to the low concentration values recorded. The average RSD is 3.7%, proving good repeatability of the experimental system employed for these studies.
<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
<th>Run 4</th>
<th>Mean</th>
<th>SD</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.007</td>
<td>0.006</td>
<td>0.007</td>
<td>0.007</td>
<td>0.007</td>
<td>0.000</td>
<td>6.796</td>
</tr>
<tr>
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<td>0.015</td>
<td>0.015</td>
<td>0.015</td>
<td>0.017</td>
<td>0.016</td>
<td>0.001</td>
<td>7.855</td>
</tr>
<tr>
<td>1.5</td>
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<td>0.026</td>
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<td>0.028</td>
<td>0.028</td>
<td>0.001</td>
<td>5.297</td>
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<tr>
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<td>0.047</td>
<td>0.042</td>
<td>0.045</td>
<td>0.045</td>
<td>0.002</td>
<td>4.376</td>
</tr>
<tr>
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<td>0.059</td>
<td>0.060</td>
<td>0.060</td>
<td>0.059</td>
<td>0.001</td>
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<td>3</td>
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<td>0.077</td>
<td>0.079</td>
<td>0.077</td>
<td>0.078</td>
<td>0.002</td>
<td>2.159</td>
</tr>
<tr>
<td>3.5</td>
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<td>0.093</td>
<td>0.094</td>
<td>0.095</td>
<td>0.093</td>
<td>0.002</td>
<td>1.919</td>
</tr>
<tr>
<td>4</td>
<td>0.125</td>
<td>0.121</td>
<td>0.113</td>
<td>0.114</td>
<td>0.118</td>
<td>0.006</td>
<td>4.765</td>
</tr>
<tr>
<td>4.5</td>
<td>0.131</td>
<td>0.137</td>
<td>0.129</td>
<td>0.127</td>
<td>0.131</td>
<td>0.004</td>
<td>3.275</td>
</tr>
<tr>
<td>5</td>
<td>0.149</td>
<td>0.150</td>
<td>0.142</td>
<td>0.139</td>
<td>0.145</td>
<td>0.006</td>
<td>3.826</td>
</tr>
<tr>
<td>5.5</td>
<td>0.167</td>
<td>0.168</td>
<td>0.154</td>
<td>0.158</td>
<td>0.162</td>
<td>0.007</td>
<td>4.079</td>
</tr>
<tr>
<td>6</td>
<td>0.172</td>
<td>0.177</td>
<td>0.175</td>
<td>0.175</td>
<td>0.175</td>
<td>0.002</td>
<td>1.207</td>
</tr>
</tbody>
</table>

Table 2.2 Measurements of degradation product formation (M) in four separate oxidations to demonstrate repeatability of experimental system

2.3. Measurements and Analysis

2.3.1. Chromatographic Analysis

Identification of oxidation products was achieved by GC-MS, using a VG AutoSpec-Q mass spectrometer fitted with a Hewlett-Packard 5890 gas chromatograph; J&W BD-5MS column with a cross linked/surface bonded 5 % phenyl, 95% methylpolysiloxane stationary phase (30 m, 0.25 mm ID, 0.25 μm). Data analysis was carried out using MassLynx MS software. Identification of oxidation products was further aided by comparison of mass spectra to those reported in the various chemical literature sources.

Quantification of identified oxidation products was carried out on samples prepared by the description in section 2.2.2. The samples were analysed by injection into a Hewlett-Packard 5890 series II gas chromatograph, fitted with a J&W DB-5 column with a cross linked/surface bonded 5% phenyl, 95% methylpolysiloxane stationary phase (30 m, 0.25 mm ID, 0.25 μm). The analysis was conducted by the use of a flame ionization detector and Clarity Chromatography Station Version 2.7.3.498, by DataApex. Method conditions were; 10 mins at 100°C, 12°C/min to 320°C with a hold for 10 mins. The carrier gas used was helium at a
flow rate of 1.6 ml/min. Injector temperature was 240°C and detector temperature was 320°C. Quantification was achieved using calibrated standards when available, and the effective carbon number (ECN) concept.\textsuperscript{146}

Figure 2.5 shows how overlapping GC peaks were resolved by fitting multiple Gaussian curves using Microcal OriginLab Version 8.5.

![Diagram](image.png)

**Figure 2.5** Overlapping peaks from GC trace (black line) and resolved peaks (red lines)

### 2.3.2. Spectroscopic Analysis

Infrared (IR) spectroscopy was carried out using a Perkin Elmer Spectrum 100 series spectrometer with a universal ATR sampling accessory and Spectrum Express software. Nuclear magnetic resonance (NMR) spectroscopy measurements were carried out at 298 K using a Bruker AV-400 spectrometer.
2.4. Model Development
Some factors were trialled during the model development phase to simulate various aspects of crankcase interactions. Not all of the trial experiments were included in the final experimental model.

2.4.1. Blow-by-Gases
Blow-by-gases have been considered for inclusion as part of the experimental model. The Rancimat apparatus has an external gas inlet allowing the capability to connect external gas sources; these can be used as alternatives to the airflow that is used under the normal operating conditions. A cylinder of a custom gas made to the following specification: NO$_2$ (766 ppm); O$_2$ (22 %); and N$_2$ (make up gas) was acquired as a model for a NO$_x$ blow-by-gas.

The model NO$_x$ gas was introduced to the Rancimat via the external gas inlet and samples of FAMEs were degraded at 110°C with the gas at a flow rate of 10 L/h. However, due to an error in the preparation of the NO$_x$ model the gas source had fully depleted after just 3 hours, a time span significantly shorter than the 48 hours that had been anticipated. IR analysis of the samples collected during the experiment showed no sign of FAME nitration that has been reported elsewhere.$^{140}$ Owing to logistical issues surrounding the acquisition of the gas, this model was not attempted again.

2.4.2. Fuel Dilution
To simulate aspects of the effects of fuel dilution, model blends of soybean methyl ester (SME) and polyalphaolefins (PAO) in a 1:1 ratio were prepared. Along with samples of neat SME and neat PAO, these solutions would later be tested under the implemented experimental and analytical procedures.

2.4.3. Acid Product Distribution Analysis
Analysis on water samples from the measuring vessel were carried out by GC in an attempt to detect and quantify the volatile acids formed from FAME oxidations that were trapped by
the measuring solution. For methyl oleate oxidised at 110°C and 150°C volatile acid content of the endpoint water samples are shown in Table 2.3.

<table>
<thead>
<tr>
<th>Oxidation Temperature (°C)</th>
<th>Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acetic</td>
</tr>
<tr>
<td>110</td>
<td>1269.6</td>
</tr>
<tr>
<td>150</td>
<td>645.9</td>
</tr>
</tbody>
</table>

Table 2.3 Volatile fatty acid (VFA) content (ppm) of Rancimat measuring solutions after 48 h oxidation of methyl oleate at 110°C and 150°C

A higher concentration of each acid detected was observed for the oxidation of methyl oleate at 110°C than 150°C, with acetic acid forming in the greatest concentration in both cases. A study has shown that formic acid has the greatest influence upon the conductivity of the measuring solution,\(^\text{147}\) whilst another has shown that formic acid forms in the highest concentration in unsaturated FAMEs oxidised under similar conditions to those carried out here.\(^\text{148}\) Unfortunately using this analytical method it is not possible to detect or quantify formic acid. This factor proved decisive in the decision not to employ it as part of the experimental model any further.

2.4.4. Temperature

Temperature is a critical aspect of the experimental model. The temperature that FAMEs and lubricating oil are exposed to in an operational crankcase ranges from 100 – 150°C.\(^\text{103}\) The experimental model should therefore reflect these conditions. A study on methyl oleate was carried out in which the FAME was oxidised at 110, 120, 130, 140, and 150°C in order to determine suitable conditions of the experimental model.
The increase in temperature results in an increase in the rate of methyl oleate oxidation (Figure 2.6 b and Table 2.4). The variation in rate constants for 18:1 oxidation at different temperatures allows for assessment of the temperature dependence of the methyl oleate oxidation by plotting an Arrhenius diagram (Figure 2.7). The data from the Arrhenius plot can be used to calculate the activation energy of the oxidation of methyl oleate, as the expression shown in Equation 2.1 can be simplified to Equation 2.2, and solved using the value obtained from the gradient in Figure 2.7 and the gas constant (R) to give an activation energy ($E_a$) for methyl oleate oxidation of 18.6 kJ mol$^{-1}$ (Equation 2.3).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$k$ (h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>0.1291 (± 0.03)</td>
</tr>
<tr>
<td>120</td>
<td>0.1521 (± 0.02)</td>
</tr>
<tr>
<td>130</td>
<td>0.1652 (± 0.03)</td>
</tr>
<tr>
<td>140</td>
<td>0.1852 (± 0.04)</td>
</tr>
<tr>
<td>150</td>
<td>0.2343 (± 0.03)</td>
</tr>
</tbody>
</table>

Table 2.4 Rate constants ($k$) for methyl oleate oxidation at various temperatures
The value for the activation energy of 18:1 oxidation obtained through the Arrhenius equation (Equation 2.1) is much lower than the typical BDE of an allylic C-H bond of 347 – 364 kJ mol\(^{-1}\).\(^{56}\) The reason for this may be due to testing at too narrow temperature range. Oxidations at temperatures lower than 110\(^{\circ}\)C and higher than 150\(^{\circ}\)C may give values closer to the literature values.

From the tests carried out it was decided to operate the experimental model at 110\(^{\circ}\)C. Though variation in the recorded oxidation rate constants was observed on varying the temperature, at the lower operating temperature the degradation of the FAME occurs at rate which is easier to analyse. 110\(^{\circ}\)C is within the operational temperature range of the crankcase and also complies with the standard test method for testing oxidative stability of biodiesel.
2.4.5. Metal Catalysis

The formation of acids from FAME oxidation can lead to an increased amount of corrosion of the metals found in the engine, which can result in higher levels of metals in crankcase lubricants from biodiesel use. Metals such as copper and lead that are used in engine bearings can be particularly susceptible to corrosion by acids, hydroperoxides and peroxides,\textsuperscript{149} whilst iron corrosion leads to the formation of rust particles. Solubilised metals can act as oxidation catalysts of the hydrocarbons present in the oil and also FAME.

Experiments with the acetylacetonate (acac) salts of Fe(II), Fe(III), Cu(II) and Pb(II) were added at various concentrations (approximately 2.5, 5, and 10 mg/ml) to methyl oleate and oxidised under standard Rancimat conditions. The results in Figure 2.8 show that under the Rancimat oxidation conditions at a metal doping level of 40 mg, Fe (II), Fe(III) and Pb(II) reduce the methyl degradation by a small amount. At lower levels of metal doping no significant effects are observed. The data points for Fe(II) and Fe(III) are very close to one another, suggesting that Fe(II) may oxidise to Fe(III) under these experimental conditions. Given the minimal effects observed from these trials, the use of metal catalysts were not included in the experimental model.
2.5. Materials

2.5.1. Rancimat Oxidation Substrates
The substrates subjected to Rancimat oxidation tests are listed in Table 2.5. The biodiesel samples were supplied with assurances that they were synthetic antioxidant free. The substrates were used without further purification.

<table>
<thead>
<tr>
<th>Name</th>
<th>Abbreviated Name</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl Stearate</td>
<td>18:0</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Methyl Oleate</td>
<td>18:1</td>
<td>Sequioa Research Products</td>
</tr>
<tr>
<td>Methyl Linoleate</td>
<td>18:2</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Methyl Linolenate</td>
<td>18:3</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Rapeseed methyl ester biodiesel</td>
<td>RME</td>
<td>Greenergy</td>
</tr>
<tr>
<td>Soybean methyl ester biodiesel</td>
<td>SME</td>
<td>Infineum U.K. Ltd</td>
</tr>
<tr>
<td>Polyalphaolefin</td>
<td>PAO</td>
<td>Infineum U.K. Ltd</td>
</tr>
</tbody>
</table>

Table 2.5 Materials used for Rancimat oxidations classified by: Name; Abbreviated Name; and Source

Figure 2.8 The influence of metals upon methyl oleate degradation at doping levels of: a) 2.5 mg/ml; b) 5 mg/ml; c) 10 mg/ml at 110°C
2.5.2. Reagents for Synthesis

Reagents and solvents used for synthesis are listed in Table 2.6. The reagents were used without further purification.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Purity</th>
<th>Supplier</th>
<th>CAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc Acetate dihydrate</td>
<td>≥ 98 %</td>
<td>Sigma Aldrich</td>
<td>5970-45-6</td>
</tr>
<tr>
<td>Phosphorus Pentasulphide</td>
<td>99 %</td>
<td>Sigma Aldrich</td>
<td>1314-80-3</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>≥ 99 %</td>
<td>VWR/Prolabo</td>
<td>603-117-00-0</td>
</tr>
<tr>
<td>Ethanol</td>
<td>96 %</td>
<td>VWR/Prolabo</td>
<td>603-002-00-5</td>
</tr>
<tr>
<td>Petroleum Spirit 60 – 80°C</td>
<td>N/A</td>
<td>VWR/Prolabo</td>
<td>649-328-00-1</td>
</tr>
</tbody>
</table>

Table 2.6 Reagents and solvents used for synthesis

2.6. Synthesis Procedures

2.6.1. Synthesis of \( ^{1} \text{Pr} \text{ZDDP} \)

\[
P_{4}S_{10} + ^{1}\text{PrOH} \rightarrow \text{Zn(OAc)}_{2} \cdot 2 \text{H}_{2}\text{O/EtOH}
\]

The method used was carried out following the procedure described in the literature.\(^{150}\) \(P_{4}S_{10}\) (5.01 g, 11 mmol) was stirred in isopropanol (9 ml, 118 mmol) for 30 mins. The pale yellow/green solution was then stirred for a further 30 mins at 80\(^{o}\)C during which the solution turned colourless. Meanwhile Zn(OAc)\(_{2}\) \(\cdot 2\)H\(_{2}\)O (4 g, 18 mmol) was dissolved in hot ethanol (14 ml), which was added to the isopropanol/\(P_{4}S_{10}\) solution and stirred for a further 15 mins. The solution was allowed to cool to room temperature then stored in a freezer at -20\(^{o}\)C for 2 h. White crystals precipitated and were separated by gravity filtration before being washed with H\(_{2}\)O. The solid product was dried in an oven at 80\(^{o}\)C (2.39 g, 31 %) before recrystallisation three time from petroleum spirit 60 – 80\(^{o}\)C. White crystals (1.17 g, 15.19 %).

\(^{1}\)H NMR (400 MHz, 298 K, CDCl\(_{3}\)): \(\delta\) (ppm) = 1.43 (d, 12H, CH-\(\text{CCH}_{3}\), \(J\) = 6.29 Hz); 4.89 (m, 2H, CH\(_{3}\)-CH, \(J\) = 6.29). \(^{13}\)C\({}^{1}\)H NMR (100 MHz, 298 K, CDCl\(_{3}\)): \(\delta\) (ppm) = 23.55 (CH(CH\(_{3}\))\(_{2}\)); 74.33 (CH(CH\(_{3}\))\(_{2}\)). \(^{31}\)P\({}^{1}\)H NMR (162 MHz, 298 K, CDCl\(_{3}\)): \(\delta\) (ppm) = 91.76. IR (ATR): \(\nu\) (cm\(^{-1}\)) = 1165, 1127 (PO-C); 984, 961 (P-OC); 650, 640 (P-S).
2.7. Conclusions
In this chapter the model for simulating aspects of the crankcase environment has been developed. Having reviewed literature and carried out a series of trial experiments, the relevant aspects of crankcase chemistry were highlighted as the operating temperature, and the issue of fuel dilution. The experimental model developed uses the Rancimat apparatus operating under a modified version of the standard test method for measuring oxidative stability as defined in EN 14112,\textsuperscript{31} in which 4 g sample of substrate is used rather than a 3 g sample. A temperature (110°C) within the range of those found in the crankcase during operation is used. Air is provided at a constant flow rate of 10 L/min. These conditions provide a suitable model that can be used to mimic the crankcase.

An analytical procedure primarily utilising chromatographic techniques is employed to allow for qualitative (GC-MS) and quantitative (GC) analysis of the degradation products formed during the oxidation. A sampling technique has also been developed to include the detection and quantification of hydroperoxides into the analysis. Overlapping GC peaks have been resolved using Microcal OriginLab Version 8.5.
3. Product Distribution Analysis of C18 FAME Degradation
3.1. Introduction
The oxidation of FAMEs leads to the formation of a number of degradation products, which can be classified as the following – volatile, monomeric and polymeric. Identification and quantification of these degradation products formed during the course of FAME oxidation provides information from which FAME oxidation pathways can be determined. In this chapter, previous literature on C18 fatty acid and FAME oxidation product distribution analysis is reviewed. This is followed by product distribution analysis carried out upon a series C18 FAMEs (Figure 3.1) with varying degrees of unsaturation using the simulated crankcase conditions developed in Chapter 2. This provides information on the oxidative pathways that are occurring under the experimental conditions, for a representative sample of FAMEs commonly found in commercially available biodiesel. This leads to progress in achieving the primary goal of the studies carried out in this chapter, of gaining an understanding of the FAME oxidation pathways under simulated crankcase conditions.

![Figure 3.1 C18 FAME series used in this study: a) methyl stearate (18:0); b) methyl oleate (18:1); c) methyl linoleate (18:2); d) methyl linolenate (18:3)]
### 3.1.1. Oleate Oxidation

In a series of papers, Frankel et al. demonstrated the value of product distribution analysis for identifying oxidation mechanisms of FAME.\(^{51,57,79,81,86,89,102,151-153}\) Others too have contributed with studies involving the photo-oxidation\(^ {154}\) and autoxidation\(^ {155}\) of fatty acids, FAMES\(^ {88}\) and triacylglycerols\(^ {156-158}\) having lead to the isolation and identification of many primary and secondary oxidation products. Photo-oxidation and autoxidation can be differentiated by the product distribution analysis, with either the generation of certain unique products or the absence of particular products indicating the oxidation pathway. In the case of methyl oleate the distribution of the hydroperoxides formed from autoxidation was reported to be fairly consistent over a range of temperatures and peroxide values (PV) as shown in Table 3.1.\(^ {57}\)

<table>
<thead>
<tr>
<th>PV (meq)</th>
<th>Temp (°C)</th>
<th>Relative Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>8-OH</td>
</tr>
<tr>
<td>461</td>
<td>25</td>
<td>26.6</td>
</tr>
<tr>
<td>72</td>
<td>40</td>
<td>26.3</td>
</tr>
<tr>
<td>200</td>
<td>40</td>
<td>27.5</td>
</tr>
<tr>
<td>401</td>
<td>40</td>
<td>27.9</td>
</tr>
<tr>
<td>282</td>
<td>60</td>
<td>27.1</td>
</tr>
<tr>
<td>597</td>
<td>60</td>
<td>26.2</td>
</tr>
<tr>
<td>791</td>
<td>60</td>
<td>27.5</td>
</tr>
<tr>
<td>355</td>
<td>80</td>
<td>26.4</td>
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<td>775</td>
<td>80</td>
<td>26.8</td>
</tr>
<tr>
<td>1232</td>
<td>80</td>
<td>26.2</td>
</tr>
</tbody>
</table>

**Table 3.1** Distribution of methyl oleate hydroperoxides determined by GC-MS from the autoxidation of methyl oleate by Frankel et al.\(^ {57}\)

When product distribution analysis was carried out on photo-oxidised methyl oleate only two hydroperoxides were detected as a result of the “ene” reaction mechanism between singlet oxygen and the olefin site in methyl oleate (Table 3.2). The lack of hydroperoxides in the 8 and 11 positions demonstrated that the oxidation was proceeding through a non-radical process.\(^ {51}\) However, when the hydroperoxides of autoxidised and photo-oxidised methyl oleate are thermally degraded, the same volatile degradation products can be
observed. This is due to significant isomerisation of the 9- and 10-hydroperoxides of the photo-oxidised product to give the 11- and 8-hydroperoxides respectively. The yields of the hydroperoxides from autoxidation and photo-oxidation before and after thermal treatment show the photo-oxidised methyl oleate still has a higher proportion of 9- and 10-hydroperoxides than the autoxidised methyl oleate (Table 3.3). This is also reflected in the yields of the volatile degradation products formed as a result of hydroperoxides decomposition.

<table>
<thead>
<tr>
<th>Methyl Ester</th>
<th>PV (meq)</th>
<th>Time (h)</th>
<th>9-OH</th>
<th>10-OH</th>
<th>12-OH</th>
<th>13-OH</th>
<th>15-OH</th>
<th>16-OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oleate</td>
<td>1727</td>
<td>6</td>
<td>47.7</td>
<td>52.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Linoleate</td>
<td>1124</td>
<td>3</td>
<td>31.9</td>
<td>16.7</td>
<td>17.0</td>
<td>34.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Linolenate</td>
<td>1566</td>
<td>2</td>
<td>22.7</td>
<td>12.7</td>
<td>12.0</td>
<td>14.0</td>
<td>13.4</td>
<td>25.2</td>
</tr>
</tbody>
</table>

Table 3.2 Distribution of methyl ester hydroperoxides determined by GC-MS from the photo-oxidation of methyl esters at 0°C by Frankel et al.51

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Pyrolysis (200°C)</th>
<th>Relative Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Autoxidation (40°C, PV 1051)</td>
<td>Before</td>
<td>27 23 23 27</td>
</tr>
<tr>
<td>Photo-oxidation (0°C, PV 1727)</td>
<td>Before</td>
<td>50 50</td>
</tr>
<tr>
<td>Photo-oxidation (0°C, PV 1727)</td>
<td>After</td>
<td>18 26 31 25</td>
</tr>
</tbody>
</table>

Table 3.3 Methyl oleate hydroperoxides distribution before and after partial pyrolysis79

3.1.2. Linoleate Oxidation

In methyl linoleate autoxidation the different hydroperoxides form in an approximately equal distribution over a range of different temperatures and peroxide values as shown in Table 3.4. Under autoxidation conditions the addition of oxygen occurs exclusively at the terminal positions of the pentadienyl system, resulting in hydroperoxides at the 9-, and 13-sites for linoleate only. When methyl linoleate undergoes photo-oxidation, the “ene” reaction results in the formation of four isomeric FAME hydroperoxides. This mechanism allows the formation of internal hydroperoxides in the 10-, and 12-positions giving non-conjugated diene products that cannot be realised by autoxidation (Table 3.2). The presence
of these species in the product distribution is a prime indication of photo-oxidation. The terminal hydroperoxides (positions 9 and 13) from linoleate photo-oxidation are still the major products and compared to the internal hydroperoxides are formed in an approximate ratio of 2:1. This preference may be explained by the stability gained through the conjugated dienes formed in these products.

<table>
<thead>
<tr>
<th>PV (meq)</th>
<th>Temp (°C)</th>
<th>Relative Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>9-OH</td>
</tr>
<tr>
<td>152</td>
<td>40</td>
<td>50.2</td>
</tr>
<tr>
<td>261</td>
<td>40</td>
<td>51.7</td>
</tr>
<tr>
<td>686</td>
<td>40</td>
<td>49.7</td>
</tr>
<tr>
<td>918</td>
<td>40</td>
<td>49.6</td>
</tr>
<tr>
<td>93</td>
<td>60</td>
<td>47.3</td>
</tr>
<tr>
<td>505</td>
<td>60</td>
<td>51.5</td>
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<tr>
<td>1403</td>
<td>80</td>
<td>49.0</td>
</tr>
<tr>
<td>1249</td>
<td>80</td>
<td>52.5</td>
</tr>
</tbody>
</table>

Table 3.4 Distribution of methyl linoleate hydroperoxides determined by GC-MS from the autoxidation of methyl linoleate by Frankel et al.\textsuperscript{89}

3.1.3. Linolenate Oxidation

Autoxidation of methyl linolenate leads to the formation of four isomeric hydroperoxides at the 9-, 12-, 13-, and 16-positions (Table 3.5).\textsuperscript{86} The distribution shows selectivity towards the terminal sites, of which hydroperoxide formation at the \( \omega \) terminal is preferred over the \( \Delta \) terminal of the pentadienyl system (for terminology see section 1.3.1). Each of the hydroperoxides formed through autoxidation of methyl linolenate results in the formation of a conjugated diene system. Photo-oxidation of methyl linolenate gives rise to six isomeric hydroperoxides, including non-conjugated diene derivatives at the 10-, and 15-positions (Table 3.2). As with autoxidation, there is a preference for the formation of hydroperoxides at the \( \omega \) terminal over the \( \Delta \) terminal of the FAME in photo-oxidation too. This trend may be attributed to steric factors.
Frankel et al. report that both linoleate and linolenate hydroperoxides derived from autoxidation and photo-oxidation showed little sign of isomerisation under thermal degradation conditions. As a result the variation in hydroperoxides yields between the two oxidations remains, and the volatile product distribution by thermal degradation of autoxidation and photo-oxidation induced hydroperoxides varies greatly in the concentrations of the products formed.

### 3.2. Real FAME Composition Analysis

Samples of soybean methyl ester (SME) and rapeseed methyl ester (RME) were analysed by the Rancimat to determine the oxidative stability and by GC to calculate the relative FAME composition of each of the samples (Table 3.6). The relative composition of the FAME
samples is made up of saturated, monounsaturated and polyunsaturated FAME ranging from 14 to 22 carbon atoms long, the majority of which are accounted for as the C18 series.

<table>
<thead>
<tr>
<th>FAME</th>
<th>Soybean*</th>
<th>Rapeseed*</th>
<th>Soybean$^{159}$</th>
<th>Rapeseed$^{159}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>14:0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>16:0</td>
<td>10.8</td>
<td>0.3</td>
<td>10.9</td>
<td>5.1</td>
</tr>
<tr>
<td>16:1</td>
<td>0.1</td>
<td>4.6</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>18:0</td>
<td>4.8</td>
<td>1.8</td>
<td>4.2</td>
<td>2.3</td>
</tr>
<tr>
<td>18:1</td>
<td>33.5</td>
<td>71.5</td>
<td>26.5</td>
<td>54.4</td>
</tr>
<tr>
<td>18:2</td>
<td>49.2</td>
<td>16.7</td>
<td>46.1</td>
<td>21.5</td>
</tr>
<tr>
<td>18:3</td>
<td>0.2</td>
<td>1.4</td>
<td>8.2</td>
<td>10.1</td>
</tr>
<tr>
<td>20:0</td>
<td>0.4</td>
<td>0.6</td>
<td>2.1</td>
<td>2.9</td>
</tr>
<tr>
<td>20:1</td>
<td>0.3</td>
<td>1.6</td>
<td>1.4</td>
<td>3.1</td>
</tr>
<tr>
<td>22:0</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>MUFAME:PUFAME</td>
<td>0.69:1</td>
<td>4.08:1</td>
<td>0.5:1</td>
<td>1.8:1</td>
</tr>
<tr>
<td>IP (h)</td>
<td>0.6</td>
<td>7.34</td>
<td>N/D</td>
<td>N/D</td>
</tr>
</tbody>
</table>

Table 3.6 Relative FAME composition (%) of SME and RME samples by GC* and literature values$^{159}$ (N/D = Not Determined)

The oxidative stability of the RME is significantly higher than that of the SME (IP = 7.34 and 0.6 hours respectively), and this can be attributed to the difference in the polyunsaturated FAME (PUFAME) to monounsaturated FAME (MUFAME) ratios. The RME has a higher proportion of MUFAME than PUFAME compared to that of the SME, this will result in a higher oxidative stability owing to the relative oxidation kinetics of PUFAME and MUFAME.

In the RME and SME samples analysed the C18 series accounts for 87.7 – 91.4 % of all the major FAME. Because of this, the C18 series were used as model FAME to carry out degradation studies upon.
3.3. Product Distribution Analysis

3.3.1. Methyl Stearate

After 48 hours oxidation at 110°C only one degradation product (stearic acid) was observed for this fully saturated FAME. This implies that autoxidation does not occur for saturated FAME under these conditions, and instead hydrolysis of the ester is the dominant degradation mechanism. Methanol would also be formed under this mechanistic pathway, but is not detected by the GC analysis. Figure 3.3 shows the formation of stearic acid over the course of the experiment. The curve resembles an induction period though Rancimat data does not give one, with the conductivity measurements staying fairly constant throughout. The curve in Figure 3.3 may represent an induction period for the hydrolysis reaction taking place. Given that no scission products were detected in the organic phase analysis and that little change occurred in the conductivity measurements it would appear reasonable to conclude that no autoxidation took place.

![Figure 3.2 Structure of methyl stearate](image)

![Figure 3.3 Formation of stearic acid from methyl stearate oxidation](image)
3.3.2. Methyl Oleate

![Structure of methyl oleate](image)

**Figure 3.4 Structure of methyl oleate**

The monounsaturated C18 FAME – methyl oleate – shows a higher propensity to oxidation than methyl stearate does, and this is reflected in both the FAME induction period and degradation product distribution. A number of volatile and monomeric degradation products are observed during the 48 hour oxidation, with many of them being identified using GC-MS (Figure 3.5) and quantified using GC (Figure 3.6).

The major monomeric degradation products formed from methyl oleate degradation are trans-epoxystearate, cis-epoxystearate, hydroxy-oleate, and oxo-oleate. The formation and decay of these compounds over 48 hours is shown in Figure 3.6. Of these compounds the trans-epoxide is formed in the greatest concentration, accounting for nearly half of all the monomeric degradation products quantified, with the cis-epoxide being formed in the next highest concentration. This preference for the trans isomer forming more than the cis isomer can be explained by the ability of the FAME to undergo isomerisation to give the less sterically hindered trans isomer during the formation of a peroxy radical, which subsequently results – via an alkoxy radical – in the formation of a trans-epoxide. Another proposed mechanism for the formation of epoxides from FAME involves the addition reaction of a peroxy radical to an olefin forming a peroxyalkyl adduct, whereby the \( \pi \) character is lost and free rotation is allowed, enabling isomerisation to occur before loss of an alkoxy radical and epoxide formation (Figure 3.7).\(^\text{94}\)
Figure 3.5: GC trace and structures of volatile and monomeric degradation products from methyl oleate oxidation after 6 hours.
Both the hydroxy-oleate and oxo-oleate degradation products are formed in moderate concentrations compared to the trans-epoxide. Along with the cis-epoxide these compounds show subsequent decay, with the concentration of all three species reaching approximately the same concentration after 48 hours oxidation. The trans-epoxide on the other hand has a much slower decay and after 48 hours the concentration is still only 25% less than at its concentration maximum.

Some unidentified species are formed in minor amounts (Figure 3.8). Compound I starts to form about 9 hours into the methyl oleate autoxidation and continues to increase in
concentration until the endpoint of the oxidation. This suggests that compound I is derived from other monomeric species as a result of further oxidation. Compounds G and H are formed in greater concentration than compound I, and start to form considerably earlier. These compounds may also be formed from other monomeric species that oxidise further to form poly-oxygenated compounds.

Figure 3.8 Poly-oxygenated monomeric degradation products from methyl oleate autoxidation

Another monomeric degradation product that forms from FAME autoxidation is the primary oxidation product – hydroperoxides. These products are not stable under the harsh conditions used in the analytical techniques so do not appear in the GC trace shown in Figure 3.5. It is known that under GC conditions hydroperoxides decompose to form ketones, alcohols and scission products,\textsuperscript{161,162} meaning that direct quantification of hydroperoxides by GC is not possible. However, hydroperoxides are readily reduced at room temperature by a reaction with triphenylphosphine – thought to be a non-radical process involving the nucleophilic displacement of the peroxide bond\textsuperscript{163} – to form the corresponding alcohol.\textsuperscript{164} When a sample is analysed by GC before and after reduction with triphenylphosphine, the difference in the measured yields of the alcohols represents the yield of hydroperoxides.
Goosen et al. used this technique in the analysis of a standard solution of 2-decyl hydroperoxides in decane by GLC. Before reduction by PPh₃ they detected decan-2-one (47 %) and decan-2-ol (10 %) as the major products. However, treatment of the sample with triphenylphosphine gave a close to quantitative yield of decan-2-ol (90 %) as the major product after GLC analysis (Figure 3.9). This lead the authors to conclude that quantification of the isomeric alcohols could be determined by direct analysis of their GLC yields before treatment with PPh₃, whilst the true yields of the isomeric ketones are those observed after reduction with triphenylphosphine.

![Figure 3.9 Products of 2-decyl hydroperoxide a) thermolysis and b) PPh₃ reduction as reported by Goosen et al.](image)

Similarly, Evans et al. analysed product mixtures from the catalytic oxidation of ethylbenzene, reporting three major products: acetophenone, 1-phenylethanol, and 1-phenyl-ethyl hydroperoxide. Further analysis of showed that 1-phenyl-ethyl-hydroperoxide degraded almost exclusively to acetophenone and the minor product benzaldehyde by thermolysis under GC conditions. After treatment of the hydroperoxide with triphenylphosphine, subsequent GC analysis showed significantly lower yields of acetophenone and benzaldehyde, while an increase in 1-phenylethanol was observed compared to those values measured before reduction by PPh₃ (Figure 3.10).
The studies by Goosen et al.\textsuperscript{161} and Evans et al.\textsuperscript{162} show that from analysis of a sample by GC before and after treatment with PPh\textsubscript{3}, the concentration of alcohols, ketones and hydroperoxides can be determined. The yield of scission products may vary between the measurements made before and after reduction with triphenylphosphine, with some scission products forming as a result of hydroperoxide thermolysis under GC conditions.

The yield of the hydroperoxides from methyl oleate oxidation is shown in Figure 3.11. The concentration is calculated from the difference in the GC yield of the alcohols formed from methyl oleate autoxidation, before and after treatment with PPh\textsubscript{3}. The plot also shows the yield of the ketones and volatiles formed from the thermolysis of the hydroperoxides prior to reduction by triphenylphosphine. This shows that approximately 39\% of the hydroperoxides of methyl oleate degrade to form ketones under GC conditions, which is comparative to the proportion of 2-decanone (47\%) formed from 2-decyl hydroperoxide thermolysis in the study by Goosen et al.\textsuperscript{161} Major volatile degradation products account for a further 12\% of the thermolysed hydroperoxides, leaving 49\% unaccounted for. Not all of the volatile products have been identified and quantified and some of these may result from hydroperoxide thermolysis. Some of the remaining unaccounted hydroperoxide may form alcohols from hydroperoxide thermolysis, though a study on the pure hydroperoxide would be required to verify this. Preparation and isolation of pure FAME hydroperoxides is a difficult and lengthy procedure that is beyond the scope of this project, so no attempts to carry out this work have been made.
Applying the PPh₃ treatment method in the volatile degradation product analysis also helps to provide information about the hydroperoxides from which they are derived. With most of the major volatile scission products identified and quantified, closer analysis of the difference in yields before and after reduction with PPh₃ shows that nonanal and methyl 9-oxo-nonanoate are approximately equal. As both compounds are products of the same scissions of the 9- and 10-hydroperoxides of oleate it may be expected that each would form in equal quantities. The differences in yields of methyl 8-oxo-octanoate and octanal before and after reduction with PPh₃ are also roughly equal, and around half that of those observed for 9-oxo-nonanoate and nonanal (Figure 3.12). This can be explained owing to each compound being derived from just one hydroperoxide, methyl 8-oxo-octanoate from the 9-hydroperoxide and octanal from the scission of the 10-hydroperoxide of oleate (Figure 3.13). The shape of the plot resembles those observed for the formation of hydroperoxides, with a sharp early peak and subsequent decay to a very low concentration. This data suggests that both the 9- and 10-hydroperoxides of methyl oleate are present in roughly equal concentrations.
The volatile degradation product of methyl oleate oxidation that forms in the highest concentration is nonanedioic acid mono methyl ester (Figures 3.14 and 3.15). This is generated in concentrations far in excess of any other volatile product. Interestingly the measured yields are unaffected by the treatment of the sample with PPh₃, indicating that it is not a direct product of hydroperoxide thermolysis or decomposition. It is likely that it
forms as a result of the secondary oxidation of methyl 9-oxo-nonanoate, a compound that is a product of hydroperoxide decomposition.

![Chemical structures](image)

**Figure 3.14** Volatiles detected by GC from methyl oleate autoxidation

![Graph](image)

**Figure 3.15** Quantification of volatiles detected from methyl oleate autoxidation (Names and structures of compounds shown in Figure 3.14)

Overall the quantity of volatiles formed as a result of methyl oleate oxidation that have been detected by GC is low, relative to the amount of monomeric degradation products quantified. Although some of the volatiles have been quantified, the data obtained does not provide an accurate picture of the real yields of these compounds that are being formed.
from secondary oxidation. The yields of the volatile degradation products detected by GC analysis may only represent a small proportion of the actual volatile degradation products formed through FAME oxidation. As the Rancimat apparatus is effectively an open system which allows those products that are able to volatilise, to leave the system. Given that this is the case and not all of the volatile degradation products formed can be detected by this experimental model, it is difficult to comment definitively about the yield of volatile degradation products and therefore analysis of scission products is limited to that discussed above in relation to methyl oleate and hydroperoxide thermolysis.

Analysis of organic residue by mass-spectrometry shows evidence of methyl oleate oligomerization. Peaks in the mass range of fragments of dimers and trimers of methyl oleate can be seen in Figure 3.16, with peak groups A and B arising from fragments of dimers, while trimer fragments are responsible for peaks grouped as C and D. The formation of the major peaks in the B group can be accounted for by the presence of a carbon linked dimer with one hydroxy group, which would have a molecular mass of 608. Loss of a CH₂CH₃ fragment gives rise to the peak at 597, and successive losses of methylene fragments give the following peaks: 565, 551, and 537. Dehydration of the dimer, converting the alcohol into an olefin accounts for the peak at 519 and the subsequent loss of methylene groups accounts for the peaks at 505, 491, and 477 (Figure 3.16 inset).
Figure 3.16 Mass spectrum of oxidised methyl oleate and suggested structures of some oligomeric products with fragments corresponding to peaks (Inset)

The polymeric species that have been detected by GC are present in relatively low concentrations, insufficient amounts to generate good enough quality mass spectra to able to identify the products. Therefore quantification of the polymeric degradation products by this method is not possible and discussion on the subject is only extended to that mentioned above.

3.3.3. Methyl Linoleate

![Structure of methyl linoleate](image)

Figure 3.17 Structure of methyl linoleate

Under the experimental conditions applied, methyl linoleate oxidation gives rise to a number of monomeric degradation products. These degradation products are a
combination of mono- and poly-oxygenated species, consisting of epoxides, alcohols, and ketones (Figure 3.18).

Figure 3.18 GC trace and structures of monomeric degradation products from methyl linoleate oxidation after 6 hours

As with methyl oleate oxidation, the major degradation products formed are epoxides, as determined by comparison of the GC-MS data with literature sources. There are more epoxide isomers formed from linolenate oxidation than that of oleate owing to its polyunsaturated nature. Whilst there are possible geometric isomers there are also positional isomers, and combining the two types of isomers results in four possible epoxide isomers being detected. The trivial names of the positional isomers are methyl coronarate (methyl 9,10-epoxy-cis-12-octadecanoate) and methyl vernolate (methyl 12,13-epoxy-cis-9-octadecanoate), the structures of which are shown for the overlapping peaks at 24.09 in Figure 3.18. Both coronarate and vernolate have cis and trans epoxide isomeric forms. It is assumed that the remaining double bond either retains its cis geometry or undergoes complete isomerisation to a trans geometry, as four peaks are detected in the epoxide region of the GC rather than eight, as would be expected if some double bond isomerisation occurred.
Similarly to the epoxides formed from methyl oleate oxidation, the trans-epoxides are generated in higher concentrations than the cis isomers, and this applies for both methyl coronarate and methyl vernolate (Figure 3.19). Interestingly, the product distribution of the positional isomers is very close, with both isomers being formed in an almost equal concentration for the majority of the oxidation. Table 3.7 shows that during the first six hours of oxidation there is a slight preference for coronarate formation, whilst after the first six hour period the selectivity switches to vernolate. Overall, the marginal selective preference for one isomer over the other is not significant, and this data suggests that the position at which the radical precursor to the epoxide forms is non-selective. Reports have shown that there is a fast inter-conversion between the 9- and 13- hydroperoxides of linoleic acid when thermally degraded leading to the same products being formed regardless of which pure hydroperoxides are decomposed.\textsuperscript{166-168} These reports support the data here, with approximately equal proportions of the two positional isomers being formed over time.

\textbf{Figure 3.19} Epoxide formations from methyl linoleate oxidation
<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Ver</th>
<th>Cor</th>
<th>Time (h)</th>
<th>Ver</th>
<th>Cor</th>
<th>Time (h)</th>
<th>Ver</th>
<th>Cor</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
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<td>46.22</td>
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</tr>
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</tr>
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<td>51.83</td>
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</tr>
<tr>
<td>4.5</td>
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<td>24</td>
<td>51.02</td>
<td>48.98</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 3.7** Product distribution (Rel %) of positional epoxide isomers from methyl linoleate oxidation (Ver = methyl vernolate, Cor = methyl coronarate)

Other major monomeric degradation products detected from methyl linoleate oxidation include hydroxy octadecadienoate methyl esters, of which there are two positional isomers. The hydroxy groups are located at either the 9 or 13 positions (methyl dimorphecolate and methyl coriolate respectively), allylic to a conjugated diene. It has been reported that under GC conditions allylic alcohols will dehydrate to conjugated dienes, or in the case of linoleate alcohols, conjugated trienes.\(^{165}\) This however has not been observed here, with a mass spectrum obtained showing a molecular ion peak at m/z 310 corresponding to the alcohols mentioned. After treatment with PPh\(_3\), the intensity of this peak increases, also confirming the presence of the alcohol. The GC peaks representing these alcohols are overlapping and are integrated as one to give one yield for the two isomers combined. The initial formation of the alcohols is very rapid, with the concentration maximum of approximately 0.04 M being reached after 3 – 4 hours, followed by a steady decomposition of the product over the remaining 40 hours of the oxidation (Figure 3.20). The subsequent decay of these alcohols may be due to the generation of poly-oxygenated species, with these alcohols acting as precursors to their formation. Other alcohols have been identified but are only present in very low concentrations and are deemed minor products.
Further major degradation products of methyl linoleate that have been observed are the two positional isomers of the oxo-octadecadienoate methyl ester. As with methyl oleate, the oxo-derivative is formed in slightly greater concentration than the hydroxy-derivative, and this finding is therefore consistent with reports in the literature\textsuperscript{169-171}. Similar to the hydroxy-derivative, the oxo-groups occupy the 9 or 13 positions and are allylic to a conjugated diene system, the presence of which increases the number of potential isomers with cis-trans and trans-trans isomers being possible. These regioisomers are detected as two overlapping peaks in the GC data. The corresponding mass spectra are similar to those of 9-, and 13-, oxo-octadecadienoate methyl esters characterised in literature sources\textsuperscript{172,173}. The two ketone isomers have been quantified together as one. The initial formation of the oxo-species is more gradual than that of the hydroxy analogues, with the concentration maximum concentration peaking at about 0.045 M after 12 hours. This is followed by a less severe decrease in concentration than that observed with the equivalent alcohol (Figure 3.19). As previously suggested this decrease in concentration may be an indicator that these compounds serve as precursors to other poly-oxygenated species.

During the oxidation of methyl linoleate the hydroperoxide concentrations are shown to be particularly high relative to the concentration of the monomeric degradation products.
formed (Figure 3.21). The hydroperoxide concentration peaks after two hours at approximately 0.22 M, roughly the same yield observed for all the epoxides combined. In methyl oleate the hydroperoxide concentration did not come close to matching that of the epoxides. As with methyl oleate it appears that the majority of the hydroperoxides are being converted to epoxides, and that the alcohols, ketones and poly-oxygenated species are being formed in much lower concentrations.

Figure 3.21 Monomeric degradation products from methyl linoleate autoxidation

The poly-oxygenated species detected from methyl linoleate oxidation contain epoxide functionality along with either a hydroxy or oxo group separated by an olefin (Figure 3.22). There are two possible positional isomers with the hydroxy and oxo groups being at the 9- or 13- position. These compounds have also been reported as products of linoleate hydroperoxide decomposition previously in the literature. 89,168,173-178

Figure 3.22 Poly-oxygenated monomeric degradation products formed from methyl linoleate oxidation
Spiteller et al. reported that the allylic epoxyhydroxy analogues are the main lipid peroxidation products of linoleic acid from their study on the Fe$^{2+}$ catalysed degradation of linoleic acid hydroperoxides. The authors did not isolate or detect the species directly but inferred their existence as intermediates by the detection of trihydroxy derivatives 9,12,13-trihydroxy-10-octadecenoic acid and 9,10,13-trihydroxy-11-octadecenoic acid which form as a result of the hydrolysis of 12,13-epoxy-9-hydroxy-10-octadecenoic acid and 9,10-epoxy-13-hydroxy-11-octadecenoic acid respectively, as had previously been reported by Gardner et al. These allylic epoxyhydroxy analogues are known to degrade to 4,5-epoxy-2-decenal. Spiteller et al. also reported the direct detection of isomeric epoxyhydroxy analogues 9,10-epoxy-11-hydroxy-12-octadecenoic acid and 12,13-epoxy-11-hydroxy-9-octadecenoic acid. These isomers are more stable than their allylic epoxyhydroxy analogues.

Other groups have reported the detection and characterisation of the allylic epoxyhydroxy species from the degradation of 13-hydroperoxy linoleic acid. Gardner et al. proposed that atmospheric oxygen was involved in the mechanism for the formation of the product from the hydroperoxides degradation. However, Tokita and Morita degraded the hydroperoxides under degassed conditions to form the same product, therefore proposing that oxygen is generated during the decomposition of the hydroperoxides.

Schieberle et al. detected equal quantities of the 9- and 13-isomers of the epoxyhydroxy- and epoxyoxyo-analogues despite starting the degradation studies exclusively with 13-hydroperoxylinoleic acid methyl ester. They proposed that the peroxy radical intermediate formed in the decomposition of the hydroperoxide is stable enough to undergo isomerisation over the conjugated diene system to form precursors for both 9- and 13-isomers in equal amounts. Two mechanisms were proposed for the formation of the hydroxy-epoxy and oxo-epoxy analogues. The first suggests that two peroxy-diene radicals disproportionate to give both a hydroxy-diene and an oxo-diene whilst releasing molecular oxygen. This is followed by the addition of oxygen from a peroxy radical across a double bond resulting in the formation of hydroxy-epoxy and oxo-epoxy analogues, both with two positional isomers (Figure 3.23).
Figure 3.23 A proposed mechanism for methyl oxo-epoxy-octadecenoate and methyl hydroxy-epoxy-octadecenoate formation by Schieberle et al., taken from reference\textsuperscript{180}

The other proposed mechanism involves the formation of molecular oxygen and caged alkoxy radicals as the result of the collision of two peroxy radicals, followed by subsequent cyclization to form an epoxy radical. This then undergoes isomerisation and reacts with \( O_2 \) to form an epoxy-peroxy radical, from which an oxo- or hydroxy-group is formed\textsuperscript{173} (Figure 3.24).

Figure 3.24 A proposed mechanism via caged alkoxy radicals for polyoxygenated monomeric degradation products formation from methyl linoleate oxidation by Schieberle et al.\textsuperscript{180}
Volatile degradation products that have been identified as resulting from methyl linoleate oxidation are; hexanal, methyl octanoate, 2,4-decadienal, methyl 8-oxo-octanoate, methyl 9-oxo-nonanoate, methyl 8,11-dioxo-9-undecanoate. Quantification of these compounds has not been carried out because, vide supra (see Section 3.3.2). But the detection of the volatile products listed above goes some way towards confirming the autoxidation pathway undertaken by methyl linoleate under the experimental conditions applied.

3.3.4. Methyl Linolenate

![Structure of methyl linolenate](image)

Figure 3.25 Structure of methyl linolenate

Figure 3.26 shows the monomeric degradation products detected and characterised from linolenate oxidation. Owing to the low yield of monomeric degradation products formed only the major products could be identified; each of those products has positional isomers, and in the case of the epoxides geometrical isomers. The alcohols formed have one hydroxy group at either the 9- or 16-position, whilst the ketones have an oxo-group at the same positions.

![Monomeric degradation products formed from methyl linolenate oxidation after 6 hours](image)

Figure 3.26 Monomeric degradation products formed from methyl linolenate oxidation after 6 hours
Similarly to methyl linoleate, the monomeric degradation products of methyl linolenate are formed in lower concentrations than those observed for methyl oleate. Overall, the total concentration of the monomeric degradation products from methyl linolenate oxidation is significantly less than those formed from methyl linoleate oxidation, as illustrated in Figure 3.27. This shows the total yield of epoxides – the most significant monomeric product – from unsaturated FAME oxidation, which can be used as a good representation of the yield of all the monomeric degradation products formed. The yield of monomeric degradation products from FAME oxidation follows the trend of 18:1 > 18:2 > 18:3, which can be attributed to the increase in unsaturation. This suggests that greater yields of volatile or polymeric degradation products are formed when FAMEs of increased degrees of unsaturation are oxidised under these simulated crankcase conditions.

![Figure 3.27 Total epoxide yield from unsaturated FAME oxidation](image)

In a study by Hejazi et al.\textsuperscript{181} in which significant fragment ions of methyl linolenate were identified (Figure 3.28), showed that knowledge of these ions and their peaks can be used to elucidate the position of the oxirane groups in the epoxides from linolenate oxidation.
According to this work it could be expected that the 12,13-epoxide will not give rise to any of these fragments as each of them requires the Δ12 olefin. Both the 9,10- and 15,16-epoxides can form the [C₆H₇]⁺ ion, whilst the 9,10-epoxide can also form the ω-ion and the [C₇H₁₁]⁺ ion, however the 15,16-epoxide cannot form these ions due the them both requiring the Δ15 olefin. The 15,16-epoxide can form the α-ion which is a fragment that contains both the Δ9 and Δ12 olefins as well as the rest of the molecule up to and including the Δ-terminal.

<table>
<thead>
<tr>
<th>Key Ion</th>
<th>Fragment</th>
<th>m/z</th>
<th>9,10</th>
<th>12,13</th>
<th>15,16</th>
</tr>
</thead>
<tbody>
<tr>
<td>α⁺</td>
<td>m/z 236</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>m/z 161</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[C₇H₁₅O₂]⁺</td>
<td>155</td>
<td>15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[C₇H₁₁O]⁺</td>
<td>111</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>ω⁺</td>
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<tr>
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<td>50</td>
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<td></td>
</tr>
<tr>
<td>[C₇H₁₁]⁺</td>
<td>95</td>
<td>50</td>
<td></td>
<td></td>
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<tr>
<td>[C₆H₉]⁺</td>
<td>93</td>
<td>80</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[C₆H₉]⁺</td>
<td>81</td>
<td>80</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>[C₆H₇]⁺</td>
<td>79</td>
<td>100</td>
<td>100</td>
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<tr>
<td>[C₅H₇]⁺</td>
<td>67</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[C₄H₇]⁺</td>
<td>55</td>
<td>90</td>
<td>70</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.8 Relative abundances (%) of key ion fragments of 18:3 epoxides from GC-MS
The presence of the 12,13-epoxides has been detected; the mass spectrum of two peaks at 21.623 and 21.728 mins show intense fragment ions where \( m/z = 111, 95, 81, \) and 67. The peak at 111 has been assigned as a \([C_7H_{11}O]^+\) fragment, which may lose oxygen to form the \([C_7H_{11}]^+\) ion giving rise to the peak at 95. Subsequent loss of two \( CH_2 \) fragments can lead to formation of ions responsible for the peaks at 81 and 67. The mass spectra that show the most intense peaks at 79 have been assigned the 9,10- and 15,16-epoxides as both of these will readily form the \([C_6H_7]^+\) ion. The main difference between the spectra of these two positional isomers is that the 9,10-epoxide forms the \( \omega \)-ion \( (m/z = 108) \), whilst the 15,16-epoxides has a peak at 236 from the formation of the \( \alpha \)-ion.

Quantification of the epoxides (Figure 3.29), shows a slight preference for the formation of the 12,13-epoxide, this isomer is derived from hydroperoxides in both the 12 and 13 positions. It is possible that two different hydroperoxides decomposing to give the same product results in the higher yields for the 12-13 epoxides. However, this result conflicts with the findings of Frankel et al. who studied the autooxidation of linolenate at various temperatures, reporting that there was a distinct preference for the formation of 16-hydroperoxide, followed by the 9-hydroperoxide over the 12-, 13-analogues.\(^86\) The difference in the yields of each of the epoxides does not appear to be significant. Two mass spectra have been observed for each positional isomer, suggesting that there are two geometric isomers for each of the three positional epoxide isomers, resulting in a total of six epoxides. The \textit{cis} and \textit{trans} isomers cannot be distinguished by their mass spectra, but based on trends from oleate and linoleate oxidation it is assumed that the \textit{trans} isomers elute first and form in the highest concentration.
The major alcohols and ketones detected from methyl linolenate autoxidation are in both the 9- and 16-positions. These sites are the terminal positions of the conjugated diene systems formed as a result of autoxidation initiation, which have been shown to be the favoured sites for hydroperoxide formation. These compounds form as a result of hydroperoxide decomposition, yielding the secondary oxidation products.

Volatile compounds detected from methyl linolenate degradation include a number of acids, aldehydes, alkenes, and heterocycles. Furyl formation may occur via a polyoxygenated precursor – an epoxyoxoene – by the mechanism proposed by Higaldo et al. The mechanism starts with a ring opening of the epoxide due to attack by the carbonyl, with the formation of a five membered ring intermediate. Rearrangement of electrons can lead to the cleavage of a C-C bond, yielding an isolated furyl and an aldehyde (Figure 3.30). Each of these compounds are detected by GC-MS, with the furyl being found in higher yields than the corresponding aldehyde (peaking at approximately 0.01 M vs. 0.005 M respectively), when it may be expected that they would be formed in equal amounts. This can be accounted for by the fact that the aldehyde is a volatile molecule that is likely to be lost from the system by evaporation rather than remaining in the organic residue.

**Figure 3.29** Quantification of epoxides formed from methyl linolenate autoxidation
3.4. Conclusions

The product distribution analysis carried out in this chapter indicates that autoxidation is the primary oxidation pathway for the C18 FAME series under the simulated crankcase conditions applied here. With the exception of methyl stearate, for which the only degradation product detected was the hydrolysis product stearic acid, the C18 FAMES produced an array of volatile and monomeric degradation products that are consistent with those reported in other FAME autoxidation studies.51,57,79,81,86,89,102,151-153

A good understanding of the FAME degradation mechanisms has been achieved with the identification and quantification of many degradation products of C18 FAMES completed, with monomeric compounds being the major products formed under these conditions. The relative yields of the monomeric degradation products formed are consistent with literature reports, i.e. epoxides (trans > cis) > ketones > alcohols.88,169-171 Hydroperoxides have been detected and quantified as well as their thermolysis degradation products that are formed under GC conditions.

Lower yields of monomeric degradation products were detected from 18:1 – 18:3, indicating that the increasing degree of unsaturation results in the formation of more volatile or polymeric degradation products. The effect of this would be of potential significance with respect to the influence of FAMES in the crankcase, as the use of fuels with higher PUFAME content could potentially introduce a greater quantity of acids and other volatile or polymeric degradation products into the crankcase.
4. Oxidative Degradation Kinetics
4.1. Introduction
In this chapter, work from Chapter 3 is extended, focusing on the kinetics of FAME degradation in model FAMEs, commercial biodiesel and mixtures of model FAME. Interesting differences are found between the degradation kinetics of FAME in single-component and multi-component systems. The influence of forming binary mixtures of SME biodiesel and PAO model base oil on the kinetics of SME and PAO degradation is also investigated, to simulate aspects of fuel dilution under the experimental conditions.

4.1.1. FAME Kinetics Literature
The oxidation of fatty acids (FA) and FAME is a well studied field with a great deal of research directed towards the oxidation kinetics of saturated and unsaturated FAs and FAMEs. The widely accepted trend regarding saturated, monounsaturated and polyunsaturated FAs and FAMEs is that oxidation rates proceed by the following order: Polyunsaturated > Monounsaturated >> Saturated. However, the literature values for the rates of oxidation of unsaturated lipids vary greatly from source to source.\(^{183-186}\) Most of the variation in these reported rates arises from the different experimental techniques and conditions applied to the investigations.

In 1947 Holman and Elmer reported the relative rates of oxidation of the polyunsaturated acids and their ethyl esters.\(^{183}\) Using a Warburg respirator to measure the uptake of oxygen by fatty acids and ethyl esters in air at 37\(^\circ\)C, they reported that the maximum rate of oxidation for ethyl linolenate (18:3) was 2.4 times that of ethyl linoleate (18:2), and the rate of oxidation for ethyl arachidonate (20:4) about two times that of ethyl linolenate (18:3). These results led them to conclude that for every single increase in the number of double bonds in a fatty acid or its ester, the rate of oxidation of the compound increases by at least a factor of two.

Howard and Ingold determined the absolute rate constants for the oxidation of a number of saturated and unsaturated hydrocarbons – including methyl oleate, methyl linoleate, and methyl linolenate – by the rotating sector method.\(^{184}\) Their experiments involved the oxidation of FAME in solution of chlorobenzene with the presence of an azo initiator at
The data garnered gave the relative rates of oxidation for the FAME as 1:23:44 for methyl 18:1, 18:2, and 18:3 respectively.

Pryor et al. evaluated the kinetics of polyunsaturated fatty acid (PUFA) autoxidation by measuring the rate of oxygen uptake of a chlorobenzene solution of a PUFA, initiated by an azo initiator, at 37°C under 760 torr of O₂ in a gas absorption apparatus. Using steady-state analysis of the autoxidation mechanisms, a term referred to as oxidizability was created. Oxidizability describes the measure of ease with which the PUFA will undergo autoxidation, and was expressed as the ratio of the rate constants for propagation and termination, \( k_p \) and \( k_t \) respectively (Equation 4.1).

\[
\text{Oxidizability} = \frac{k_p}{(2k_t)^{1/2}} \quad \text{[Eq 4.1]}
\]

The authors determined the relative oxidizibilities of 18:2, 18:3, 18:4 and 18:6 to be 1:2:3:5 respectively, declaring that for every additional bis-allylic position present in the PUFA, the relative oxidizibility increases by 1, and not by 2 as declared by Holman and Elmer.

Adachi et al. evaluated the autoxidation kinetics of several neat PUFAs and their corresponding ethyl esters, by measuring the change in concentration of the starting material over the course of the oxidation. They developed an expression based on a well established kinetic equation describing olefin autoxidation by Bolland, using the concentrations of unreacted substrate, oxidised substrate and oxygen to give Equation 4.2, where \( C_{RH}, C_{ROOH}, \) and \( C_x \) are the concentrations of unreacted ethyl linoleate, hydroperoxides, and oxygen respectively. \( k_\alpha \) is the rate constant and \( K \) is the saturation constant.

\[
\text{rate} = k_\alpha \frac{k_x C_x C_{RH}}{K + C_x} C_{ROOH} \quad \text{[Eq 4.2]}
\]

After making some modifications to the expressions based on assumptions about the concentrations of the substrates and oxidation products, Equation 4.3 and its integrated form Equation 4.4 were derived, where \( Y = \) the fraction of unoxidised substrate.

\[
\frac{dy}{dt} = -k_1 Y(1 - Y) \quad \text{[Eq 4.3]}
\]

\[
\ln \frac{1-Y}{Y} = k_1 t + \ln \frac{1-Y_0}{Y_0} \quad \text{[Eq 4.4]}
\]
Ultimately these expressions showed that the relative autoxidation rates of \( \omega-6 \) PUFA ethyl esters followed the expected order of 20:4 > 18:3 > 18:2 whilst satisfying first order kinetics. However a series of \( \omega-3 \) PUFA ethyl esters were shown to only satisfy the rate expression when the unreacted substrate concentration was above 0.5, below which the linearity of the fit deviated from the plot. Another expression was developed to express the autoxidation process when substrate concentration reached less than \( \frac{1}{2} \), as shown by Equation 4.5, where \( t_{0.5} = t \) when \( Y = 0.5 \).

\[
\ln(2Y) = -k_2(t - t_{0.5}) \quad \text{[Eq 4.5]}
\]

Differential scanning calorimetry was employed by Litwinienko and Kasprzycka-Guttman to assess the oxidative stability of unsaturated fatty acids and their esters.\(^{186}\) The fatty acids oleic, linoleic, linolenic and erucic and their ethyl esters were oxidised without solvents or free radical initiators by linear programmed heating rates of 1 – 25 K/min at 50 – 300\(^\circ\)C. The relative rate constants of 18:1, 18:2, and 18:3 at 90\(^\circ\)C were reported as 1:3:12 respectively.

### 4.2. Kinetics of Individual FAME

<table>
<thead>
<tr>
<th>Name</th>
<th>Abbreviated Name</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl Stearate</td>
<td>18:0</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Methyl Oleate</td>
<td>18:1</td>
<td>Sequioa Research Products</td>
</tr>
<tr>
<td>Methyl Linoleate</td>
<td>18:2</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Methyl Linolenate</td>
<td>18:3</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Rapeseed methyl ester biodiesel</td>
<td>RME</td>
<td>Greenergy</td>
</tr>
<tr>
<td>Soybean methyl ester biodiesel</td>
<td>SME</td>
<td>Infineum U.K. Ltd</td>
</tr>
</tbody>
</table>

**Table 4.1** Materials used for Rancimat oxidations classified by: Name; Abbreviated Name; and Source

In this work a series of neat C18 FAME (Table 4.1) with varying degrees of unsaturation (18:0, 18:1, 18:2, 18:3) were oxidised individually without the use of initiators, by a Rancimat apparatus at 110\(^\circ\)C and with 10 L/h air flow rate. The product distribution analysis of these FAME in Chapter 3, has indicated that the unsaturated FAME degraded by normal hydrocarbon autoxidation pathways under these conditions. Periodic sampling of the FAME
over the course of the oxidation and subsequent analysis by GC, allows the FAME concentration to be calculated using a calibrated standards and the effective carbon number (ECN) concept. In Figure 4.1 the calculated concentrations for each individual FAME are plotted together vs. time.

**Figure 4.1** Plot of FAME concentration vs. time for the oxidative degradation of C18 FAME series at 110°C

Under these conditions, the FAMEs undergo oxidative degradation following first order rate kinetics. Little distinction between the rates of degradation for the individual unsaturated FAME is observed. Relative rate constants ($K_{rel}$) can be determined by plotting the natural logarithm of the FAME concentration against time, giving linear fits. The gradients of the resulting plot are equal to $K_{rel}$ of the FAME oxidation (Figure 4.2). The values for $K_{rel}$ of the three unsaturated FAMEs are: 1, 1.18, and 1.25 for 18:1, 18:2, and 18:3 respectively over a period of 0 – 6 hours oxidation (Table 4.2).
Chapter 4

Figure 4.2 Plot of natural logarithm of FAME concentration vs. time

![Plot of natural logarithm of FAME concentration vs. time](image)

Table 4.2 Relative rate constants ($k_{rel}$) of unsaturated FAME oxidative degradation

<table>
<thead>
<tr>
<th>FAME</th>
<th>$k_{rel}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>18:1</td>
<td>1</td>
</tr>
<tr>
<td>18:2</td>
<td>1.18</td>
</tr>
<tr>
<td>18:3</td>
<td>1.25</td>
</tr>
</tbody>
</table>

The values of $k_{rel}$ obtained from the experimental data here are unusual, as they show little difference between the FAMEs despite the increasing degrees of unsaturation. Under the experimental conditions carried out, the oxidation kinetics of the individual FAMEs are very different to those reported in the literature.\textsuperscript{183-186} It is possible that the experimental conditions provide an excess of thermal energy required for activation, removing the significance of the difference in activation energies of each FAME.

4.3. Kinetics of FAME Mixtures as RME and SME

The following experiments are carried out in order to discover if the values of $k_{rel}$ for each of the FAMEs is the same when oxidised as mixtures as those recorded when oxidised individually, using the same experimental conditions.

Samples of an American Soybean Methyl Ester (SME) and European Rapeseed Methyl Ester (RME) – both additive free and commercially available – were analysed by GC and their fatty acid profiles determined (Table 4.3), prior to oxidation by the Rancimat. RME shows a high
proportion of 18:1 and as a consequence has a high monounsaturated FAME to polyunsaturated FAME (MUFAME/PUFAME) ratio (4.08:1). SME on the other hand, is composed by nearly half of its total fatty acid profile by 18:2, resulting in a MUFAME/PUFAME ratio of 0.69:1. The contrasting ratios are reflected in the oxidative stability of the two FAMEs (Figure 4.3), with RME exhibiting a relatively high induction period of 7.34 hours, while SME – with its high proportion of polyunsaturated FAME – has an induction period of 0.6 hours.

<table>
<thead>
<tr>
<th>FAME</th>
<th>Trivial Name</th>
<th>Relative % of FAME</th>
</tr>
</thead>
<tbody>
<tr>
<td>16:0</td>
<td>Palmitate</td>
<td>0.3</td>
</tr>
<tr>
<td>16:1</td>
<td>Palmitoleate</td>
<td>4.6</td>
</tr>
<tr>
<td>18:0</td>
<td>Stearate</td>
<td>1.8</td>
</tr>
<tr>
<td>18:1</td>
<td>Oleate</td>
<td>71.5</td>
</tr>
<tr>
<td>18:2</td>
<td>Linoleate</td>
<td>16.7</td>
</tr>
<tr>
<td>18:3</td>
<td>Linolenate</td>
<td>1.4</td>
</tr>
<tr>
<td>20:0</td>
<td>Arachidoate</td>
<td>0.6</td>
</tr>
<tr>
<td>20:1</td>
<td>Gondoate</td>
<td>1.6</td>
</tr>
</tbody>
</table>

| MUFAME/PUFAME Ratio | 4.08:1 | 0.69:1 |
| Induction Period (h) | 7.34   | 0.60   |

Table 4.3 Fatty acid profile of biodiesel samples

![Figure 4.3 Rancimat plots of conductivity vs. time for RME and SME at 110°C](image)
4.3.1. Oxidation of RME

The induction period of the RME is also observed in Figure 4.4. In this graph the concentration of FAME as Mol % is overlaid with the Rancimat conductivity curve vs. time. The induction period – as indicated by the inflection of the Rancimat curve – coincides with the rapid decrease in FAME concentration, after a period where the concentration remains roughly constant. This induction period may be due to the high proportion of 18:1 and lower amount of polyunsaturated FAME present. Or, alternatively it may be an effect of the presence of some natural antioxidants that were not removed from the sample during manufacture.

![Figure 4.4](image)

Figure 4.4 Plot of Conductivity (solid line) and FAME concentration (Mol %) vs. time for RME oxidative degradation

The values of $K_{rel}$ for each of the individual FAME in the biodiesel FAME mixture is shown in Table 4.4. As a mixture, there becomes a clearer distinction between the values of $K_{rel}$ for each FAME during oxidation. When the $K_{rel}$ of 18:1 is given an arbitrary value of 1, $K_{rel} = 4.33$ and 1.83 for 18:2 and 18:3 respectively, while the saturated FAME 18:0 oxidises markedly slower with $K_{rel} = 0.08$. The fact that the polyunsaturated FAMEs show faster oxidation rates
than 18:1 is significant, as it is more in line with reports from the literature. The recorded values of $K_{rel}$ for 18:3 is lower than that of 18:2, however this is likely to be due to the large error in sampling of 18:3 due to the small quantities of 18:3 present in the original sample (<0.2 % cf. 50+ % for 18:2). With this factor considered the value reported for $K_{rel}$ of 18:3 may be inaccurate.

<table>
<thead>
<tr>
<th>FAME</th>
<th>$K_{rel}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>18:0</td>
<td>0.08 ($\pm 5.1 \times 10^{-4}$)</td>
</tr>
<tr>
<td>18:1</td>
<td>1 ($\pm 5.8 \times 10^{-4}$)</td>
</tr>
<tr>
<td>18:2</td>
<td>4.33 ($\pm 2.4 \times 10^{-3}$)</td>
</tr>
<tr>
<td>18:3</td>
<td>1.83* ($\pm 2.3 \times 10^{-2}$)</td>
</tr>
</tbody>
</table>

Table 4.4 Calculated relative rate constants ($K_{rel}$) of individual C18 FAMEs in RME. * $K_{rel}$ for 18:3 is not definitive

4.3.2. Oxidation of SME

Oxidation of SME under the conditions of crankcase simulation results in the degradation of the individual unsaturated FAME from the outset. The SME has an induction period of just 0.6 hours so no significant delay in the decrease of FAME concentration is observed in Figure 4.5. The Rancimat conduction curve overlaid on the graph shows a good correlation between the data obtained by GC and that generated by the automated oxidation apparatus.
The values of $K_{rel}$ for the C18 FAMEs obtained from the degradation of SME indicate a significant difference between those with differing degrees of unsaturation (Table 4.5). When 18:1 is given a value of $K_{rel} = 1$, subsequent values of $K_{rel} = 4.64$ and 2.32 are determined for 18:2 and 18:3 respectively, whilst $K_{rel} = 0.06$ for 18:0. As with the oxidative degradation of RME, SME exhibits similar values for the relative rate constants, with the tri-unsaturated FAME 18:3 showing a lower $K_{rel}$ than that of 18:2. Again, this may be due to the small amount of 18:3 present in the SME sample and the error incurred in measuring the concentration over time. When comparing the two data sets of FAME kinetics from the oxidation of RME and SME, the values obtained are reasonably consistent with one another, falling within a margin of 25 %. Though, the values for 18:3 may be disregarded, owing to inaccuracy of the measurements due to the low concentration of 18:3 present in each of the samples.
<table>
<thead>
<tr>
<th>FAME</th>
<th>$K_{rel}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>18:0</td>
<td>0.06 ($\pm 8.6 \times 10^{-3}$)</td>
</tr>
<tr>
<td>18:1</td>
<td>1 ($\pm 1.7 \times 10^{-3}$)</td>
</tr>
<tr>
<td>18:2</td>
<td>4.64 ($\pm 1.9 \times 10^{-3}$)</td>
</tr>
<tr>
<td>18:3</td>
<td>2.32* ($\pm 9.1 \times 10^{-3}$)</td>
</tr>
</tbody>
</table>

Table 4.5 Calculated relative rate constants ($K_{rel}$) of individual C18 FAME in SME. *$K_{rel}$ for 18:3 is not definitive

4.4. FAME Mixtures as 1:1:1:1

Investigations into mixtures of model FAME oxidation kinetics were carried out to compare with the FAMEs in RME and SME biodiesel samples. By preparing a model FAME mixture of the C18 series in equal quantities (1:1:1:1 ratio by mass), the problems encountered in evaluating the FAME kinetics in RME and SME could be avoided. Oxidation of the mixture by the Rancimat apparatus gives rise to the degradation profiles observed in Figure 4.6 a. Interestingly no induction period was observed for this model FAME mixture, though given the relatively high concentration of PUFAME present only a small induction period may have been expected. The presence of natural antioxidants in the RME and SME biodiesel samples could account for the induction periods observed, however in the model FAME mixture it is likely that there are absolutely no antioxidants present. Similarly to the RME and SME samples, the FAMEs degrade at different rates in the order 18:0 $<<$ 18:1 $<$ 18:2 $<$ 18:3, also in accordance with the relative rates stated in the literature. 183-186

![Figure 4.6](image_url)

Figure 4.6 Plots of a) FAME concentration vs. time and b) natural logarithm of FAME concentration vs. time for C18 FAME in an equal 1:1:1:1 mixture when oxidised at 110°C
Plotting the natural logarithm of the FAME concentration against time to give $K_{rel}$ for the FAME oxidation, demonstrates a change in the $K_{rel}$ for 18:1 and 18:2 during the observed degradation (Figure 4.6 b). When the gradients for the data obtained in the first six hours and the data obtained from hour nine to the end of the test are plotted independently (Figure 4.7), the change in $K_{rel}$ becomes apparent. During the first six hours of the oxidation 18:3 is entirely consumed with $K_{rel} = 11.1$ compared to 18:1 and 18:2 with $K_{rel} = 1$ and 5.1 respectively (Figure 4.7a). These values correspond well with those published by Litwinienko et al. who reported $K_{rel}$ values of 1, 3, and 12 for 18:1, 18:2, and 18:3 respectively.¹⁸⁶

**Figure 4.7** Plots of the natural logarithm of C18 FAME concentration vs. time for C18 FAME in an equal 1:1:1:1 mixture for a) 0 – 6 hours and b) 9 – 48 hours

After the first six hours of oxidation, 18:3 has completely degraded. The remaining unsaturated FAMEs appear to increase in their respective relative oxidation rate constants, with 1.33 and 7.82 being observed for 18:1 and 18:2 respectively, relative to that of 18:1 during 0 – 6 hours (Figure 4.7 b). The increase in $K_{rel}$ for the oxidation of 18:1 and 18:2 coincides with the complete oxidation of 18:3 implying that the presence of other FAMEs may influence the oxidation kinetics of a mixture.

An example in the literature shows similar experimental methodology to that carried out here, with FAME mixtures analysed. Adachi et al., investigated the oxidation kinetics of binary mixtures of FAMEs and showed that the presence of another FAME affected the rate of autoxidation of a FAME.¹⁸⁹ When methyl linoleate (18:2) was combined with ethyl arachidonate (20:4) in 1:3, 1:1, and 3:1 ratios and oxidised at 65°C, the rate of the methyl linoleate autoxidation was increased on increasing the concentration of ethyl arachidonate in the binary mixture. Conversely, the rate of the autoxidation of ethyl arachidonate
decreased when methyl linoleate was present in higher concentrations. The reports of Adachi et al. imply that the more easily oxidised ethyl arachidonate acts as a catalyst for increasing the oxidation rate of methyl linoleate, with the FAMEs diluting one another and the formation of oxidation products of one affecting the other. Taking this into consideration, the oxidation products of the 18:3 autoxidation may also increase the rate of other FAMEs present. However in the work carried out here, the data from the quaternary FAME mixture oxidation study suggests that an effect opposite to that reported by Adachi et al. is occurring, with the presence of the more readily oxidised methyl linolenate suppressing the oxidation kinetics of methyl linoleate and methyl oleate.

When comparing the relative rate constants ($K_{rel}$) obtained from the individual FAME oxidations relative to those recorded during the oxidation of the quaternary FAME mixture, it is possible to assess the influence of the other FAMEs in the mixture upon each other’s $K_{rel}$ (Table 4.6). Methyl oleate appears to oxidise at a much slower rate when in a mixture than when oxidised individually. During oxidation of the model FAME mixture, the oxidation rate constants for methyl oleate are 22% and 29% that of the neatly degraded FAME, for the period of 0 – 6 hours and 9 – 48 hours respectively. However, compared to the $K_{rel}$ of methyl linoleate when degraded individually, in the model FAME system during the initial 6 hour period the values of $K_{rel}$ are relatively close (1.18 vs. 1.11). During the remaining period of linoleate autoxidation in the mixture, the $K_{rel}$ then exceeds the recorded rate constant from individual degradation studies (1.18 vs. 1.72), though the difference between $K_{rel}$ does not compare to the relative proportions observed for methyl oleate. With methyl linolenate, the FAME has a much greater $K_{rel}$ when oxidised in the presence of other FAME than it does when oxidised individually. In the model FAME system, 18:3 oxidises approximately twice as fast compared to a single component system.

<table>
<thead>
<tr>
<th>System</th>
<th>18:0</th>
<th>18:1</th>
<th>18:2</th>
<th>18:3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Individual</td>
<td>0.014</td>
<td>1.00</td>
<td>1.18</td>
<td>1.25</td>
</tr>
<tr>
<td>1:1:1:1 (0 – 6 h)</td>
<td>0.022</td>
<td>0.22</td>
<td>1.11</td>
<td>2.44</td>
</tr>
<tr>
<td>1:1:1:1 (9 – 48 h)</td>
<td>0.016</td>
<td>0.29</td>
<td>1.72</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 4.6 Relative rate constants ($K_{rel}$) for the autoxidation FAME when oxidised individually and in a quaternary mixture model FAME system (1:1:1:1)
Given these comparisons it would appear that in the mixed system the rate of oxidation of methyl oleate and methyl linoleate is being suppressed by the presence of the more readily oxidised methyl linolenate, with methyl oleate affected the most. There may be an effect as Adachi et al. suggested, where the oxidation products of one FAME can increase the oxidation rate of another FAME, though here it may not be able to occur until all of the methyl linolenate has itself been oxidised. The key degradation product formed is the FAME peroxy radical, which can propagate the autoxidation by abstracting hydrogen from a FAME molecule and in doing so forms the primary oxidation product, a FAME hydroperoxide. Each of the unsaturated FAMES in the quaternary mix will produce FAME radicals at different rates, as determined by the number and relative C-H bond strengths of allylic and bis-allylic positions. These FAME radicals react rapidly with O₂ to form the corresponding peroxo radicals.

The fate of those individual peroxo radicals is determined by some kinetic and thermodynamic factors. As discussed in greater detail in section 1.2.3., there are competing pathways that peroxo radicals can take, with the reverse reaction of the addition of O₂ to a pentadienyl system, β-fragmentation allowing for isomerisation to take place, as well as the hydrogen atom transfer route that propagates the autoxidation pathway further. In order for rapid H-abstraction to take place, the resulting bond formed must be at least as strong as the bond being broken. Typically the strength of the ROO-H bond in a FAME hydroperoxide is about 90 kcal mol⁻¹, whilst allylic C-H bonds are in the region of 84 kcal mol⁻¹, meaning that a peroxo radical should be able to easily abstract hydrogen from any unsaturated FAME molecule. The defining factor in the competition between the FAME molecules undergoing H-abstraction comes from the selectivity of the peroxo radicals towards the weakest bound H atom, which in this case will be those of linolenate. It has been reported that H-abstraction is facilitated in neat lipids and aprotic solvents as is the case under these experimental conditions. So all the while linolenate is present in the model FAME system it is likely that it will be reacting with the majority of the peroxo radicals formed by oleate and linoleate oxidation as well as the linoleate peroxo radicals. This may explain the apparent suppression of linoleate and oleate oxidation rates when degraded as an equal mixture of FAME (Figure 4.8).
4.5. PAO Degradation

Studies into the relative degradation rates of neat PAO and PAO in the binary mixture of SME/PAO were carried out in an attempt to understand more about the possible interaction between the two under the simulated crankcase environment. This would be achieved by firstly analysing PAO and assessing its oxidative stability to use as reference point to compare further studies against. Secondly the SME/PAO mixture was degraded under the same conditions as neat PAO and the concentration of the PAO in the sample monitored over time to determine the relative rates of degradation.

PAO (polyalphaolefins) are high quality, synthetic base oils produced from linear alpha olefins by an oligomerization and hydrogenation process. A PAO was selected as the example model base oil for this study as it was expected to have a much simpler GC spectrum than a mineral base oil. A mineral base oil would comprise a multiplicity of different compounds.

In the literature reports of PAO oxidation have been documented by various groups: Butt et al. developed an oxidation kinetic model for PAO and carried out a product distribution analysis. In a study by Gamlin et al. PAO was reported to have an onset activation energy of 118 kJ mol$^{-1}$ and a peak activation energy of 130 kJ mol$^{-1}$. The authors also reported induction periods ranging from 117.29 – to 13.18 minutes between temperatures of 140°C.
and 170°C, as determined by pressure differential scanning calorimetry (PDSC). More recently Bantchev et al. calculated onset and peak activation energies of PAO as 74 kJ mol\(^{-1}\) and 120 kJ mol\(^{-1}\) respectively, whilst acknowledging that their recorded values were less than those observed by Gamlin et al. the authors failed to comment further.

### 4.5.1. PAO Analysis

Analysis of PAO by GC-MS indicated that the PAO is composed of several compounds of similar molecular mass, which elute from the column within a two minute retention time range. The mass spectra for each of the corresponding peaks of the GC are very similar to one another, each with a molecular ion peak at 394, which correlated to a C\(_{28}\) hydrocarbon. The GC-MS software – MassLynx – suggests the structure of a branched hydrocarbon 9-octyl eicosane for the peaks with the molecular ion of 394 (Figure 4.9 a). Though, this structure is not consistent with the structures of known products from PAO production methodology. Isomeric structures that would be more likely products would be that of the C14 feedstock dimer 14-methyl heptacosane (Figure 4.9 b) or the C7 feedstock tetramer 8,10-dipentyl 12-methyl heptadecane (Figure 4.9 c).

![Figure 4.9 a) 9-octyl eicosane, b) 14-methyl heptacosane, c) 8,10-dipentyl 12-methyl heptadecane](image)

The infrared spectrum of PAO shows all the characteristic peaks for CH\(_3\), CH\(_2\) and CH stretches, as well as the bands for CH deformations, CH\(_3\) symmetrical deformation and CH\(_2\) rocking. Whilst the NMR spectrum for the PAO integrates to give 58 hydrogen atoms, 9 of which are from methyl groups and show as a triplet as a result of splitting from the adjacent methylene groups. This data is consistent with structures a and b in Figure 4.9, the most likely of which being structure b, 14-methyl heptacosane.
Conventional PAOs are often made from oligomerisation of 1-decene. Alternative PAOs based on C12 or C8/C10/C12/C14 mixtures are also now commercially available. The PAO used was sourced through Infineum UK Ltd. Further information on the particular PAO structure was not provided.

### 4.5.2. PAO Oxidation

The oxidation of PAO by the Rancimat method was carried out for 60 hours and the degradation monitored by periodic sampling and GC analysis. Quantification of the PAO was achieved by two methods whereby the sum peaks of the PAO were integrated together as one and another where one individual peak of the chromatogram is integrated on its own. Both calculation methods used the ECN concept against an internal standard. Figure 4.10 shows the GC trace of the PAO and the peaks used to calculate the “all peak” method, also highlighted is the individual peak used to calculate the “single peak” method.

![Figure 4.10 GC of PAO showing peaks used to calculate the concentration by the “all peak” method and highlighting the peak used by the “single peak” method](image)

The results of these two methods correlate well with the gradients for the plots of \( \ln[\text{PAO}] \) vs. time being in close accordance with one another, with values of \( 0.0059 \text{ h}^{-1} (\pm 2.2 \times 10^{-3}) \) and \( 0.0062 \text{ h}^{-1} (\pm 9.8 \times 10^{-4}) \) recorded for the all peak and single peak methods respectively over 0 – 60 hours (Figure 4.11).
Figure 4.11 Plots of ln[PAO] vs. time for the: a) all peak, b) single peak methods of determining $K_{rel}$ for PAO degradation

A Rancimat induction period was observed for the PAO and was found to be 33.15 hours. This reflects a greater stability for PAO compared to FAME. If the ln[PAO] vs. time data points from 30 – 60 h are analysed then the rate constant of the PAO degradation is observed. The gradients of the plots for both the all peak and single peak methods correlate well with values of 0.0093 and 0.0104 h$^{-1}$ respectively (Figure 3.12).

Figure 4.12 Plots of ln[PAO] vs. time from 30 – 60 hours for the a) all peak and b) single peak methods of determining $K_{rel}$ for PAO degradation

The infrared spectrum of PAO subjected to 60 hours oxidation shows little difference from that of PAO prior to oxidation. There is a peak at 1715 cm$^{-1}$ in the oxidised sample that does not appear in the original PAO spectrum, which is likely to arise from a carbonyl (C=O) stretch as a result of the oxidation. NMR analysis shows no significant evidence of PAO
oxidation with both the $^1$H and $^{13}$C spectra being virtually the same for neat PAO and that of PAO oxidised for 60 hours by the Rancimat.

4.5.3. Binary Mixture of SME and PAO Oxidation
An induction period of 1.13 hours was recorded for the oxidation of the binary SME/PAO mixture by the Rancimat method. The oxidation was carried out for 48 hours and the degradation of the PAO monitored by periodic sampling and GC analysis. A plot of the natural logarithm of PAO concentration – as determined by the single peak method – against time for the SME/PAO gives a gradient of 0.0051 h$^{-1}$ (Fig 4.13 a), which is relatively close to the 0.0062 h$^{-1}$ (Fig 4.13 b, black gradient) observed for neat PAO using the single peak method over 0 – 60 hours. Using this value obtained for the oxidation of PAO over 60 hours may imply that the PAO in the mixture is degrading at a similar rate to neat PAO.

![Figure 4.13](image_url) Plots of natural logarithm of PAO concentration vs. time for PAO in a) PAO/SME mixture and b) neat PAO

The binary mixture of SME and PAO has the significantly shorter Rancimat induction period of 1.13 hours than the 33.15 hours observed for neat PAO, which may imply that the oxidation of the FAME influences the stability of the PAO. Though the Rancimat induction period recorded for the binary mixture may well reflect the relative ease through which the FAME is oxidised rather than the stability of the PAO in the mixture. When GC data is taken into consideration, the PAO in the binary mixture appears to start degrading soon after the Rancimat induction period (Figure 4.13 a), similarly the concentration of neat PAO does not decrease significantly until after the 33 hour Rancimat induction period (Figure 4.13 b). The
gradients observed in each plot after the respective Rancimat induction periods, indicate that the PAO in the binary mixture with SME degrades at close to half of the rate of the neat PAO, with relative rate constants of 0.0051 h\(^{-1}\) and 0.0091 h\(^{-1}\) respectively. So for PAO in the binary mixture, despite starting to oxidise a lot sooner than the neat PAO, after 48 hours both systems show similar overall degradation of 20 % and 23 % loss from initial concentrations respectively.

The cause of the reduced degradation rate of PAO in the mixture could be attributed to similar effects as those observed in the mixture of C18 FAME where, the most reactive substrate oxidises at its normal rate, causing the less reactive components in the mixture to oxidise slower than their normal rate whilst there are still more reactive species present. This could be thought of in the context of antioxidants, whereby the more readily oxidised substrate acts as an antioxidant to the less readily oxidised substrate, thereby slowing the oxidation rate of the less reactive substrate. The formation of FAME peroxy radicals may facilitate the propagation of the oxidation of PAO, though when competing with the more reactive FAME molecules to interact with the peroxy radicals, the PAO may be less competitive and ultimately oxidise at a slower rate.

4.6. Conclusions
This chapter has examined the oxidation kinetics of single-component and multi-component systems under Rancimat oxidation conditions. Under these conditions, a difference in the oxidation kinetics of a given FAME in a single component and multi component system has been observed. Further to this, changes in the rate constants of FAMEs have been observed within a multi component system (Table 4.6).

<table>
<thead>
<tr>
<th>System</th>
<th>FAME</th>
<th>18:0</th>
<th>18:1</th>
<th>18:2</th>
<th>18:3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Individual</td>
<td></td>
<td>0.014</td>
<td>1.00</td>
<td>1.18</td>
<td>1.25</td>
</tr>
<tr>
<td>1:1:1:1 (0 – 6 h)</td>
<td></td>
<td>0.022</td>
<td>0.22</td>
<td>1.11</td>
<td>2.44</td>
</tr>
<tr>
<td>1:1:1:1 (9 – 48 h)</td>
<td></td>
<td>0.016</td>
<td>0.29</td>
<td>1.72</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 4.7 Relative rate constants (\(K_{rel}\)) for the autoxidation FAME when oxidised individually and in a quaternary mixture model FAME system (1:1:1:1)
The oxidation of C18 FAMEs in single-component systems gives comparatively close $K_{rel}$ values for each of the unsaturated FAMEs, contrary to the findings reported in the literature.\textsuperscript{183-186} However, in both commercial biodiesel and blends of model FAME, the studies have shown significant differences between $K_{rel}$ values of the unsaturated FAMEs, with polyunsaturated FAME depleting at a faster rate in the mixture.

Changes of degradation rate are observed when a particular FAME becomes depleted in the mixture, as demonstrated by the reported changes in value of $K_{rel}$ for 18:1 and 18:2 which coincide with the complete oxidation of 18:3 in the quaternary model FAME mixture.

Studies on the oxidation kinetics of a binary mixture of SME and PAO indicate that under the experimental conditions applied, PAO starts to oxidise earlier in the binary system with SME than when PAO is oxidised as a single component. However, the PAO in the binary mixture oxidises at approximately half the rate of the neat PAO. This kinetic data suggests that the oxidation of SME does not adversely accelerate the oxidation rate of PAO.

The multi-component FAME system and the binary PAO and SME mixture have both exhibited similar behaviour, with both systems displaying a reduction in the oxidation rates of less readily oxidised components when a more reactive species is present. To this extent, the more readily oxidised component may be described as a pseudo-antioxidant to the other less reactive species, in the manner that affects their oxidation rates.
5. Investigating the Influence of Additives on the Induction Period of FAMEs and PAO
5.1. Introduction
This chapter investigates the oxidative stability of FAMEs, PAO (used as model base oil) and binary combinations of the two when additives are included. The effect of primary and secondary antioxidants upon the substrate system is primarily investigated and instances of synergy are identified. The work is extended to consider the effect of surfactants on the oxidative stability of these model systems. Antioxidants and surfactants are two important classes of additive content found in engine-lubricating oils and therefore their influence upon biodiesel and base oil oxidative stability are of particular interest.

5.1.1. Antioxidants in Fuels and Lubricants
The oxidative stability of biodiesel varies depending on the source of the FAME, as the oils from different plant sources contain different levels of natural antioxidants and contain variation in the relative fatty acid composition. Biodiesel containing more polyunsaturated FAME (PUFAME) tend to have poorer oxidative stability than those with lesser concentrations of PUFAME. As a result, the amount of antioxidants required to stabilise FAME varies on a case to case basis, with a target value of 6 hours to be met to satisfy the European standard outlined by EN14 112.  

Numerous studies have been carried out to assess the use of different antioxidants to stabilise biodiesel from various sources. Some examples of antioxidants (AO) commonly tested in the chemical literature are shown in Figure 5.1.

![Selected synthetic AOs commonly tested in the literature](image)

**Figure 5.1** Selected synthetic AOs commonly tested in the literature (see text below for definitions of abbreviations)

There is no clear agreement in the literature on the most effective antioxidant for use with FAME. Some of the antioxidants are reported to be better than others in different FAME or...
biodiesel sources. The means of evaluating the AOs performance also varies across the range of studies conducted. Dunn reported the relative antioxidants activities of the following AOs in SME by static pressure differential scanning calorimetry (PDSC) as: butylated hydroxyanisole (BHA) ~ propyl gallate (PG) > t-butyl hydroxyquinone (TBHQ) ~ butylated hydroxytoluene (BHT) > α-tocopherol > none. Dunn subsequently reported that the same AOs in SME had the following relative antioxidant activities, as determined by dynamic PDSC: BHT ~ PG > BHA > TBHQ > α-tocopherol > none. In a study by Tang et al., soybean-, cottonseed-, and yellow grease-based biodiesels induction periods (IPs) were extended by the following AOs in the order of: PG ~ pyrogallol (PY) > DTBHQ ~ TBHQ > BHA ~ BHT, which were related by the authors to the relative electronegativities of the phenolic AOs, which they report to be in the same order as the antioxidant activities.

Antioxidants that are effective in neat FAME may also be unsuitable for use in lubricating oils or petrodiesel, or blends thereof with biodiesel, due to poor solubility in non-polar base oil or volatile loss when exposed to high temperatures.

The use of sulphur and phosphorus as antioxidants in base oils has been known from the early stages of lubrication science. Elemental sulphur and phosphorus were both used for their oxidation inhibiting properties but proved to be problematic owing to the corrosive effect on certain metals and alloys. Consequently organic sulphur and phosphorus containing compounds such as sulphides, phosphates and phosphites (Figure 5.2) were employed with positive results.

![Figure 5.2 Selected Phosphorus and sulphur containing antioxidants](image)

One commonly used type of additive in lubricant formulations is zinc \( OO' \)-dialkyldithiophosphate (ZDDP). ZDDP is a coordination complex of zinc and 2 \( OO' \)-dialkyldithiophosphate ligands as represented by the structure shown in Figure 5.3.
alkyl moiety can be aliphatic, cyclic or aromatic, which influences the physical state of the complex, its solubility in various solvents, and its thermal or oxidative stability properties. Mixtures of low molecular and higher molecular weight alkyl moiety ZDDPs are produced for performance and economic reasons.

ZDDP is widely employed for its antiwear properties, as well as its antioxidant action as a hydroperoxide decomposer. It is one of the most effective and economically viable additives in lubricants, but it does contain phosphorus and sulphur. Lower levels of phosphorus and sulphur are required in certain of today’s oil formulations to help meet industry standards on lower emissions. Phosphorus is believed to bind to the precious metals used in catalytic converters in modern engines, thus potentially poisoning them and compromising emission standards. Sulphur affects emissions directly as well as potentially indirectly through the negative interaction with the catalysts in exhaust after-treatment devices. As a result, combinations of ZDDP and organic antioxidants may be employed when ZDDP content is constrained by chemical limits on phosphorus and sulphur content.

### 5.1.2. Antioxidant Synergy

The term synergy refers to the work of two or more components working together to achieve results greater than the sum of those components working individually. The synergistic relationship between two antioxidants can be expressed and quantified by equation 5.1. Any value below 0 % can be considered as antagonistic, whilst any value above 0 % is deemed as synergistic.

\[
\% \text{ Synergism} = \frac{(IP \cdot AO_{1} + AO_{2} \text{ combined}) - (IP \cdot AO_{1} + AO_{2} \text{ alone})}{(IP \cdot AO_{1} + AO_{2} \text{ alone})} \times 100
\]

[Eq 5.1]

An adaptation of this equation is used throughout this chapter to assess the synergic potential of combinations of antioxidants. Equation 5.2 shows working for a term dubbed
the ‘synergy baseline’ which can be shown in plots to represent the minimum induction period that could defined as synergistic effect. Where \( IP_{AO} \) is the Rancimat Induction Period recorded using antioxidant \( x \), and \( IP_0 \) is the induction period of the substrate without any antioxidants.

\[
\text{Synergy Baseline} = IP_{AO_1} + IP_{AO_2} - IP_0
\]  

[Eq 5.2]

Antioxidant synergy arises through a number of different possible interactions between the components and the substrate being stabilised. As discussed in the section 1.6.1. there are various modes of antioxidant activity, ranging from radical chain-breaking AOs to metal chelators. When two AOs with the same mechanistic action are combined to provide a synergistic effect, for example when two chain-breaking, hydrogen donating AOs are used together, it is termed homo-synergism. A good example of this is the interaction between tocopherol (vitamin E) and ascorbic acid (vitamin C), which when used individually can both act upon peroxy radicals through hydrogen transfer reactions, thus preventing propagation of the autoxidation. When those two antioxidants are used together, the tocopherol is more kinetically labile and therefore reacts faster with the peroxy radicals than the ascorbic acid. The role of the ascorbic acid has been identified as a synergist that regenerates the faster and more effective tocopherol\textsuperscript{211-213} (Figure 5.4).

![Figure 5.4 Tocopherol-ascorbic acid synergy mechanism](image_url)

When two AOs with different activities such as a chain-breaking hydrogen donor and a hydroperoxide decomposer are used together it is termed hetero-synergism. By combining the non-propagating action of one AO with the non-radical product forming action of
another AO, a more complete form of synergy can be observed than with those of homosynergistic combinations.

5.2. Antioxidant Screening in Neat SME

Initial antioxidant screening was carried out in neat SME biodiesel to evaluate the performance of a selection of known antioxidant types in the Rancimat oxidation tests at 110°C (Table 5.1). SME was selected for the tests as it was the least stable of the biodiesels evaluated (see Section 4.3), and would therefore provide an indication of worst case performance in neat biodiesel. The chosen antioxidants are all soluble in lubricating base oil and represent classes widely used in engine lubricating oils, plus two phenol antioxidants (BHT and Toco) more commonly associated with biodiesel use.

<table>
<thead>
<tr>
<th>Abbreviations to be used in Figures and Tables</th>
<th>Antioxidant Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADPA</td>
<td>Alkylated diphenylamine</td>
</tr>
<tr>
<td>HPh</td>
<td>Synthetic Phenol</td>
</tr>
<tr>
<td>OS</td>
<td>Organic Sulphur</td>
</tr>
<tr>
<td>BHT</td>
<td>Butylated Hydroxytoluene</td>
</tr>
<tr>
<td>Toco</td>
<td>α-Tocopherol (Vitamin E)</td>
</tr>
<tr>
<td>ZDDP</td>
<td>Zinc ( OO^- ) diisopropylidithiophosphate</td>
</tr>
</tbody>
</table>

**Table 5.1** Antioxidants used in initial screenings, defined by: name (abbreviated) and type

The alkylated diphenylamine (ADPA), synthetic phenol (HPh), and organic sulphur (OS) antioxidants were supplied by Infineum UK Ltd. The butylated hydroxytoluene (BHT) and α-tocopherol (Toco) were purchased from Sigma Aldrich. The zinc \( OO^- \) diisopropylidithiophosphate (ZDDP) was prepared according to the procedure reported in the literature\(^{150}\) (see Section 2.6.1.).

Figure 5.5 a shows the performance of these antioxidants at various concentrations (0 – 5000 ppm) in neat SME as evaluated in the Rancimat apparatus at 110°C. BHT appears to be the best antioxidant under these conditions across all concentrations, with HPh also demonstrating good activity. α-tocopherol shows a moderate response, whilst ZDDP, ADPA
and OS antioxidants all show poor antioxidant activity at the range of concentrations and conditions tested. Initially ZDDP appears to perform moderately at the lower concentrations, but induction periods actually become smaller at 2000 and 5000 ppm.

Figure 5.5 Plots of: a) Induction period of SME under the influence of AOs at various concentrations, b) The natural logarithm of AO concentration vs. induction period in SME, c) Linear fits for AOs showing 1st order AO activity, d) inverse AO concentrations raised to the power of $n$ vs. induction period for HPh and BHT in neat SME

A plot of the natural logarithm of antioxidant concentration vs. induction period provides a useful representation of the relative antioxidant activity of each compound screened (Figure 5.5 b). This data indicates the reaction orders of the consumption of the antioxidants, with the ADPA, OS and Toco antioxidants exhibiting first order reaction kinetics, given their straight line plots (Figure 5.5 c). The organic sulphur (OS) compound shows pro-oxidant activity under these conditions as it possesses a negative gradient. No straight line fits were
made for HPh, BHT or ZDDP by the transformation shown. For ZDDP the data points failed to show a consistent trend between concentration and induction period so therefore did not give a linear fit. Whilst for HPh and BHT linear plots were achieved by raising the antioxidant concentrations to the power \( n \). Figure 5.5 d shows the linear fits for HPh and BHT where \( n = 0.50 \) and 0.55 respectively, giving partial reaction orders of 0.50 and 0.45 respectively. The relative antioxidant activity as determined by the gradients of the linear plots, give values of 1 and 1.06 for HPh and BHT respectively.

The partial reaction orders for HPh and BHT are indicative of participation of the antioxidants in multistep reactions. In a kinetic study on BHT and the 2,2-diphenyl-1-picrylhydrazine (DPPH) radical by Berset and co-workers, it was found that the antioxidant BHT had a partial order of 0.4, and overall pseudo 2\(^{\text{nd}}\) order reaction in the quenching of the radical.\(^{215}\) The authors proposed a multi-step reaction mechanism for the antioxidant activity of BHT, offering three different fates for the antioxidant. Two of the routes allowed the quenching of two radicals each, and the other involved the dimerization of two intermediates followed by further reactions with DPPH radicals, with 3 DPPH radicals being quenched for every molecule of BHT (Figure 5.6).

![BHT reaction mechanism as proposed by Berset et al.](image)

The close accordance of the literature value of the partial orders of the antioxidant and the experimental values obtained in this study suggests that the BHT under the described conditions, undergoes a similar reaction mechanism to the one described by Berset et al.
Also, given the close partial orders calculated for BHT and HPh, the two antioxidants may follow similar reaction mechanisms.

5.3. Antioxidant Synergy in Neat SME

After the initial screening of antioxidants, three were selected to use in synergy screening experiments. The antioxidants used were ADPA, HPh, and ZDDP, at concentrations of approximately: 250, 500, 1000, 2000, 5000, and 10,000 ppm. In order to test the synergistic relationship between two components, two of the antioxidants were combined together in approximately equal concentrations in SME to form a binary antioxidant system. The induction period of the resulting solution was measured by the Rancimat apparatus at 110°C. If the Rancimat induction period was greater than the induction periods of the two individual components added together with the induction period of neat SME subtracted then synergy could be inferred.

5.3.1. ADPA in Neat SME

This alkylated diphenylamine (ADPA) shows limited antioxidant activity at all concentrations tested under these conditions (Table 5.2). Even at an antioxidant concentration in excess of 10,000 ppm the induction period of SME is extended by less than one hour more than with no antioxidants. This is in agreement with previous work by Sharma et al. who reported the performance for an ADPA in soybean oil, noting that the oxidation induction time (OIT) for ADPA at 2% concentration has a similar value to that of neat soybean oil.216 As Sharma comments, such results with ADPA exhibiting poor antioxidancy may be due to the relatively low temperatures used in this study.
### Table 5.2 Induction periods of SME with the antioxidant ADPA at varying concentrations

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>Induction Period (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.60</td>
</tr>
<tr>
<td>273</td>
<td>0.69</td>
</tr>
<tr>
<td>555</td>
<td>0.75</td>
</tr>
<tr>
<td>1100</td>
<td>0.81</td>
</tr>
<tr>
<td>2198</td>
<td>0.89</td>
</tr>
<tr>
<td>4988</td>
<td>1.02</td>
</tr>
<tr>
<td>10015</td>
<td>1.53</td>
</tr>
</tbody>
</table>

5.3.2. **HPh in Neat SME**

The performance of the synthetic phenol antioxidant shows an excellent response in SME at all concentrations (Table 5.3). This antioxidant outperforms ADPA and ZDDP when screened individually under these conditions, as seen previously. Hindered phenolic antioxidants are known to be one of the most effective types of antioxidants for stabilising hydrocarbons.\(^{204}\)

### Table 5.3 Induction periods of SME with the antioxidant HPh at varying concentrations

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>Induction Period (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.60</td>
</tr>
<tr>
<td>267</td>
<td>0.95</td>
</tr>
<tr>
<td>510</td>
<td>1.61</td>
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<tr>
<td>1014</td>
<td>2.24</td>
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<tr>
<td>2029</td>
<td>3.34</td>
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<tr>
<td>5010</td>
<td>5.08</td>
</tr>
<tr>
<td>10044</td>
<td>12.97</td>
</tr>
</tbody>
</table>

5.3.3. **ZDDP in Neat SME**

Table 5.4 shows the induction period values for Zinc $OO'$-diisopropylidithiophosphate (ZDDP) at varying concentrations in SME under the same conditions. Initially the relationship between concentration and induction period shows little increase between 0 – 2000 ppm,
indicating that the antioxidant is having little effect at this concentration range. A more substantial increase in IP is observed when SME is treated with ZDDP at 10,000 ppm.

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>Induction Period (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.60</td>
</tr>
<tr>
<td>252</td>
<td>0.84</td>
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<tr>
<td>500</td>
<td>1.14</td>
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<td>999</td>
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<tr>
<td>1999</td>
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<tr>
<td>5144</td>
<td>1.20</td>
</tr>
<tr>
<td>9846</td>
<td>2.47</td>
</tr>
</tbody>
</table>

Table 5.4 Induction periods of SME with the antioxidant ZDDP at varying concentrations

5.3.4. ADPA and HPh Synergy in Neat SME
Results for Rancimat Induction Period at 110°C obtained from the pairing of ADPA and HPh antioxidants in a 1:1 ratio in neat SME are shown in Figure 5.7. This data shows a response which is slightly above the synergy baseline for the combination of antioxidants at lower concentrations (250 – 2000 ppm), a large synergy effect at 5000 ppm, whilst no synergy at 10,000 ppm is observed. Given the magnitude of the synergy at 5000 ppm, it may be that the data point is an outlier as the other values trend towards a minimal synergistic response. The IPs recorded for HPh alone exceeded those obtained by the synergy pairing of the two antioxidants at equal total antioxidant concentration. For instance the IP for HPh at a concentration of 10,000 ppm is greater than the IP for ADPA/HPh at approximately 5000 ppm each (total antioxidant concentration of 10,000 ppm). This trend was observed at all equivalent antioxidant concentrations.
Reports in the literature suggest that there can be a significant synergy between these two classes of antioxidants in base oils. Both species are known radical scavengers, and their synergistic properties are thought to arise from a hydrogen radical donation interaction. ADPAs react quickly with alkyl, alkoxy, and peroxy radicals, forming aminyl radicals in the process. The slower hindered phenol acts as a hydrogen donor to regenerate the ADPA. The hindered phenol is able to react with peroxy radicals until it is consumed, after which the ADPA will begin to be consumed by the oxidation reactions (Figure 5.8).

**Figure 5.7** Plot of antioxidant concentration for the synergy pairing of ADPA and HPh vs. induction period in SME (HPh + ADPA = theoretical synergy baseline (from Equation 5.2), HPh/ADPA = experimental values)
5.3.5. ADPA and ZDDP Synergy in Neat SME

Both of these two antioxidants performed relatively poorly when screened individually in SME. However, when combined the response to SME was excellent (Figure 5.9) under the given Rancimat conditions. At lower concentrations (250 – 2000 ppm) the synergistic effect was minimal, but at 5000 ppm and above the synergy increases with increasing antioxidant concentration. There is a dramatic rise in performance with 300% synergism being reached and a linear relationship is found for this combination of antioxidants between 2000 and 10,000 ppm. This effect may arise from the hetero-synergism between the two different types of antioxidant actions of the components, ADPA being a radical scavenger, and ZDDP a hydroperoxide decomposer. Cases of ADPA and hydroperoxide decomposer antioxidant synergism in base oils have been reported as effective in increasing induction periods and lowering sludge formation,\textsuperscript{220} whilst in soybean oil synergy between ADPA and antiwear additives with 2\textsuperscript{0} antioxidant activity has been observed.\textsuperscript{216}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{synergistic_mechanism.pdf}
\caption{Proposed synergistic mechanism between ADPAs and BHT by references\textsuperscript{218-220}}
\end{figure}
Chapter 5

Figure 5.9 Plot of antioxidant concentration for the synergy pairing of ADPA and ZDDP vs. induction period in SME (ADPA + ZDDP = theoretical synergy baseline (from Equation 5.2), ADPA/ZDDP = experimental values).

The Induction period recorded for this AO pairing at 5000 ppm each is far greater than the values recorded for either antioxidant individually at 10,000 ppm and the theoretical synergy baseline for the synergy pairing at 10,000 ppm each. Also, the induction period at a concentration of 10,000 ppm each is greater than the induction period observed for the equivalent concentrations for the pairing of ADPA and HPh (Figure 5.8).

5.3.6. HPh and ZDDP Synergy in Neat SME
As with the pairing of ADPA and ZDDP, the combination of HPh and ZDDP couples a 1° and 2° antioxidant, resulting in good synergy at higher concentrations. In this case however, at the lower concentrations (250 – 2000 ppm) the experimental results show lower induction periods than the theoretical synergy baseline, and lower than the values of HPh alone at the corresponding concentrations (Figure 5.10). At antioxidant concentrations of 5000 and 10,000 ppm the synergism is good but the improvement relative to the individual
components is not as good as is it in ADPA and ZDDP, possibly due to the strong antioxidant activity of HPh on its own under these conditions. However, the Rancimat induction periods at 5000 and 10,000 ppm are greater for the pairing of HPh and ZDDP than ADPA and ZDDP at the same concentrations. At 10,000 ppm HPh singularly outperforms the synergy pairing of HPh and ZDDP at 5000 ppm each.

![Figure 5.10](image)

**Figure 5.10** Plot of antioxidant concentration for the antioxidant pairing of HPh and ZDDP vs. induction period in SME (HPh + ZDDP = theoretical synergy baseline (from Equation 5.2), HPh/ZDDP = experimental values)

### 5.3.7. Neat SME Summary

The source of the synergy between ZDDP and both ADPA and HPh may arise due to the hetero-synergism exhibited. When ZDDP is used alone it performs poorly, possibly due to the stoichiometry of ZDDP’s hydroperoxide decomposition mechanism. Four equivalents of ZDDP are required to reduce one equivalent of a hydroperoxide during the initial stages of the decomposition mechanism (Equation 5.3). \(^{221}\)

\[
4 \text{[}((\text{RO})_2\text{PS}_2)_2\text{Zn}] + \text{R}_1\text{OOH} \rightarrow [((\text{RO})_2\text{PS}_2)_6\text{Zn}_4\text{O}] + 2 ((\text{RO})_2\text{PS}_2) + \text{R}_1\text{OH} \quad [\text{Eq 5.3}]
\]
During FAME autoxidation its autocatalytic nature results in the formation of hydroperoxides at an exponential rate if left uninhibited. If the concentration of hydroperoxides is in excess of the ZDDP then the influence of the AO may be minimal. However, if a radical chain breaking AO such as ADPA or HPh is used to inhibit the propagation step of the autoxidation, then the rate of hydroperoxide formation can be significantly reduced. With the hydroperoxide concentration suppressed by a primary AO, if the ZDDP concentration is in sufficient excess of the hydroperoxide concentration, then the ZDDP can decompose the hydroperoxides more effectively, resulting in a synergistic effect. Therefore the concentration of the ZDDP relative to hydroperoxide concentration may be important as to its ability to function as an effective antioxidant.

Examples in the literature report synergy between phenolic antioxidants such as BHT and antiwear agents such as antimony dialkyldithiocarbamate and zinc diamyldithiocarbamate. Improved results in oxidation induction times and rotary bomb oxidation tests for synergy combinations in soybean oil were observed compared to when the antioxidants are used individually, though no explanations as to why were made.  

If we consider the overall performance of each of the synergy combinations compared to one another (Figure 5.11), we observe that at the lower concentrations between 250 and 2000 ppm, the combinations containing ZDDP have very close induction periods. At concentrations above 2000 ppm a substantial increase in induction periods is realised. One may hypothesise that under these particular conditions a certain threshold quantity of ZDDP and primary antioxidant between 2000 and 5000 ppm, is required for the AOs to act as effective synergists. This concentration range whereby ZDDP and a primary AO become effective synergists may relate to the stoichiometry of ZDDP and the hydroperoxide concentrations. Both ADPA and HPh when combined with ZDDP gave longer induction periods at 10,000 ppm each than the synergy pair of ADPA and HPh together at the same concentration. This result implies that at higher concentration under the Rancimat conditions in neat SME, the hetero-synergy action from combining two antioxidants with different mechanisms working together appears more effective than the homo-synergism of two antioxidants with the same action, as is the case with ADPA and HPh. At lower concentrations the homo-synergy mechanism appears to be better than hetero-synergism.
for SME under the experimental conditions applied, this may be due to the concentration
dependence of ZDDP discussed previously.

![Graph](image.png)

**Figure 5.11** Comparison of Rancimat induction periods from different antioxidant
combinations at varying concentrations in neat SME

### 5.4. Antioxidant Synergy in Binary Mixture of SME and PAO

The same antioxidants in the same concentrations and under the same conditions as were
used for the individual and synergy pair screenings in neat SME, were also screened in a
binary mixture of SME and polyalphaolefins (PAO) in an approximately 50:50 ratio. The PAO
is used as model base oil in order to simulate some of the conditions under which FAME and
the components of an engine lubricant may come into contact with one another in the
crankcase and oil sump.
5.4.1. ADPA in Binary Mixture of SME and PAO
The response of the SME/PAO mixture to ADPA (Table 5.4) is slightly better than the response of neat SME to the same antioxidant. The relative increase of the induction periods at 10,000 ppm compared to the mediums when no antioxidants are used is 2.55 for neat SME, and 3.1 for SME/PAO.

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>Induction Period (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.13</td>
</tr>
<tr>
<td>257</td>
<td>1.50</td>
</tr>
<tr>
<td>504</td>
<td>1.53</td>
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<tr>
<td>1003</td>
<td>1.81</td>
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<td>2009</td>
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<tr>
<td>4968</td>
<td>3.09</td>
</tr>
<tr>
<td>9943</td>
<td>3.50</td>
</tr>
</tbody>
</table>

Table 5.5 Induction periods of SME/PAO with the antioxidant ADPA at varying concentrations

5.4.2. HPh in Binary Mixture of SME and PAO
The antioxidant HPh shows an excellent linear response to the SME/PAO medium under the prescribed conditions (Table 5.5), with the highest concentration extending the induction period by 37.5 times that of the SME/PAO without antioxidants. Comparing this effect of HPh to the analogous observation in neat SME, whereby the highest induction period is an increase by a factor of 21.6 on that of the medium with no antioxidants, suggests dilution of the FAME with PAO is beneficial to the antioxidant response.
Table 5.6 Induction periods of SME/PAO with the antioxidant HPh at varying concentrations

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>Induction Period (h)</th>
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<tr>
<td>0</td>
<td>1.13</td>
</tr>
<tr>
<td>255</td>
<td>2.56</td>
</tr>
<tr>
<td>507</td>
<td>3.73</td>
</tr>
<tr>
<td>1011</td>
<td>5.62</td>
</tr>
<tr>
<td>2022</td>
<td>9.68</td>
</tr>
<tr>
<td>5022</td>
<td>21.70</td>
</tr>
<tr>
<td>10046</td>
<td>42.41</td>
</tr>
</tbody>
</table>

5.4.3. ZDDP in Binary Mixture of SME and PAO

In SME/PAO under the Rancimat test conditions, ZDDP exhibits relatively little antioxidant activity at low AO concentrations (250 – 1000 ppm), but above 1000 ppm an improvement in the performance of the antioxidant is observed, with a maximum observed induction period of 12.95 hours reached at approximately 10,000 ppm. The response of SME/PAO to ZDDP is considerably better than that of SME at equivalent concentration, with a relative increase of induction period at maximum concentration of 11.46 times that without antioxidants, compared to an increase of just 4.12 times for the equivalent amounts of ZDDP in neat SME. Based on the result for ZDDP in neat SME as discussed in Section 5.3.7, the performance of ZDDP in SME/PAO under the Rancimat conditions may be concentration dependant, with a threshold level between 1000 and 2000 ppm possibly indicating the point at which the ZDDP – hydroperoxide stoichiometry is greater than 4:1. It may be at this threshold level that the ZDDP’s hydroperoxide decomposing mechanism become more effective and results in greater antioxidancy being observed.
### Table 5.7

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>Induction Period (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.13</td>
</tr>
<tr>
<td>255</td>
<td>1.11</td>
</tr>
<tr>
<td>507</td>
<td>1.12</td>
</tr>
<tr>
<td>1011</td>
<td>0.95</td>
</tr>
<tr>
<td>2022</td>
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<tr>
<td>5022</td>
<td>5.01</td>
</tr>
<tr>
<td>10046</td>
<td>12.95</td>
</tr>
</tbody>
</table>

Induction periods of SME/PAO with the antioxidant ZDDP at varying concentrations

#### 5.4.4. ADPA and HPh Synergy in Binary Mixture of SME and PAO

Figure 5.12 shows the induction periods for both ADPA and HPh individually and in synergy pairings at various concentrations. As with neat SME, the response of the SME/PAO to HPh is significantly better than that of ADPA. At all concentrations there is little or no synergy between the two components under these conditions, a similar trend was observed for the same combination of antioxidants in neat SME.
5.4.5. ADPA and ZDDP Synergy in Binary Mixture of SME and PAO

In the binary mixture of SME and PAO, the combination of ADPA and ZDDP provided interesting results. As observed previously, at low antioxidant concentrations a minimal synergy effect was observed. When the antioxidants are used at concentrations of 2000 ppm and above significant synergistic effects are observed, although at the maximum concentration tested, 10,000 ppm, no induction period value was recorded (Figure 5.13). Despite numerous attempts to report an induction period at the maximum concentration, the Rancimat conductivity curve failed to provide a clear inflection to indicate an induction period. Instead the curve gradually increased until it reached the maximum conduction measurement. This information may indicate that the design of the Rancimat method might not be well suited to the use of relatively high levels of antioxidant.

The synergistic effect that is observed at the concentrations where Rancimat induction periods were obtained may be resultant of a hetero-synergy mechanism whereby ADPA
suppresses the hydroperoxide formation, allowing ZDDP to decompose the hydroperoxides more effectively.

![Plot of antioxidant concentration for the synergy pairing of ADPA and ZDDP vs. induction period in SME/PAO (ADPA + ZDDP = theoretical synergy baseline (from Equation 5.2), ADPA/ZDDP = experimental values)](image)

**Figure 5.13** Plot of antioxidant concentration for the synergy pairing of ADPA and ZDDP vs. induction period in SME/PAO (ADPA + ZDDP = theoretical synergy baseline (from Equation 5.2), ADPA/ZDDP = experimental values)

### 5.4.6. HPh and ZDDP Synergy in Binary Mixture of SME and PAO

The data from Figure 5.14 shows that at lower concentrations the induction periods for the synergy pair are slightly lower but close to the values obtained for HPh alone. Although they are generally slightly lower this may be due to minor variations in concentrations of antioxidants used in each test. It appears that at these lower concentrations the ZDDP is inactive, given that induction periods almost match those for HPh alone, suggesting that HPh may be working independently. Experiments with ZDDP at a fixed concentration and varying the synergist concentration could support this. Again, as with this synergy pair in neat SME, at a concentration above 2000 ppm excellent synergy is observed. Given these findings and those for ZDDP in SME/PAO on its own, there is further support to the idea of
that under these conditions a threshold level is required for ZDDP to become effective as an antioxidant and synergist.

**Figure 5.14** Plot of antioxidant concentration for the synergy pairing of HPh and ZDDP vs. induction period in SME/PAO (HPh + ZDDP = theoretical synergy baseline (from Equation 5.2), HPh/ZDDP = experimental values)

### 5.4.7. Binary Mixture of SME and PAO Summary

Comparison of all the synergy pairings in the SME/PAO medium (Figure 5.15) shows a clear difference in the response of the antioxidants. Similar trends to those seen with same AO pairings in neat SME under the same experimental conditions are also observed, but in SME/PAO the Rancimat induction periods are extended further. The strongest antioxidant activity is observed with the combination of HPh and ZDDP with the highest induction periods being reached. Again, in this medium ZDDP also displays good AO action when used above a threshold level as an antioxidant and a synergist.
Although the longest induction periods are a result of the pairing of HPh and ZDDP, ADPA and ZDDP have the highest synergist relationship and hence synergistic interaction under these Rancimat conditions at 110°C (Figure 5.16). Also from this data it is possible to observe the lack of synergism between ADPA and HPh. As good a method as it is for evaluating the synergism and interaction between antioxidants, the term synergy is relative to the activity of the individual components and does not necessarily reflect the best performance.

Figure 5.15 Comparison of induction periods from different synergy combinations vs. antioxidant concentration in SME/PAO
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5.5. Antioxidant Synergy in Neat PAO
In these experiments the same antioxidants were screened at the same concentrations in neat PAO as were used for the experiments reported in sections 5.3 and 5.4.

5.5.1. ADPA in Neat PAO
The response of ADPA to neat PAO is considerably better than that observed for neat SME or SME/PAO. Even at the low antioxidant concentration of 253 ppm, the induction period is extended almost 6 times over that with no antioxidant. The increases in induction period with concentration show a non-linear relationship, with the relative effectiveness of the antioxidant decreasing at higher concentrations.

Figure 5.16 Synergy percentages for antioxidant pairs in SME/PAO
### Table 5.8 Induction periods of PAO with the antioxidant ADPA at varying concentrations

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>Induction Period (h)</th>
</tr>
</thead>
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<td>33.2</td>
</tr>
<tr>
<td>253</td>
<td>198.4</td>
</tr>
<tr>
<td>501</td>
<td>318.4</td>
</tr>
<tr>
<td>1007</td>
<td>373.1</td>
</tr>
<tr>
<td>2022</td>
<td>475.7</td>
</tr>
</tbody>
</table>

5.5.2. **HPh in Neat PAO**

At the modest concentration of 250 ppm, HPh responded exceptionally well to PAO during an oxidation test. The induction period was extended by over 15 times compared to the recorded value for PAO without additives (Table 5.8). Owing to the excessive induction periods expected for higher concentrations of HPh in PAO, the experiments required to obtain the data were aborted at approximately 844 hours. The magnitude of the response at only 250 ppm demonstrated the stability of the PAO with respect to oxidation and the effectiveness of HPh as an antioxidant in this medium.

### Table 5.9 Induction periods of PAO with the antioxidant ADPA at varying concentrations

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>Induction Period (h)</th>
</tr>
</thead>
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<td>507.58</td>
</tr>
<tr>
<td>499</td>
<td>N/D (&gt; 844)</td>
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<td>999</td>
<td>N/D (&gt; 844)</td>
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<tr>
<td>1999</td>
<td>N/D (&gt; 844)</td>
</tr>
</tbody>
</table>

5.5.3. **ZDDP in Neat PAO**

The additive ZDDP showed an excellent response to neat PAO. Figure 5.17 illustrates the linear relationship between ZDDP concentration and the induction period of PAO. This relationship was not observed in either the neat SME or SME/PAO. Given the excellent oxidative stability of the PAO, hydroperoxide formation will occur at a much slower rate than in FAMEs, therefore allowing ZDDP to display AO activity at low concentrations,
suggesting that in this system there may be a lower threshold for ZDDP to become active. At 2000 ppm ZDDP, the induction period is extended by nearly 20 times that of neat PAO. This significantly exceeds the response of the other mediums to ZDDP.

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>Induction Period (h)</th>
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<tr>
<td>1998</td>
<td>650.10</td>
</tr>
</tbody>
</table>

Table 5.10 Induction periods of PAO with the antioxidant ADPA at varying concentrations

5.5.4. Neat PAO Summary

The data in Figure 5.17 shows the magnitude of the PAO stability through the use of relatively low concentrations of AOs. Considering the performance of the same AOs in neat SME and the binary mixture SME/PAO at equivalent concentrations, this data goes some way to supporting the findings in section 4.5 whereby it was established from degradation studies that FAME and PAO oxidise independently of one another. The induction periods obtained for the SME/PAO mixture with AOs are far more representative of those from neat SME oxidation than those of neat PAO, indicating that the Rancimat IPs are induced from FAME oxidation rather than PAO. It is likely that the antioxidants in the mixture are consumed almost entirely by preventing the oxidation of the FAME present.
Surfactants

Lubricant surfactants are an important class of compounds which includes dispersants and detergents. Their primary roles in lubricating oil are to prevent particles and debris from adhering to the surfaces of an engine. Structurally dispersants and detergents are similar and both contain long non-polar hydrocarbon chains connected to a polar head group. The size of these groups however are what distinguish themselves apart, with dispersants typically having longer hydrocarbon chains and weaker head groups compared to detergents which have shorter non-polar tails and stronger polar heads (See Figure 5.18 for schematic representations). Detergents can also be made to be “over-based” whereby during their synthesis an excess of a metal oxide and carbon dioxide are used. The resulting product has a metal carbonate core which is useful for the neutralisation of acids that are present as blow-by-gases. Dispersants do not contain a metal and are often referred to as “ash-less dispersants”.

Figure 5.17 Plot of antioxidant concentrations vs. induction period in neat PAO
5.7. The Influence of Surfactants on Binary Mixture of SME and PAO

Three surfactants were supplied by Infineum UK Ltd for screening by the experimental crankcase model. These surfactants are simply referred to as dispersant A, detergent A and detergent B. These compounds are used at concentrations of 2000 and 5000 ppm and in combination with the synthetic phenol (HPh) and zinc $\text{OO}^\prime\text{-diisopropylidithiophosphate}$ (ZDDP) antioxidants at 2000 and 5000 ppm also. The induction periods of SME/PAO mixtures (50:50) containing various combinations of the surfactants and antioxidants were measured using the Rancimat at 110°C, with an upper limit of 24 hours. All induction periods presented in the following tables with a value above are data values taken from previous antioxidant screenings.

5.7.1. Dispersant A

The induction period for SME/PAO was marginally extended when dispersant A was introduced at concentrations of 2000 and 5000 ppm (Table 5.11). When dispersant A is used with other antioxidant components (at fixed concentrations, 2000 ppm) it is shown to act as either a pro-oxidant or an antioxidant depending on the AO that it is mixed with. When paired with HPh the IP of SME/PAO is increased rather more significantly than when the dispersant is on its own. When dispersant A is used in combination with ZDDP, the dispersant has the effect of a pro-oxidant by decreasing the induction period of the SME/PAO. It has been reported that succinimide complexes with ZDDP in fresh oil,\(^{222}\) which may explain the apparent decrease in AO activity of ZDDP. Basic aminic dispersants may also be expected to react with carboxylic acids, which may assist the induction period for
dispersant A alone or when combined with HPh. When dispersant A is used with both HPh and ZDDP the trend is less well defined. At a concentration of 2000 ppm dispersant A decreases the effectiveness of the two antioxidants, as seen by the decrease in recorded IP. Though, when dispersant A is used at the higher concentration of 5000 ppm, there is an improvement in the IP of the SME/PAO relative to the use of the two AOs without the surfactant (9.94 vs. 9.41 h respectively). With dispersant A having opposing effects on HPh and ZDDP individually, it would appear that the conflicting influence of dispersant A upon each AO, prevents neither an antioxidant or pro-oxidant effect of any real significance from prevailing when the HPh and ZDDP are combined.

<table>
<thead>
<tr>
<th>[Surfactant] (ppm)</th>
<th>No AO</th>
<th>HPh</th>
<th>ZDDP</th>
<th>HPh/ZDDP</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.06</td>
<td>9.68</td>
<td>1.97</td>
<td>9.41</td>
</tr>
<tr>
<td>2000</td>
<td>1.15</td>
<td>12.11</td>
<td>1.62</td>
<td>8.17</td>
</tr>
<tr>
<td>5000</td>
<td>1.28</td>
<td>13.44</td>
<td>1.51</td>
<td>9.94</td>
</tr>
</tbody>
</table>

Table 5.11 Recorded induction periods (h) for SME/PAO with dispersant A at varying concentrations and antioxidants at fixed concentrations (2000 ppm)

Similar results are observed for dispersant A when the concentration of antioxidants used is increased to 5000 ppm (Table 5.12). Again, the IP for SME/PAO is increased by using dispersant A in combination with HPh, with induction periods exceeding 24 hours. With ZDDP a decrease in the IP is observed on use of dispersant A. The increase in surfactant concentration from 2000 to 5000 ppm has little effect on the IP with almost identical values being recorded. When the pairing of HPh and ZDDP is used in combination with dispersant A the IP is decreased significantly when each component is at concentration of 5000 ppm. It is unclear as whether the general trend is that the IP decreases on increasing concentration of dispersant A as the value at a concentration of 2000 ppm was recorded as above 24 hours. Obviously that could mean it is greater than 50.13 h too, but given the trends observed at AO concentrations of 2000 ppm, it would be reasonable to assume that the value would not exceed the IP for the combination of antioxidants without dispersant A present.
Table 5.12 Recorded induction periods (h) for SME/PAO with dispersant A at varying concentrations and antioxidants at fixed concentrations (5000 ppm)

5.7.2. Detergent A
Detergent A shows pro-oxidant effects throughout the screening with and without antioxidants except for one result when the AOs are combined together and detergent A is present at a concentration of 5000 ppm (Table 5.13). On its own, detergent A decreases the oxidative stability of SME/PAO on increasing surfactant concentration. This trend continues when detergent A is combined with HPh. The same effect is observed for ZDDP and detergent A only the pro-oxidant activity is less effective, with a smaller decrease in IP observed than for HPh. When both antioxidants used in combination with detergent A, a slight decrease is observed at a surfactant concentrations of 2000 ppm, but at an increased concentration of 5000 ppm, the induction period is increased significantly to 13.12 h. This single result is surprising given the pro-oxidant effects otherwise observed for detergent A when used with each of the individual AOs.

Table 5.13 Recorded induction periods (h) for SME/PAO with detergent A at varying concentrations and antioxidants at fixed concentrations (2000 ppm)

The use of antioxidants at the higher concentration of 5000 ppm in combination with detergent A continued to show a decrease in SME/PAO IP (Table 5.14). For HPh a steady decrease in SME/PAO IP is observed on increasing surfactant concentration, whilst for ZDDP
an initial decrease in IP is seen when detergent A is introduced at a concentration of 2000 ppm, on increasing the surfactant concentration to 5000 ppm, a similar IP is recorded as when no detergent A is used. When both antioxidants are combined the IP of the SME/PAO without detergent A is about 50 hours, on the addition of detergent A at 5000 ppm this value decreases to around 20 hours. An IP above 24 hours is recorded for detergent A in combination with both AOs, this value is likely to be below the 50 hours seen for the two AOs without any surfactant given the trends already seen.

<table>
<thead>
<tr>
<th>[Surfactant] (ppm)</th>
<th>No AO</th>
<th>HPh</th>
<th>ZDDP</th>
<th>HPh/ZDDP</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.06</td>
<td>21.7</td>
<td>5.01</td>
<td>50.13</td>
</tr>
<tr>
<td>2000</td>
<td>0.74</td>
<td>16.88</td>
<td>3.59</td>
<td>24 &lt;</td>
</tr>
<tr>
<td>5000</td>
<td>0.63</td>
<td>11.04</td>
<td>4.94</td>
<td>20.02</td>
</tr>
</tbody>
</table>

Table 5.14 Recorded induction periods (h) for SME/PAO with detergent A at varying concentrations and antioxidants at fixed concentrations (5000 ppm)

5.7.3. Detergent B

On its own, detergent B displays some inherent antioxidant properties for a surfactant. An increase in IP is observed on increasing concentration of detergent B, with almost a three-fold increase in the oxidative stability of SME/PAO when the surfactant is present at a concentration of 5000 ppm. At the lower antioxidant concentrations of 2000 ppm, detergent B shows similar properties as dispersant A with strong antioxidant effects displayed when used with HPh, but slight pro-oxidant activity when used with ZDDP. When the two antioxidants are combined and detergent B is introduced an apparent pro-oxidant effect is observed at 2000 ppm, whilst at 5000 ppm a relatively strong antioxidant effect is seen.

<table>
<thead>
<tr>
<th>[Surfactant] (ppm)</th>
<th>No AO</th>
<th>HPh</th>
<th>ZDDP</th>
<th>HPh/ZDDP</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.06</td>
<td>9.68</td>
<td>1.97</td>
<td>9.41</td>
</tr>
<tr>
<td>2000</td>
<td>1.38</td>
<td>10.25</td>
<td>1.97</td>
<td>7.95</td>
</tr>
<tr>
<td>5000</td>
<td>3.00</td>
<td>17.01</td>
<td>1.73</td>
<td>12.09</td>
</tr>
</tbody>
</table>

Table 5.15 Recorded induction periods (h) for SME/PAO with detergent B at varying concentrations and antioxidants at fixed concentrations (2000 ppm)
From the experimental data where detergent B was combined with antioxidants at higher concentrations (5000 ppm) it is difficult to gauge the relative antioxidant activity of the surfactant. When used in combination with HPh there is a slight pro-oxidant effect at a surfactant concentration of 2000 ppm, whilst on increasing the concentration of detergent B to 5000 ppm an antioxidant effect is observed with the IP being in excess of 24 hours. A pro-oxidant effect is observed for the increase in surfactant concentration when used with ZDDP as demonstrated by subsequent the decreases in IP. However for the combination of both AOs with detergent B it is impossible to make any conclusions as at both surfactant concentrations the IP is in excess of 24 hours.

<table>
<thead>
<tr>
<th>[Surfactant] (ppm)</th>
<th>No AO</th>
<th>HPh</th>
<th>ZDDP</th>
<th>HPh/ZDDP</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.06</td>
<td>21.7</td>
<td>5.01</td>
<td>50.13</td>
</tr>
<tr>
<td>2000</td>
<td>1.38</td>
<td>21.27</td>
<td>4.58</td>
<td>24 &lt;</td>
</tr>
<tr>
<td>5000</td>
<td>3.00</td>
<td>24 &lt;</td>
<td>2.95</td>
<td>24 &lt;</td>
</tr>
</tbody>
</table>

Table 5.16 Recorded induction periods (h) for SME/PAO with detergent B at varying concentrations and antioxidants at fixed concentrations (5000 ppm)

It is hard to draw firm conclusions from the data reported above regarding the antioxidant activity (or lack of) of the surfactants screened. It would appear that the different surfactants interact differently with each of the AOs and when the surfactants are screened with HPh and ZDDP combined. The possibly conflicting interactions make the data as it stands insufficient to interpret more fully, so no clear trends emerge. The data from trials with AOs at 2000 ppm may provide the most useful information given the upper recorded IP limit set at 24 hours. In retrospect carrying out the experiment with AO concentrations at 1000 ppm or 3000 ppm may have been more appropriate as lower induction periods are likely to have been recorded.

5.8. Conclusions
In this chapter the work completed has given information on the kinetics and performance of various classes of antioxidants in neat FAME and FAME/PAO mixtures.
Phenolic antioxidants when used on their own exhibited good antioxidant performance in extending the Rancimat induction period at $110^\circ C$ in neat SME with BHT performing best. Other type of antioxidant such as alkylated diphenylamines, organic sulphur compounds, and ZDDP were relatively ineffective when used as the sole antioxidant under these conditions.

Different kinetic behaviour was observed for the different classes of antioxidants in neat FAME. Alkylated diphenylamine, an organic sulphur antioxidant, and the natural antioxidant $\alpha$-tocopherol, were consumed by first order rate kinetics in SME. However, the synthetic phenolic antioxidants HPh and BHT showed partial antioxidant orders of 0.5 and 0.45, which suggest that they participate in multi-step reaction mechanisms. The close accordance with the partial rate orders of HPh and BHT may indicate that they undergo similar antioxidant reaction mechanisms.

Further experiments on the selected antioxidants alkylated diphenylamine (ADPA), synthetic phenol (HPh) and Zinc $\text{OO}^\prime$-diisopropylthiophosphhate (ZDDP) have been carried out on the antioxidants individually and in pairs, in biodiesel (SME), model base oil (PAO), and a binary combination of the two with differing results. Individually, only HPh consistently displayed good antioxidant activity across all mediums, though PAO responded excellently to both ADPA and ZDDP. PAO exhibited excellent oxidative stability even at AO concentration of 250 ppm, providing further evidence to the findings from the kinetic experiments in Chapter 4, that PAO is very stable with respect to oxidation under the experimental conditions applied.

Synergistic effects have been observed for the different combinations of ADPA, HPh and ZDDP in SME and SME/PAO, with the greatest AO synergism displayed in SME/PAO. Evidence has been recorded to suggest that there is a strong relationship between the concentration of ZDDP and its effectiveness as an antioxidant. The hetero-synergistic effect observed between ZDDP and both ADPA and HPh suggests that the hydroperoxide decomposing mechanism of ZDDP is much more effective when the concentration of hydroperoxides is controlled or suppressed, such as in the instances when ZDDP is paired with a radical chain breaking antioxidant such as ADPA or HPh. This hypothesis is based on the data accumulated from the studies carried out here with antioxidant pairs, and
knowledge of the initial stages of the antioxidant mechanism of ZDDP and the 4:1 stoichiometry of ZDDP that is required to decompose a hydroperoxide (Equation 5.3).

\[
4 \left( [(\text{RO})_2\text{PS}_2]_2\text{Zn} \right) + R_1\text{OOH} \rightarrow \left( [(\text{RO})_2\text{PS}_2]_6\text{Zn}_4\text{O} \right) + 2 \left( [(\text{RO})_2\text{PS}_2] \right) + R_1\text{OH} \quad \text{[Eq 5.3]}
\]

The data collected in the antioxidant studies also indicates that there may be a threshold level of concentration, above which ZDDP becomes an effective antioxidant or synergist. This may relate to the ZDDP-hydroperoxide stoichiometry present in the oxidising sample.

The surfactants have displayed a combination of both anti- and pro-oxidant effects when screened in PAO/SME, and also in combination with HPh and ZDDP. Dispersant A and detergent B had similar effects when used with and without antioxidants, with both exhibiting antioxidant effects in combination with HPh, whilst both also showed pro-oxidant effects when screened with ZDDP. For dispersant A, this may be attributed to the dispersant coordinating with the ZDDP, as reported in the literature.\(^{222}\) Detergent B generally exhibited pro-oxidant behaviour. The surfactant influence tended to be relatively small compared to the main antioxidant effects. However, the lack of structural detail known for the surfactants limits the capacity to interpret the results of the experiments effectively, and hence draw any definitive conclusions.
6. Product Distribution Analysis of Methyl Oleate with Antioxidants
6.1. Introduction
Experiments to investigate the influence of antioxidants upon the product distribution of methyl oleate oxidation by monitoring the monomeric degradation products were undertaken. The antioxidants tested were synthetic phenol (HPh), Zinc OO’-diisopropylthiophosphate (ZDDP), and a combination of these two antioxidants in equal concentrations. When used together, these AOs showed a synergistic effect (vide supra Chapter 5). The product distribution analysis proves informative in elucidating the mechanism by which the HPh and ZDDP exhibit a hetero-synergism in inhibiting FAME oxidation.

Experimental conditions were as in the previous chapters, with methyl oleate oxidation in the Rancimat apparatus at 110°C and product distribution analysis by GC. The antioxidants were evaluated at a concentration of 2000 ppm.

6.1.1. Methyl Oleate Model
Methyl oleate (18:1) is a good model FAME with which to investigate the influence of antioxidants upon product distribution analysis in a model system. It is monounsaturated so is easily susceptible to autoxidation, whilst the product distribution as described in section 3.3.2, is considerably less complicated than that of polyunsaturated FAMEs or of a biodiesel sample, allowing for easier analysis and conclusions to be drawn. The major monomeric degradation products detected as a result of autoxidation, in the absence of antioxidants, were trans- and cis- epoxides, with an alcohol and ketone also formed in significant quantities.

6.2. HPh in Methyl Oleate
The use of the synthetic phenol (HPh) antioxidant primarily affected the onset of oxidation, whilst having a minimal influence upon the product distribution. The induction period of methyl oleate increased from 0.14 hours to 12.83 hours (as determined by the Rancimat) in the presence of HPh, whilst Figure 6.1 shows the increased induction period in that the degradation products start to form between 12 and 15 hours, in close accordance with the Rancimat value (12.8 h). After this initial delay, the degradation product concentrations
follow much the same reaction profile as that of methyl oleate oxidation without antioxidants (Figure 3.3), with products peaking at roughly the same concentrations. This radical chain breaking AO therefore appears to delay the autocatalytic period of the autoxidation by interrupting the chain propagating step in 18:1 autoxidation. By possessing an X-H bond with a lower bond dissociation energy than the allylic hydrogen on 18:1, the oleate peroxy radical will selectively abstract a hydrogen radical from HPh rather than the 18:1 allylic hydrogen. This generates an oleate hydroperoxide and a relatively stable HPh radical. When HPh is fully consumed the autocatalytic nature of the FAME autoxidation and similar product distribution to 18:1 oxidation with no AO use is observed.

![Figure 6.1 Degradation product formations from methyl oleate oxidation with HPh](image)

**Figure 6.1** Degradation product formations from methyl oleate oxidation with HPh

### 6.3. ZDDP in Methyl Oleate

Metal dialkyl dithiophosphate compounds are known hydroperoxide decomposers\textsuperscript{221,223-229}, and that antioxidant action is reflected in the results obtained here with Zinc O\textsuperscript{O'}-diisopropylidithiophosphate (ZDDP). A decrease in hydroperoxide yields was observed, as determined by PPh\textsubscript{3} treatment and GC analysis (Figure 6.2). When ZDDP is introduced the hydroperoxides concentrations are reduced by approximately one third compared to the
concentrations observed with no antioxidants present. There is also an influence upon the induction period when using this antioxidant which is reflected in the formation of the hydroperoxides. The induction period recorded by the Rancimat when ZDDP is used is 2.5 hours, which correlates well with the rise of the hydroperoxides at about 2.5 hours in Figure 6.2.

Figure 6.2 Hydroperoxide formations from methyl oleate oxidation with and without ZDDP

The reported mechanism of the antioxidant action of ZDDP upon hydroperoxides is shown in Figure 6.3. The first stage of the reaction involves the reduction of one mole of an alkyl hydroperoxide to the corresponding alcohol by 4 equivalents of neutral ZDDP, also forming 1 equivalents of basic ZDDP and two equivalents of the $OO'$-dialkyldithiophosphoryl radical, which terminate with one another to form the corresponding disulphide (Figure 6.3 a). The basic ZDDP salt undergoes thermal degradation to form 3 equivalents of neutral ZDDP and 1 equivalent of zinc oxide (Figure 6.3 b), a process which causes the rate of hydroperoxide decomposition to slow down owing to the ZDDP being tied up as a basic salt. Bridgewater et al. showed that disulphides also play a role in the decomposition of hydroperoxides and postulated that the disulphide reacts with a hydroperoxide via the $OO'$-dialkyldithiophosphoryl radical, to form the corresponding $OO'$-dialkyldithiophosphoric acid
and a peroxy radical$^{224}$ as in Figure 6.3 c. This theory was later confirmed by Sexton who realised that when the ZDDP concentration is low, the relative concentration of $OO'$-dialkyldithiophosphoryl radicals is low enough to prevent the recombination termination reactions that form the disulphides. The $OO'$-dialkyldithiophosphoric acids are then able to react rapidly with more hydroperoxides, forming disulphides, alcohols and water$^{221}$ (Figure 6.3 d).

![Figure 6.3 Mechanism of hydroperoxide decomposition by ZDDP and $OO'$-dialkyldithiophosphate derivatives](image)

Interestingly the epoxide yields from 18:1 oxidation are dramatically decreased as a result of the inclusion of ZDDP. The cis-epoxide is affected by the ZDDP the most, with its yield peaking at a mere 21% of that when no antioxidants are used. The trans-epoxide forms to a maximum concentration that is approximately 56% of that of the epoxide yield for normal methyl oleate oxidation. Both the cis and trans epoxides concentrations decline rapidly after reaching their peaks, with minimal traces remaining after 21 hours and 35 hours for the cis and trans isomers respectively. This suggests that the epoxides may form from alkoxy radical precursors. The alkoxy radical is generated by the homolytic scission of hydroperoxides, a process that is less frequent when in the presence of ZDDP.

Overall the degradation products are formed in lower yields than those observed through oxidation with no antioxidants, with the exception of the hydroxy and oxo derivatives (Figure 6.4). The oxo degradation product is largely unaffected by ZDDP, with the concentration in which it is formed comparable to that without ZDDP. The hydroxy degradation product shows a significant increase in concentration in the presence of ZDDP,
with the yield increasing by over 50% compared to that formed without ZDDP, which could be expected owing to the peroxide decomposition mechanism of ZDDP converting hydroperoxides to alcohols. The reaction profile also shows that the concentration of the alcohol is maintained until the end of the oxidation after 48 hours, instead of decreasing after its peak, as is the case in the absence of ZDDP. The fact that the alcohol concentration remains relatively constant during this period suggests that the rates of formation and decomposition of the alcohol are in equilibrium.

![Degradation product formations from methyl oleate oxidation with ZDDP](image.png)

**Figure 6.4** Degradation product formations from methyl oleate oxidation with ZDDP

### 6.4. HPh and ZDDP Synergy in Methyl oleate

When these antioxidants are used together they exhibit a synergistic effect, with induction periods greater than the sum of those observed with the individual components. This is reflected in Figure 6.5, which shows the reaction profiles for the formation of trans-epoxides from methyl oleate oxidation with no antioxidants (black marker), HPh (red marker), ZDDP (green marker), and the HPh and ZDDP synergy combination (blue marker). For HPh/ZDDP, the epoxide concentration starts to increase around 6 hours after it does for
just HPh, whilst for ZDDP the epoxide begin to form after approximately 2.5 hours, showing a synergy effect of induction period extension by over 3 hours.

Figure 6.5 Formation of trans-methyl epoxystearate as a result of methyl oleate oxidation with (red, green, and blue markers) and without antioxidants (black markers)

Using the blend of HPh and ZDDP, a combination of the effects of each are observed in the product distribution analysis of methyl oleate oxidation. For HPh a significant increase of the induction period is observed, followed by a normal degradation product reaction profile. ZDDP has less impact on the induction period but a significant effect on the yield of the degradation products formed. The combination of the two antioxidants shows both a large increase in oxidative stability (induction period of ca. 15 h vs. 12.8 h for HPh and 2.5 h for ZDDP), and variation in the concentration in which the oxidation products are formed. These trends apply for each of the degradation products quantified, resulting in a higher concentration of the hydroxy derivative, roughly the same amount of the oxo product, and much less trans- and cis-epoxides being formed than under normal conditions (Figure 6.6).
Figure 6.6 Formation of monomeric degradation products from methyl oleate oxidation with HPh and ZDDP (15 – 48 hours only)

The use of ZDDP both independently and with HPh appears to affect the total monomeric degradation compounds formed under the Rancimat oxidation conditions. Oxidation of methyl oleate without any antioxidants, results in the sum concentration of the epoxides, alcohol, and ketone reaches approximately 0.73 M at its highest, whilst the use of HPh in 18:1 generates a comparable total yield of monomeric compounds at approximately 0.72 M. However, when ZDDP is screened the value of the concentration maximum for the same group of compounds reaches just 0.46 M, and when coupled with HPh the overall yield of these monomeric degradation products amounts to 0.56 M (Figure 6.7).

From the data on monomeric oxidation products presented in Table 6.1 below, two trends appear. Firstly, the proportion for each of the total monomeric degradation products varies according to which antioxidant is used, with ZDDP having the greatest influence over this distribution under the experimental conditions applied. Secondly, there appears to be a correlation between the decrease in concentration of total monomeric degradation products and a noticeable decrease in yield of epoxides, products which are normally the major degradation products formed during the Rancimat oxidation conditions.
Figure 6.7 Sum concentrations of monomeric degradation products from methyl oleate oxidation

<table>
<thead>
<tr>
<th>Product</th>
<th>No AO</th>
<th>HPh</th>
<th>ZDDP</th>
<th>HPh/ZDDP</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-epoxy</td>
<td>41</td>
<td>42</td>
<td>33</td>
<td>36</td>
</tr>
<tr>
<td>cis-epoxy</td>
<td>25</td>
<td>26</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>Hydroxy</td>
<td>16</td>
<td>14</td>
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<td>33</td>
</tr>
<tr>
<td>Oxo</td>
<td>18</td>
<td>18</td>
<td>24</td>
<td>24</td>
</tr>
</tbody>
</table>

Table 6.1 Relative proportions (%) of individual monomeric products formed from methyl oleate oxidation in the presence and absence of antioxidants

The formation of epoxides from secondary reactions between alkylperoxy radicals and olefins is a well-known mechanism (Figure 6.8 a). The reduced yield in epoxides coincides with the reduced yield of hydroperoxides, which in turn could affect the yield of the precursor of the hydroperoxide – the peroxy radical. If lower concentrations of peroxy radicals are formed, then this would support the hypothesis that the main mechanism for the formation of epoxides is via the reaction shown in Figure 6.8 a, rather than by the intramolecular rearrangement of an allylic alkoxy radical$^{88}$ (Figure 6.8 b).
Figure 6.8 Epoxide formation mechanisms: a) intermolecular addition to an olefin via peroxyalkyl adduct; b) by intramolecular rearrangement of an allyl alkoxy radical

Analysis of the hydroperoxide yields with each of the antioxidants may also give further support to the proposed source of the synergy between HPh and ZDDP (Figure 6.9). The concentration of hydroperoxides formed through use of HPh is similar to those observed when no antioxidant is used to oxidise 18:1 under the Rancimat oxidation conditions. However, the use of the ZDDP antioxidant lowers the hydroperoxide yield. The combination of both HPh and ZDDP appears to decrease the hydroperoxide yields further than when ZDDP is used individually under the Rancimat oxidation conditions, as reflected in Figure 6.9. This supports the hypothesis that the source of the synergy between HPh and ZDDP is derived from suppression of the hydroperoxide formation, allowing ZDDP to exist in sufficient excess concentration to the hydroperoxides (4:1 stoichiometry), thereby allowing for it to decompose the hydroperoxides more effectively.
Figure 6.9 Formation of hydroperoxides from methyl oleate (18:1) oxidation with antioxidants

6.5. Conclusions

The work carried out in this chapter demonstrates the influence of the synthetic phenol (HPh) and zinc OO’-diisopropylidithiophosphate (ZDDP) AOs upon the induction period and product distribution of methyl oleate oxidation. Individually HPh and ZDDP have differing effects upon both induction period and product distribution of methyl oleate. When the AOs are combined in equal concentration a mixture of effects is observed, reflecting the main influence of each AO on the oxidative stability and product distribution.

HPh had little impact upon the product distribution of methyl oleate oxidation, with no significant changes in monomeric degradation product concentrations being observed. However, HPh does extend the Rancimat Induction Period and it is possible to observe the influence of HPh on the oxidative stability of methyl oleate from the GC data, which correlates well with the induction period as determined by the Rancimat.
The addition of ZDDP to methyl oleate causes a noticeable decrease in the hydroperoxide yield, in accordance with literature reports of ZDDP’s hydroperoxide decomposer activity.\textsuperscript{221,223-229} Other significant effects upon the formation of monomeric degradation products as a result of ZDDP are; a decrease in epoxide concentrations, and increase in alcohol concentration relative to the yields of those degradation products formed from methyl oleate oxidation without antioxidants. These trends may lend support to the hypothesis that the primary mechanism for the formation of epoxides is from the reactions between olefins and hydroperoxides.\textsuperscript{88}

When ZDDP and HPh are combined, the results are synergistic and reflect a combination of both of the individual antioxidants influences, with lower hydroperoxide and epoxide yields, and higher alcohol concentration after an extended induction period. These findings support the proposed origin of the synergy between ZDDP and primary antioxidants, previously discussed in Chapter 5.
7. Conclusions and Future Work
7.1. Conclusions
The investigations carried out in this work have provided an improved understanding of
FAME oxidation under experimental crankcase simulation conditions. The main objectives of
the project have been to design an experimental model that is capable of simulating certain
aspects of FAME and lubricant oxidation in a diesel engine crankcase, and then to use that
set-up to carry out a series of experiments. This has been achieved through firstly carrying
out a series of initial tests that helped design the experimental model and ensure that it was
capable of providing reproducible results. The method has been based on the Rancimat
apparatus and the test method defined by EN 14112. Secondly, this method has been
coupled with a GC analysis procedure, which together has provided much data leading to
some key findings:

1. Product distribution analysis on a C18 FAME series has shown that the primary
oxidation pathway under the Rancimat oxidation experiments applied is
autoxidation, with the formation of major degradation products correlating well to
previous literature reports.\textsuperscript{57,86,88,89,169} The only exception to autoxidation was
observed in the hydrolysis of methyl stearate, as determined by the detection of
stearic acid as the only degradation product.

2. The oxidation kinetics has revealed the interesting behaviour of substrates in single-
component and multi-component systems. FAMEs have been shown to oxidise at
different rates when oxidised as mixtures in multi-component systems compared to
their individual oxidation rates in single-component systems.

3. Model FAME mixtures have shown similar behaviour to real FAME biodiesel samples
with respect to oxidation, with comparable relative rate constants ($K_{rel}$). Though in
the model FAME mixture no Rancimat induction period was observed, whereas in
biodiesel samples a small Rancimat induction period was observed for SME (0.60 h)
and a relatively large Rancimat induction period was recorded for RME (7.34 h).

4. Methyl oleate (18:1) and methyl linoleate (18:2) have demonstrated changes in
relative rate constants ($K_{rel}$) over the course of an oxidation in a multi-component
system (Table 7.1). The change in $K_{rel}$ coincided with the complete oxidation of
methyl linolenate (18:3) in the system, leading to the suggestion that a more readily
oxidised substrate may suppress the oxidation of other less readily oxidised substrates in a multi-component system, through acting as a pseudo-antioxidant.

### Table 7.1

<table>
<thead>
<tr>
<th>System</th>
<th>FAME</th>
<th>18:0</th>
<th>18:1</th>
<th>18:2</th>
<th>18:3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Individual</td>
<td></td>
<td>0.014</td>
<td>1.00</td>
<td>1.18</td>
<td>1.25</td>
</tr>
<tr>
<td>1:1:1:1 (0 – 6 h)</td>
<td></td>
<td>0.022</td>
<td>0.22</td>
<td>1.11</td>
<td>2.44</td>
</tr>
<tr>
<td>1:1:1:1 (9 – 48 h)</td>
<td></td>
<td>0.016</td>
<td>0.29</td>
<td>1.72</td>
<td>N/A</td>
</tr>
</tbody>
</table>

5. In a binary mixture of SME and PAO the $K_{rel}$ of oxidation for PAO is smaller than that of neat PAO and therefore the SME did not adversely accelerate the oxidation rate of the PAO. This finding is consistent with the observations made with the model FAME mixtures whereby the oxidation of 18:1 and 18:2 were suppressed by the presence of 18:3.

6. Screening of selected antioxidants has shown that alkylated diphenylamine (ADPA), organic sulphur (OS) and $\alpha$-tocopherol (Toco) have first order antioxidant orders. Synthetic Phenol (HPh) and butylated hydroxytoluene (BHT) antioxidants have close antioxidant orders (0.5 and 0.45 respectively), indicating that they may operate by similar reaction mechanisms.

7. Synergistic effects have been reported between $1^\circ$ and $2^\circ$ antioxidants in neat FAMEs and in a binary system of SME and PAO. The strong synergistic action of ZDDP has been hypothesised to be due to the importance of ZDDP concentration relative to that of hydroperoxides. When combined with a radical chain breaking antioxidant such as ADPA or HPh, the hydroperoxide concentration may be suppressed sufficiently so that the ZDDP-hydroperoxide stoichiometry is in excess of 4:1 as in the early stages of the ZDDP’s hydroperoxide decomposing mechanism (Equation 7.1). This factor could be significant in the effectiveness of ZDDP as an antioxidant, though other explanations may be possible.

$$4 \left[ (RO)_2PS_2Zn \right] + R_1OOH \rightarrow [\left( (RO)_2PS_2 \right)_6Zn_4O] + 2 \left( (RO)_2PS_2 \right) + R_1OH \quad [Eq \ 7.1]$$

8. The use of surfactants has provided examples of both anti- and pro-oxidant effects when screened with the binary combination of PAO and SME. When used in
combination with antioxidants a variety of anti- and pro-oxidant effects are again observed. It is difficult to draw clear conclusions from these results. The surfactant influence was generally small compared to the main antioxidant effects. A consistent effect was seen when dispersant A and ZDDP are combined, this may possibly be attributed to the dispersant coordinating with the ZDDP, an effect previously reported in the literature.\textsuperscript{222}

9. The influence of antioxidants upon 18:1 product distribution has been demonstrated, with HPh showing little effect on the concentration of the major degradation products formed, only impacting the induction time after which they begin to form. ZDDP shows a significant decrease in the hydroperoxide and epoxide yields, but an increase in the alcohol yield. This finding supports the mechanism of epoxide formation from secondary reactions between peroxy radicals and olefins.\textsuperscript{88}

10. When HPh and ZDDP are used together during methyl oleate autoxidation a combination of effects is displayed in the product distribution analysis, with the increased induction period of HPh and the changes in the product yields associated with ZDDP use both reflected in the product distribution.

To summarise, the work carried out in this thesis has led to considerable insight into the model systems being gained. The initial goals of the project have been achieved with successful product analysis carried out on C18 FAMEs, leading to the confirmation of the autoxidation pathway being the primary degradation mechanism. Kinetic data has suggested that the influence of the FAME upon the PAO in the model system does not increase the oxidation of the base oil. The use of antioxidants has demonstrated a range of effects upon the oxidative stability of the FAMEs and PAO under the experimental conditions, as well as the product distribution of model FAME.

The results presented here are from experiments carried out on a simplified model designed to represent certain aspects of crankcase chemistry. They should not be misconstrued as an exact representation of the chemistry that occurs in a real working diesel engine crankcase. The complexity of a crankcase under operating conditions is tremendous, and therefore extremely difficult to recreate under laboratory bench test methods. The modelling of aspects such as fuel dilution is still some way from realistic fuel dilution levels (up to \( \sim 10\% \)) which is also made more complex by the formulation of a real engine lubricant. The
experimental conditions carried out in this thesis could be considered as a good model for evaluating certain aspects of the influence of FAMEs, model base oils and additives given the results obtained through it, though there are numerous other test methods that could be equally important to use in understanding the complexity of FAME use and its influence on the diesel engine crankcase.

7.2. Future Work

7.2.1. Further Investigations into Fuel Dilution
In this thesis, data was obtained through kinetic and antioxidant studies in mediums consisting of neat SME, neat PAO, and a binary mixture of SME and PAO at approximately a ratio of 50:50. Further work could be carried out in the binary mixture of SME and PAO at different ratios, including 25:75, and 75:25. By carrying out the same kinetic and AO studies using these intermediate ratios, the influence of fuel dilution could be examined further with possible implications relating to the linearity of a dilution effect.

7.2.2. Investigations into the Hetero-Synergism Between 1° and 2° Antioxidants
With the proposed hetero-synergy mechanism between HPh and ZDDP in this thesis relating to the concentration of ZDDP, further investigations using different treat ratios of the antioxidants may provide further evidence to support this proposed mechanism. The AO studies carried out have used pairs of antioxidants in the same ratio (equal treat ratios, 1:1). By fixing the concentration of one AO and varying the concentration of the other (to give an experiment matrix as shown in Table 7.2), the Rancimat induction periods recorded could provide information relating to the threshold concentration of ZDDP in a synergy pairing with HPh. Though many combinations will screen the treat ratio of 2:1, at different concentrations, the Rancimat induction periods may vary significantly within a single treat ratio as already observed for 1:1. The data obtained from carrying out these experiments may provide further information relating to the AO treat ratios and relative concentrations that should be used. This matrix system could also be applied to other AO combinations.
Table 7.2 Experiment matrix for investigating AO combinations at different treat ratios and concentrations

<table>
<thead>
<tr>
<th>[HPh] (ppm)</th>
<th>250</th>
<th>500</th>
<th>1000</th>
<th>2000</th>
<th>4000</th>
<th>8000</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>1:1</td>
<td>1:2</td>
<td>1:4</td>
<td>1:8</td>
<td>1:16</td>
<td>1:32</td>
</tr>
<tr>
<td>500</td>
<td>2:1</td>
<td>1:1</td>
<td>1:2</td>
<td>1:4</td>
<td>1:8</td>
<td>1:16</td>
</tr>
<tr>
<td>1000</td>
<td>4:1</td>
<td>2:1</td>
<td>1:1</td>
<td>1:2</td>
<td>1:4</td>
<td>1:8</td>
</tr>
<tr>
<td>2000</td>
<td>8:1</td>
<td>4:1</td>
<td>2:1</td>
<td>1:1</td>
<td>1:2</td>
<td>1:4</td>
</tr>
<tr>
<td>4000</td>
<td>16:1</td>
<td>8:1</td>
<td>4:1</td>
<td>2:1</td>
<td>1:1</td>
<td>1:2</td>
</tr>
<tr>
<td>8000</td>
<td>32:1</td>
<td>16:1</td>
<td>8:1</td>
<td>4:1</td>
<td>2:1</td>
<td>1:1</td>
</tr>
</tbody>
</table>

7.2.3. Investigations into the Influence of ZDDP and its Derivatives Upon Epoxides

The support for the proposed mechanism of epoxide formation via peroxide radical addition to olefins proposed in this thesis is one hypothesis. Another that may merit further investigation involves the direct interaction between ZDDP derivatives and epoxides, rather than ZDDP indirectly affecting the formation of epoxides.

Clive and Menchen reported the use of alkali metal $O,O$-dialkyl phosphorotelluroates for the deoxygenation of epoxides to convert to the corresponding alkenes. $^{230}$ The reagents used for this procedure show some similarities to the dialkyl dithiophosphate ligands and consequently ZDDP compounds may act in a likewise way (Figure 7.1).

Figure 7.1 Possible mechanisms for conversion of methyl epoxystearate to methyl oleate by dialkyl dithiophosphate ligand
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