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The Effect of Biofuel on the Corrosion and
Wear of Automotive Engine Components

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Abstract

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Soot particles produced during diesel engine combustion process are of strong interest within the fields of environmental science (global warming, air pollution), air filtration and combustion science (the optimization of the combustion process).

Diesel fuel production from renewable resources such as vegetable oils and animal fats offer the potential to reduce fossil carbon emissions and produce alternative ultra-clean fuels for transport and industrial use. It is well known that biodiesel, neat or in blends, can provide reduced particulate matter (PM) mass emissions through either oxygen content or enhanced air due to the higher boiling range of biodiesel.

Recent observations have shown an oxidation reactivity variation with soot derived from different fuels. However, the manner in which crystallinity or nanostructure affects soot oxidation rates has not been clarified for diesel fuel soot, whether it is derived from conventional or alternative (e.g. renewable) fuel sources.

This study has looked at the comparison of soot nanostructures of particulates produced from three different fuels (an ultra-low sulphur diesel fuel, its B20 blend and pure biodiesel B100) with a diesel engine by means of high resolution transmission electron microscopy (TEM) imaging.

TEM studies of soot samples collected on a soot catcher under conditions relevant to different biodiesel blends, revealed a nanostructure that to our knowledge, has not been previously reported for diesel soot particulates. The immersion corrosion tests of biodiesel B100 were conducted at six different temperatures; 25°C, 80°C, 90°C, 100°C, 110°C and 120°C, each for 270 hours. Each sample was weighed at the commencement of the tests and again at the end.

Any difference in those weights was used to inform on the corrosion characteristics of the particular fuel on each metal type. Under the experimental conditions, copper and brass were more susceptible to corrosion in biodiesel than aluminium and steel.

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CHAPTER 1

1.The use of biofuels in automotive applications

1.1 Introduction – Why biofuels?

Diesel engines are used for the majority of heavy goods vehicles, as well as in countless agricultural applications and industrial plants. The efficiency and durability of the engine has made them the ideal power plant for these applications. However, there is a need to reduce the impact of CO₂ emissions from the vehicle fleet [1]. Biofuels offer potential advantages over conventional fuels within the medium term (10 years). However, there is a tension between the global need for procuring biofuels and the need for producing food [2]. A recent report by the Royal Academy of Engineering on the Sustainability of Liquid Biofuels notes that the development of second generation biofuels derived from waste and agricultural, forest and sawmill residues should be incentivised [3]. They also recommend that there is a cap on the supply of crop-based biofuels to reduce the tension between food and fuel production [3].

Biofuels are fuels that are produced from biological sources such as trees, plants or micro-organisms. They are carbon neutral, because they do not result in fossil carbon being released into the atmosphere. All of the carbon contained in a biofuel is absorbed from the atmosphere by photosynthesis in plants [4]. This means that when you burn a biofuel, you simply release the carbon back into the atmosphere, and have no overall effect on atmospheric CO₂ levels. In contrast, fossil fuels contain carbon that has been locked up underground for millions of years. Burning a fossil fuel increases the level of CO₂ in the atmosphere, but it is not balanced out

by photosynthesis. The three biofuels which are most widely used are bioethanol, biodiesel and wood [5].

Biofuels have the potential to work with existing diesel engine technology as they can be introduced as blends mixed with conventional diesel fuel. The advantage is that they are said to “decarbonise” the fuel reducing the overall carbon dioxide generated, either through fuel switching or by reducing the amount of CO₂ involved in production of the fuels, sometimes, a combination of both [5].

Some biofuels have a strong effect on reducing CO₂ but other types of biofuels have a very limited effect on reducing CO₂ therefore the amount of reduction in CO₂ emission depends on using low-carbon biofuels and also the type of feedstock which is being used for producing the biofuels. It is maybe important to consider using the varieties of feedstock which need the minimum of agricultural land for growing the feedstock [5].

The refinery methods used to produce biofuels also have a strong effect on the CO₂ emission - different refinery methods have very different CO₂ life-cycles even though the biofuel product is the same. Therefore, one of the main challenges in production of biofuel is to harmonise biofuel production and ensure each method of production has the same CO₂ life-cycle [6].

It is also important that a standard method exists for evaluating CO₂ emissions and the CO₂ life-cycle for both the combined fuel and all types of biofuel on the market [6].

1.2 The use of biofuels in transport

Using biomass for producing biofuels for the transport industry has significant potential to reduce carbon emissions where alternative sources of renewable energy are not available.

The E.C. directive 2009/28/EC requires that by 2020, all E.C. member states will have 10% of their transport energy source (fuel) derived from renewable resources, e.g. biofuels. The E.C. Fuel Quality Directive (FQD) also requires that by 2020 all members should reduce carbon emissions from the transport sector by 6% [7].

In the U.K the directives are implemented by the renewable transport fuel obligation (RTFO) order 2017 [8]. The RTFO states that road transport fuel supplies must ensure 4.75% of fuel comes from renewable sources. Biofuels also have to meet sustainability criteria which thus ensure that greenhouse gas savings are also met. RTFO amendments are published annually by the government [8].

Nearly 30% of the total energy consumption in the U.S is used by the transport industry. The total energy consumed by the residential and commercial sectors in the U.S is only 10% of the total energy used. Thus in industrialised countries, people are consuming 3 times more energy to move themselves and their goods than they do for their daily cooking and heating (or cooling) their premises [9].

Globally, transport accounts for 62% of total oil production in the world. The population of the world is nearing its maximum use of oil products. Natural resources of crude oil are reducing. When we consider that at some point all easily available crude oil will be completely used and likewise consider the negative environmental effects of using fossil fuels, then the need to find replacement clean, renewable fuels for now and future use becomes imperative [10].

Utilising renewable energy sources, such as wind or solar, present obvious problems for transport use using current technology and are thus impractical. For example, the storage of enough electrical power within a vehicle for a 100 mile trip requires good battery technology. Scientists and

engineers believe that it will take decades to make the appropriate technology efficient and fully operational at an economic cost. Thus, the main challenge at the current time is to find a fuel which is able to easily replace current fossil fuels and which has very low emissions of pollutants [10].

In the E.C., the quantity of biofuels used in the transport sector is 4.7% of the total amount of fuel consumed. This quantity has been measured as 13.985 kilo tonne of oil equivalent (or ktoe), comprising of 10.644 ktoe as biodiesel, 2.892 ktoe as biogasoline and 422 ktoe other liquid biofuels [10].

Biofuels blend easily with fossil fuels and can be used to power modern internal combustion engines with very little, if any, adaptation required.

Figure 1.1 shows the available alternative fuels and their suitability for use in journeys of different types. Note that the first three alternatives are still fossil fuels.

Fuel	Road passenger			Road freight		
	short	medium	long	short	medium	long
LPG						
LNG						
CNG						
Electricity						
Biofuels (Liquid)						
Hydrogen						

Figure 1.1: Coverage of transport modes and travel range by the main alternative fuels such as Liquefied Petroleum Gas (LPG), Liquefied Natural Gas (LNG) and Compressed Natural gas (CNG), dark boxes indicate the fuel is suitable [11].

The uptake and use of biofuels is dictated by both political drivers and the economics of producing the fuel as compared to the price of extracting and refining crude oil. As we have seen, the 10% target for the use of renewable fuels by 2020 for the transport sector is a requirement of EU energy and environmental policy. This shows the importance of policy in driving change [10].

In 2013, the European parliament announced their decision to replace 6% of fuels for transport with the first generation of biofuels. However, the additional decision to replace a further 2.5% by using advanced biofuels produced from waste or algae was not activated. It remained as a draft requirement until June 2014 when it was cancelled after consideration was taken on the amount of land which was needed to produce these advanced fuels [10].

Following this cancellation, a new plan was formulated to revise the earlier 6% level passed in 2013, by raising it to 10% by 2020. In 2015, 7% of fuel was biofuel. The projected road transport fuel demand biofuel 2030 is illustrated in figure 1.2 below [11].

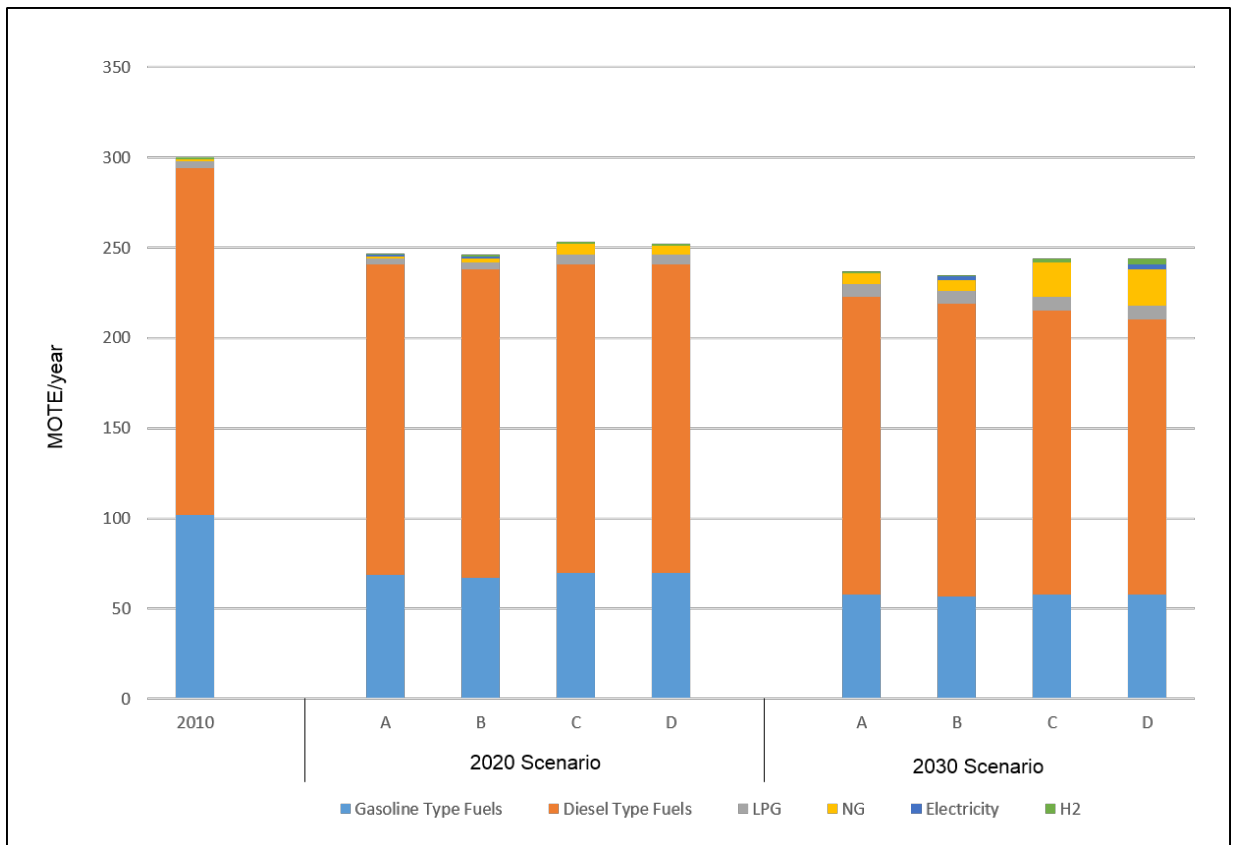


Figure 1.2: Road Transport Fuel Demand [11].

Biodiesel fuel has a similar performance in diesel engines to fossil diesel fuel. High energy prices, increasing energy imports, concerns about fuel supplies, and the environmental consequences of fossil fuels have driven interest in transportation biofuels [12].

Meanwhile, laboratory and road tests on internal combustion engines proved that biofuels produce a similar performance as normal fossil fuels in terms of torque (the amount of force available to rotate an object) and power (the amount of energy available per unit time).

Used on a large scale, biodiesel is a clean and economical fuel for HGV's, buses, agricultural equipment and other heavy plant vehicles [12].

Biofuel refineries are simpler to build and easily adapted to meet environmental concerns than their equivalent petrochemical refineries. Biofuels can also be applied to other transport modes such as rail, sea and air. More information about the potential use of biofuels for these uses is available within the Low Carbon Transport Innovation Strategy [12].

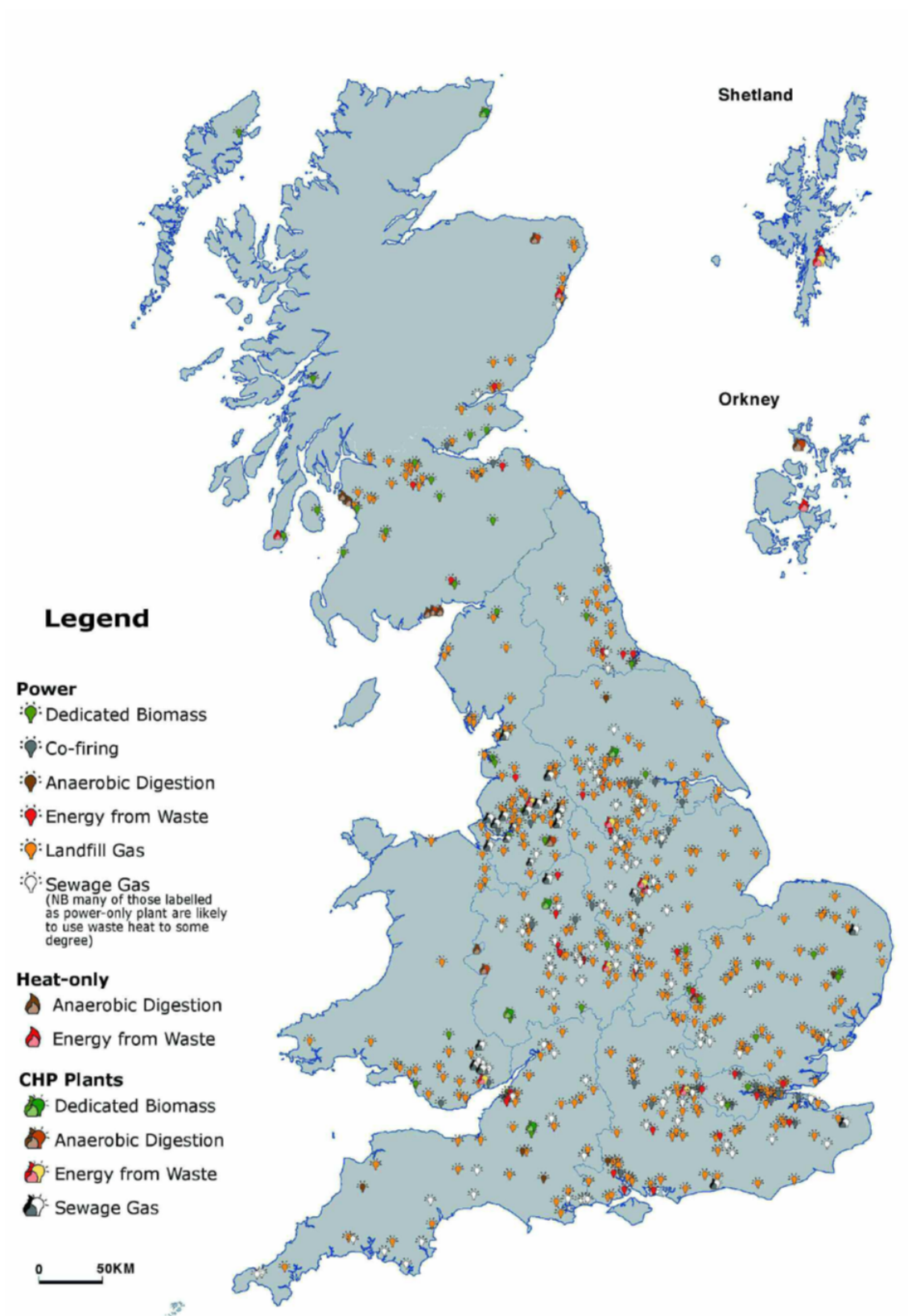


Figure 1.3. Location of Biofuels and Solid Biomass Installations in the U.K [12].

1.3 Thesis aims and objectives.

Engines produce soot as a result of incomplete fuel combustion. Normally, complete combustion in a cylinder would only produce carbon dioxide and water, but no engine is completely efficient. As the result of the way that fuel is injected and ignited, soot formation occurs more in diesel than in petrol engines. Unlike petrol engines where the ignition process happens with a spark, fuel and air entering the diesel cylinder ignite as the result of the high pressure in the combustion chamber. The fuel and air mixture in diesel engines typically does not mix as thoroughly as in petrol engines. This makes fuel-dense points that produce soot when ignited. While the majority of soot easily escapes through the exhaust, some particles get past the piston rings and ends up in the oil [13].

The long term effects of using biofuels on the engine performance are currently not fully understood and this fact, combined with the differing feedstocks from which biodiesel may be produced, gives a wide variability in the potential effects of soot and particulate matter generation [13].

There is far less information available regarding the long effects of vegetable oil based fuels on the engines performances and maintenance, but they are gaining popularity as it provides a use for spent oils from the catering industry which otherwise would be sent for waste disposal. For example, the fast food chain McDonalds actively recycles its cooking oil to biodiesel, providing 40% of the fuel required by their delivery fleet. The company says that this contributes to a saving over 6,000 tons of CO₂ each year [14].

1.3.1 Thesis aims.

The main aim of this thesis is to study the use of biofuels in diesel engines and in particular to understand the issues from the use of biofuels that influence the wear and corrosion of typical engine components.

The plan of the project had been, through the use of a wear rig test, running engine testing and laboratory static tests, to study the major wear and corrosion mechanisms of diesel engines components which are in contacts of the exhaust soot, soot contaminated oil and biofuels.

In order to understand how biodiesel fuel influences engine wear, the thesis will consider the role played by soot produced during the combustion process, in influencing engine component wear.

Two types of test have been used to understand the wear performance. Firstly, the wear produced by soot particles has been studied using a specially designed rig to allow samples to be run immersed in soot loaded oil at temperatures relevant to the engine, 80°C. The wear rig test has been developed to be capable of providing a simulation of the wear for the critical engine components which are in contact of soot contaminated oil.

The wear has then been characterised using scanning electron microscopy and EDX. Secondly, the soot particles themselves were analysed by modern microscopy techniques (transmission electron microscopy) to better understand the morphology and agglomeration characteristics of the soot particles and to compare the key differences between biodiesel soot and soot produced from 100% diesel.

Tests were conducted using a baseline fuel and two different biodiesel blends. Ultra-Low-Sulphur diesel fuel (ULSDF) was used as the baseline fuel for this study, as it is the standard diesel fuel in use for road vehicles today. Biodiesel can be blended and used in different percentages such as; B100 (pure biodiesel), B20 (20% biodiesel, 80% fossil diesel), B5 (5% biodiesel, 95% fossil diesel) and B2 (2% biodiesel, 98% fossil diesel). For this study, two biodiesels were used. The first of these was a vegetable oil-derived biodiesel fuel blend which comprised of 20% biodiesel and 80% diesel blend. Biodiesel originating from vegetable oil is widely available and there have been a number of studies investigating its effects on

engine wear. The second fuel used for comparison was B100 - 100% biodiesel.

B20 and lower-level blends are popular because they represent a good balance of cost, emissions and materials compatibility. They also generally do not require engine modifications.

However, one of the problems with some B100 fuels is that they have poor viscosity at low temperatures. Engines operating on B20 have similar horsepower and torque to engines running on fossil based diesel.

In order to develop the emission control and engine performance necessary when operating with biodiesel fuels, it is important to understand the diesel combustion processes and the formation mechanism of diesel soot particles.

In this research, the engine used to test the various fuels was a British made four-stroke internal combustion diesel engine type Petter PJ2, 22 horse power at 2100 rpm (Revolution per minute) water cooled, situated at the Internal Fire Museum of Power, Wales. Soot particles were collected from the exhaust and subsequently scanned with transmission electron microscopy (TEM).

For each biodiesel blend, the morphology and nanostructure of soot particles from the exhaust gasses were studied.

Image analysis of these soot samples allowed the development of the soot particles from different blends of biodiesel to be described.

Additionally, wear testing with different soot concentrations in oil using a laboratory pin on disk wear tester has been conducted. This research leads to an improved understanding of wear and corrosion from biofuels.

The second aim of this thesis was to understand how the biodiesel impacted on the corrosion of common engine components. Although

there are many studies on the preparation and characterisation of biodiesel, there is currently still little information available about the corrosive effects of biodiesel on the metallic components of a diesel engine. Copper, carbon steel, aluminium, brass and cast iron are the five main metals widely used for diesel engine construction. It is essential therefore, that the influence on corrosion by biodiesel, together with their corrosion mechanisms is better understood.

For this thesis, the corrosion reactions of five metals in contact with biodiesel were carried out using simple immersion tests at different temperatures. The results from different temperatures biodiesel in contact of different metals were compared with those from the same tests using pure biofuel in room temperature and not contacting any metals.

Wear rig tests and static immersion tests are usually used to investigate the wear and corrosion mechanisms of biofuels as candidate engine materials.

This study will, therefore, begin to provide some of the information that will help in the design of diesel engines suitable for use with a variety of diesel fuels.

The aim of this project was studying the wear and corrosion mechanisms of critical engine components in contact of the soot contaminated oil and biofuels. The wear rig test, engine running tests and the static immersion tests were conducted to meet this aim. This information and other test data could be used by the engine manufacturers and designers to reduce the engine wear and corrosion.

Whilst there is a wealth of studies on the wear and corrosion of components in the engine, much of the research is focused on the effects of petroleum or diesel fuels and there is much less emphasis on wear and corrosion involving biofuels, thus this thesis will benefit users of biofuels in

engines by providing new insights into how biofuels lead to engine wear and corrosion.

1.3.2 Objectives

To achieve the thesis aims therefore, the research had the following objectives:

- To design and build a lab based wear rig for evaluating wear rates from soot contaminated oil. The rig had to simulate the real working conditions of the engine valve train by using suitable contact loads, speeds, temperatures and lubricants;
- To evaluate soot particle morphology using Transmission Electron Microscopy (TEM). Soot particles were obtained from engine running tests using biodiesel blends and diesel;
- Studying how biodiesel corrodes typical engine components such as brass, copper, aluminium and mild steel by performing immersion tests in B100 biodiesels at different temperatures;
- Understanding the degradation and corrosion mechanisms that occur in biodiesel at different temperatures in contact with typical engine materials by investigating the chemical changes using GCMS (Gas chromatography-mass spectrometry) and ICP-MS (Inductively coupled plasma-mass spectrometry) to study the constituents of the various fuels before and after exposure to the different engine materials. FEG-SEM (Field Emission Gun-Scanning Electron Microscopy) was used to investigate the surface morphology and EDS (Energy Dispersive Spectroscopy) analysis were used to investigate the corrosion products on the sample surfaces after exposure to biodiesel.

1.4 Thesis Structure

The structure of the thesis is outlined below:

Chapter one of this thesis provides an introduction to the biofuel and use of biodiesel in the transportation system. The effect of biodiesel on soot production during the combustion is explained in this chapter.

Chapter two presents a detailed literature survey of biodiesel production and blends, diesel engine particulate matters emission and biodiesel effects on engine performance.

Next, chapter three presents engine tribology related to the soot contaminated oil. Chapter four describes the experimental materials and methods. In chapter five the wear results and soot characterisation were investigated.

Chapter six introduces other experimental tests regarding the corrosion behaviour of 5 different metallic samples such as brass, copper, pure Aluminium, Aluminium alloy and steel in contact with biodiesel. A general discussion is presented in chapter seven and followed by conclusions and suggestions for future work in chapters eight and nine.

CHAPTER 2

2.Literature Review

The previous chapter considered the context for the use of biofuels in diesel engines and the drivers for the increased use of them in transport. Biodiesel appeals to us because it can be made from plants grown locally and burns far cleaner than ordinary diesel fuel. It results in 67% less unburned hydrocarbons (helping to reduce smog and ozone), 48% less carbon monoxide and 47% less particulate matter, according to an analysis of heavy-duty engines by the U.S Environmental Protection Agency.

This chapter will consider biodiesels in detail and also the research to date into the effect of biodiesel on friction, wear and corrosion of engine components.

2.1 Wear and corrosion from biodiesel

Dhar *et al* [15] investigated the wear and durability of a range of engine components (piston top, cylinder head and injector tips for example running in long (250 hours) tests with a 20% Karanja biodiesel blend (KOME20). They found that there was relatively lower wear with a biodiesel fuelled engine as compared to a similar test endurance test for mineral diesel. They did however find high carbon deposits and higher wear on components such as the big end bearing and crank pins. They found that the Karanja biodiesel had lower volatility which increased heat release in the late combustion phase and that soot particles formed during late combustion do not oxidise to the same extent. Thus, the incomplete combustion of the fuel led to increased carbon deposits.

Fazal *et al* [16] showed that biodiesels provide a protective layer on metal surfaces. They investigated pure diesel, B100 and three different biodiesel blends (B10, B20 and B50) using ball on flat wear testing at different speeds. The friction and wear decreased as the proportion of biodiesel in the fuel increased with a 20% reduction in wear for the B100 as compared to the pure biodiesel. They attributed the improved performance to the presence of an aliphatic fatty acid forming on the surface and developing a lubricating film.

Haseeb *et al* [17] investigated the effect of temperature on the efficacy of biodiesel. They showed that friction and wear increased with increasing temperature for temperatures between 30, 45, 60 and 75 °C. They attributed this to a decrease in viscosity of the biodiesel as the temperature increased. They also considered that it was possible that the ester ends of the fatty acid chain become adsorbed to the metal surfaces. They suggested that at higher temperatures, the lubricant films become less stable. Haseeb *et al* also discussed the fact that free fatty acids which increase the total acid number (TAN) number can cause significant changes in reducing wear but that despite this not have a significant impact on corrosion.

Haseeb *et al* [18] investigated the corrosion behaviour of commercial bronze and pure copper which are frequently used in the fuel supply systems in diesel engines. They carried out static immersion tests in B0, B50 and B100 fuels at room temperature for 2640 hours and at 60°C for 840 hours. To find the acid concentration of fuel samples, the TAN analyser was used. Increasing of TAN number, oxidation products rate and free water content, caused significant degradation of biodiesel in contact with copper or bronze. Corrosion behaviour of each fuel samples was investigated by weight loss measurements and changes in surface morphology of metallic coupons. At the end of tests, it was conducted that

under the experimental conditions, copper was more corrosive in contact of biodiesel than the bronze.

Kaul *et al* [19] conducted a detailed study on material compatibility of IC engine components in M3 fuels (a blend of methanol and gasoline) in their laboratory. Some reports are available in the literature of material solvency and compatibility with biodiesel. Metallic elements such as copper, bronze, lead, brass, zinc and tin may oxidize diesel or biodiesel and create condensates. However, it was found that stainless steel and aluminium are compatible materials with biodiesel. The major fatty acids present in biodiesel are in the range of C16-C18. Geller *et al* [20] reported that corrosion of steel is not very clear and data differ. Steel is mostly comprised of iron and contains carbon in ranging 0.2 to 2.1%. Prieto *et al* [21] reported that the electrical conductivity of biodiesel may cause galvanic metal corrosion in steel.

Singh *et al* [22] has investigated the advantages and disadvantages of biodiesel in diesel engines against diesel fuel. At the moment, diesel engines are suited for a low-ratio blend of biodiesel with diesel because of corrosion problems. According to Nernst's theory, all metals have a tendency to pass into solution. However, the corrosion behaviour of metal ions depending on its oxidation potential and many other conditions such as temperature, water content, etc. in the fuel. Metal ions in contact of fuel, can cause corrosion. Biodiesel has a good lubricity property; however, it has a higher trend to dissolve the metallic parts, compared to diesel fuel. The level of corrosiveness property in biodiesel is usually specified by the 'copper strip corrosion test' which is a determined method by ASTM D 93 [22]. The type of alloy has a direct effect on the level of metallic material corrosion in contact with biodiesel fuel. Ferrous alloys have been found to be less corrosive than copper alloys [22].

Agarwal *et al* [23] found corrosion mechanisms in carburettors in contact with ethanol in three ways such as: corrosion, dry corrosion and wet corrosion. General corrosion occurs from ionic soilage from contact with acids and chloride ions. Dry corrosion happens as the result of polarity of the molecule. And finally, wet corrosion is the results of the azeotropic water and oxidizes various metals [23]. Biodiesels hold water around 20–30 times more than diesel fuel. The impregnation amount of water in the biodiesel was 1395 ppm while it was 62 ppm in diesel fuel [23] and this water content can lead to increased corrosion.

Mankowski *et al* [24] studied pitting corrosion mechanisms. He found that copper interacts with oxygen in atmosphere to make CuO/CuCO_3 in the outer layer and Cu_2O in the inner layer of copper. The same mechanism happens in biodiesel fuel which contains approximately 11% elemental oxygen. Fazal *et al* [25] found that biodiesel changed color as the results of formation of metal oxide. Copper carbonate creates a light green color in biodiesel, diesel causes a dark red color oxide.

Fazal *et al* [25] tested the effect of corrosion on mild steel dipped in biodiesel and diesel at temperatures of 27, 50, and 80 °C. The corrosion rate increased with increasing temperature in the diesel (B0) and biodiesel, especially B50 and B100. The surface morphology of copper and aluminum strips showed a higher pitting corrosion value for biodiesel (80% and 18%, respectively) compared to diesel (54% and 10%, respectively). Stainless steel, however, did not show any change on its surface exposure to biodiesel [25].

Fontaras *et al* [26] investigated the concentration of the metallic particles in pure soybean oil biofuel (B100) and its 50 vol% blend with diesel (B50) on diesel engine to demonstrate the biodiesel impact on engine components wear. He found that the use of B50 and B100 increase engine components wear as the result of the higher amounts of metallic

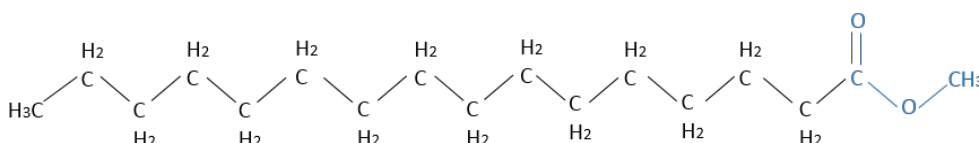
elements, originated from the different moving parts. Although, biodiesel has better lubricity properties than the diesel fuel, but the wear rate of many engine components was higher during the engine running test. The hygroscopic property of biodiesel causes the moisture absorption which increase the corrosive wear in engine parts.

The following section considers the chemical structure of biodiesel.

2.2 Biodiesel

Biodiesel is a type of fuel which is produced from vegetable oil or animal fat with a long chain of methyl, propyl or ethyl esters. It is commonly produced by chemical reaction between vegetable oil or animal fat and an alcohol.

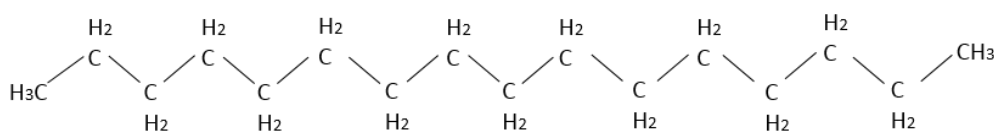
A molecule of biodiesel looks like the structure below. Mostly it is a long chain of carbon atoms, with hydrogen atoms attached, at one end is an ester functional group (shown in blue).



Diesel engines can burn biodiesel with no major modifications. Some fuel lines are made of rubber which high blends of biodiesel will degrade them over time. Biodiesel concentration affected the properties of the elastomer and making them swelling. Fuel lines are made up mostly of elastomers. A noteworthy biodiesel property is its auto oxidation. The presence of

unsaturated fatty acids methyl esters makes biodiesel more susceptible to oxidation than diesel. This process can change fuel acid number, causing a more severe damage to the polymeric materials contacted.

This is because biodiesel is chemically very similar to regular diesel, shown below. The regular diesel also has the long chain of carbon and hydrogen atoms, but doesn't have the ester group shown in blue above.



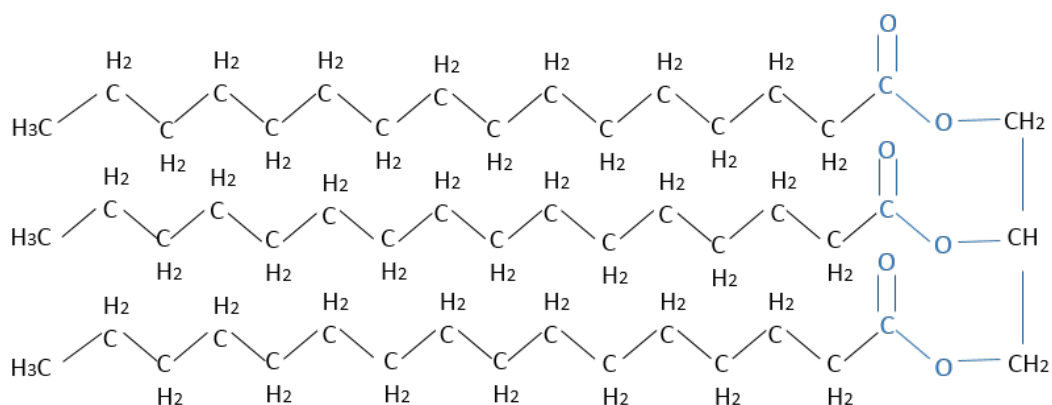
2.2.1 Blends

Blends of biodiesel and fossil fuels are now commonplace in the world's fuel market. Most countries are using a system based on "B" factors to state the proportion of biodiesel / fossil fuel mix, wherein the number suffix after the "B" signifies the percentage of biodiesel in the product. For example, 100% biodiesel is labelled as B100, whilst a 20% biodiesel and 80% fossil diesel fuel is labelled as B20. Blends of less than 20% of biodiesel are able to be used in the diesel engines directly without any modifications to the fuel supply system of the engine. However, most of the fuel injection manufacturers will not provide any warranty for their products which are damaged as a result of using biodiesel fuels, unless the blends (usually of B6 to B20) are recognised by ASTM D7467 standard [4].

Requirements for Biodiesel B6-B20 ASTM D7467			
Property	Test Method	Limits	Units
Acid number	D664	0.3 max	mg KOH/g
Viscosity at 40°C	D445	1.9-4.1 ^a	mm ² /s
Flash point	D93	52 ^b	°C
Cloud point	D2500	Report to customer	°C
Distillation temperature, 90% evaporated	D86	343	°C
Ramsbottom carbon residue on 10% bottoms	D524	0.35 max	% mass
Sulphur	D5453	0.0015 max (S15) 0.05 max (S500)	% mass
Cetane number	D613	40 min ^c	-
Ash content	D482	0.01	% mass
Water and sediment	D2709	0.050 max	% mass
Copper corrosion 3 h at 50°C	D130	No. 3	-
Biodiesel content	D7371	6-20	% (V/V)
Oxidation stability	EN15751	6 min	Hours
Lubricity at 60°C	D6079	520 max ^d	micron

Table.2.1. Requirements for Biodiesel B6-B20 ASTM D7467 [5].

It is possible to use 100% pure biofuel in diesel engines, the first diesel engines didn't run on the petroleum diesel fuel, but on vegetable oil, a sample molecule of which is shown below.



The use of biodiesel could also lead to some major problems, particularly in relation to blocked injector systems and reduced performance of the engines owing to greater corrosion and water contents.

The process of blending B100 biofuel with fossil diesel takes place using one of the following methods:

- Blending biodiesel and diesel fuel in the refinery before delivering the fuel to the tanker trucks.
- Splash mixing the fuels in the tanker trucks. In this process a certain percentage of biodiesel and diesel are mixed inside the tanker trucks.
 - In-line mixing—in this process both biodiesel and diesel arrive at the tanker at the same time by using a static mix.
 - Metered pump mixing—in this process meters are fixed for a certain percentage of biodiesel and diesel fuel. Transfer pumps pull fuels from two main tanks and the fuels mixed on the leaving pipe [27].

2.2.2 Applications

As previously mentioned, use of biodiesel in blends up to B100, is possible without engine modification, especially in older style engines. However, the modern high pressure common rail fuel injection system which works at 2000 bar, is limited to fuels in the B5 to B20 range, depending on the individual manufacturer's recommendation and their warranties terms and conditions.

The solvent characteristics of biodiesel are different to those of fossil diesel. A consequence of this is that the rubber parts, including the gaskets and hoses of engines for example may be damaged by switching to biodiesel. This effect is a more significant problem for engines and vehicles built prior to 1990, where biodiesel can remove deposits from the fuel pipes and fuel tank. At best this can lead to fuel filter elements becoming clogged, requiring them to be replaced more frequently, whilst at worst, minute particles might fail to be filtered and pass to the injectors causing them to fail to function properly [28].

2.2.3 Distribution

After the United States passed the Energy Policy Act of 2005, the use of biodiesel was increased in that country. In the U.K the Renewable Transport Fuel Obligation forced fuel manufacturers to add at least 5% renewable fuels to their products by the end of 2010, so that by that date, all fuel retail outlets sold fuel containing 5% bio-product [29].

However, since that date, the global price of crude oil has dropped by more than 50% (to 2015) and given that the prediction for the next two years is that prices will remain static, the incentive and economics to use biofuels is likely to remain equally static.

2.2.4 Vehicle use and manufacturer's acceptance

In 2005, the United States Chrysler Corporation introduced their Jeep model cars utilising a CRD (Common Rail Diesel) diesel engine, designed to work with biodiesel B5. It was the first time that a car manufacturer officially had accepted and established the blend of biodiesel with fossil diesel. Following this project, in 2007 Chrysler decided to apply a full warranty covering all its diesel engines using up to B20 biodiesel blend, if the quality of biodiesel product used had been recognised by United States standards.

In another project, Halifax City (U.S.) decided to convert its bus transport system. The new buses were powered by biodiesel produced from fish-oil feedstock. Initially, this project caused some high maintenance costs associated with the use of the fuel, but after further refining processes for the fuel, use in the bus engines was acceptable and the replacement with this biodiesel proved successful.

In the U.K., the Virgin Train company claimed they were the first company in the world to utilise biodiesel in its locomotives. They used the B20 biodiesel blend, and the company claimed that this would reduce its emissions by 14%. Again in the U.K., the train used by the Royal Family is hauled by locomotives using B100, a unique success in the world [4].

2.2.5 Properties

Biodiesel has better lubricating properties and also a higher Cetane Number (CN) when measured against low sulphur diesel fuel. CN is related to fuel's ignition delay, and the time between the start of injection and starting the combustion of the fuel.

Although B100 biofuel can cause component wear, actual biodiesel blends reduce wear of fuel injection systems [30]. The use of low blends of

biodiesel in the common rail (CR) fuel injection systems (where greater lubrication is necessary as a result of the high pressure working condition) gives an increase in the life of the system components such as fuel injection pumps or injector units [31].

The calorific values of biodiesels varies according to the feedstock used. An average working figure for the fuel is from 27 to 37 MJ/kg (Mega joules per kilogram) which is 9% less than the calorific value of normal fossil diesel [32].

The output energy of biodiesel depends on its quality blend and the conditions which the fuel is ignited. The thermal efficiency of B100 as compared to B20 is vary due to the content of the blends. Thermal efficiency of a fuel is part of fuel characteristics such as: viscosity, density, and the flash point; these characteristics are changing in the different blends as well as the quality of biodiesel.

Biodiesel is a liquid with a colour range from golden to dark brown, depending on the feedstock. It is immiscible in water and has a higher boiling point and lower vapour pressure compared to fossil diesel. The flash point of biodiesel ($>130^{\circ}\text{C}$) is higher than diesel (64°C) and its density (0.88 g/cm^3) is higher than diesel (0.85 g/cm^3) [31].

An added bonus in favour of biodiesel is its lubricating qualities. In fossil diesel, sulphur has historically provided lubrication, but in modern ultra-low sulphur fuels, this has been greatly reduced. The addition of biodiesel restores this lubricity [32].

2.2.6 Material Compatibility

Plastics—High density polyethylene (HDPE) is compatible with biodiesel while polyvinyl chloride (PVC) and blends of polystyrenes are vulnerable to degradation on contact with biodiesel.

Metals—Biodiesel affects materials based on the pure metal or alloys of copper, zinc, tin, lead and cast iron. Biodiesel does not have any effect on stainless steel and aluminium alloy.

Rubber—Biodiesel has detrimental effect on all natural rubbers used on older engines through repeated exposure. However, modern synthetic rubbers (such as Viton) now commonly used in new engines are compatible with biodiesel in all working conditions [31].

2.2.7 Low Temperature Gelling

The temperature at which a fuel molecule freezes is polarity. The more polar a molecule is, the more easily it forms crystal structure and becomes solid. Biodiesel is more polar than standard diesel as it contains for oxygen, and thus is more prone to freezing. The fuel usually does not change to solid, it changes to crystals which is referred to gelling.

Biodiesel begins to gel at temperatures around 16°C depending on the feedstock used in its production. As the temperature drops further, the crystals grow in size - up to 0.1 µm or larger. The biodiesel also changes appearance, becoming cloudier. The point that this occurs is known as the cloud point (CP) of biodiesel. Further temperature drops cause the crystal size to increase until it reaches a point where it will not pour – the Pour Point (PP) [31].

Crystallisation of the biodiesel then continues to a point called the cold filter plugging point (CFPP) which is the point when the biodiesel can still

pass through a 45 μm filter. Below this temperature, it starts to become jellified and eventually solid.

The CP of biodiesel is variable, depending on the feedstock oil used for its production. For example, biodiesel produced from erucic acid base and canola seed has a CP beginning at $-10\text{ }^{\circ}\text{C}$, while that produced from tallow tends to start to crystallise at $+16\text{ }^{\circ}\text{C}$ [13]. There are many commercial additives which reduce the pour point and CFPP of biodiesel. Working with biodiesel in winter is possible by preparing blends of low sulphur diesel fuel (No. 2 grade) or kerosene (No. 1 grade) with biofuel B100 [14].

A way of avoiding gelling of the biodiesel during cold temperatures is to use a twin-compartment fuel tank. One compartment contains regular fossil diesel, whilst the other tank is insulated and perhaps fitted with a heater coil. In use, the engine is started on the normal diesel and once the biodiesel is heated, the tanks can be switched over allowing this fuel to be used in preference [32].

2.2.8 Contamination by water

Biodiesel may contain small quantities of water which can cause serious problems within the fuel supply system of diesel engines. Although miscible in water, biodiesel has some similar properties to ethanol in that it is able to absorb moisture from the atmosphere i.e. it is hygroscopic. One of the reasons for this is the remnants of mono-and diglyceride compounds produced as the result of incomplete reaction during the biodiesel production [32]. These molecules behave in a similar way to emulsifiers, allowing water to mix with the biodiesel. The source of water found in diesel is usually condensation produced within the fuel storage vessel.

The presence of water in biodiesel is an issue because;

- It reduces the combustion temperature causing incomplete combustion, hence more smoke, hard starting and less output power from the engine.
- It can cause corrosion in the fuel supply system components such as the fuel pump, injector and pipes.
- It can allow the propagation of certain microbes that are able to easily utilise biodiesel as a food source. Rapid growth of this microbe causes the so called “diesel bug”, a black jelly-like substance that can block pipes and filters and may even cause damage to the fuel pump. This is a particular issue for common rail (CR) injection systems where diesel, warmed from its passage through the hot engine supply system, is returned to the fuel tank, thereby heating the tank and promoting condensation.
- It starts to freeze at 0 °C and this property can accelerate gelling in the biodiesel.
- It can cause specific wear issues within the engine, such as pitting on the pistons.

Excessive water contamination of the biodiesel feedstock also contributes to poor performance of base compounds used in the catalytic production process by affecting the pH of the reaction. However, the methanol production process is unaffected by the presence of water as the transesterification process between oil feedstock and methanol occurs under high pressure and temperature [32].

2.2.9 Availability and prices

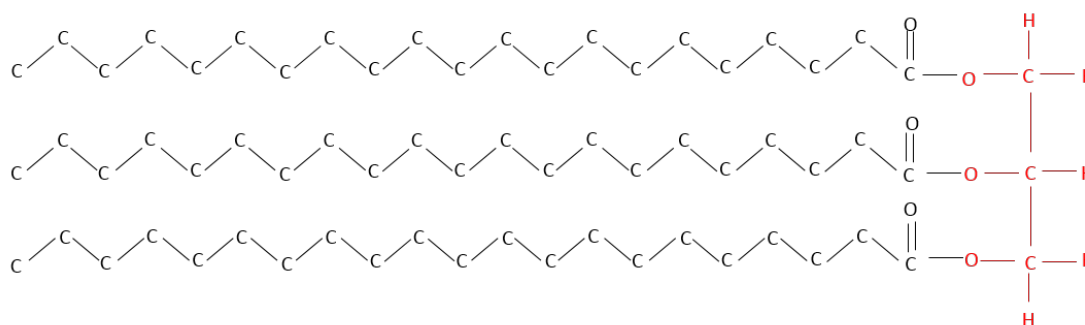
The price of biodiesel varies across the world and in some countries, it is cheaper than fossil diesel fuel. The production of biodiesel reached 4

million tonnes in 2006, approximately 85% of this produced within the European community. In the United States in 2007 the selling price of B2/B5 (excluding the federal and state duty) was 12 cents per gallon cheaper than diesel whilst the price of B20 was the same as fossil diesel. However, a large increase in price of crude oil from 2009 raised the price of B20 to 15 cents per gallon higher than diesel. Exceptions to this did occur where governments paid a subsidy to the manufacturers or charged a preferential rate of fuel tax. The severe fluctuation in crude oil prices over recent years means that now (2015) biodiesel production and future investments are in a state of flux, with uncertain long-term prospects.

2.2.10 Production

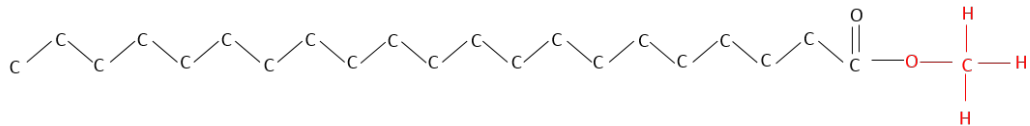
Biodiesel is mainly produced by a transesterification process applied to vegetable oil or animal fat feedstock. There are several chemical methods for transesterification triglycerides process, the main ones being common batch, supercritical process, ultrasonic methods and microwave methods.

Triglycerides are a type of biological molecule common in plants and animals. They are made up of three atoms, oxygen, carbon, and hydrogen. They look something like this:

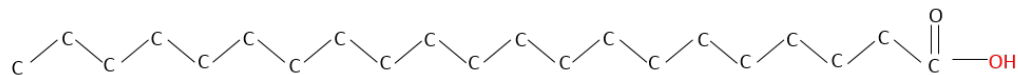


The red part is glycerol and the three black chains are fatty acids. So, a triglyceride molecule is made from a glycerol molecule and three fatty acid

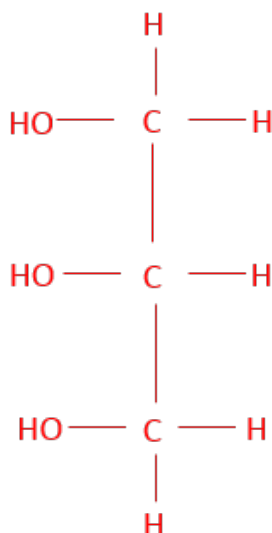
molecules. The fatty acid chains are similar to hydrocarbons, then scientists break off the glycerol and release the fatty acids by applying transesterification process. It produces an ester. An ester looks like this:



The red part is the R group and can be any length of one carbon. Biodiesel also contains fatty acid alcohols, which look like the following:



The transesterification also produces glycerol, a type of alcohol, as a by-product. For every metric ton (tonne) of biodiesel that is produced, 100 kilograms of glycerol is produced. Glycerol looks like the following:



Biodiesel produced by transesterified processes contains blends of mono-alkyl esters of long chain fatty acids. The most common alcohol used for the process is methanol because it is currently very priced advantageous. Ethanol or other higher molecular weight alcohols such as butanol and isopropanol are also used for producing ethyl ester biodiesel, where it has been found useful in increasing the flow properties of product at low temperatures, whilst remaining a cost effective transestrification process.

A lipid transesterification process can be used for converting base oil to esters. During this process, all free fatty acids in the base oil either convert to soap, which is removed from the product process or esterifies due to the presence of acidic catalysts. The biodiesel produced as a result of the lipid transesterification process has similar combustion properties to fossil diesel [33]. Crude glycerol produced from the process has a further use where, after refining and purification by vacuum distillation it is used as a raw material in the production of epoxy resins [33].

2.2.11 Biodiesel Chemical Overview

As indicated previously, biodiesel is a fuel derived from fats and oils composed of triglycerides, i.e. molecules consisting of a single glycerol molecule in combination with three fatty acid molecules (hydrocarbon chains terminating in a carboxyl group). These oils are converted to biodiesel in a process known as transesterification. In this process, the triglycerides are converted to mono alkyl esters by reaction of the fat or oil with an alcohol (usually methanol) in the presence of a catalyst. This produces glycerol and esters which, when methanol is used, are known as fatty acid methyl esters or FAME. The transesterification reaction is illustrated below in figure 2.1.

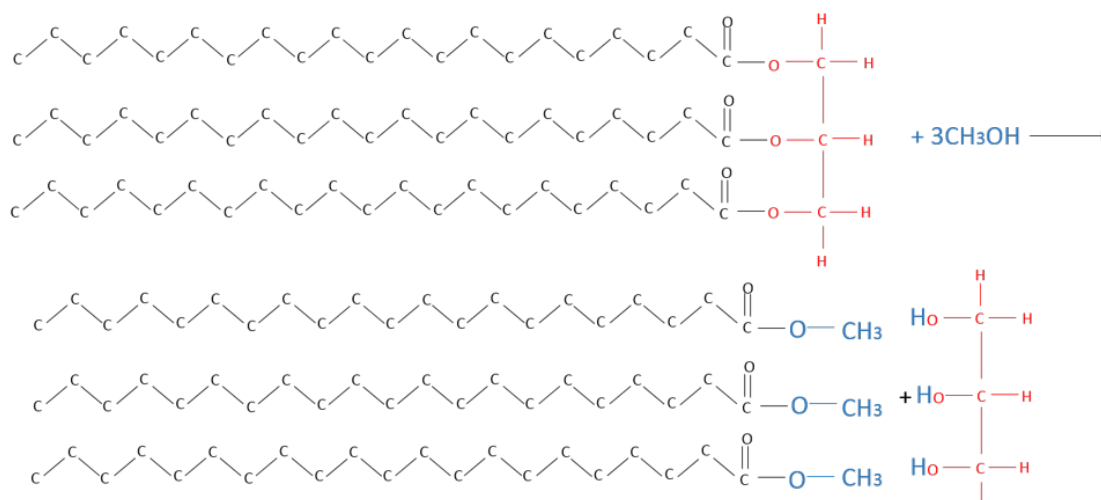


Figure 2.1: Transesterification of triglycerides with methanol.

Most biodiesel fuels derived from vegetable oil, animal fat or waste grease feedstock consist of fatty acids with 12 to 18 carbon atoms. The conversion process allows these hydrocarbon chains to be chemically fully-saturated i.e. the carbon atoms only have a single bond between them and the adjacent atoms, though depending on process efficiency a very small proportion of unsaturated molecules will exist (i.e. possessing the aromatic double or even triple bonding between atoms).

2.2.12 Production level

In 2007, biodiesel production across the world increased dramatically by more than 40%. The total quantity of world production for that year was near to 6 million tonnes. Europe produced almost 5 million tonnes of which 3 million tonnes was by Germany alone. The remaining production was by the United States. In 2008, production in Europe had increased to 8 million tonnes. To support the European biodiesel producers, an import duty was considered applicable to imported American biodiesel in 2009. Today (2014) the total production capacity of biodiesel in Europe is about 18 million tonnes whilst the global demand for biodiesel is estimated at 500 million tonnes. Meanwhile total global production of vegetable oil for all

uses is about 200 million tonnes, far less than global demand for biodiesel fuel [34].

2.2.13 Biodiesel feedstock

A large range of bio-oils are capable of being used for biodiesel production. The most common oil feedstocks are;

- Virgin oil — rapeseed and soya bean are the most common feedstock. In the United States, soya bean accounts for 90% of the raw material.
- Waste vegetable oil (WVO).
- Animal fats.
- Algae, which could be grown with waste materials (such as waste water) and without using agriculture lands, are important aspect as it does not take up land used for food production.
- Oil from the Halophyte plant which grows in salt water and hence use land not required for agriculture. It could be a good replacement for soya bean and other oil seeds which need fresh water [35].

It is generally accepted that waste vegetable oils are the best feedstock for biodiesel production, but as its total production amount is much less than world demand, then clearly it is not going to be possible to satisfy all market requirements. Animal fats are a by-product of the meat production industry. There are currently many factories producing animal fat based biodiesel. An example of this is a factory in the United States producing 0.014 million tonnes of biodiesel per year from 1.2 million tonnes of chicken fat. There are some other factories which are using waste fish oil as the feedstock in their factories [35].

2.2.14 Energy security

One of the main reasons for considering biodiesel for the energy market is the need by governments to secure energy supplies. Biodiesel reduces the dependence of countries on crude oil and additionally concentrates their minds on utilising their local natural resources such as coal, gas and renewable sources. By adopting extensive use of biofuels, countries would be reducing greenhouse gas emissions.

In today's world, many governments, especially those of the leading nations, have to strike a balance between political power and energy supplies to the point where their strategy has to include reducing the dependence to crude oil.

The U.S National Renewable Energy Laboratory (NREL) and the White House announced in their annual reports that energy security is a major factor for the U.S government to become involved with and investment in the development of biodiesel industries. The European Community is adopting the same strategy [36].

2.2.15 Environmental effects

Biodiesel is confirmed as having a positive effect in reducing greenhouse gas emissions, especially particulates. According to a U.S. Environmental Protection Agency (EPA) report, biodiesel produced from soya oil feedstock is able to reduce greenhouse gases emissions by 57% when compared against fossil fuels. When waste grease feedstock is used, the reduction leaps to a 86% reduction. An additional benefit is that biofuel degrades twice as fast as fossil fuel and also degrades more completely. In salt water, degradation is likewise quicker than for fossil fuel [36].

2.2.16 Food versus fuel

In poorer countries the increasing price of vegetable oil is becoming a problem for the population. There is a belief that biodiesel should only be produced from non-edible vegetable oil seeds such as Camelina or Jatropha. These plants are able to grow on land unsuitable for human food crops. The issue is more serious because farmers might produce biofuel crops in preference to those for food in order to earn a better profit. The competition between growing crops for fuel as opposed to food is therefore likely to increase the price of the latter, making the population more reliant on imported food [35].

2.3 Overview of biodiesel effects on engine emissions

The result of transesterification production of biodiesel is an oxygenated fuel with effectively no aromatic or sulphur content. In general, reports indicate a slight decrease in particulate matter (PM), hydrocarbons (HC) and carbon monoxide (CO) emissions compared to fossil diesel when biodiesel fuels are used. The reduction in PM emissions is understood to mainly be a consequence of the oxygenated methyl ester group in the biodiesel molecule.

However, this reduction in PM may also, at least partly be attributed to the lack of aromatics molecules and sulphur. Conversely, it is generally reported that emissions of oxides of nitrogen (NO_x) either remain constant or are slightly increased when biodiesel fuels are used. With regard to the oxygenated nature of the biofuel, it has been observed that biodiesel (B100) derived soot is more reactive than that derived from fossil diesel. This is thought to be mainly due to the surface oxygen reactivity of B100 derived soot, but may also be related to the soot structure.

In the combustion chamber, soot could undergo different fates; it may become oxidized by the reaction with O₂, CO₂, and other oxidizing compounds or be emitted as sub-micrometre particles [37].

The reduction in PM mass emissions can be partly explained by the decrease in size of particles emitted from engines fuelled with biodiesel. There is a decrease in the concentration of accumulation mode particles (50 nm and 1 µm), accompanied by a relative increase in the concentration of nucleation mode particles (size ≤50 nm). Since, as previously mentioned, most of the PM mass is emitted as accumulation mode particles, this reduction in accumulation mode particles leads to a decreased PM mass emission [37].

This is partly explained by the advanced combustion timing which is associated with biodiesel fuels – especially in older engines with mechanical fuel injection systems.

2.4 Effects of biodiesel fuelling on soot structure

Focusing on the soot nanostructure, B100 is seen to produce soot particles with a typical shell-core structure exhibiting an amorphous core with highly ordered outer structure. Diesel soot displays a slightly less ordered structure, while B20 soot is extremely disordered. These are the characteristics of the initial soot particles, but there are structural changes that become apparent during early oxidation stages – especially with B100-derived PM. B100-derived PM undergoes drastic changes during early oxidation, showing a tendency to become far more disordered; developing short, defective graphene layers. The primary soot particles are spherical and consist of layer plane segments. They may be stacked concentrically around the particle centre, this structure is known as a shell-core structure.

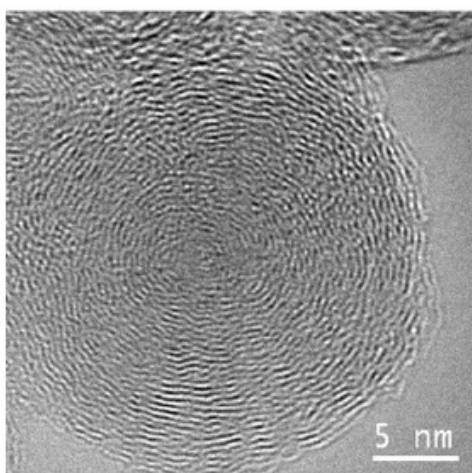


Figure 2.2: A TEM image of a Shell-core structure soot particle [38].

This shell-core structure is what is thought to be typical of diesel engine soot.

2.5 Diesel particulate matter overview

Particulate matter (PM) is a major regulated emission from the combustion of diesel in an engine. It is one of the more difficult emissions to reduce and a great deal of research has been completed, or is currently underway with the aim of gaining a stronger understanding of PM.

Diesel PM generally consists of soot generated during combustion, which may adsorb some organic compounds onto its surface. Most of the PM is the result of incomplete combustion of fuel hydrocarbons, though some is derived from the engine lubricating oil.

A number of methods are employed in attempting to limit PM emissions. Some of these concentrate on dealing with the issue within the combustion chamber, such as modified injection strategies, whilst others deal with the combustion products once produced, primarily by the use of Diesel Particulate Filters (DPF).

Diesel particulate matter mainly consists of highly agglomerated, solid carbonaceous material, ash and volatile organic and sulphur compounds.

The solid carbon is understood to originate within the cylinder during the combustion process.

The particles are believed to be formed in fuel rich regions of the cylinder combustion chamber under high-temperature conditions. These solid particles often undergo oxidation, with the residue from this process being emitted in the exhaust.

Particle characteristics can therefore potentially vary depending upon the level of engine technology. A modern engine with a high-pressure injection system and perhaps multiple injections per cycle (pilot injections, or late injections) can lead to different emissions compared to a traditional pump-line-nozzle setup.

2.6 How Does a Diesel Engine Work?

A diesel engine is an internal combustion engine which uses the high temperature of the compressed air in the cylinder to start the ignition process and burn the diesel fuel which is injected into the combustion chamber before the final stage of compression. It is generically known as a compression ignition engine. Compression ignition engines and their thermodynamic cycle were invented and developed by Rudolf Diesel in 1897. Diesel's work has been used as the basis for all subsequent technology and development of this engine, which subsequently became commonly referred to as a "diesel engine" after its inventor.

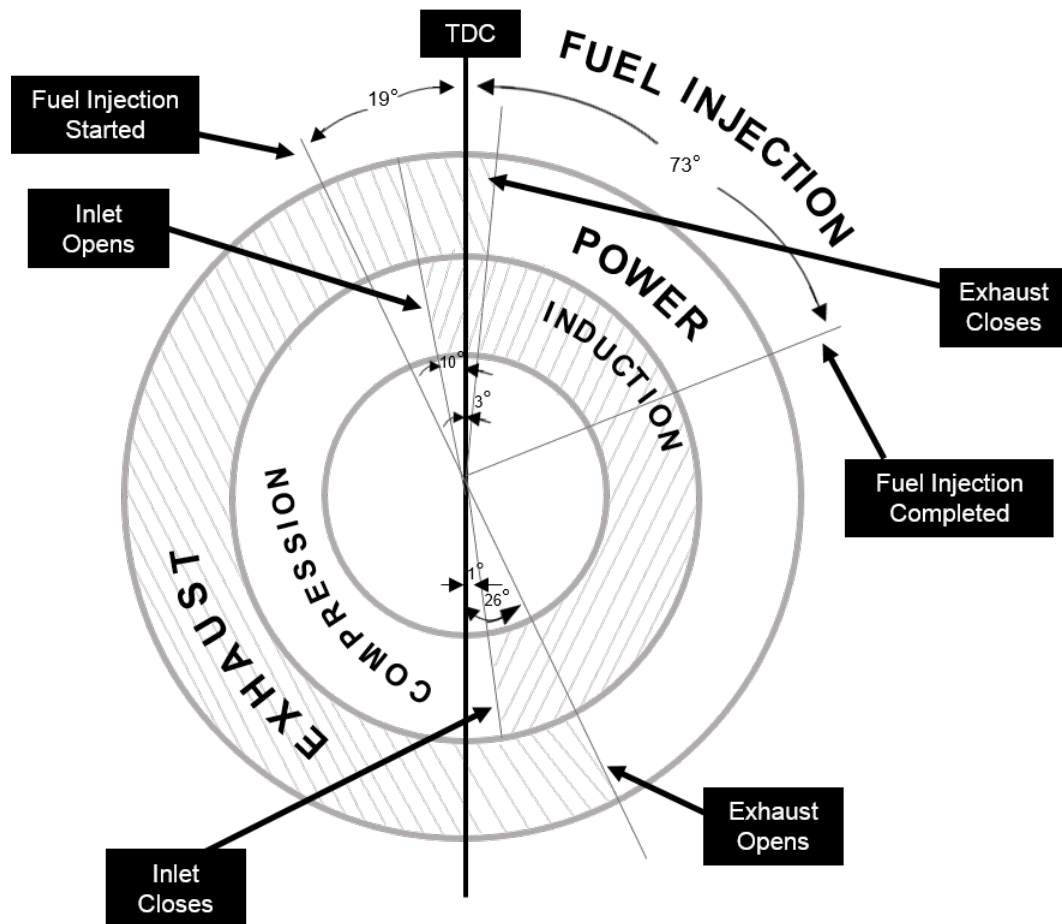


Figure 2.3 A timing diagram for a typical diesel engine [39].

A piston engine, which includes the diesel type, converts the chemical energy of the ignited fuel to mechanical energy to move pistons along a closed cylinder. The pistons are connected to a crankshaft which converts the linear motion of piston to a rotary motion. The complete cycle of work happens over four “strokes” of the piston and hence is known as a “four-stroke” engine. Although the compression ignition engine has undergone extensive development since it was invented by Rudolf Diesel, the basic concepts of this four-stroke design have not changed during the last 100 years.

With reference to Figure 2.3 above, the first stroke consists of fresh air drawn through open inlet valves into the cylinder as a result of the vacuum created by the downward piston motion. When the piston assembly is at the bottom of this stroke, the inlet valves close, sealing the air within the cylinder.

In the next (second) stroke the piston starts to move up the cylinder, compressing the air that as a result, increases in temperature, typically in the region of 400° C. At a point just before the piston reaches top dead centre (TDC) diesel fuel is injected into the compressed air, whereupon spontaneous ignition of that fuel occurs. The expanding hot combustion gases push the piston down the cylinder with great force – the third or power stroke.

In the fourth and final stroke, the piston again moves up the cylinder, expelling the spent gases through exhaust valves timed to open at this particular moment. Once at the top of its stroke again, the exhaust valves close and the next compression ignition cycle begins again.

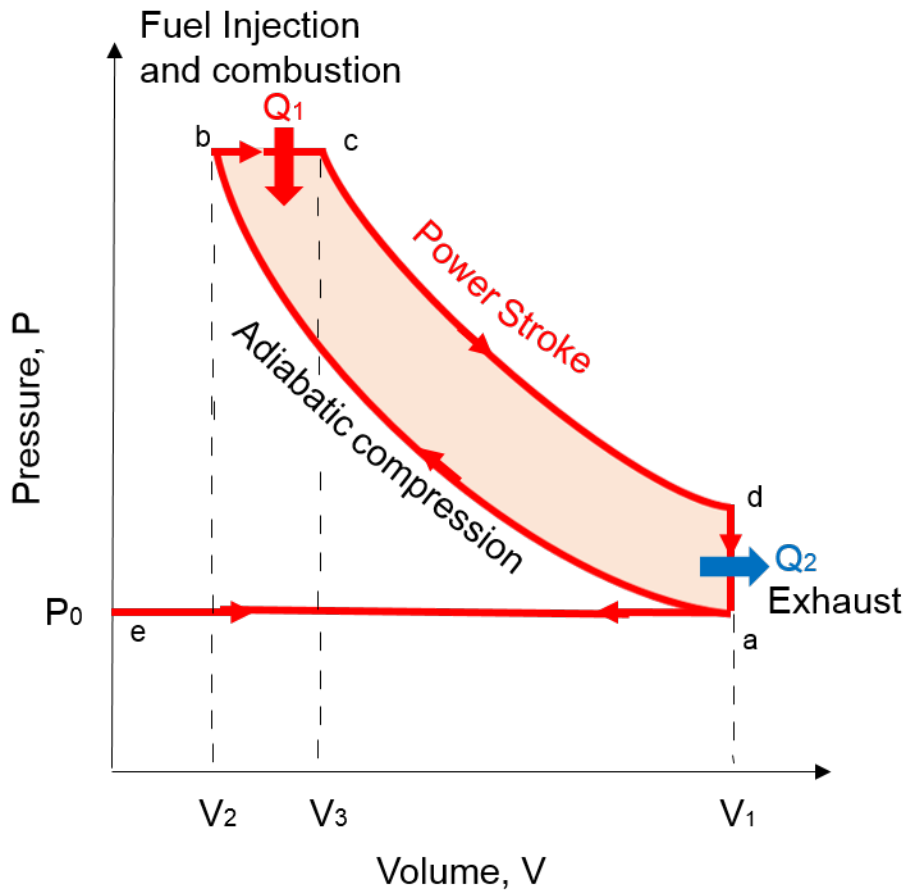


Figure 2.4 – p - V (Indicator) diagram for the ideal diesel cycle. The cycle follows the numbers 0-4 in clockwise direction. In the diesel cycle the combustion occurs at almost constant pressure and the exhaust occurs at constant volume. On this diagram the work that is generated for each cycle corresponds to the area within the loop [40].

In early design diesel engines, the injection point of the diesel fuel is controlled mechanically, with all the limitations of such systems when working at speed. Consequently, incomplete fuel combustion was common, especially at low speeds and light loads, resulting in wasted fuel and poor emission quality of the exhaust gasses.

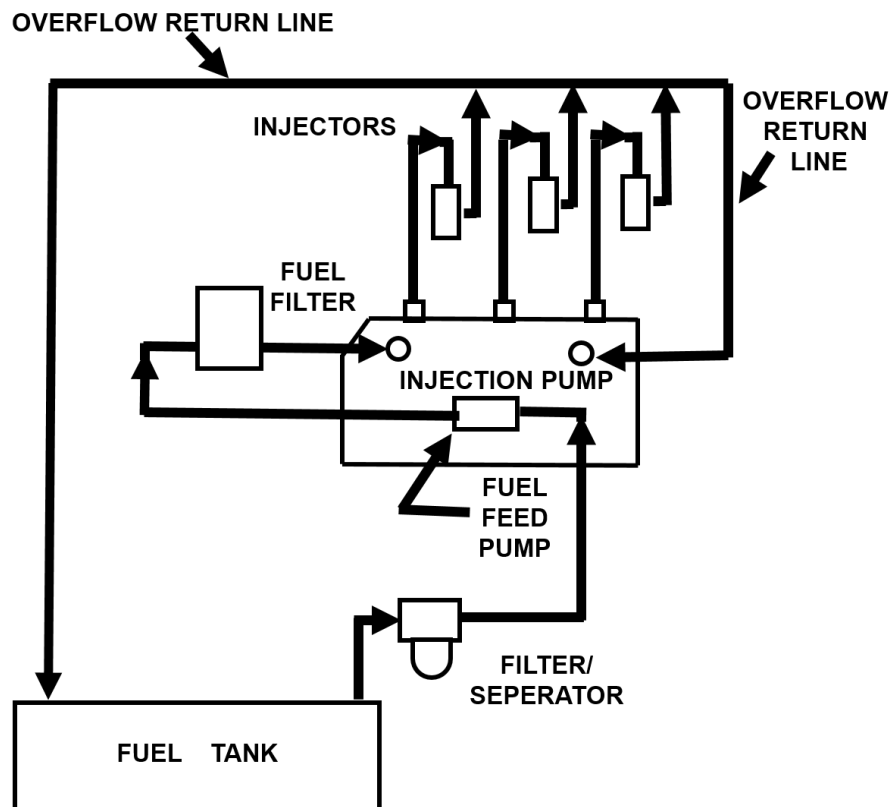


Fig 2.5 –Illustration of mechanical fuel injection system [41].

In modern, new diesel engines, the diesel fuel is injected directly into the combustion chambers through a common rail fuel injection system with a high pressure typically 1,500 bar to 1,800 bar.

In such modern diesel engines, all functions are controlled by a computer known as an engine control unit (ECU). Connected by sensors located in strategic places within the engine, the ECU monitors such parameters as engine speed, oil and coolant temperatures and even the piston's position within the cylinder. Having assessed these, the ECU then determines the exact amount of fuel required for those particular conditions.

These tight controls allow for better fuel combustion and increased engine power, giving greater fuel economy with less emission as compared to the old diesel engines.

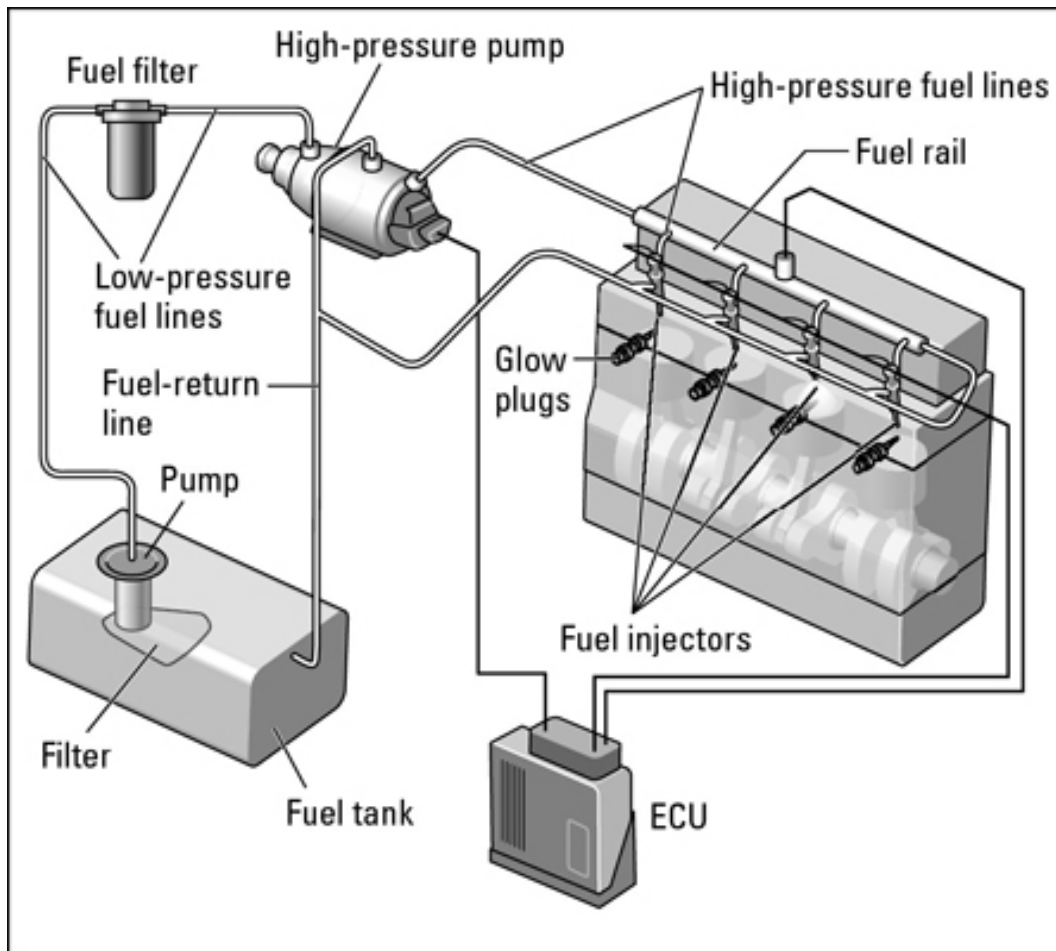


Fig 2.6 – The fuel supply and the fuel injection system of in modern diesel engine [41].

This chapter has discussed the key issues around biodiesel fuels and their use as an energy source. The next chapter will introduce issues related to engine tribology.

CHAPTER 3

3. Engine Tribology

3.1 Tribology

Tribology is the science and study of interacting surfaces which are in relative motion.

Tribology is a branch of materials science that studies the principles of friction, lubrication and wear. The tribological interactions between an unprotected solid surface and another surface or material, may cause loss of material from those solid surfaces, a process commonly referred to as “wear”. Tribology involves research from many different disciplines including materials science, mechanical engineering and chemistry for example.

The main types of wear are abrasion, friction and erosion, all of which can be minimised by modifying the properties of the solid surfaces. Applying one or more surface engineering processes or providing lubricants can limit this wear.

The study of tribology is important for any application where surfaces are in contact. In automotive applications this may be bearings, piston liners, camshafts, crankshafts. Tribology also covers other areas such as hair conditioners and downhill skis for example. Wherever there are materials sliding or rubbing against each other, complex tribological interactions occur that will vary according to whether the surfaces are lubricated or un-lubricated.

When two solid bodies are in contact, subject to forces that produce sliding motion, stresses develop on the surfaces to oppose that motion.

This phenomenon is called friction and is often discussed as a result of the contact stresses that result from e.g. friction force.

Wear can be defined as the loss or displacement of material from a solid surface as a result of mechanical action. Material can be removed in the form of debris, however material can be transferred from one surface to another. Wear is almost inevitable when two solid surfaces which are in contact are moving relative to each other. Wear can appear in different ways depending on the material properties, the environment, and the running conditions. The wear rate of a surface is defined as the volume or mass of lost surface per unit of distance slid. From an engineering view, wear is often classified as either mild with a low wear rate or severe with a high wear rate [42].

A practical aspect of tribology is in the role of mechanical production. For example, in a metal-forming process, friction causes wear upon the tools used, rendering them gradually more inefficient. A consequence of this is the need for more power to drive that tool during the production of the work piece. It also leads to increased tool replacement and wasted energy during the production process.

A lubricant is a substance used to reduce friction and wear and to provide smooth running and satisfactory life for machine components. The lubrication of moving parts in machinery is generally carried out using oil or grease. Most lubricants are liquid, but they can also be solid or gaseous.

A simple lubricant layer reduces friction across the contacting surfaces, thereby prolonging the life of the tool piece and reducing the energy requirements needed [43].

3.2 Wear

In materials science, wear is a consequence of interactions between surfaces. More specifically, it is related to the removal and deformation of surface material as a result of its contact and mechanical actions against an opposing surface.

It can also be defined as the process of interaction between two or more solid surfaces or solid bonding faces that as a consequence of environmental conditions, suffers a dimensional loss, with or without loss of the parent material.

The environmental conditions affecting wear include the load applied, the direction of sliding or rolling, speed of contact, temperature and type of contact (ranging between single phase and multi-phase). For example, a multi-phase process could be a combination of a liquid with solid particles (soot contaminated oil is a good example of this type) and also gas bubbles.

There are several established standard wear test methods currently used for different types of surface contact. These tests are based on calculating the volume of material removed within a specified time under clearly defined conditions.

The American Society for Testing and Materials (ASTM) International Committee has established a number of standard wear rig tests for different applications. These are updated regularly as a result of gaining a better understanding of tribological actions.

The Society for Tribology and Lubrication Engineers (STLE) likewise has defined a large number of frictional wear and lubrication tests. However, all test methods have their own limitations and none can individually give a complete picture of all the different aspects. This is due to the nature of

the wear process, particularly for industrial wear characteristics and the difficulties in providing simulated wear process effects.

Based on the established standard from the ASTM, results for wear effects are reviewed based on calculations of the volume of material lost or affected. Loss of material volume gives a truer picture of the wear process compared to weight loss as the density of the material under test will vary greatly.

For example, the weights of 1 cm³ of two materials tungsten carbide (density of 14000 kg/m³) and aluminium alloy (density of 2700 kg/m³) are 0.014 kg and 0.207 kg respectively. Clearly, comparison of wear for these two materials using weight as a measure would prove fallacious, whereas measurement of volume loss would give a set of results comparable across different materials. The service life of an engineering component can be defined as the point at which its dimensional loss exceeds the tolerance limit for that application.

Wear and other ageing processes such as fatigue, creep and other stress concentration factors (such as fracture toughness) can cause the fast degradation of material and engineering components. Understanding wear and the behaviour of bearing surfaces is one of the unique factors that has allowed massive economic improvements in industrial processes to be achieved [44].

3.2.1 Stages of Wear

In a normal mechanical working situation, the wear-rate changes over three different stages as outlined below:

- Primary Stage or Early Run-In Period

In this stage, as surfaces adapt to each other and “bed-in”, the wear-rate changes from low to high.

- Secondary Stage or Mid-Age Process
Once “bedded-in”, the materials undergo a steady rate of ageing is in progress with minimal wear occurring. Most of the operational life of the engineering components occurs during this stage.
- Tertiary Stage or Old-Age Period
This is reached when the components begin to reach and exceed their tolerance limits. Rapid wear begins to occur and the only cure is replacement.

The life of the materials within the secondary stage will be shortened as a result of severe environmental conditions such as excess temperature, a heavy working load, material stress and sliding velocities [45].

3.2.2 Types of Wear

Study of the wear process is one of the disciplines of tribology science. The complex nature of the wear process leads to studies of wear mechanisms and processes to determine how wear occurs. Common wear mechanisms include adhesive wear and abrasive wear. These two wear mechanisms do not necessarily occur independently from each other and they are also not mutually exclusive.

Wear mechanisms (or sub-mechanisms) frequently occur together. In such circumstances, the wear rate is cumulative and therefore greater than those for each individual wear mechanisms.

3.2.2.1 Adhesive Wear

Adhesive wear occurs between surfaces subject to frictional contact. It normally causes displacement of material compounds from one surface to another as a result of partial binding of two surfaces. Adhesive wear occurs as a result of motion of surfaces as they slide past each other, or make contact as a result of pressure. The direct contact, if excessive

factors come into play, can cause plastic deformation of the material surface allowing material transfer from one surface to another.

Much engineering science and industrial research goes into studying adhesive wear as it is a common fault in industrial applications. It occurs as a result of lubricant failures and is referred to as “galling” or “welding” wear. It occurs extensively when like materials are in contact, e.g. steel on steel or brass on brass. Therefore reducing the number of like materials in contact with each other reduces wear rates.

In adhesion, after possibly extant protective surface layers have been broken through, atomic bonds (microwelds) form above all on the plastically deformed microcontacts between the base body and counterbody. If the strength of the adhesive bonds is greater than that of the softer friction partner, material eventually detaches from the deformed surface of the softer friction partner and is transferred to the harder one. The transferred material can either remain on the harder friction partner or detach, or even return.

If the contact interface between two surfaces under plastic contact has enough adhesive bonding strength to resist relative sliding, large plastic deformation caused by dislocation motion is introduced in the contact region under compression and shearing. As a result of such large deformation in the contact region, a crack is initiated and is propagated in the combined fracture mode of tensile and shearing. When the crack reaches the contact interface, a wear particle is formed and adhesive transfer is completed. This type of wear, which occurs when there is enough adhesive bonding at the contact interface, is called adhesive wear.

In practice, the size of the particles does not correspond to the size of the contact area. A wear particle is not always generated from the soft material and could occur from both materials. The wear particle generation at each contact point is also not equal and depends on the shape of the

contact and the microstructure of the material in the contact area, microscopic surface contamination, and other disturbances in the surroundings. In the adhesive wear mechanism, transfer and retransfer from one surface to another surface takes place in many ways. The large wear particles composed of two surfaces are formed. It is another basic part of the adhesive wear mechanism [45]. In the process of repeated sliding, these particles leave the contact surface as free wear particles or stay on another surface and scratch the counterface [45].

If the contact is made between flat surfaces of similar materials and the contact interface is at first parallel to the sliding direction, the interface rotates as a result of the effect of normal and tangential forces in sliding [45]. This is another aspect of deformation at a contact interface which explains why the adhesive wear mode occurs commonly in practice.

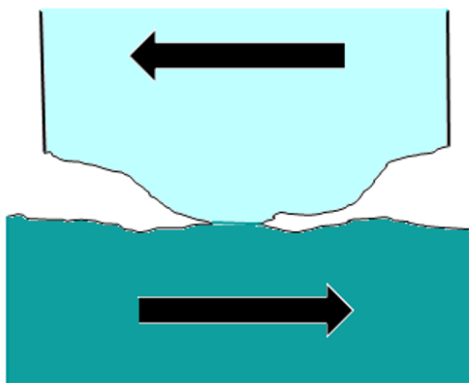


Fig 3.1. Illustrating the adhesive wear process. Arrows indicate direction of sliding.

3.2.2.2 Abrasive Wear

Abrasive wear happens when a hard and rough surface slides over a softer surface. The ASTM defines abrasive wear as the removal of surface materials by hard particles or hard protuberances which are sliding on a

solid surface. Abrasive wear is commonly classified by types of contact and contact environment.

3.2.2.2.1 Mechanisms of Abrasive Wear

It was originally thought that abrasive wear occurred by grits or hard cutting by a series of machine tools. Microscopic investigation has shown that the cutting process is approximated by the sharpest of grits and other mechanisms are also involved. The grits may remove material by micro cutting, pull-out of individual grains [7] or accelerated fatigue by repeated deformations as illustrated in Figure 3.2.

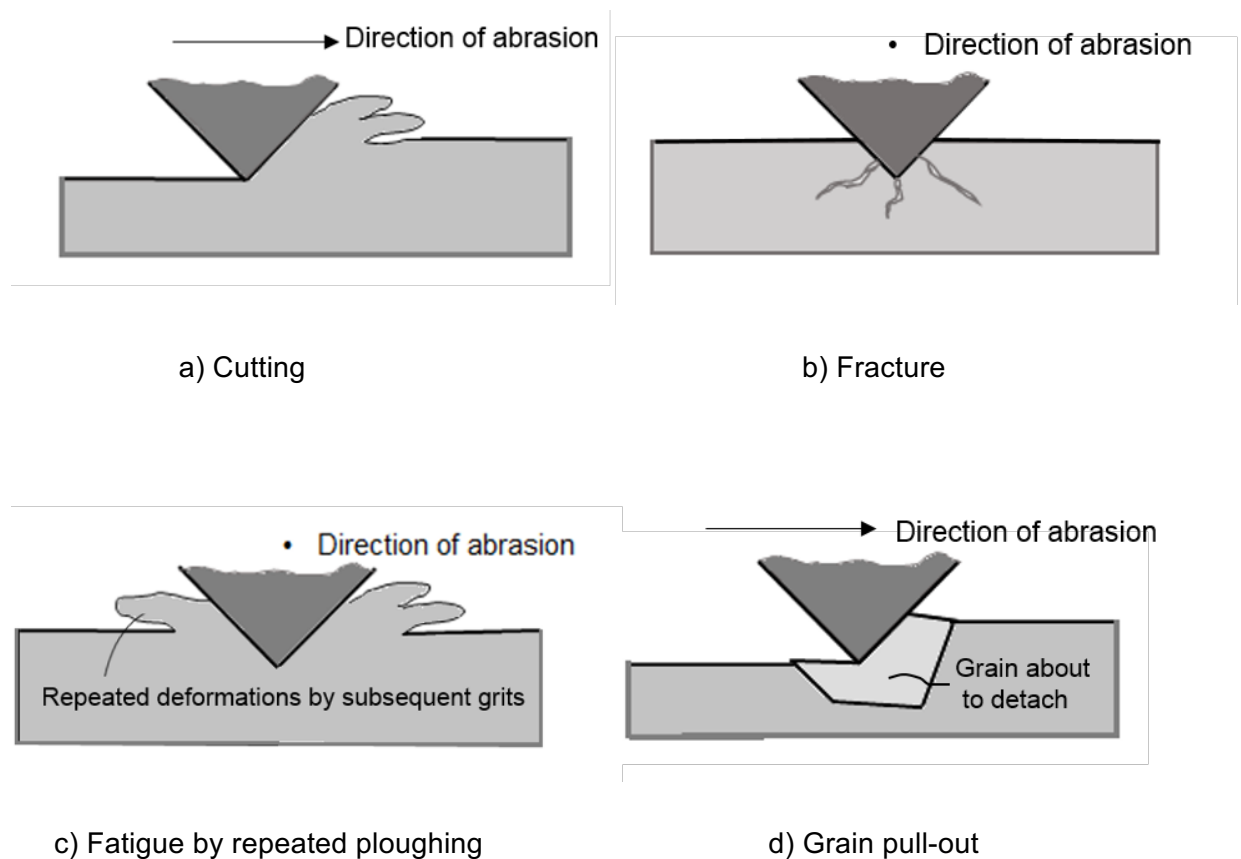


Fig. 3.2. Mechanisms of abrasive wear: microcutting, fracture, fatigue and grain pull-out [46]

The first mechanism illustrated in Figure 3.2.a, cutting, shows the model where a sharp grit cuts the surface. The material is removed as debris.

When the abraded material is brittle, fracture of the worn surface may occur (Figure 3.2.b).

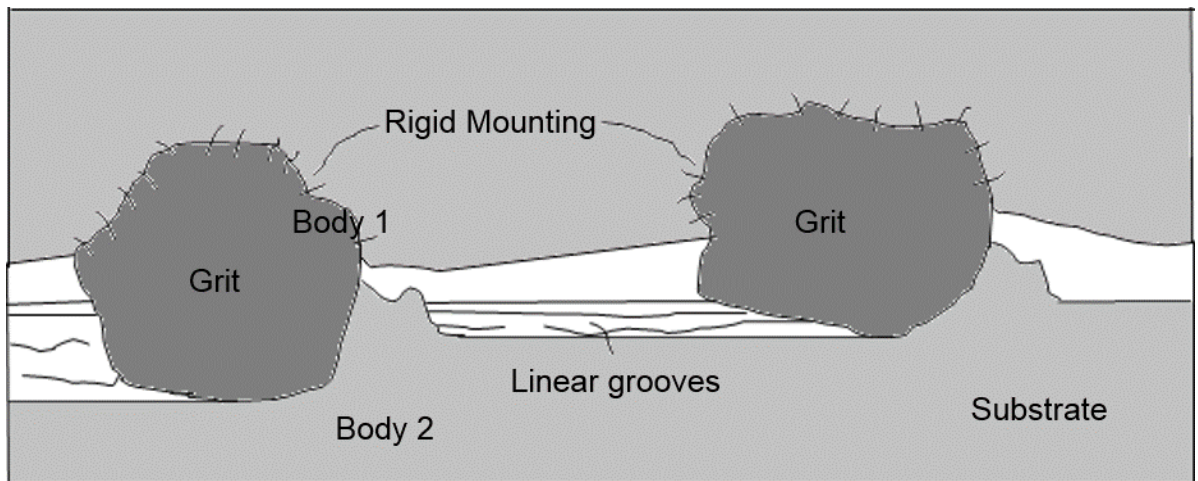
When a material is abraded by a grit then cutting is unlikely and the worn surface is deformed (Figure 3.2.c). In this case debris is as the result of metal fatigue.

The last mechanism illustrated (Figure 3.2.d) is grain pull-out. This mechanism applies for type of materials where the boundary between grains is relatively weak. In this mechanism, the entire grain is lost as wear debris.

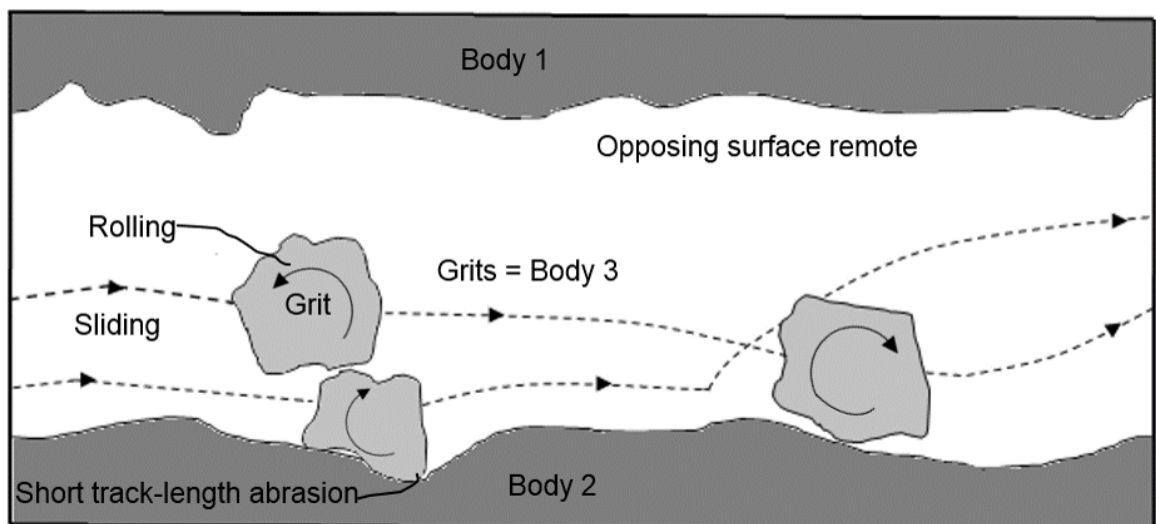
3.2.2.2.2 Modes of Abrasive Wear

The way which the grits pass over the worn surface determines the type of abrasive wear. Two basic modes of abrasive wear are two-body and three-body types.

Two-body wear occurs when hard grits pass over the surface like a cutting tool. In the three-body mechanism the grits are free to roll as well as slide over the surface. The two and three-body mechanisms of wear are illustrated in Figure 3.3.



Two-body mode



Three-body mode

Fig. 3.3 Two and three-body modes of abrasive wear [46]

These two mechanisms of wear were thought to be very similar, however, some major differences between them have been found [46]. It was found that three-body abrasive wear is ten times slower than two-body wear [46]. Properties such as hardness of the “backing wheel”, which forces the grits onto a particular surface, were found to be important for three-body but not for two-body abrasive wear. Two-body wear corresponds to the material

removal where three-body wear have slower mechanisms of removal, however only little is known about the wear mechanisms involved [46]. The worn material is not removed by a series of scratches, as is the case with two-body wear. The worn surface displays a topography suggesting for removal of surface layers by the contact of grits [46].

3.3 Friction

Friction is a force occurring between two surfaces when they are in contact with each other. This force can be categorised as below.

3.3.1 Dry Friction

Dry friction is a force between two solid surfaces. This kind of friction results from the movement, relative to each other, of two surfaces in contact with each other. The direction of the frictional force is usually opposite to the direction of movement and acts to prevent that movement.

The equation for this situation can be stated as:

$$F_f \leq \mu F_n \quad (\text{Equation 3.1})$$

where F_f is friction force, μ is coefficient of friction and the F_n is the normal force acting upon the surfaces. The coefficient of friction, μ , is independent of the mass of the material and mainly depends on its type. For example, μ for a small cube of steel and a big block of steel is the same. The μ can range from zero to 1 or greater.

During frictional contact, the energy generated usually appears as heat. For example, the generation of fire by rubbing two sticks of wood against each other. Friction is an element of the study of tribology. During the last century, most research in this area focused on finding physical mechanisms for the friction. Dry friction is further categorised by

subdivision into static friction between non-moving surfaces and dynamic friction between moving surfaces [46].

3.3.2 Static Friction

Static friction is the friction occurring between two surfaces in stationary contact that prevents the two surfaces from moving. In order to get the two surfaces to move, a kinetic force greater than the static friction force existing must be applied. An example would be the force required to overcome the static friction existing between a book resting on a table in order to push that book across the table.

3.3.3 Dynamic Friction

Compared to static friction, dynamic friction happens when two moving surfaces rub together. The frictional force for this type of interaction is lower than static frictional force. In friction equations, there is normally an assumption which believes that the surfaces contact each other on an atomic scale. This means there is contact across smaller regions, as compared to the whole area. It is usually found that the frictional force is independent of contact, unless the contact area changes.

Although larger contact area between surfaces could create larger frictional forces, it also could reduce the pressure of surfaces for a given force. The increase in friction area is offset by the reduction in pressure.

3.3.4 Fluid Friction

Fluid friction occurs in the flow of liquids or gases. It depends on the chemical properties of the fluid and the structure of the surface where the fluid is passing. Fluid friction is affected by increased velocities. This type of friction also happens when a fluid layer is interposed between moving objects. In this case the viscosity of the liquid acts as the resisting element and gives rise to fluid friction against the motion. A relationship between

viscosity and the thickness of the fluid layer exists that means a thicker layer will increase the viscosity [45].

3.3.5 Lubricated friction

In some ways, this type of friction is similar to fluid friction and occurs when there is a fluid between two hard surfaces. However, lubricated friction is mainly used to reduce component wear. The layer of lubricant allows the two surfaces to slide over each other smoothly, especially when a load is applied. If the lubricant layer fails, then the surfaces rub on each other in the manner of dry friction, damaging one or both of them. The different lubrication regimes are discussed in section 3.6.

3.3.6 Reducing friction

In order to reduce friction, lubricants such as water, oil, grease and also solid lubricants, often, but not always, working in conjunction with devices like ball bearings, wheels, air cushions or fluid bearings, are utilised [31]. They are all designed to separate surfaces or convert sliding friction into rolling friction.

3.4 Engines and Tribology

Engines are common machines currently in use. They are crucial for economic success in both the developing as well as developed nations of the world. In many countries, they add greatly to the quality of life. Engines contain many components, such as bearings, pistons, gears and valves that can be affected by their surface tribology. Understanding tribological principles is essential for the reliability of the engines and their mass production during the last century which led to enormous developments in the science of tribology. The rapid development of lubrication and bearing surface technology resulted from the requirements for increasing capacity and durability of engines for industry. The internal combustion engine as

shown diagrammatically in Figure 3.2 is the prime power mover in many modes of ground, sea and air transport such as vehicles, trucks, buses, trains, ships and small planes. They are also used in electrical power generation for prime and standby electrical power generation. The popularity of internal combustion engines is related to their performance, reliability and versatility. However, they also have many weaknesses. Thermal and mechanical efficiencies of internal combustion engines are low with most of the fuel's energy being wasted through friction and heat loss. The efficiency of internal combustion engines varies. Generally most petrol engines, even when equipped with turbochargers, have a mechanical efficiency of 20%. These engines waste about 36% of the energy as heat lost to the cooling system and another 38% through the exhaust.

The rest of 6% is lost as the friction. Most engineers have not been able to successfully harness wasted energy for any meaningful purpose, although there are various add on devices and systems that can greatly improve combustion efficiency.

Internal combustion engines are also the main contributor to atmospheric pollution by producing hydrocarbon, particulate and NO_x emissions. They also exhibit an effect on greenhouse gasses via carbon dioxide (CO₂) emissions.

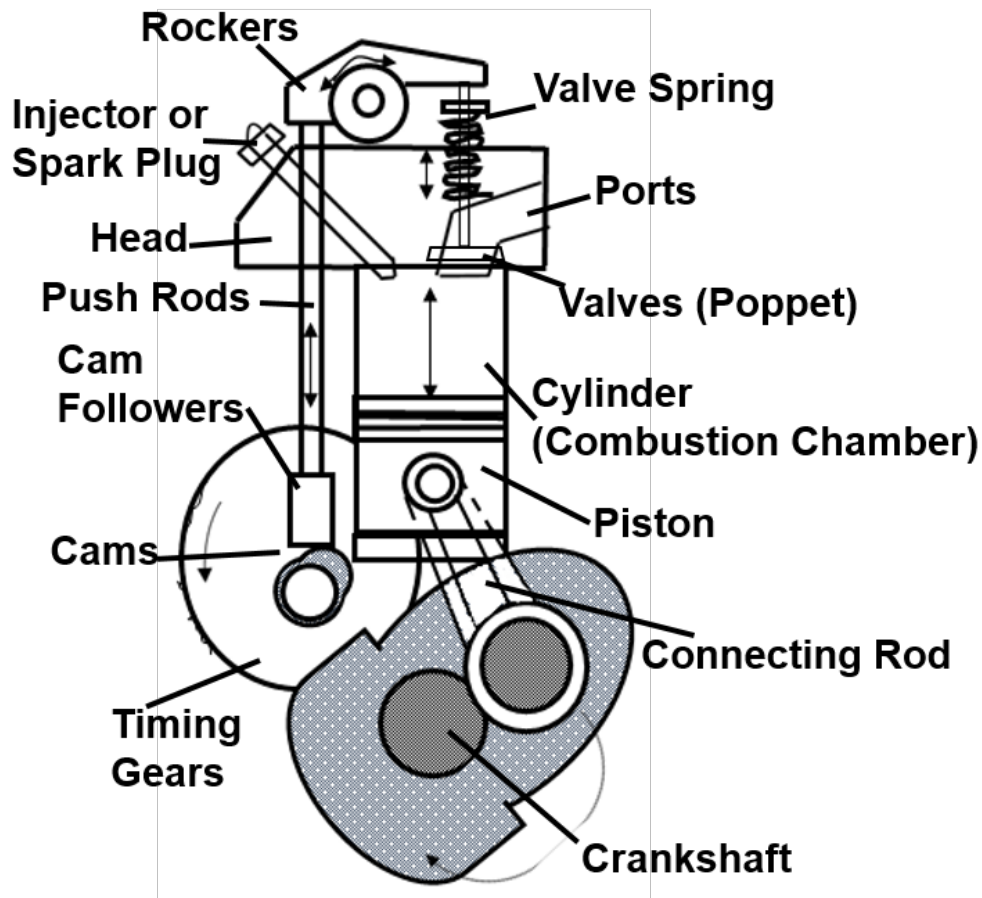


Figure 3.4: Typical internal components of an engine [47].

3.5 Importance of Engine Tribology

For reducing friction and wear, engineers need to achieve effective lubrication of all moving engine components. It is a hard aim to achieve as the wide range of operating conditions within the engine, such as load, speed and temperature need to be considered. The tribological performance of engines has a direct effect on factors such as fuel consumption, engine output power, oil consumption, decreasing exhaust emissions, improving engine life and reducing maintenance. With huge numbers of internal combustion engines in service, the smallest improvements in engine performance could have a major effect on the

global emission levels and the world economy. It is worth considering the fact that only 14% of fuel energy is used to drive a medium sized car wheels, with more than 13% of the fuel energy being wasted as mechanical friction. A 7% reduction in friction could lead to a 1.6% reduction in fuel consumption. The major source of friction losses in an engine occurs as the piston rings slide against the cylinder walls. The valve train and bearings are the next source of frictional losses in a rotating engine. Other minor sources of these losses relate to operation of parts such as the oil, water and fuel pumps. There are some other losses relating to engine type, components design, operating conditions, type of engine lubricants and service history.

3.6 Lubrication in the Engine

The main operating tribological factor in an engine is the film thickness of the lubricant separating the component surfaces. The lubricant film thickness ratio compares the lubricant film to the combined roughness of two contact surfaces. The thickness of the fluid film describes the type of lubrication in an engine. The following regimes or types of lubrication may be considered in the order of increasing severity or decreasing lubricant film thickness (Fig. 3.5):

Hydrodynamic lubrication

1. Elastohydrodynamic lubrication
2. Transition from hydrodynamic and elastohydrodynamic lubrication to boundary lubrication
3. Boundary lubrication.

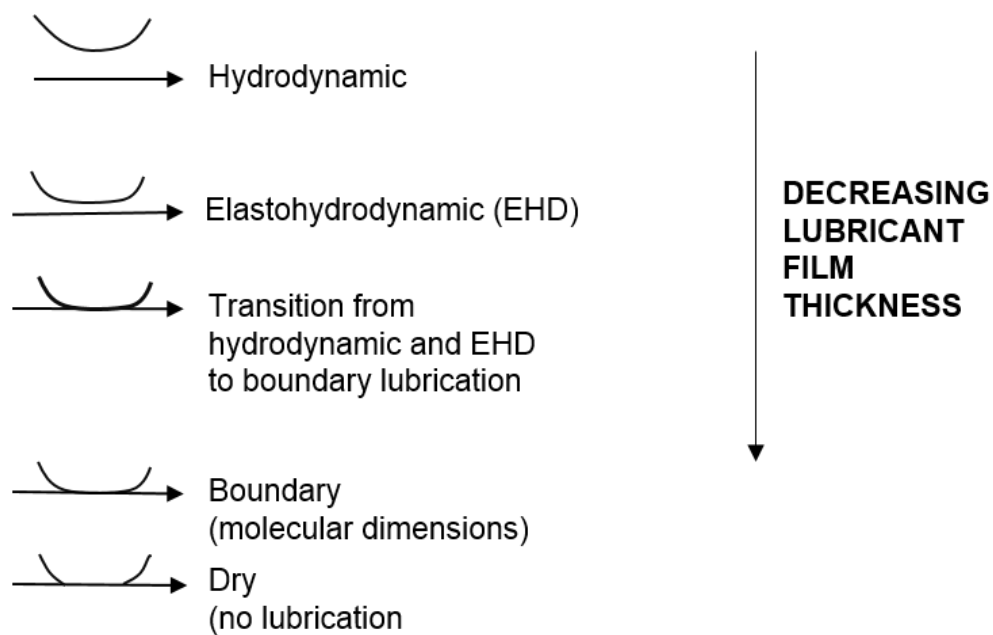


FIGURE 3.5 Regimes of lubrication [48].

In the regime of lubrication film, there is no contact between the surfaces. The film thickness is related to the physical properties of the lubricants such as viscosity.

Although prevention of contact is probably the most important function of a lubricant, there is still much to be learned about the transition from hydrodynamic and elastohydrodynamic lubrication to boundary lubrication. Boundary lubrication is the area in which lubrication changes from the condition of no contact to the acceptable “boundary” condition, where increased contact usually leads to higher friction and wear [48].

However, it is often described as a condition of lubrication in which the friction and wear between motion surfaces are determined by the surface properties of the solids and the chemical nature of the lubricant rather than its viscosity.

3.7 Engine Bearings

Engine bearings are used to support some main engine components such as the crankshaft, camshaft and the connecting rod and are usually constructed as metal acting upon metal, known as “plain journal” bearings. They are manufactured using a steel back shell overlaid with a soft material such as tin-aluminium or lead-bronze as the bearing material. Shafts made to rotate inside the bearing shells are composed of heat-treated steels or spheroidal graphite irons with a hardness of 3 times that of the bearing material. Engine oil is pumped to the bearings by passing through a drillway bored within the shaft or from channels in the cylinder and cylinder head.

Bearing erosion is a failure mechanism in engines and it is important to understand their tribology and how factors such as lubricant supply, dynamic load and thermal effects affect them.

Cavitation erosion damage in engine bearings has increasing importance during the past 5–10 years, as a result of the design higher rotational speeds, and, in some cases, higher rates of change of cylinder pressure rise. Cavitation damage could occur when surfaces in contact with fluid are subjected to vibrations, e.g. water-cooled diesel-engine cylinder liner.

Cavitation damage in oil lubricated plain bearing is also observed in medium or slow speed diesel marine engine or power station applications. Because of instability of lubricant flow, variation of oil pressure can be sufficient to produce bubble inception, collapse and microjet formation process [49].

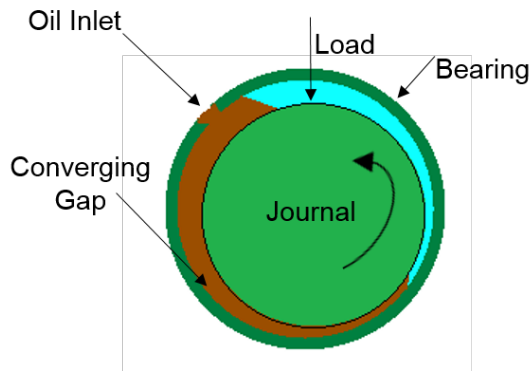


Figure 3.6 Journal Bearing [49].

3.8 Piston Assembly

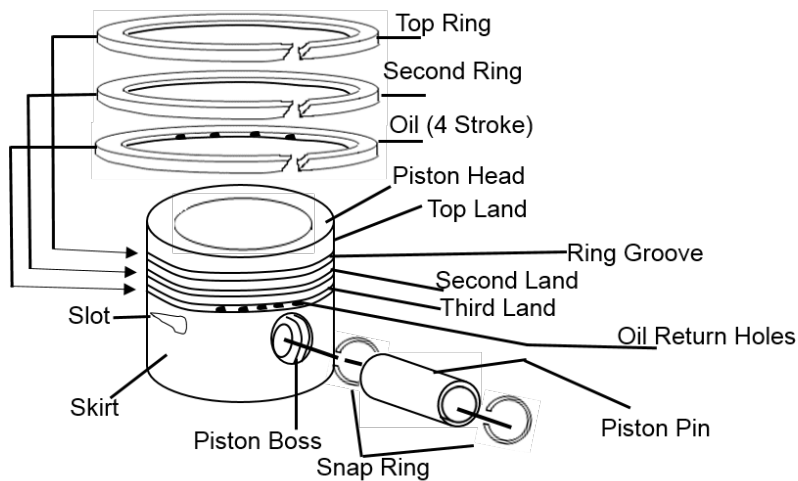


Figure 3.7. Typical piston assembly [49].

The top compression ring is the first gas sealing ring and suffers the highest loads and temperatures during the combustion cycle. This ring set has a barrel-faced shape with a wear resistant coating such as chromium. The second compression ring (scraper ring) acts as a secondary gas sealing device and also limits the upward flow. The oil ring at the bottom of piston assembly has two faces and a spring to promote a radial load. This ring has no gas sealing ability, its main role is to limit the amount of oil transported from the crankcase to the combustion chamber.

The piston ring is the most complicated tribological component to analyse in engines. In each stroke of the piston assembly, the piston ring in contact with the cylinder wall may exhibit all lubrication regimes such as boundary, mixed, elastohydrodynamic and hydrodynamic lubrication.

Investigating and studying the wear of pistons and ring sets is a main factor to improving engine performance. Manufacturers have only recently fully understood the complex interactions between wear and lubrication of these engine components.

3.9 Valve Train

The valve train system includes components such as valves, springs, keys, rocker arms, the camshaft, tappet and pushrod. The primary duty of the valve train is to convert rotary camshaft motion into linear valve motion for controlling the inlet and outlet of gas flow into and out of the combustion chamber

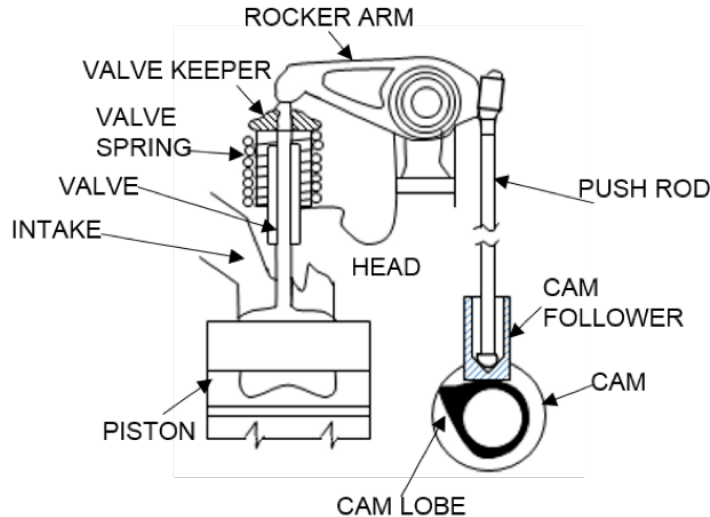


Figure 3.8. Valve train system [50].

Friction and wear play important roles in the selection of a valve train mechanism for engines, in particular, the selection of the type of rocker assembly. The assembly where the rocker arm pivots at one end has been shown to have the best configuration as it can reduce valve train friction significantly (see table 3.1)

The valve train system deals with some tribological problems in relation to the cam and followers, valve guides, valve seats, camshaft bearings, pivots and lifter guides. Wear is a problem at the valve/seat contacts, cams and followers. However, this is not the sole consideration.

The valve train system must be looked at from all component aspects and also how it sits within the whole engine. And thus illustrate how tribology, applied to the whole machine, results in optimum design.

Mechanism Feature	 Type 1	 Type 2	 Type 3	 Type 4	 Type 5
Natural Frequency (Hz)	2000-3000	1200-1500	900-1400	900-1400	400-700
Effective Mass @ Valve (gr.)	140-160	80-120	120-160	130-170	240-290
Maximum RPM	6500++	6500+	6000+	6000+	4000 - 6000
Friction (A-E)	E	A	B	C - D	C - D
Overall Engine Packaging (A-E)	D - E	D - E	B	C	A

* A = Best, E = Worst

Table 3.1 Comparison of friction, effective mass, engine speed, and overall engine package among five types of valve train systems [51].

3.10 Engine Oil

Oil is used to lubricate internal combustion engine components. Whilst its main function is lubrication of the moving components, it also cleans the internal surfaces, reduces corrosion, increases the sealing ability of piston rings and cools the engine by heat transfer from the moving components.

Traditionally, engine oil is produced from mineral based crude oils, however, modern oils are now frequently based on fossil synthesised hydrocarbons. These new formulas of engine oil are common blends of the chemical compounds from the base oils such as; hydrocarbons, poly alpha olefin (PAO) and poly internal olefins (PIO).

Whilst the majority of organic compounds in engine oil are based on carbon and hydrogen, some high performance engine oils contain more than 20% by weight of esters [52]. Synthetic oil is a lubricant consisting of chemical compounds that are artificially made (synthesised). Synthetic oil can be produced using chemically modified petroleum components than using crude oil, but can also be synthesised from other raw materials.

3.10.1 Types of engine oil

3.10.1.1 Single-Grade Oil

Single or mono-grade engine oil does not contain any polymeric viscosity modifier additives and is known as “straight” oil. It has eleven viscosity grades - six are winter-grades designated by the letter W. The eleven viscosity grades are 0W (Winter Grade), 5W, 10W, 15W, 20W, 25W, 30, 40, 50, and 60.

Automotive Lubricant Viscosity Grades¹					
Engine Oils – SAE J 300, Dec. 1999					
SAE	Low Temperature Viscosities		High-Temperature Viscosities		
Viscosity Grade	Cranking ² (mPa.s) max at temp °C	Pumping ³ (mPa.s) max at temp °C	Kinematic ⁴ (mm ² /s) at 100°C		High Shear ⁵ Rate (mPa.s) at 150°C, 10/s
			min	max	min
0W	6200 at -35	60 000 at -40	3.8	—	—
5W	6600 at -30	60 000 at -35	3.8	—	—
10W	7000 at -25	60 000 at -30	4.1	—	—
15W	7000 at -20	60 000 at -25	5.6	—	—
20W	9500 at -15	60 000 at -20	5.6	—	—
25W	13 000 at -10	60 000 at -15	9.3	—	—
20	—	—	5.6	<9.3	2.6
30	—	—	9.3	<12.5	2.9
40	—	—	12.5	<16.3	2.9 ⁶
40	—	—	12.5	<16.3	3.7 ⁷
50	—	—	16.3	<21.9	3.7
60	—	—	21.9	<26.1	3.7

¹ All values are critical specifications as defined by ASTM D3244

² ASTM D5293

³ ASTM D4684. Note that the presence of any yield stress detectable by this method constitutes a failure regardless of viscosity.

⁴ ASTM D445

⁵ ASTM D4683, CEC L-36-A-90 (ASTM D 4741) or ASTM DS481

⁶ 0W-40, 5W-40 & 10W-40 grades

⁷ 15W-40, 20W-40, 25W-40 & 40 grades

Table 3.2. SAE Viscosity Grades for Engine Oils [52].

The viscosity grade of an oil is established by the Society of Automotive Engineers. For example SAE-15W40 for a multigrade oil and SAE-40 for a single grade oil. The first number (15W) indicate the viscosity grade at low temperatures (W from winter). The second number (40) refers to the viscosity grade at high temperature.

3.10.1.2 Multi-Grade Oil

Engine oil should be able to maintain its performance over a wide temperature range – the extremes of a cold winter, before starting the engine, to the hot weather of summers.

Single grade oils have a high viscosity at cold temperatures and conversely, a low viscosity at hot engine temperatures. This property can cause faults in the engine components. The solution for this problem is adding some specific polymer additives to the oil. These additives are referred to as VIIs (Viscosity Index Improvers) and the resulting oil product is the multi-grade variety.

Multi-grade engine oil has a base grade viscosity for cold temperatures, but when the temperature increases, the viscosity of the oil increases as well. This property enables the oil to be appropriate for all seasons.

The Society of Automotive Engineers (SAE) uses two viscosity grades when referring to multi-grade engine oils. For example, 10W-40 is the common multi-grade oil and this oil has passed the SAE J300 standard for both 10W and 40 viscosity grade oils [52].

There is the potential for more internal wear over time, due to soot-loaded engine oil. Soot consists of micrometer-scale particles of elemental carbon.

As the piston goes down, soot can be scraped down by the piston rings. Soot can be go to the crankcase via blow-by of combustion gases past the piston rings. Soot loading also causes a viscosity increase.

3.11 Soot formation in a direct injection engine

3.11.1 Introduction to the combustion of compression-ignition engine

In a compression ignition engine, air alone is drawn into the combustion chamber. The fuel is injected after the air has been highly compressed and just before the Top Dead Centre (TDC) position of the piston. The high pressure causes a sharp increase in the air temperature and this causes the fuel to self-ignite. This cycle of work is a thermodynamic cycle, first described in 1897 by Rudolph Diesel.

There are two types of diesel engine, categorised depending on where within the cylinder head the fuel is injected, either indirect injection or direct injection. In an indirect injection diesel engine, the fuel is not injected directly into the combustion chamber but into a separate pre-chamber connected to the main cylinder by a small passage. The combustion process starts in the pre-chamber and expands into the main cylinder. Pre-chambers are designed to promote a better air - fuel mixing and reduce the rate of combustion as well as reducing the noise associated with “diesel knock”, however their use increases heat loss and therefore reduces engine efficiency. Within a pre-chamber, good mixing is achieved by a design that gives rapid air flow and turbulence whilst allowing low injection pressures for fuel delivery [53].

The design and manufacture of indirect injection diesel engines is therefore easier than a corresponding direct injection engines which require high pressure fuel injection systems and high in-cylinder gas velocity flow. Progress in injector technology together with improved designs of combustion chambers has now allowed production of direct injection engines to become commonplace. Thus we find that older, first generation diesel engines were almost always of an indirect injection design, whereas nowadays, all engines have direct injection systems.

In a direct injection engine, the fuel injectors are placed to spray their fuel directly into the combustion chamber of the main cylinder. Injectors are usually multi-holed and located at the top of the chamber. Compared to previous indirect diesel engines, these new direct injection diesel engines, with their higher injection pressures, are more efficient, giving improved power, having lower polluting emissions and developing more torque at lower engine speeds. One negative result though is that they are noisier in operation. The recent High-pressure-Direct Injection (HDI) technology has become very popular and is now used in almost all new diesel engines. In the HDI systems, the high pressure fuel feed (>2000 bar) generated by the fuel pump is fed to electronically controlled injectors fed by a common rail. This high pressure electronic injection system causes a better atomisation of the fuel together with the ability to control the point of injection, injection duration and also allow for multi-injections of fuel – a new strategy found to be advantageous for combustion characteristics.

When the fuel is injected into the compressed air, the mixture does not ignite immediately, instead there is a delay between injection and the beginning of combustion. After injection of the liquid fuel into the combustion chamber, the atomised fuel liquid drops heat-up and changes to its gas-phase. The fuel vapour and oxygen from the compressed air then mix together and react by burning, producing the combustion.

This delay in ignition is dependent upon the fuel properties (Cetane number), the injection mechanism (Fuel atomisation) and the in-cylinder conditions (temperature and pressure). Increases in the in-cylinder temperature or pressure reduce the ignition delay. The amount of oxygen in the fuel/air mixture is also an important factor affecting the fuel burn and oxidation rate and again, if more oxygen is present, the ignition delay is reduced.

The oxygen content can be increased by the application of turbo chargers to diesel engines which forces air into a cylinder at an increased pressure and hence volume, thereby increasing the amount of oxygen available. However Exhaust Gas Recirculation (EGR) has the opposite effect by decreasing the oxygen content within the combustion chamber.

The start of combustion can be determined in two ways. The common method is to use the in-cylinder pressure curve (via a pressure sensor) or Heat Release Rate (HRR) obtained from the pressure curve. The increase of pressure around TDC causes a rising of the HRR which instigates the spontaneous combustion of the fuel. Figure 3.9 shows HRR diagram that shows the combustion processes in the chamber.

Once ignited, the fuel vapours burn initially in a pre-mixed combustion phase. This phase happens over only a few degrees of crankshaft rotation, but the combustion is fierce, releasing large amounts of energy at peak pressure and HRR. This is the reason for the typical “knock” in diesel engines. Immediately after the combustion within the pre-mixed phase, the HRR decreases.

A second phase of combustion then occurs as the flame arising from the pre-mixed detonation expands and diffuses into any remaining unburned fuel and also the fuel still being injected at the end of the injection cycle. This phase takes place over approximately 40 degrees of crankshaft rotation. During this period, pressure and HRR decrease.

The combustion finally ends in a low pressure and temperature phase where the fuel and combustion products are mixed with what is left of the remaining air.

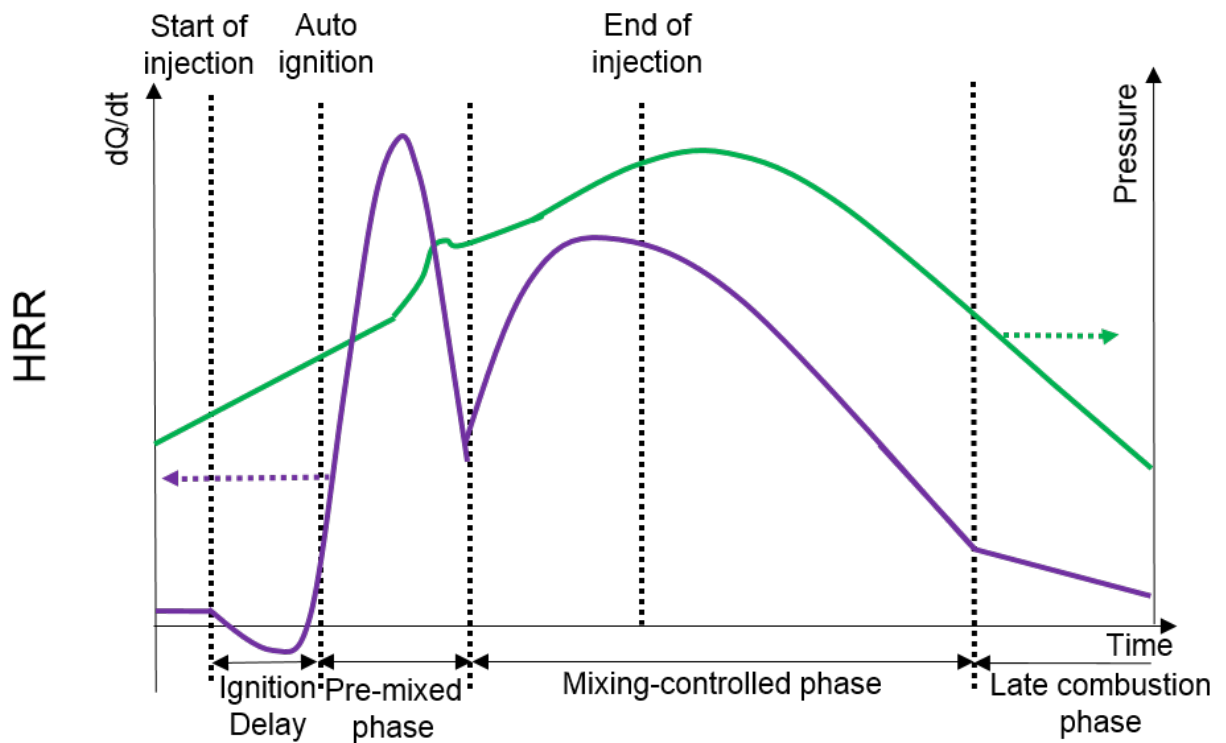


Figure 3.9 – Heat Release Rate Diagram [54].

Experimental research has also shown that the higher fuel injection pressure reduces the amount of soot production due to a better atomisation of the fuel and a better mixing of the fuel and air. The relationship between equivalent ratio, temperature and pollutant formation (soot and NO_x) are showed in figure 3.10, which is called an Flame Temperature (**f-T**) map.

The map shows that, with lower flame temperature, production of soot and NO_x can be avoided. The Exhaust Gas recirculation (EGR) technology applied to the modern diesel engines is based on a part mixing of a portion of exhaust gases with the fresh air at the intake manifold, the aim being to reduce the oxygen ratio in the combustion chamber, which then reduces the combustion temperature. When in use, EGR decreases the combustion temperature to a low enough level to sharply reduce NO_x emission levels, but does not have any effect on the soot production.

However soot production increases with an increase in the EGR level, because in addition to reducing the combustion temperature, the amount of oxygen is also reduced, which has the knock-on effect of lowering the level of soot oxidation and hence an increase in the soot released.

Meanwhile, there comes a point in the delivery of EGR when soot emissions actually start to decrease, a phenomenon that is not well understood. This behaviour is known as the Soot Bump. Most studies conclude that with high EGR, the ignition delay inherent in diesel engines is prolonged. As such, the fuel and air have, of course, more time to thoroughly intermingle creating a combustible mix that burns more efficiently due to the better dispersion of oxygen from the air. Some even say it creates a temporary artificial lean-burn condition (that would not, of course, favour soot production).

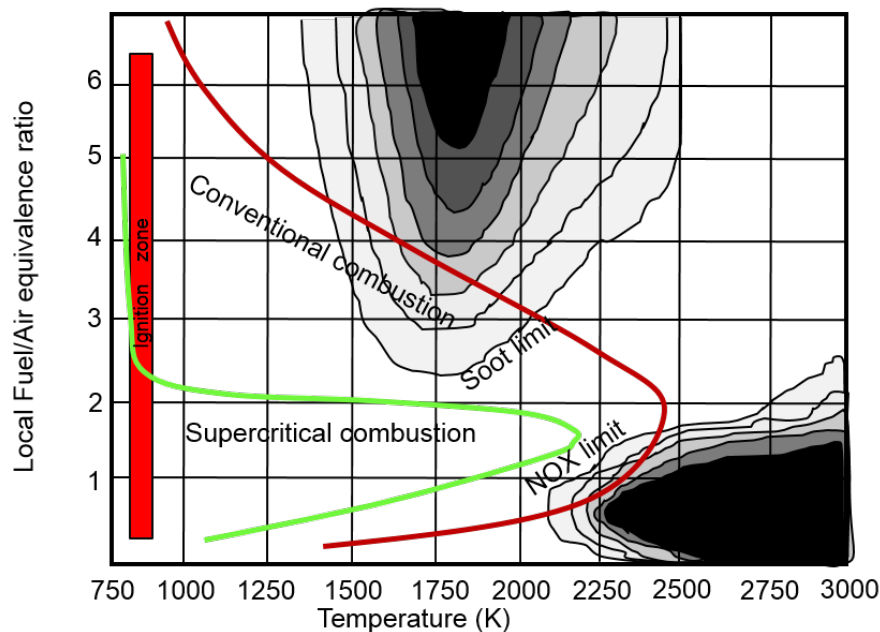


Figure 3.10. Schematic of equivalence ratio versus adiabatic mixture flame [55].

3.12 Physical parameters influencing soot formation

3.12.1 Temperature and Pressure

Temperature is the main factor in the soot formation process. This parameter increases all reaction rates within the soot formation mechanism but soot formation rate does not increase as fast as its oxidation rate. In a well-stirred reactor, the maximum rate of soot formation has been found to be around 1600 K -1650 K [56].

Above this peak, the amount of soot produced decreases in the premixed phase flames but in the second diffusion phase flame this soot production increases with the temperature. Soot formation begins around 1400 K and combustion ceases at temperatures below 1300 K.

In fact, depending on the gas temperature, soot formation is a trade-off between its oxidation and formation rates.

The pressure factor relates to other factors such as temperature, air flow velocity, flame structure and density. In the diffusion flame step, combustion occurs at the interface between the mixed gases and the flame, therefore any effect on pressure within the combustion zone may affect the flame propagation. In the premixed flame, the burning rate increases with pressure increase.

Soot formation increases at higher pressures during the premixed flames as higher pressure means larger particles, higher particle density and lower peak flame temperatures. Density has a direct relation to pressure, for example, for a specific volume; the soot density will be higher at the higher pressure.

3.12.2 Fuel Structure and Composition

The effects of the fuel structure on the soot formation in diesel engines has been largely investigated but there is no chemical agreement on the results. The main question is whether the fuel structure (straight chain, branched chain and aromatic hydrocarbons) has an influence on soot formation.

Comparing different fuels in the research is difficult because the composition of fuel affects the combustion conditions, i.e. there are too many variables to separate out the different effects. Research on different diesel engines when using different fuels showed that engine technology is the major factor in soot level production during the combustion process. It has been found that aromatic hydrocarbon content and Cetane number has no affect if the engine passes the low soot level emission standards, but has the significant effect in older engines that tend to emit high levels of soot.

3.13 Diesel combustion fundamentals

The four-stroke piston engine is commonly used in transport, marine and light aviation applications [63].

Most diesel engines operate on the four-stroke principle, where two revolutions of the crankshaft are needed to complete a working cycle. The movement of the piston assembly from the top dead center (TDC) to the bottom dead center (BDC) and its return to TDC is one cycle. A complete working cycle is shown in figure 3.9. In the intake cycle, air is sucked in the combustion chamber via the open inlet valves while the piston is going downwards and inlet valves are closed at the BDC. In the compression cycle, the air is compressed by the upward movement of the piston assembly while both inlet and outlet valves are closed.

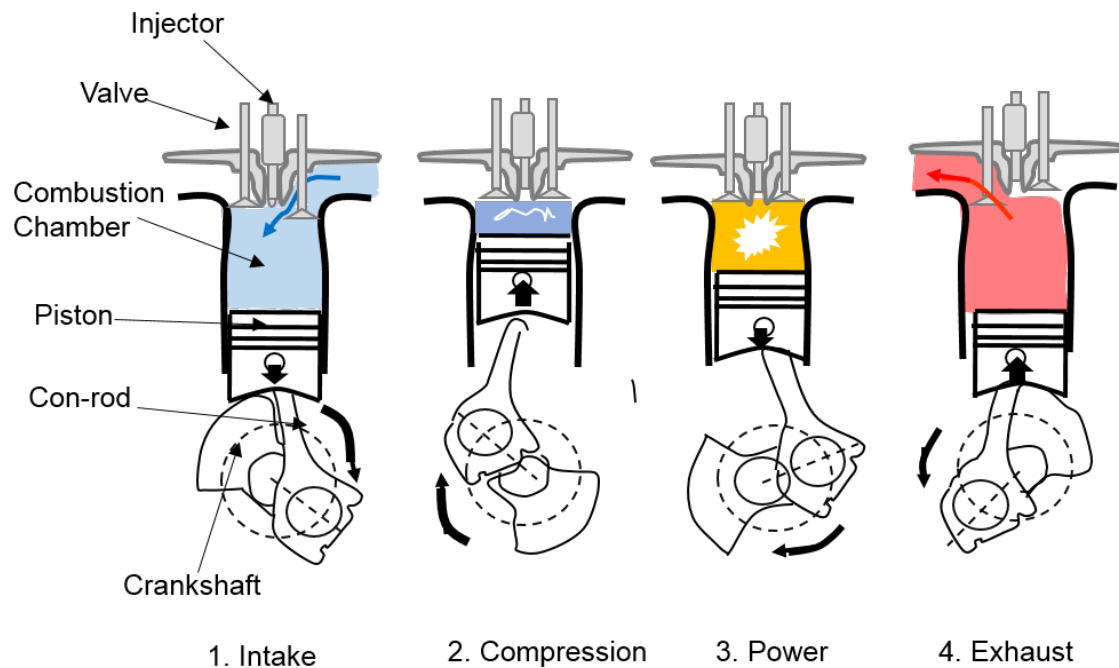


Figure 3.11 - Illustration of one complete working cycle of a four stroke diesel engine [50].

The temperature of the air in the combustion chamber at the top dead compressor (TDC) position reaches up to 800°C . At approximately 24 degrees angle on the flywheel before the TDC, fuel injection begins and the atomised fuel drops mix intimately with the compressed air, then evaporate and ignite due to the high temperature. The reaction of the mixture which is formed during the injection period (also known as ignition delay) is called the premixed burn. At the end of injection, the injector nozzle is closed and the flow of diesel fuel is stopped.

In the power cycle the increase in pressure caused by combustion, moves the piston assembly down the cylinder, making mechanical work, which is transferred by the crankshaft into rotary motion.

In the exhaust cycle, the exhaust gases are pushed out by the upward movement of the piston assembly while the exhaust valves are opened. Engine speed is normally measured in revolutions per minute (rpm). Several studies of diesel combustion processes have been researched. A cross-section model of diesel combustion is shown in figure 3.11, where the reacting of diesel jet during the quasi-steady phase of combustion is shown.

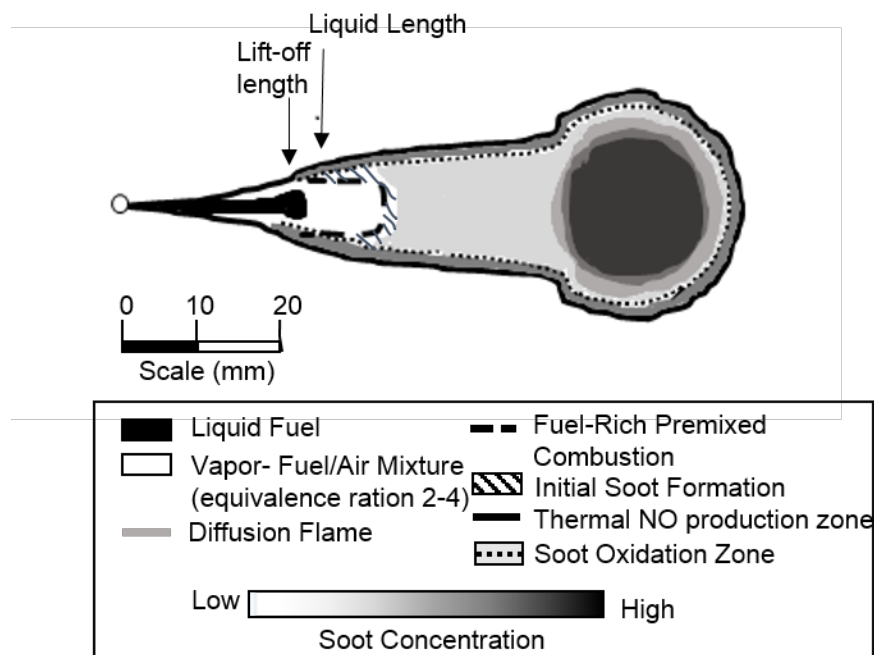


Figure 3.12. Reacting diesel spray during the diffusion phase of combustion [57].

As the fuel jets enter into the cylinder (in figure 3.12 from left to right), it absorbs heat from the hot gases in the cylinder, as it forms a cone-shaped spray (black region). The maximum penetration length of the liquid fuel

into the cylinder is called the liquid length. The location of the flame is dependent on the jet velocity (injector nozzle pressure) and the time of reaction between the fuel/air mixtures [57].

3.14 Possibilities for reduction of soot particle formation

3.14.1 Injection pressure

One of the main factors necessary to reduce soot emissions is to optimize the injection system of the diesel engine [57]. Injection usually commences in the region of 24 degrees before TDC. An earlier injection of the diesel fuel causes an increase of pressure within the combustion chamber, with a corresponding increase in the temperature, which causes a more homogeneous combustion process.

However, a later fuel injection causes an incomplete combustion process, as the pressure and temperature within the combustion chamber are reduced. The increase of the injection pressure, achieved by using a common rail injection system, also reduces soot emissions (see figure 3.13). In the common rail injection system, the start of injection can be altered at will since the required injection pressure of up to 2000 bar is always available. The high injection pressure allows for an improved spraying behavior of the fuel, which causes a more homogeneous combustion process. Furthermore, a fast switching magnetic valve enables multiple injections, which allows a free configuration of the injection with a variation of pre, main and post-injection and then an optimisation of the soot emission reduction. A post-injection causes a reduction of soot particles by oxidation.

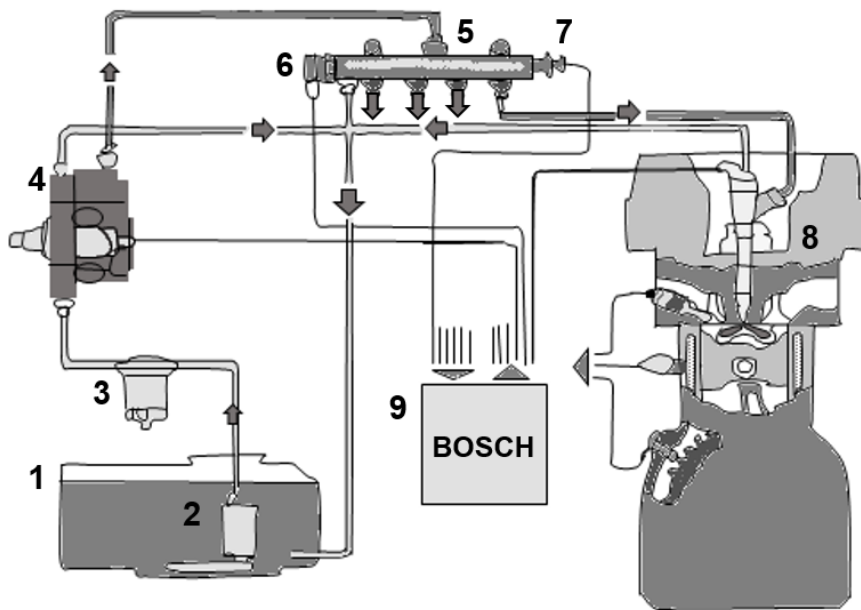


Figure 3.13 - Common rail injection system. 1 - Fuel tank, 2 - Fuel pump with filter, 3 - Fuel filter, 4 - High pressure pump with dosing unit, 5 - Rail, 6 - Pressure regulation valve, 7- Rail pressure sensor, 8 - Injector, 9 - Control unit with inputs for sensors and outputs for a actuators [58].

3.14.2 Injector design

A sectional diagram of a typical fuel injector is shown in figure 3.14. It consists of an injector body with a high pressure fuel feed, the needle channel and hub, injector needle, injection hole and stud hole. The injector design is sized specifically to the engine it serves to ensure optimum performance. During an injection cycle the injector needle moves upwards allowing diesel fuel to stream through the injection hole into the combustion chamber, where it is burnt. The injector design has a marked influence on just how the fuel/air mixture disperses by optimising atomisation of the fuel prior to ignition. Furthermore, they affect the engine performance, exhaust emissions and noise level of the engine, as well as seal the injection system from the combustion chamber between power strokes.

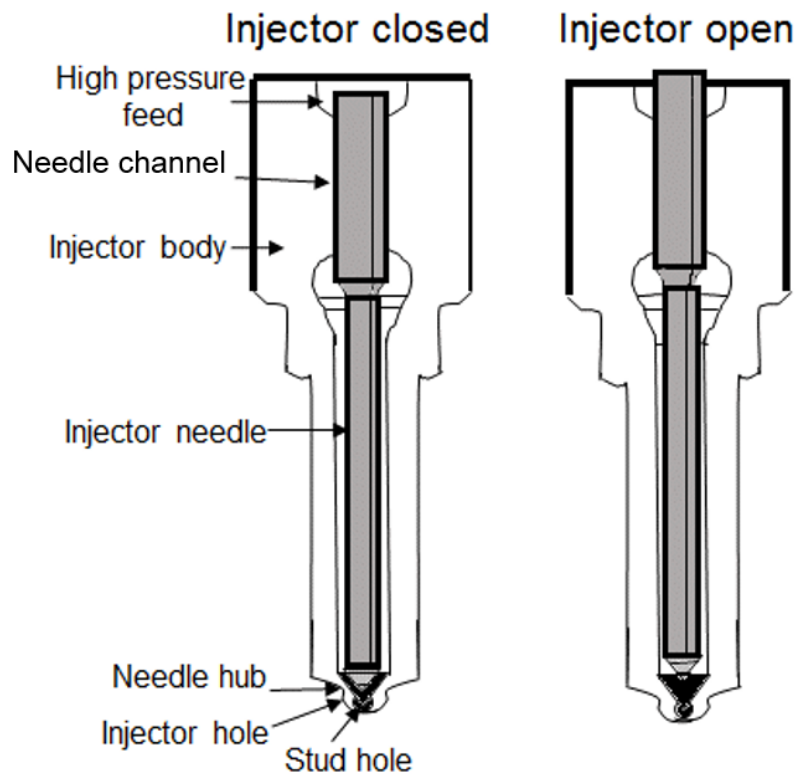


Figure 3.14 - Sectional diagram of a typical fuel injector [57].

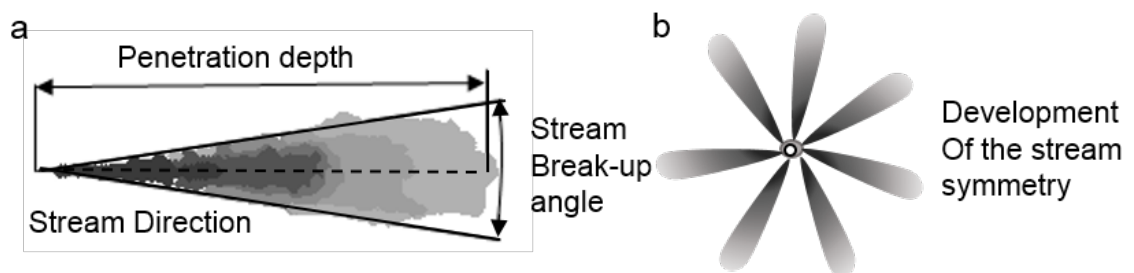


Figure 3.15. a) Illustrates the stream analysis of the diesel fuel injection, b) Principle of a stream image analysis [57].

The penetration depth, stream direction and stream break-up angle as the fuel sprays into a cylinder are important factors for good combustion. In modern diesel engines, injectors with multiple injection holes (see figure

3.17) are used, with the aim of optimising their performance by symmetrically separating the fuel into several sub-streams. Failure to ensure this separation and hence dispersion can negatively affect combustion characteristics, leading to poor combustion and loss of performance.

Reducing the orifice diameter of the injector nozzle holes slightly reduces the liquid length and the fresh air charge entering the jet. It also reduces the fuel flow from the nozzle, which causes a better air/fuel stoichiometric at the lift-off length and in the premixed burning area, and then reducing the soot formation. Increasing the injection pressure improves the atomisation, the velocity of the fuel and the lift-off length, which causes decreased soot formation [59].

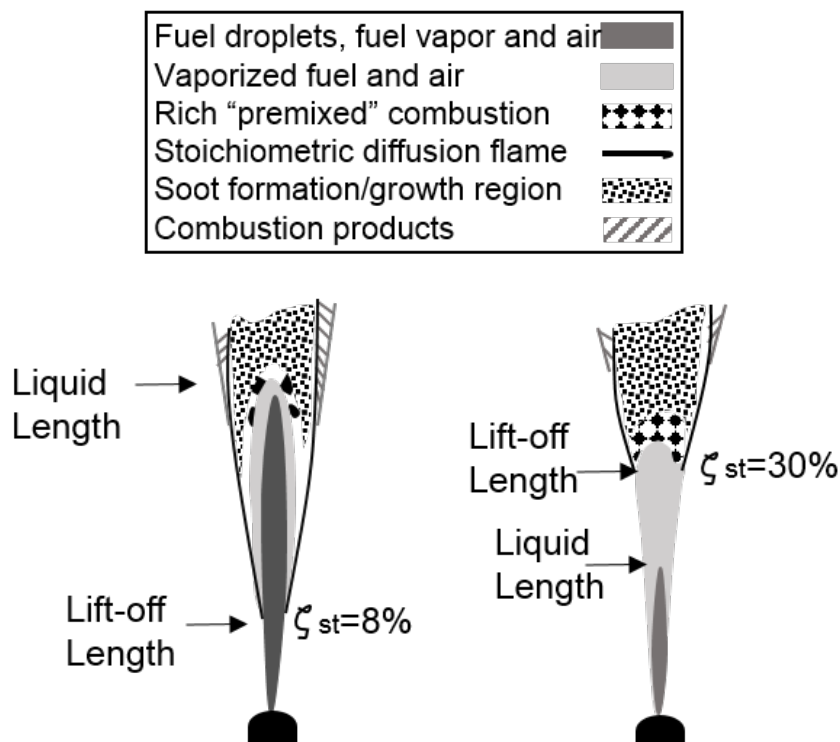


Figure 3.16 – Injector Fuel Jet illustration [59].

3.14.3 Injection timing

Injection timing has an important role in pollutant emissions and engine performance. An advanced timing will reduce the soot emissions but increase the NO_x content. However, retarded timing causes more soot formation and less NO_x emissions due to temperature and equivalence ratio in the combustion chamber [59].

3.14.4 Multiple injections

Multiple injection method is a new technique to reduce soot emissions by injecting the fuel in stages during the injection cycle. This method is possible due to high-pressure common rail fuel systems and electronic control units. Research has been conducted to fully understand the mechanism of how this technique reduces particulate and NO_x emissions [46]. The multiple injection system usually consist of three steps, pilot injection, main injection and post injection. Pilot injection increases the temperature within the cylinder before the main injection, thereby reducing ignition delay of the main injection. This decrease in ignition delay reduces the fuel fraction necessarily burnt in the premixed combustion phase, which reduces the pressure rise and peak during that phase. Pilot injection increases the amount of particulates produced because of the higher temperature during the main injection step. Lift-off length and air (which contains a small proportion of fuel from the pilot injection step) mixing with fuel will both be reduced [59].

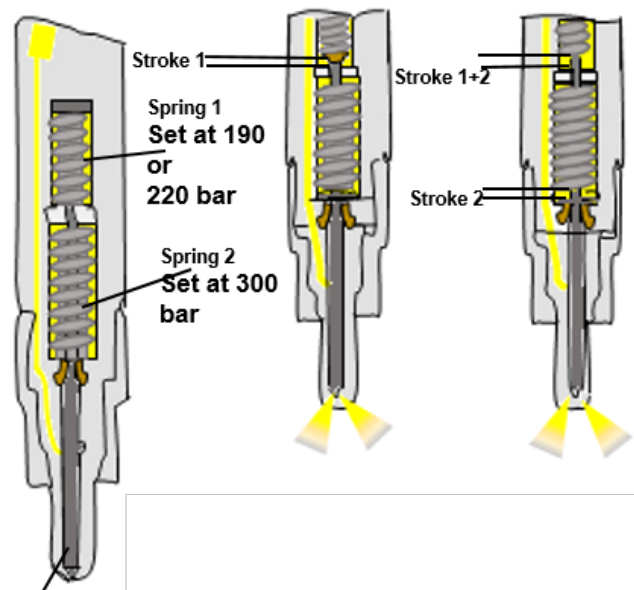


Figure 3.17 – Sectional view of a multiple injector [58].

The multiple injector functions starts with the pre-injected fuel at low fuel pressure and continues to the main injection cycle at higher fuel pressure.

Two springs with different thicknesses are used in the multiple injector holders. These two springs are applied in such a way that the injector needle is lifting against the force of the first (weaker) spring when the injecting starts. During this pre-injection phase, a small quantity of fuel is injected through the small gap between two springs.

This pre-injection phase in the combustion chamber increases the combustion pressure and creates better conditions for igniting the main fuel injection phase.

As the fuel pressure is rising by delivering more fuel from the injection pump, the force of the second (stronger) spring is overcome and the injector needle lifting more and then the main injection phase starts.

3.14.5 Combustion Chamber Design

Soot formation is dependent on two key factors of combustion chamber design. These are the internal air flow and the effects of its shape on the liquid fuel components. Swirl within a combustion chamber increases turbulence and improves mixing of the fuel and air and therefore the subsequent rate of combustion during and after injection [59]. Soot is oxidised more quickly while the gas temperature remains high during early expansion of the gases. The swirl rate can be limited by interaction between two adjacent jets of injected fuel or by a jet reaching the cylinder wall. When liquid fuel impinges on the inner wall of the combustion chamber or piston, homogenous mixing with the air charge is reduced. Liquid impingement can happen with early injection (piston is too close to the injectors), with late injection (in-cylinder temperature not high enough to evaporate the fuel), low cylinder pressure, over-fuelling or a variation in fuel enthalpy of vaporisation (water-fuel emulsions) [59].

These effects can, however, be limited by good design. If the combustion chamber is constructed in such a way that its surfaces retain heat easily and uniformly (i.e. there are no “cool spots”), liquid impingement upon them improves the atomisation leading to a better fuel/air mixing and consequently a decrease of soot level. Likewise, the design should be such that any contact of the liquid jet with solid surfaces is dissipated and not allowed to rebound back into the mixture. It has been found that the impingement of the leading edge of the jet onto a hot surface led to a decrease in soot emissions but when jets were scattered back in the same direction they came from, the opposite effect occurred. A similar situation occurs if two adjacent jets cross each other [59].

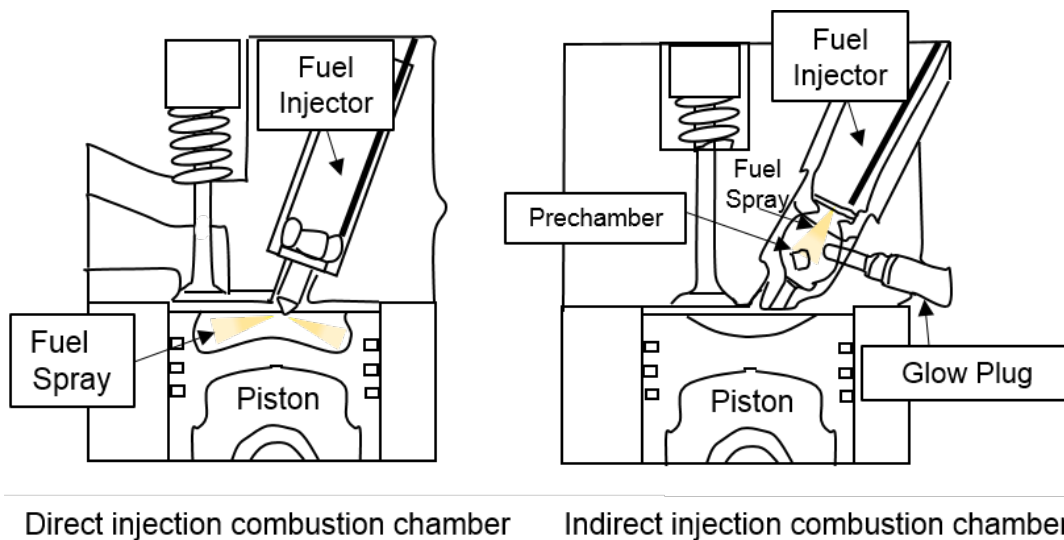


Figure 3.18 – Sectional diagram of combustion chambers.

3.14.6 Engine Transient

An engine's speed and applied load will have an obvious effect on its emissions. A rapid change from idle or low load to high load and high speed (quick acceleration at low gears) is the moment when a significant amount of soot is produced, due to a temporary increase in fuel (as the throttle is applied) compared to the air charge passing into the engine.

The fuel/air ratio becomes too high and more liquid fuel impinges on the cylinder wall due to the low air charge density (which allows a higher fuel penetration). The mixture in the cylinder becomes temporarily too rich in fuel and poorly mixed with the air. This problem has fortunately been largely resolved following the implementation of electronic fuel injection regulated by computer, together with variable geometry turbochargers [59].

3.15 SOOT FORMATION REVIEW

This section reviews the literature on soot characteristics, properties, formation processes and the influence of the main parameters in an internal combustion engine on soot formation.

3.15.1 Soot formation mechanisms

The evolution from liquid or vapour phase hydrocarbons to solid soot particles involves five processes occurring in the following order: pyrolysis, nucleation, coalescence/surface growth, agglomeration and oxidation (Figure 3.19). Only oxidation can convert hydrocarbons to CO, CO₂ and H₂O at any time in the sequence. The term “net soot formation” includes the formation and the oxidation of soot. The full process can proceed in a spatially and separated sequence in a laminar flame or simultaneously in a well-stirred reactor. In a combustion engine, the sequence varies between these two limits.

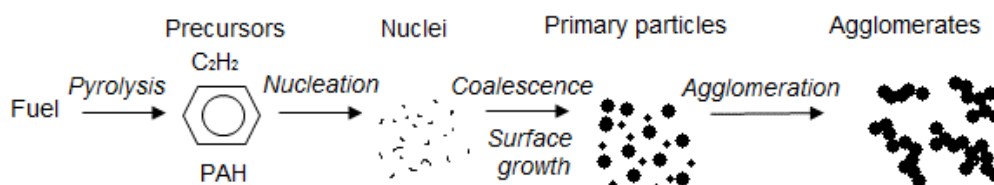


Figure 3.19 - Schematic diagram of the soot formation steps [59].

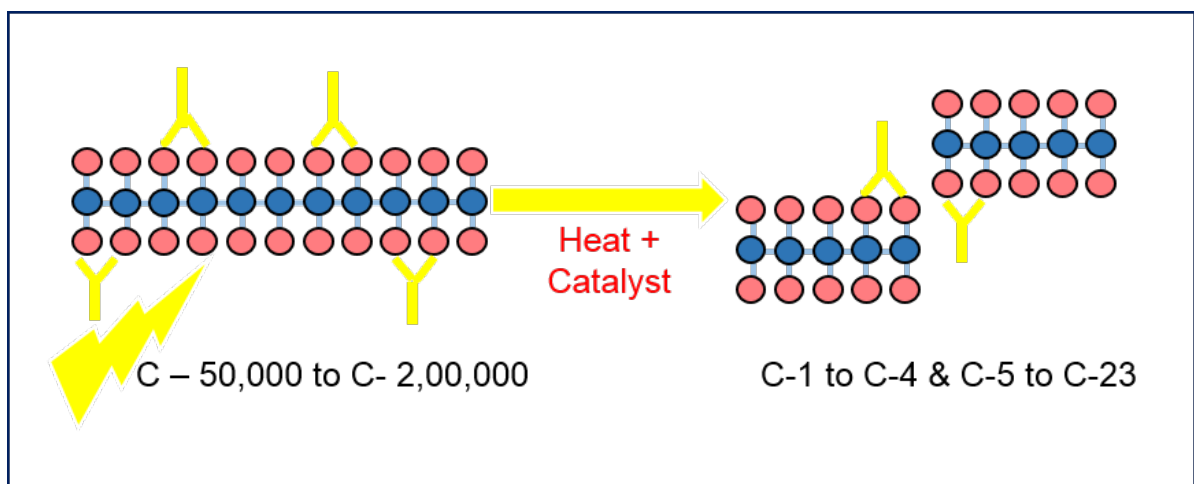
3.16 Oxidation

Oxidation is the transformation, by chemical reaction, of carbon or hydrocarbons into the combustion products. If a carbon based molecule

has partially oxidised, it will not evolve into a soot particle even if the molecule goes through a fuel-rich zone. Oxidation can happen at any point from pyrolysis to agglomeration. It depends on the oxygen presence and on the temperature conditions. Soot oxidation happens at high temperatures, above 1300 K [60]. The presence of some species such as; O_2 , O, OH, CO_2 and H_2O during the combustion process can cause the soot to oxidise. The more agglomerated the soot particles become, the less likely they are to oxidise and the net soot production is highly dependent on the oxidation process and the combustion temperature [59].

3.17 Fuel pyrolysis

Pyrolysis is a chemical reaction in which large molecules are broken down into smaller molecules, usually in the presence of heat. A simple example of pyrolysis is cooking in which complex food molecules are broken down into smaller and easy to digestible molecules.



Long Chain Polymer

Short Chain Carbon Black (C1 to C5)

Figure 3.20 – Pyrolysis process.

During pyrolysis, high temperatures change the molecular structure of the fuel. This change starts with the breakdown of aromatic carbon bonds, followed by the combination and saturation of the free-radicals. Even if oxygen is present, there is no significant oxidation. The result of the pyrolysis is the production of soot precursors. All fuels undergoing a pyrolysis process produce the same base molecules - polycyclic aromatic hydrocarbons (PAH) and acetylene (See figure 3.20) [61].

3.18 Nucleation

Nucleation, also called soot particle inception, is the formation of a great many solid soot particles (nuclei) from gas-phase reactants. The smallest detectable nuclei in a very light flame are in the range of 1.5 nm to 2 nm in diameter [61].

3.19 Surface growth

Surface growth is the process by which mass is added to the nuclei. There is no clear point marking the end of the nucleation process and surface growth beginning. In surface growth, gas-phase hydrocarbons (mainly acetylene) are deposited on the hot reactive surface of the nuclei. The growth continues until the soot nuclei particle leaves the primary reaction zone into cooler and less reactive regions of the combustion chamber [61].

It has been found that the smallest size of nuclei have the highest potential for surface growth, due to them having more reactive radical sites. The number of soot particles remains the same but the weight of soot and the soot volume increase, thus the major addition to the soot mass is produced during this step. Therefore, any steps that can be taken to reduce the time of the surface growth process will also reduce soot production [61].

3.20 - Coalescence and agglomeration

Coalescence and agglomeration are both processes by which the soot particles come together. Coalescence (also called coagulation) happens when the soot particles collide with each other and remain together. Coalescence reduces the number of soot particles but the soot mass remains constant because the mass of the new spherical soot particle is equal to the sum of the two initial particles. Agglomeration occurs when coalesced particles stick together to form a cluster. This cluster has a chain-like form that is composed of spherical particles. Again the number of particles is reduced but the weight and soot volume remains the same.

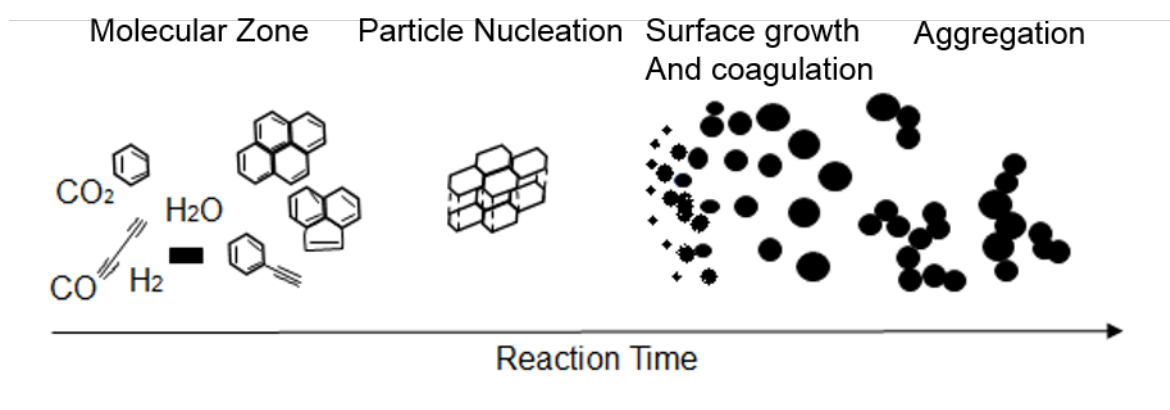


Figure 3.21. Schematic view of the soot formation process [61].

3.21 Soot characteristics

Soot is a harmful pollutant and an indicator of low combustion efficiency. It can be defined as an agglomeration of spherical carbon particles formed during an incomplete combustion of hydrocarbons in a high fuel to air ratio. Carbon is the main component of soot in a ratio of 10:1 with hydrogen, while a small fraction of other elements is also present (see table 3.3). The considerable hydrogen content of about 1%wt corresponds

to the formula C_8H of soot [61]. Sulphur is bonded as sulphate on the surface, while oxygen is strongly bonded into the structure of soot particles.

Table 3.3 : Chemical composition of diesel soot, given in wt. % .

Element	C	H	N	O	S
Virgin soot	83.5	1.04	0.24	10.5	1.13
Degassed soot	83.8	0.85	0.22	10.7	0.10

In general, diesel soot forms chain-like agglomerates, which can be several hundred nanometers in size, as clearly illustrated in figure 3.22. The chain-like agglomerates (also known as secondary soot particles) are composed of spherical or nearly-spherical basic units, the so called primary soot particles [61]. The size of the primary soot particles, which contain 10^5 - 10^6 C-atoms, varies between 10 and 80 nm, but is mostly between 15 and 50 nm. Viewed through a transmission electron microscope (TEM) small steps on the surface of the primary soot particles are visible, caused by the concentric arrangement of numerous graphitic crystallites [61].

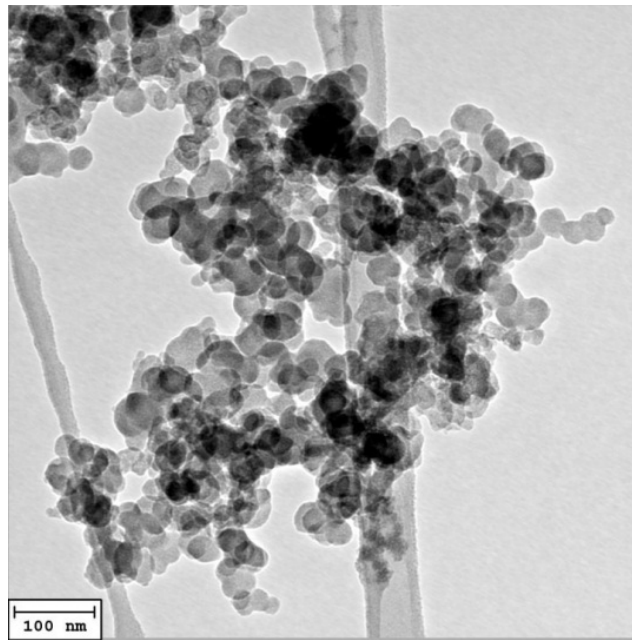


Figure 3.22. A TEM picture of Diesel soot agglomerate composed of multiple primary soot particles [61].

The C-atoms in the primary soot particles are packed in hexagonal face-centered array, the so called platelets (see figure 3.23). Multiple platelet-layers form crystallites, consisting of 2-5 platelets per crystallite. The mean distance between the platelets of 0.355 nm only slightly deviates from the one known for graphite (0.335 nm) [61]. The crystallites show a turbostratic arrangement, but they are nearly parallel ordered relatively to the surface.

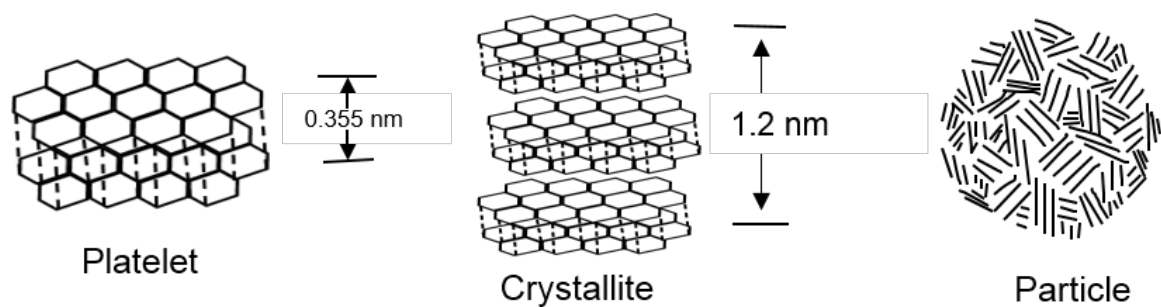


Figure 3.23 – Schematic of substructure of carbon particle [61].

The particle size is dependent of many factors such as fuel used, flame characteristics, engine type, injector types and operating conditions, as well as where and how the soot particles have been sampled and measured. In diesel engine conditions, at the exhaust the primary particle size has been found to be from 20 to 50 nm with a mean diameter of around 30 nm.

Figure 3.22 shows typical TEM micrographs of soot agglomerates from small spheres that typically contain 5 to 10 sheets containing on the order of 100 carbon atoms each. The structure within each sheet is similar to graphite, but layers are randomly ordered in turbostratic structure. The soot particles continue to grow through chemical reactions at their surface at which they begin to coagulate to form chain agglomerates [61].

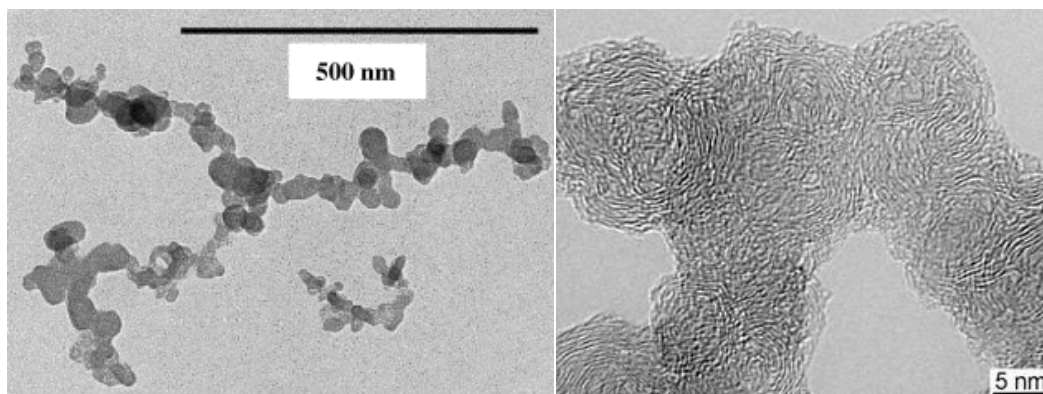


Figure 3.24 – TEM images of agglomerates and primary particles [61].

3.22 Effects of Engine Soot

Engine soot is a by-product of internal combustion engines which is produced by incomplete fuel combustion.

Hydrocarbon fuels are made up of carbon and hydrogen and if combusted completely the only by-products will be carbon dioxide and water.

Although there are many engines which work efficiently, complete combustion rarely happens in any engine.

For complete combustion, an exact ratio mixture of fuel and air is required, but in real working conditions the ratio of fuel is always greater than the air. As the ratio of air reduces in the combustion chamber, the amount of soot will increase. Diesel engines produce more soot than petrol engines, because the fuel injection and fuel ignition mechanisms are different for these two types of internal combustion engines.

In petrol engines, fuel is mixed in the intake stroke and ignited by a spark, while in diesel engines fuel is injected in the compression stroke and it ignites spontaneously as a result of hot compressed air in the cylinder.

The combustion mechanism in petrol engines is more efficient than diesel engines, because in petrol engines fuel and air have more chance to be mixed, while in diesel engines, the late fuel injection may cause poor mixing and fuel to gather in what might be regarded as more remote parts of the combustion chamber, thereby causing more soot to be produced during ignition.

Under normal conditions nitrogen does not mix with oxygen to form an oxide but when combustion reactions in diesel engines reach high temperatures, the normally inert nitrogen gas reacts with oxygen to produce nitrogen oxides like NO or NO₂. These compounds are a major contributor to air pollution. Environmental protection protocols are adopting more severe nitro-oxidation and hydrocarbon emission policies for diesel engines. These new environmental policies are good news for the environment, but bad news for lubricants as manufacturers use exhaust gas recirculation (EGR) to reduce soot emissions.

The new exhaust gas recirculation (EGR) system is applied to diesel engines in order to reduce NO_x (Nitrogen oxides) emissions. NO_x is a combustion by-product that combines in the atmosphere to create ozone and smog. It is controlled by reducing the combustion temperature inside the cylinder.

In the EGR system (shown in figure 3.25) a part of the exhaust gases are returned into the intake manifold after passing through an intercooler to reduce its temperature. The purpose of this reintroduction of the exhaust gases, although it is still very hot, is that containing no fuel or oxygen, it behaves as an inert gas in the combustion process. A computer controls the EGR mechanism in accordance with the engine load or speed. The result is a cooler combustion temperature which raises the density of the intake air so that the volume of oxygen within the air entering the combustion chamber increases [60].

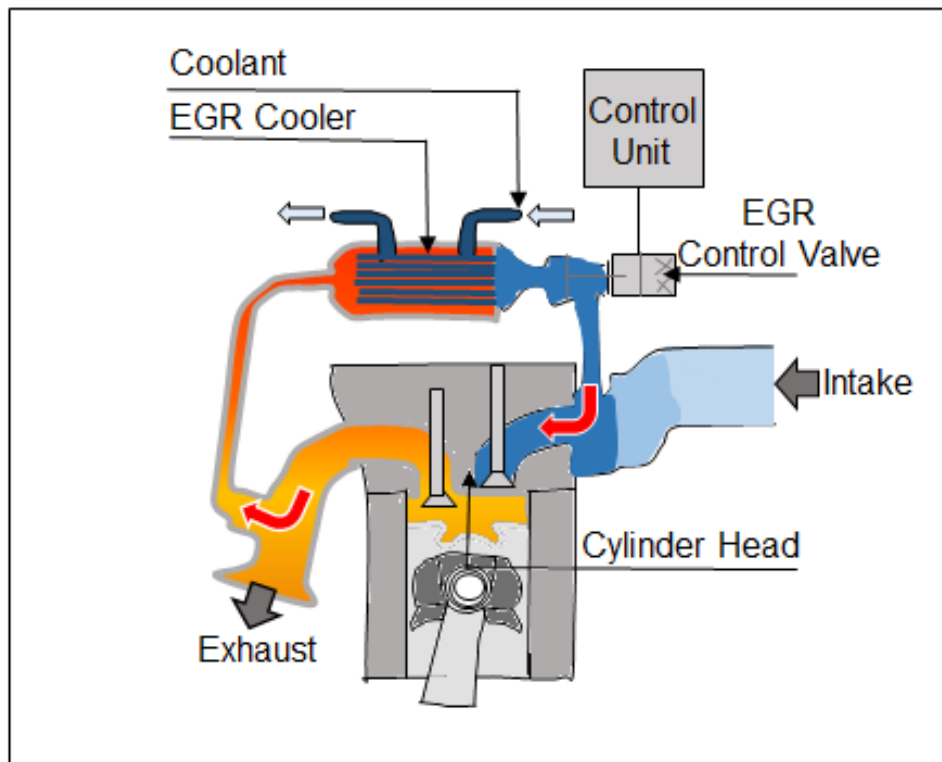


Figure 3.25 – Sectional diagram of an EGR system [62].

Figure 3.26 shows NO_x emission versus brake power for two different engine speeds with different proportions of EGR. As the % of EGR increases it can be seen that for both engine speeds the ppm NO_x decreases. As the engine speed increases the decrease in ppm NO_x is more significant.

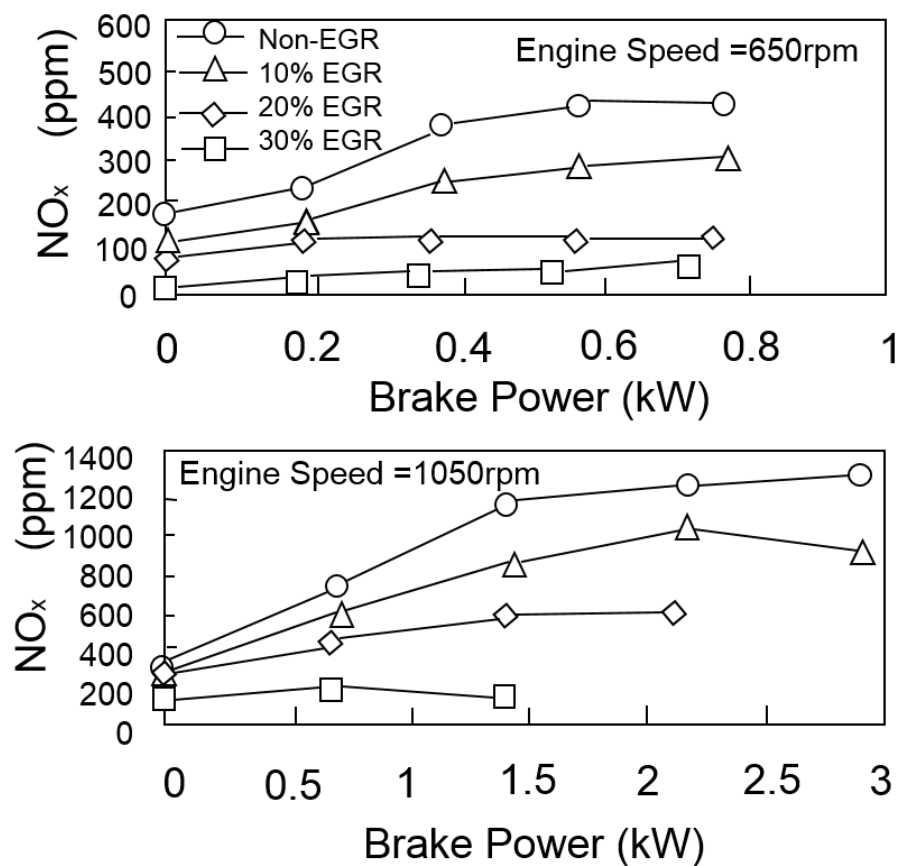


Figure 3.26 – Shows variation of NO_x emissions with brake power from diesel engine at different engine speeds and loads with and without different EGR rates. When EGR is applied, NO_x is decreased with increasing EGR rates. The reasons for reduction in NO_x emissions using EGR in diesel engines is thanks to the reduced oxygen concentration and thereby decreased flame temperatures. The degree of reduction in NO_x at higher loads is higher [60].

Additionally, the combustion temperature is reduced, the amount of particulate matter (PM) generated and the contribution of soot particles to the engine oil increases. Figure 3.27 shows particulate matter versus brake power for the same tests as in figure 3.26. In this case; as the % EGR increases the proportion of particulate matter increases.

PM increases with increasing engine load and speed. At 650 rpm (revolutions per minute) and no-load conditions without EGR, the PM emission is about 45 mg/m³. However, PM emissions increase to 176 mg/m³ at full load. By changing the mode from no-EGR to 10% EGR, PM concentrations decrease, but increase with further increase in % EGR at these lower engine speeds. This might be due to better evaporation of fuel particles at 10% EGR. At 1050 rpm, on no load condition without EGR, the PM emission is about 94 mg/m³. However, PM emission is increased to 266 mg/m³ at full load [60].

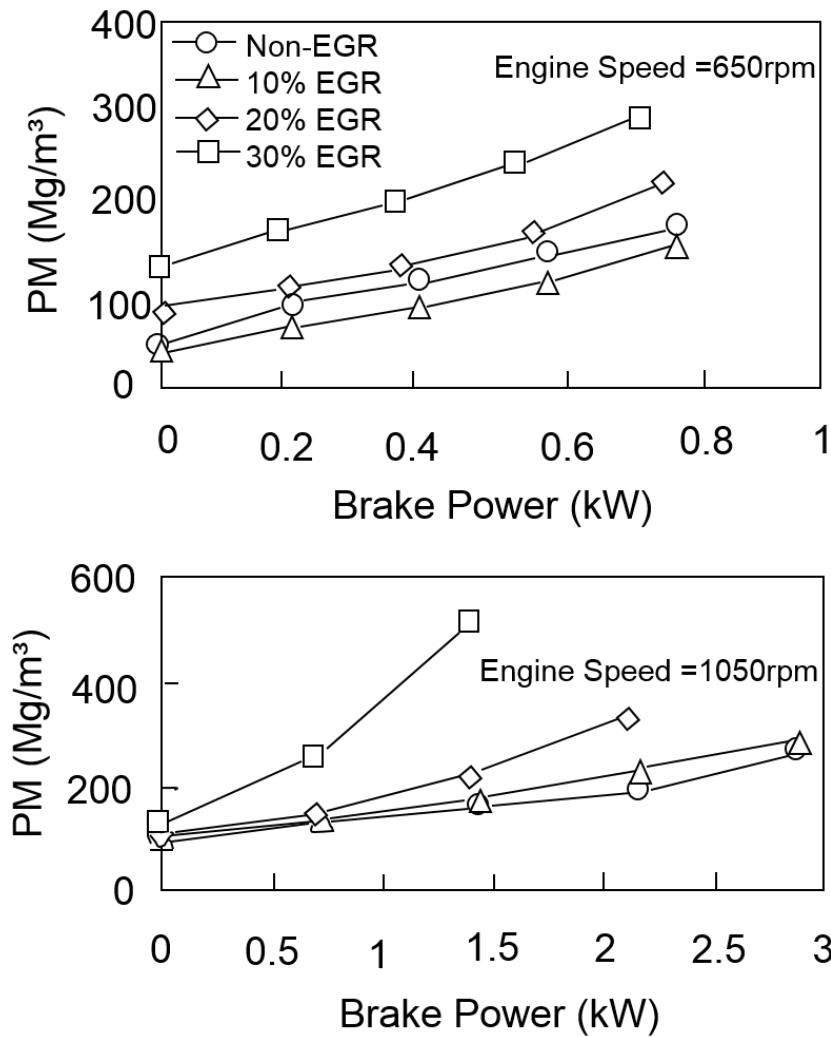


Figure 3.27 – PM emission with and without EGR at different engine speeds and loads [60].

Although most of the soot is removed through the exhaust, some soot passes by the piston rings during the power stroke and enters into the oil sump thereby contaminating the engine oil. The soot particles suspended in the oil can increase the wear of engine components by means of three-body wear.

Motor oil dispersant additives separate the soot particles from the oil molecules to allow them to be removed from the oil via the oil filter. These

dispersants also prevent the accumulation of soot deposits on the cylinder walls and other component parts of an engine.

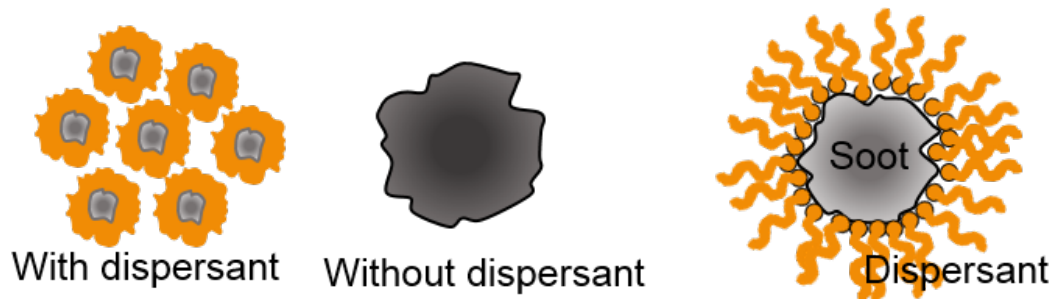


Figure 3.28 – Dispersant additives are designed to hold soot in suspension, until they can be filtered out, or otherwise removed through an oil change. The chemistry of a dispersant consists of a polar head group with along hydrocarbon tail.

However, when high concentrations of soot particles are present, the dispersants are quickly used up and if not replaced, allow the build-up of soot on engine surfaces.

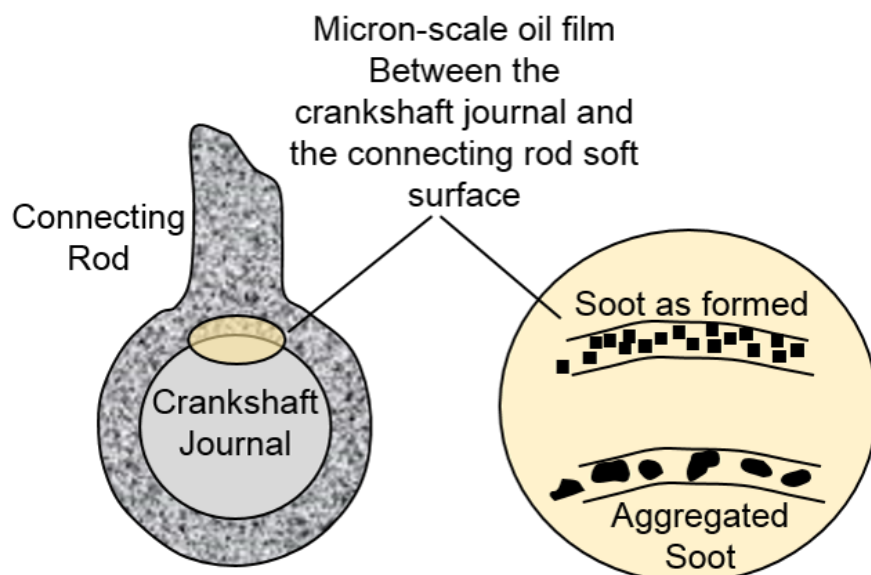


Figure 3.29 – Oil film between different engine components.

Soot particles and sludge decreases the flow of oil round the engine, clog the oil filter and in serious cases, block small oil passageways. The soot particles also increase viscosity of oil which has a negative effect on its flow. Research suggests that a conventional spark-ignition engine has oil contaminated with 1- 3% soot, but in a diesel engine, this can be as much as 10%.

A particular issue known as blow-past arises from excessive soot. In normal conditions, combustion gases and unburnt fuel pass to the piston ring, but get trapped behind it and together with the natural spring of the metal, causes the ring to make good contact and seal the combustion chamber. Soot from the combustion process, over time, begins to accumulate round the piston rings and the movement of those rings becomes restricted, especially their ability to spring out against the cylinder wall and form the seal. Consequently, “Blow-past” occurs, when the gases are forced past the rings into the crankcase.

The piston ring is said to be “stuck” and the result is wasted fuel, loss of engine power and potentially overheating as the contact is lost between piston and cylinder wall. (Fig 3.30 below)

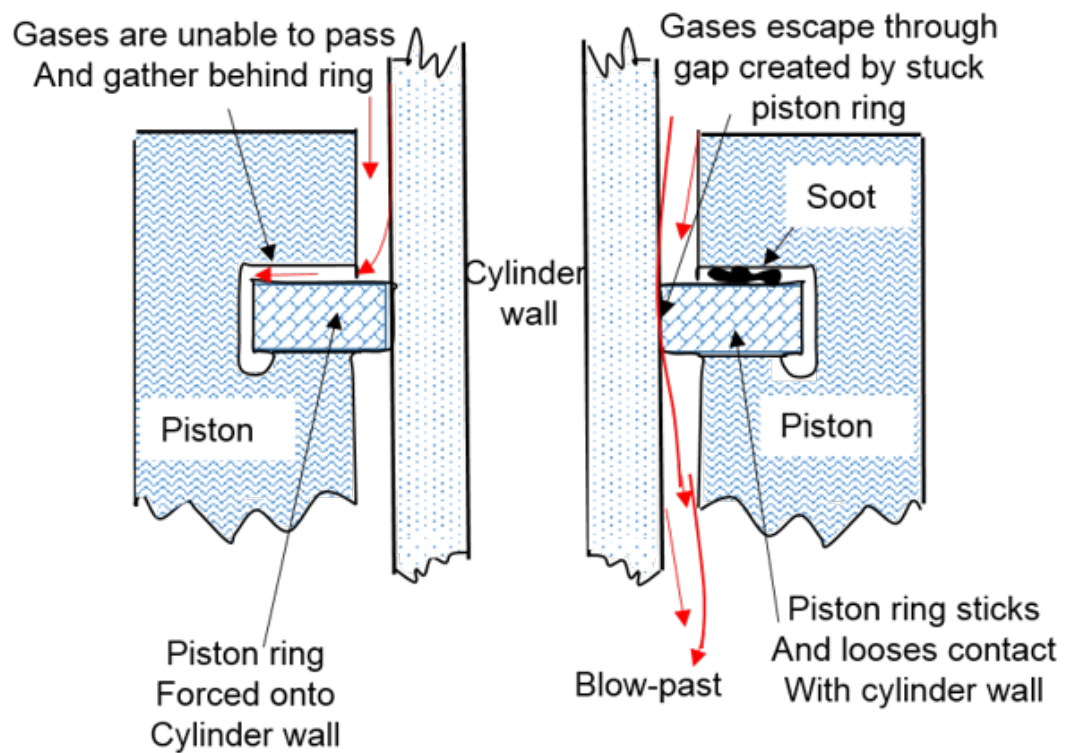


Figure 3.30 – schematic showing Blow-past. Normal conditions are left, whilst a blow-past situation is illustrated on the right.

The present chapter has discussed the major frictional components of the engine that are, the bearings, the valve train system and the piston assembly. The following chapter will describe the experimental methods and materials that were used for this study.

CHAPTER 4

4.Experimental Materials and Methods

4.1 Introduction

This section will discuss details of the experimental procedures used to establish the effects of soot contaminated oil on engine components. It describes the parameters used for testing. It also considers the materials, equipment and development of wear test rig and the corrosion testing.

4.2 Uncoated M2 Steel Samples

Sample steel rods for wear tests were cut from stock to a thickness of ~10 mm. Each was cut using a spark-erosion technique and then polished with silicon carbide paper. The roughness of samples was measured using a Surtronic 3⁺ profilometer (Taylor-Hobson, U.K) and it was found to be ~0.08 μm . According to the SAE J438B, the composition of M2 high speed steel is 0.85% carbon, 4.0% chromium, 5.0% molybdenum, 2.0% vanadium, 6.0% tungsten together with the remaining 82.15% iron. The hardness of this steel was first assessed via micro Vickers indentations using weights of 300g, 500g and 1 kg. Based on the indentation results it was found that the hardness of the samples is ~3000 **MPa**.

4.3 Diesel Soot

Soot was taken from a Crossley HD3 horizontal diesel engine of 10HP (Crossley, U.K) situated at Internal Fire Museum in Wales and used for the wear experiments. The engine had been running on idle and has a tendency to generate considerable amounts of soot under these conditions. 100 grams of soot was used in the testing. The fuel was 100% diesel.



Fig 4.1 – Crossley HD3 horizontal diesel engine (Crossley, U.K).

4.4 Lubricating Oil

The lubricating oil used for testing was Castrol Q 556 Flushing Oil 20W40 which is a mineral oil with a kinematic viscosity of $12 \text{ mm}^2 \text{ s}^{-1}$ (12 cSt) at 100°C .

4.5 Soot contaminated oils

As previously mentioned, an excess of soot produced as part of the fuel combustion, can, via blow-blast, gain access to the engine oil.

It is necessary to characterise the soot in order to have a better understanding of its morphology and mechanical properties. This morphology helps to better determine information about interactions between soot and engine oil. Previous soot morphology studies showed

that there was no difference between the industrial black carbons and diesel engine soot [63].

In order to find an exact determination of the wear process on uncoated M2 steel samples, two soot contaminated oils were prepared at 5% and 2.5% soot by weight in oil. Using volumes of 400 cc Castrol Q 556 oil, the soot weight used was 20 g and 10 g.

A stable soot suspension was prepared in the following manner:

400cc clean oil was poured into a screw-capped container. The appropriate amount of diesel soot was then added. The container was sealed, then shaken vigorously for one minute, after which, the mixture was allowed to stand for a further minute. A check was made to see if any soot had settled out and if so, this was disturbed with a stainless steel spatula until the sediment layer had been completely disturbed. The mixture was again shaken and allowed to stand until no soot layer was visible settled in the container. Once thoroughly mixed, this stable soot suspension could be used for up to two hours before the soot started to settle at the bottom of the container.

4.6 The Instruments used for testing

A number of different experimental techniques and instruments have been used in this thesis and this section introduces the relevant background to show how these provide useful insights into the experimental work.

4.6.1 Scanning Electron Microscopy (SEM)

The scanning electron microscope is an instrument which gives detailed information about the morphology and composition of natural and manufactured materials. SEM was used for studying the surface structure of the samples before and after the wear tests. It was the key instrument

for studying the wear mechanism in respect of the soot contaminated oil in this project.

A schematic diagram of an SEM is shown in figure 4.2.

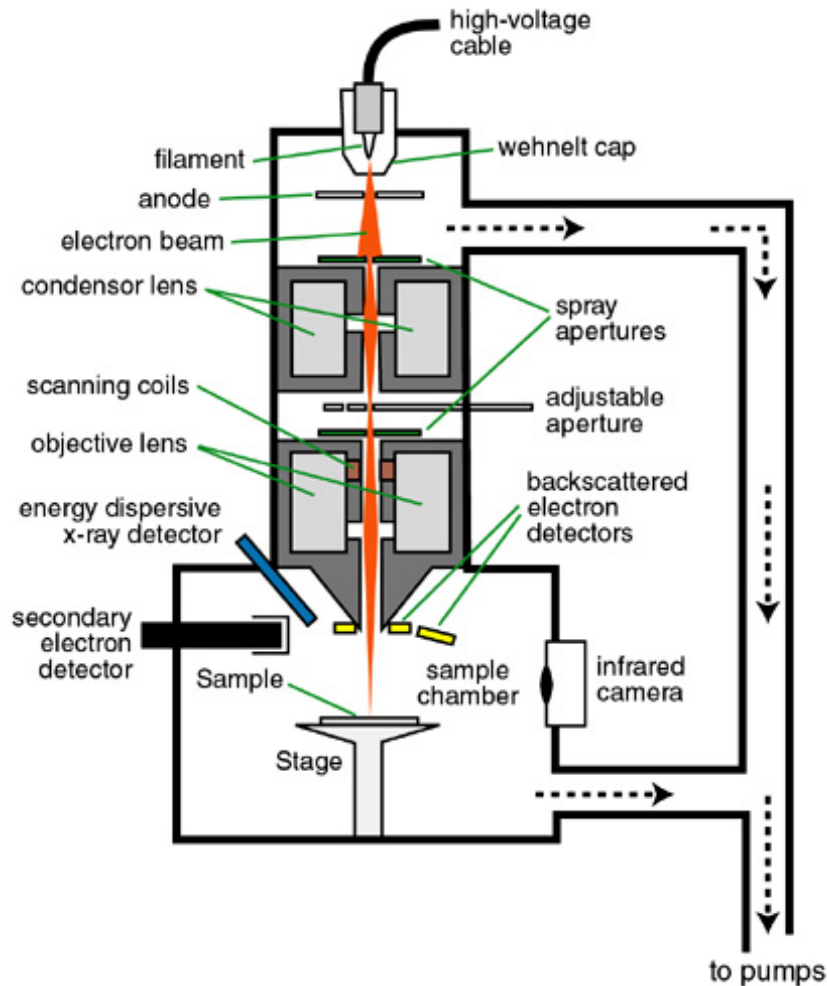


Fig 4.2 – A schematic of a typical scanning electron microscope. SEM, as its name suggests, uses electrons instead of light to image a sample. The electrons are generated by thermionic emission from a metal filament and accelerated up to 25keV. A system of electrical and magnetic fields is used to focus the beam to a spot 10 nm in diameter on the sample surface [64].

Figure 4.3 shows the signals that can be generated when the electron beam interacts with the specimen surface. In this project, secondary electrons were used for analysis the topographical features of the wear

scars. Backscattered electrons were used for identifying wear debris by atomic number contrast and X-rays were used to identify composition.

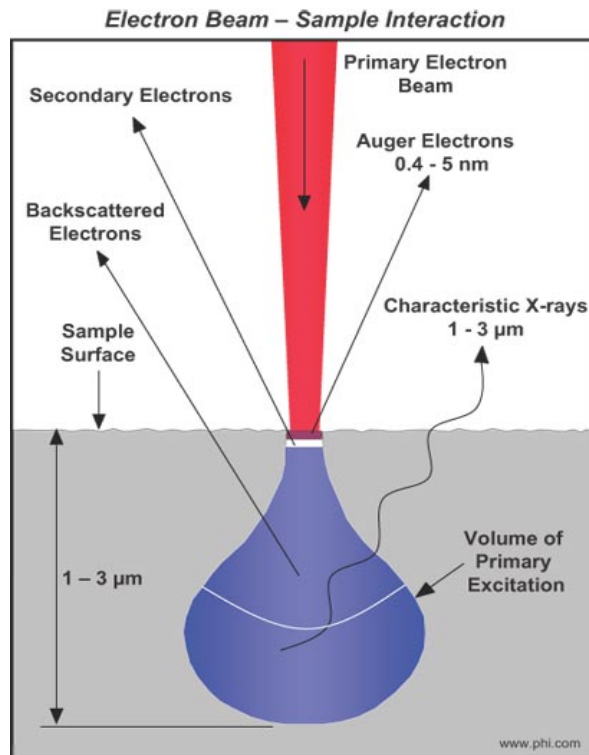


Figure 4.3 – Schematic representation of the energies produced from electron beam interaction with solid matter. The sample is bombarded by an electron beam. Due to the interaction of the beam with the sample different electromagnetic waves and electrons are generated; X-rays, Auger, Secondary and back-scattered electrons [65].

4.6.1.1 Field Emission Gun-Scanning Electron Microscopy (FEG-SEM)

This microscope is equipped with an extra field-emission cathode in the electron gun providing narrower probing beams with high electron energy. This gives improved resolution and minimizes damage to the samples.

4.6.1.2 Emitter

The main difference between SEM and FEG-SEM is the type of the emitter. The Thermionic Emitter uses electrical current to heat the

filament. When sufficiently hot electrons escape from filament. The weakness of this type of emitter is low brightness and evaporation of the cathode material. The field emission gun (FEG) which is also called a cold cathode field emitter, produces a cleaner image, less static distortions and 3 to 6 times better resolution than a tungsten filament SEM.

4.6.1.3 EDX (Energy Dispersive X-Rays)

The EDX detector is mounted on a suitable vacuum port on the SEM chamber. The SEM is equipped with the EDX analysis in order to analyse the elemental composition of materials. Figure 4.4 shows a schematic diagram of an EDX detector.

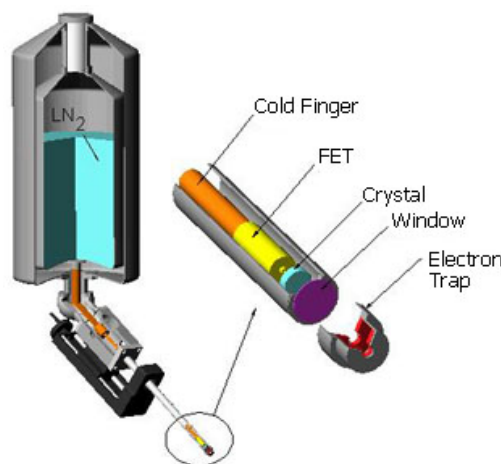


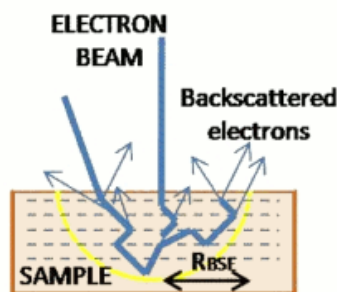
Figure 4.4 – An EDX analyser system is designed to analyse X-ray photons emitted from a sample. The photons are generated when a sample is exposed to an electron or X-ray beam, such as in a SEM or X-ray fluorescence instrument. The EDX detector is a self-contained vacuum system with cryogenic pumping created by liquid Nitrogen cooling. The principal elements of an EDX detector are the entrance window, the Si (Li) Crystal, a Field Effect Transistor (FET) and Pre-amplifier [66].

4.6.1.4 Backscattered and Secondary Electrons

When a sample is bombarded with electrons, high energy electrons interact with valence electrons of the sample atoms. The valence electrons are released from the atoms and emerge from the surface. The emergent electrons with energies less than 50 eV are referred to the secondary electrons. Figure 4.5 shows the way in which secondary and backscattered electrons are generated when an electron beam interacts with a specimen surface.

When the electrons strike the sample, some of the electrons will interact with the nucleus of the atom in the same way as space craft interacts with the gravity of a planet. The negatively-charged electrons attract to the positive nucleus. But at certain angles, electrons instead of being captured by the nucleus, are circled the nucleus and back out of the sample.

(a)



(b)

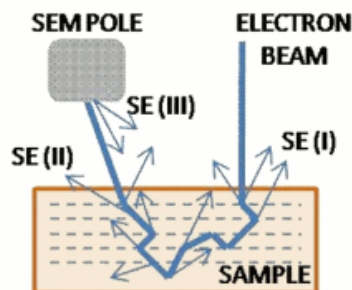


Figure 4.5 – (a) Backscattered electron generation. (b) Secondary electron generation [67].

Backscattered electrons give atomic number contrast and can be used to identify different phases or wear particles of different composition for example.

Figure 4.6 shows how the electron beam interacts with the atom.

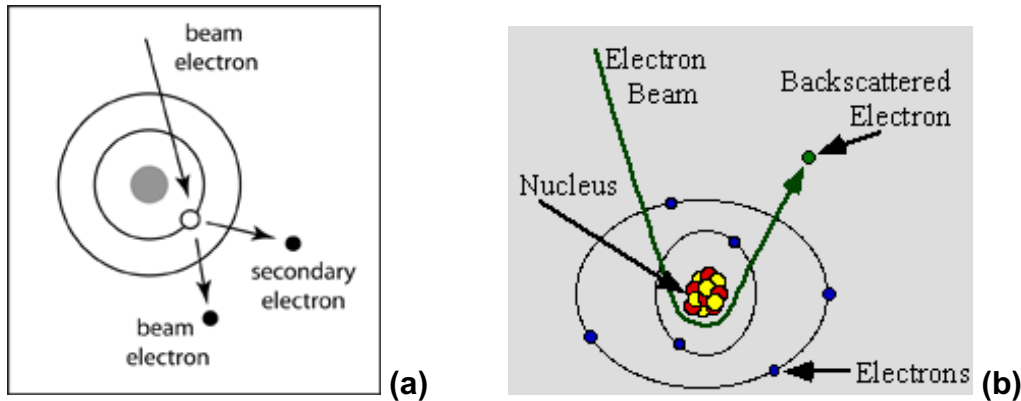


Figure 4.6 – (b) Backscattered electrons produced by elastic interactions of beam electrons with nuclei of atoms in the specimen. (a) Sometimes beam electrons interact with the electrons present in the atom rather than the nucleus. Since all electrons are negatively charged, the beam electrons will repel the electrons present in the sample. This interaction causes a beam electron to slow down as it repels the specimen electrons, the repulsion may be so great that the specimen electrons are pushed out the atom, and exit the surface of the sample, these are called secondary electrons [68].

4.6.1.5 X-Rays

When a high-energy beam of electrons bombards a sample, the electrons in the inner shells are ejected creating an electron hole. An electron from the outer energy shell fills the hole and the difference in energy between the higher and lower energy shells may be released in the form of an X-Ray photon. The energy can also be transferred to another electron and eject it from the atom. This ejected electron is an Auger electron.

The electron orbits of each element are unique and therefore the set of X-Rays emitted from these electron interactions are characteristic in respect of energy and wavelength for each element.

Figure 4.7 shows how the characteristic X-rays and the Auger electrons are produced.

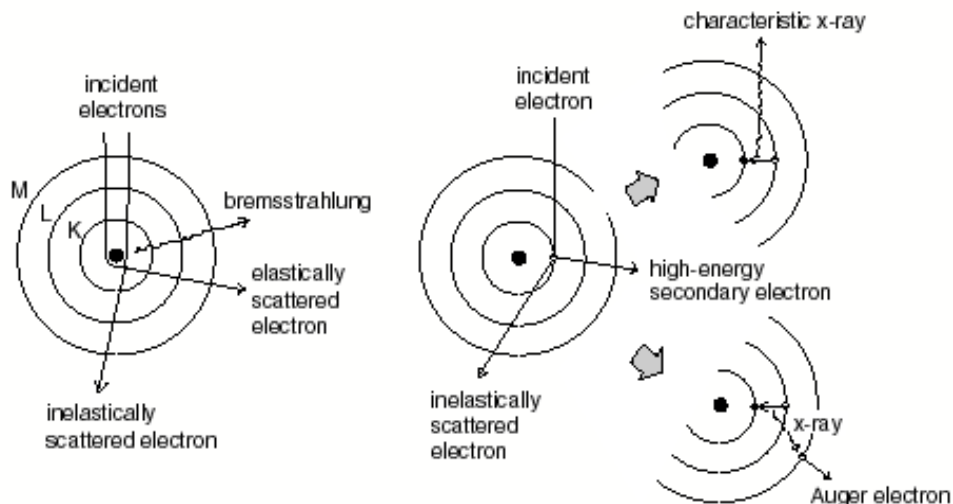


Figure 4.7 - Classical models showing the production of X-rays, and Auger electrons. (Left) Electrons are scattered elastically and inelastically by the positively charged nucleus. The inelastically scattered electron loses energy, which appears as bremsstrahlung. Elastically scattered electrons (which include backscattered electrons) are generally scattered through larger angles than are inelastically scattered electrons. (Right) An incident electron ionises the sample atom by ejecting an electron from an inner-shell (the K shell, in this case). De-excitation, in turn, produces characteristic X-radiation (above) or an Auger electron (below) [69].

4.6.2 - Transmission electron microscopy (TEM)

In transmission electron microscope (TEM) an electron beam and magnetic lenses are used instead of visible light and glass lenses used in optical transmission microscopy [70].

The electrons are typically accelerated with 200 kV and transmit onto the thin specimen. A schematic ray path for a transmission electron microscope is shown in figure 4.8.

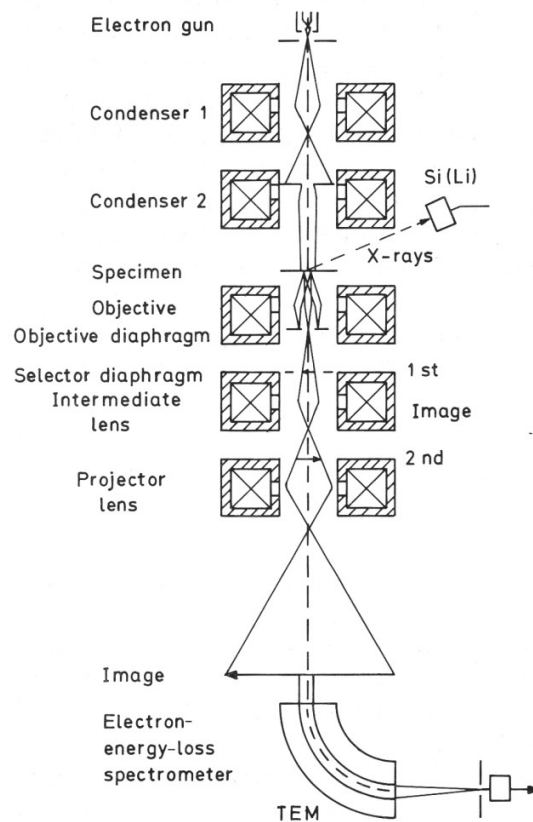


Figure 4.8: Schematic X-ray path for a TEM, equipped with detectors for X-ray spectroscopy and electron energy loss spectroscopy (EELS) [71].

The electrons are emitted in the electron gun and interact with atoms by scattering. The scattered electrons from the specimen are imaged with a three or four-stage lens system onto a fluorescent screen.

Condenser lenses, which are between the electron source and the specimen, force the electrons into a parallel beam. The first image is generated by the objective lens. The first intermediate lens is coupling projector lenses to the first image generated. The projector lenses are responsible for the image magnification. The wavelength of the electrons can be reduced by accelerating electrons with high voltages. This is used

for imaging atomic features. The lenses in a TEM are electromagnetic, which makes it possible to adjust the magnification and defocus without physically changing or moving the lenses.

4.6.3 Transmission Electron Microscopy of Diesel PM

There has been much research regarding the morphology of diesel particulate matter. A number of these studies have used Raman Spectroscopy, which provides a quantitative measure of the graphitic nature of soot particles.

Another technique, which seems to be more common, but remains a qualitative study, is the use of transmission electron microscopy (TEM), which allows a view of the inner structure of soot particles.

To provide a reference for the sizes of features viewed, in several studies the particles were viewed with a JEOL 2010F Transmission Electron Microscope, which has a point to point resolution of 0.23nm. A large number of TEM studies have been completed with a variety of different sample preparation techniques used, and a wide range of different fuels studied.

Usually the studies seem to be completed on common fuel blends such as diesel fuel and soya or other vegetable oil based B20 blend. However, some less common fuels have also been studied, such as Fischer-Tropsch fuels and B100 blends [70].

As mentioned above, a variety of sampling methods have been used to collect samples for TEM analysis, and different TEM techniques and equipment were also used for the final analyses.

Muller et al. (2007) devised a sampling system where exhaust is allowed to flow into a separate chamber attached to the exhaust line. Between this chamber and the exhaust line, a TEM grid is inserted, through which the

exhaust gases flow, with the grid effectively being used as a filter to trap particulate matter.

The samples were then examined under a TEM operating with a beam acceleration voltage of 200kV, while trying to avoid viewing the underlying carbon film, which was part of the whole carbon coated TEM grid.

Kirchner et al. (2009) opted for two techniques which were different to the one listed above.

The first technique collected samples by diffusion. In this setup, the grids were attached to membrane filters, and collected soot as exhaust was drawn through the filters.

The second method collected PM onto lacey carbon coated grids electrostatically, in which the grid was charged differently than the PM, resulting in a deposition of PM on the grids. Lacey carbon grids are used as they provide a strong support for the PM.

Soot does not necessarily have to be collected directly onto grids. Several researchers have used techniques in which soot is transferred from other collection media onto the grids. Most interpretations of this technique create a suspension of soot in some solvent, drops of which are placed on the grid, leaving particles behind as the solvent dries.

In the case of Chen *et al* (1990) the PM powder was ultra-sonicated in acetone before being transferred to holey-carbon grids, while Vander Wal (2003) used a similar method, except the suspension was made with ethanol. Vander Wal obtained the PM by creating a reverse flow through a DPF and collecting the soot.

The technique which appears to be the most commonly used is the thermophoretic sampling technique. Essentially, this technique takes advantage of the temperature gradient between the PM in the hot exhaust stream and the relatively cool TEM grid. This temperature gradient results

in an attraction of the hot particles to the cool grid, thus depositing the particles on the grid.

In most situations, a lacey carbon grid is used, which is connected to a pneumatic probe and inserted into the exhaust stream for a short period of time to collect a sample. Some researchers have also used silicon-oxide coated grids.

There are a number of good practices which should be followed with the thermophoretic sampling system for best results. The grid should be kept parallel to the exhaust flow, to ensure the deposition is thermophoretic and not simply due to gravity.

Also, the exposure time of the TEM grid should be limited so that the PM coverage of the grid is limited to less than 15%. This will help to avoid aggregation and overlapping of the particles.

This method has been used for the collection of soot from flames, but has proven to also be useful when discussing engine exhaust. In some ways it is simpler for engine exhaust as precise location of the probe is not critical, so probe deflection is not a major issue.

4.6.4 - Contact Profilometer

The Taylor Hobson contact profilometer was used for measuring the surface roughness of metal samples. In use, it measures the depth of wear area on the surface of the samples. Computer software then measures the volume of the hole after wear testing.

The mechanism of profilometer is based on a diamond stylus moving vertically in contact with the sample and then moves across the sample for a specified distance. The height position of the diamond stylus generates a digital signal then analysed and displayed. A schematic diagram of an profilometer is shown in figure 4.9.

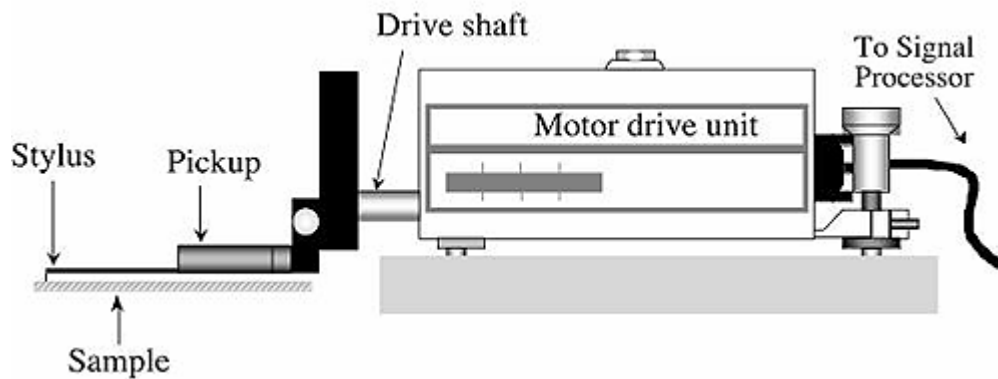


Figure 4.9 – Illustration stylus profilometer sketch [72].

4.6.5 The SZX Optical Microscope

The SZX microscope system Olympus was used for optical microscopy. This instrument was used to investigate and measure the wear area on each sample.

4.6.6 Wear Test Rig

The wear test rig for this project was redesigned and modified from equipment used for student projects during previous years. The aim of this experimental test is to simulate the real working conditions of the camshaft tappets in a diesel engine and investigate the effects of the soot contaminated oil on tappets wear.

The test rig shown in figure 4.10 consists of a variable speed electrical motor which is coupled to a cast iron disk to simulate the camshaft. According to the ASTM A339, the nominal composition of the disk which was ductile or nodular iron is carbon-3.4, manganese-0.4, nickel-1.0, magnesium-0.06 and iron-Fe 95.14 % by weight and is the general cast iron used for gears, camshafts and crankshafts. The hardness of the cast iron disk was measured using the micro indentation method and found to be ~2400 MPa. The diameter of the disk used was 50 mm, and the width was 8 mm.

An aluminium beam was arranged so that pivoting at a point, it rests upon the cast iron disc. 500mm from the pivot point, provision was made to attach weights to the beam creating a down-force upon the disc. A maximum 2kgf (19.62 N) load at the disk was used to simulate the pressure of the valves spring found in real working engines and used for all the tests. The sample holder was located 80 mm from the pivot point, so that the load at the sample contact point is a multiple rate of 6.26. To allow proper comparison between wear measurements, certain variables such as load, velocity, temperature, contacting area, surface finishing and vibration were controlled during the tests. The test rig also had a sump of oil which was equipped with a mica band heater in order to keep the oil temperature at 80 °C during the tests. This temperature was chosen as being similar to that of engine oil in real working conditions. For controlling and fixing the temperature, an extra voltage rheostat was added to the heater and monitored by a digital thermometer during the test.

The M2 steel samples were polished prior to the test using a silicon carbide paper to obtain a roughness of 0.08 μm , measured with the contact profilometer.

The first test was started by using 5% soot contaminated oil. The speed of motor was fixed at 400 rpm which is the ideal speed for the diesel engine camshaft. It is the speed when the most soot particles are produced in the combustion chamber. The test was run for 30 minutes with the aim of generating measureable wear. During the test some vibration was noted. The disk and motor were checked and the problem determined to originate from the rotor. However, the level of vibration was not considered serious enough to void the test. This test was repeated two more times with oil contaminated with 2.5% soot and clean oil. The wear scars obtained for each of these tests is shown in figures 4.10a, 4.10b and 4.10c.

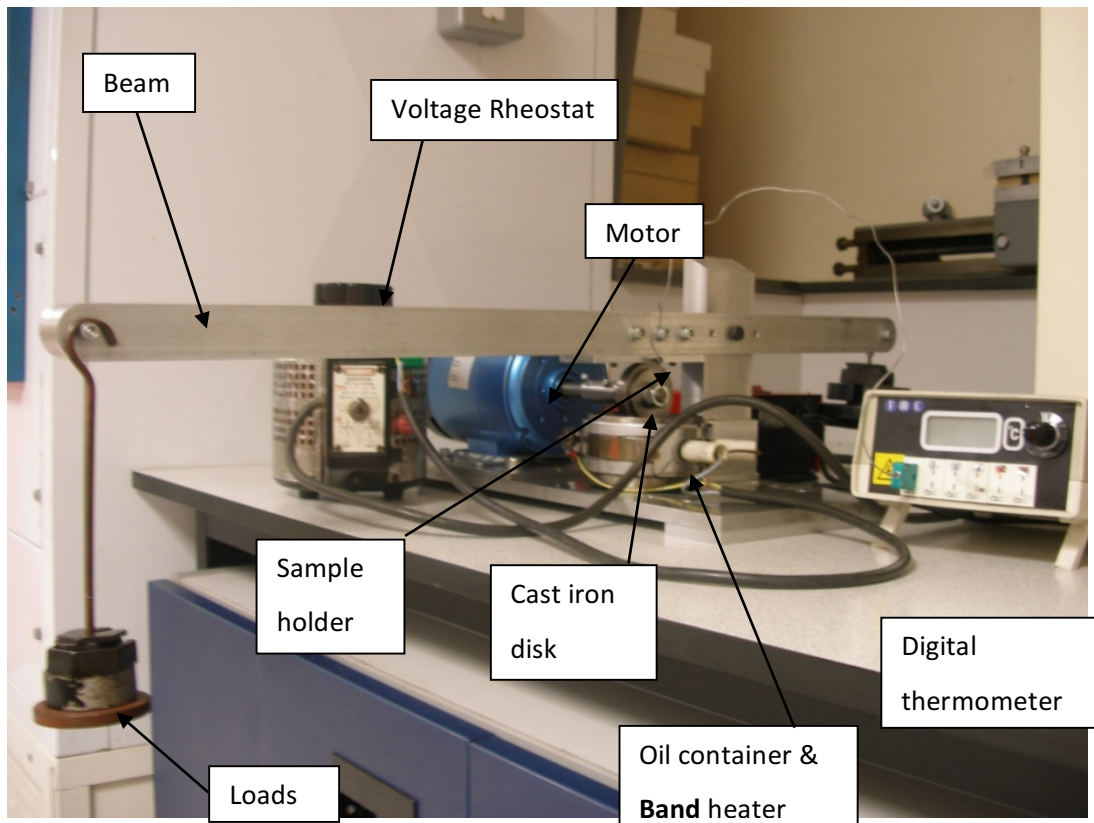


Figure 4.10 – Photo of wear test rig and its main components.

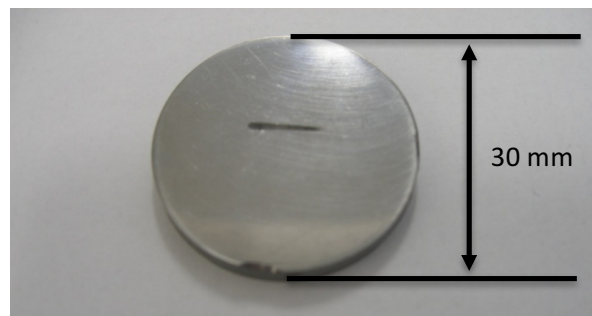


Figure 4.10.A – Image of the wear scars produced on M2 steel sample one lubricated with 5% soot contaminated oil.

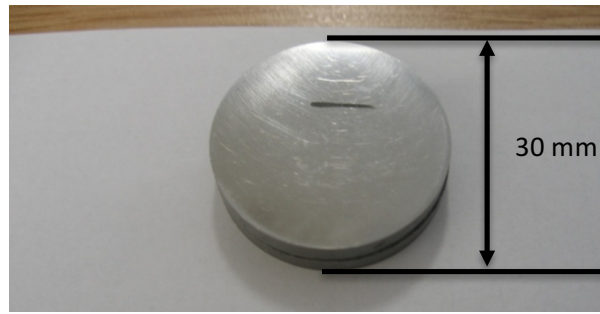


Figure 4.10.B – Image of the wear scars produced on M2 steel sample two lubricated with 2.5% soot contaminated oil.

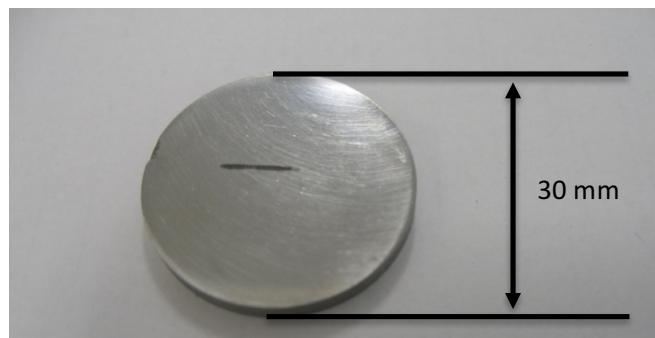


Figure 4.10.C – Image of the wear scars produced on M2 steel sample three lubricated with clean oil.

After the initial tests it was noted that the wear scars were not consistent. Investigation suggested that the cause was vibration. This meant that certain modifications were required to components on the test rig.

The sample holder was modified to a solid fixture which was resistant to heat and oil. In the initial tests, silicon adhesive tabs were used for mounting the sample to the beam. These tabs failed at the working temperature of the lubricating oil (80 °C) and also when the beam at the mounting point became oily.

The modification for specimen mounting consisted of an aluminium mounting plate, machined to accept the steel test sample and then bolted

to the beam. The second modification was needed on the pin that mounted the beam to its upright (the pivot point). The pin was found to be too loose and a new pin machined to a much finer tolerance was made, which cured that vibration source.

A further issue considered was the lateral angle between the disk and the samples. It was very important to be sure that the cast iron rotating disc made contact with the steel sample across its entire width. It was found that the kinetic loads produced when the rig was operational caused changes in the lateral angle between the samples and the disc, compromising full width contact. Although no modification was made, it was agreed that if the tests were to be repeated in the future, an extra bearing would need to be mounted outboard of the cast iron disc so that it was supported on both sides when rotating.

4.7 Collection of soot particles (Soot samples from the exhaust)

4.7.1 Experimental assembly at Internal Fire Museum of Power Wales

Exhaust soot samples for TEM investigations were collected using a special particle collector, designed and built by Paul Evans, Curator at Internal Fire Museum in Wales. The particle collector was attached to the exhaust pipe of a diesel engine, in this case a Petter PJ2 model, as shown in figure 4.11.

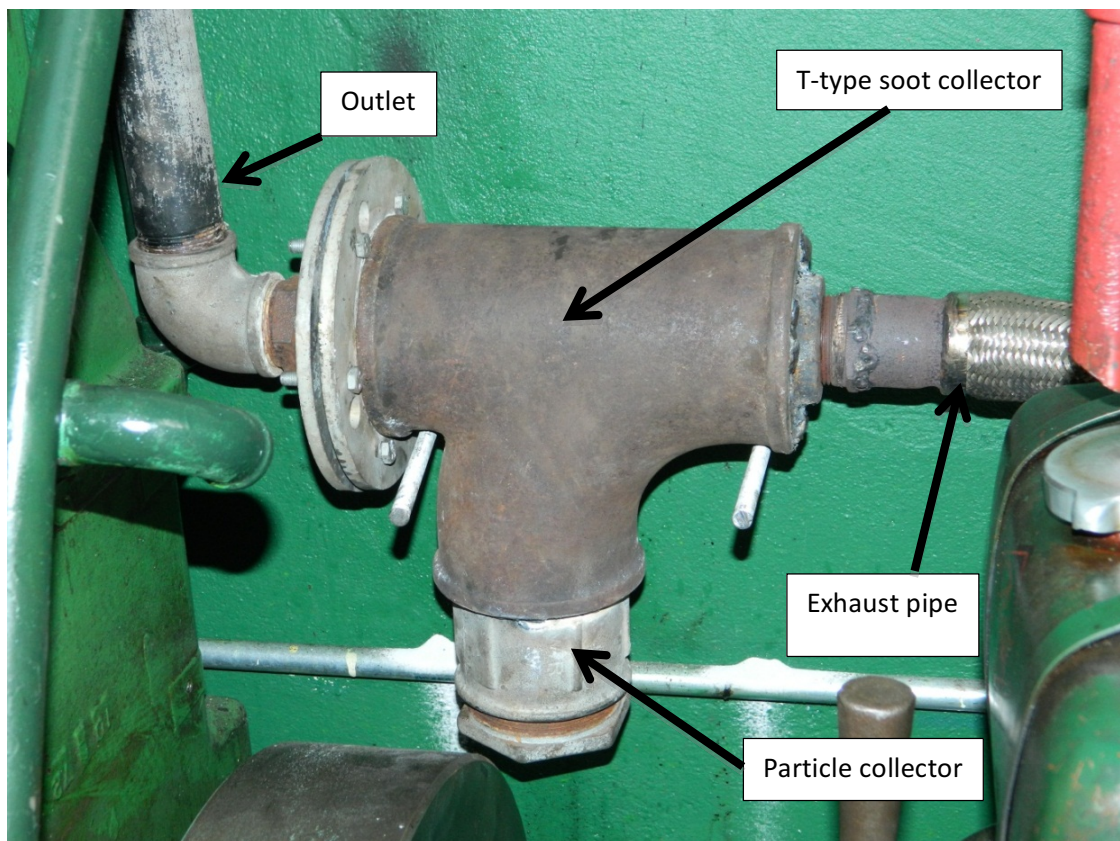


Figure 4.11. Particle collector attached to the exhaust pipe of a Petter PJ2 diesel engine at Internal Fire Museum.

Constructed from a water pipe Tee-piece fitting, exhaust gases entered one end of the Tee, towards the exit opposite. Interposed at the exit was a cone shaped porous substrate made of aluminium. This allowed gases to pass, but disturbed the flow sufficiently to cause soot to be deposited within the Tee-piece, with any loose particles falling into the stem of the Tee that had been sealed with a removable plug. This is illustrated in figure 4.12.



Figure 4.12 – Aluminium Cone in situ with trap.

This system allowed sufficient quantities of soot particles necessary for the TEM investigations to be collected.

Table 4.1 shows the details of these biodiesel variation tests performed at Internal Fire Museum, Wales. Where possible, engine parameters were kept constant, while the biodiesel blends were varied.

Type of Fuel	Fossil Diesel	B20	B100
Engine Speed (rpm)	1800	1800	1800
Load (%)	75.0	75.0	75.0
Engine power (bhp)	18.0	18.0	18.0
EGR (%)	0.0	0.0	0.0
Injection pressure (bar)	180	180	180
Exhaust Temperature (°C)	450.0	480.0	510.0
Engine Temperature (°C)	82.0	79.0	80.0
Inlet air temperature (°C)	-4.0	-4.0	-4.0
Fuel Temperature (°C)	71.5	69.6	74.0

Table 4.1 – Engine parameters for each diesel/biodiesel blend.

4.8 Corrosion Characterisation Tests

Corrosion characterisation tests were carried out for copper, brass, aluminium, aluminium 7075 alloy and steel when in contact with biodiesel B100 at 25°C, 80°C, 90°C, 100°C, 110°C and 120°C for 270 hours. During the tests, fuel temperature was maintained and monitored.

The samples used for the tests were brass (51 mm X 30 mm X 1.6 mm) with the composition of 70:30 Brass and Copper, copper (51 mm X 25 mm X 2 mm) with the composition of 100% Cu, steel (50 mm X 30 mm X 2 mm) with composition of 100% Fe, aluminium (51 mm X 20 mm X 1.5 mm) with composition of 100% Al and Al7075 (51 mm X 20 mm X 1.5 mm) with composition of Al+Mg+Cu+Zn. One 5 mm diameter hole was drilled at the corner of each metal sample, with nylon fishing line used for hanging the samples in the fuels. Before starting the immersion corrosion tests, all metallic samples were prepared using the process outlined below:

All samples were manually polished using silicon carbide abrasive paper (400 to 1200 grade) and then washed with acetone in an ultrasonic bath for 20 minutes before being dried by a heater.

Following the conclusion of the immersion corrosion tests, the now oily samples were again lightly washed with acetone to remove the testing fuels from the surfaces. To avoid damaging any potentially corroded surfaces, the samples were not re-washed by ultrasonic device or any other mechanical instrument at this stage.

Before and after the immersion corrosion tests, all metal samples were weighed by an electronic balance accurate to four decimal points. One sample from each metal was used at 25°C, 80°C, 90°C, 100°C, 110°C and 120°C.

Following the tests' conclusion, the weight loss for each sample was measured. This allowed the corrosion behaviour of the metal samples when in contact with biodiesel and diesel fuel to be observed through measurement of their corrosion rates and studying the morphology surface changes for them. The average weight loss for each sample was converted to corrosion rate by using the below equation:

$$\text{Corrosion Rate (mpy)} = \frac{W \times 534}{D \times T \times A}$$

Where; Corrosion rate “mpy” = mill (0.001 inch) per year, W = weight loss in milligrams (mg), D = density in g/cm³, A = surface area in contact of fuels (square inch), T = test duration in hours.

Changes in the surface morphology were characterised by optical microscopy and SEM. Fuel samples were analysed before and after corrosion immersion tests by the Gas Chromatography Mass Spectroscopy (GCMS) in the chemistry department at the University of Leicester. Both fuel compositional changes and the presence of metal

species were investigated by Inductively Coupled Plasma (ICP). Fuel samples were sent to Oil Check Laboratory Ltd for this analysis as the relevant instrumentation was not available at the University. Degradation of fuel properties was investigated by measuring Total Acid Number (TAN), density and viscosity of each fuel sample before and after the corrosion immersion tests. Figure 4.13 show the immersion corrosion rigs and figure 4.14 illustrates the corrosion immersion tests colour change.



Figure 4.13. Immirson Corrosion Rig

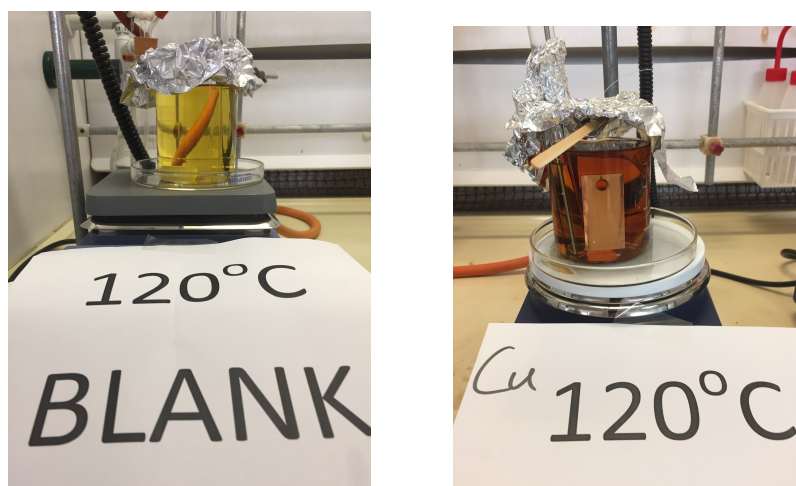


Figure 4.14. Color changes at 48hrs

The objective of this test was to study the interaction of biodiesel B100 and the five alloys over a period of time, and to evaluate their resistance to corrosive biodiesel fuel. The investigated biodiesel B100 was purchased from Biofuel Refineries Ltd. The physical, mechanical, chemical behaviour of the alloys before and after immersion test were characterised by optical microscope and SEM.

Physical and chemical characteristics of the fuel after immersion test were also determined by total acid number (TAN) by sending fuel samples to Oil Check Laboratory Services Ltd in Doncaster. The colour change of the fuel was also noted. Furthermore, the full-submerged position of specimens in biodiesel was designed to simulate the fuel–oil interface area inside real engine fuel supply systems and the oil sump, where oil, biodiesel, and engine’s material meet. Each glass jar contained one specimen of the alloys samples, and each specimen was removed for visual inspection and surface analysis after 270 hrs. An oven was used to keep the coupon samples at 40°C and the temperature was monitored by thermocouple. Figure 4.15 is showing the oven with the coupons in.



Figure 4.15. Oven with fuel jars in

CHAPTER 5

5. Wear Results and Soot Characterisation

Fuels from biological sources, such as biodiesel, and other biomass fuels, are contributing to reducing exhaust emissions and reducing the dependence on fossil fuels. Engines powered by these fuels can also benefit improved fuel economy. Soot is a by-product of the combustion process that cannot easily be reduced.

Most of the soot generated during the combustion process is emitted through the exhaust however it can also contaminate the oil within the sump as a result of blow-by gasses. This effect can be worsened when exhaust gas recirculation (EGR) is used.

Soot contamination of the oil can lead to increased wear in critical components as well as shortening of oil life and an increased frequency of oil changes. Therefore, an understanding of the effects of soot contamination on the lubricating oil is required. Soot contamination can cause serious issues and it is important that engine manufacturers and lubrication producers understand the issues. Soot can damage the engine bearings, cams valve train, piston rings, cylinder liners, etc.

The operating lubrication regimes for these components are possible boundary lubrication or liquid full film lubrication and these are dependent the viscosity of oil, the applied load, the surface roughness, etc. As such there are many different theories regarding the properties, formation and effects of soot particulates on the performance of a lubricating oil. However, the mechanisms of wear affected by the soot, and how these changes in the presence of oil additives are not clear.

The collection of soot particles to study their tribological properties is very time-consuming and challenging. In order to produce reliable data, soot with consistent properties is needed for use in contamination tests.

This chapter describes a series of experiments designed to address the influence of soot contamination on the tribological behaviour of engine lubricants by describing a systematic approach to establish basic wear data.

This chapter also describes a series of experiments designed to assess the performance of simulated soot contaminated engine oil, the results reported and discussed here provide useful insights on the role of such soot particles in oil.

In particular, the mechanisms of wear induced by the soot have been studied.

The lubricant used was Castrol Q556. Soot particle contamination was simulated using exhaust soot engine emitted from a Crossley HD3 horizontal diesel engine of 10HP. The exhaust engine soot of Crossley diesel engine was obtained from the Internal Fire Museum in Wales.

Wear testing was performed using the pin on disk cam-tappet rig that was described in section 4.10. Tests were conducted with an applied normal load of 20 N and at 400 rpm. The oil temperature for testing was set to 80°C using a thermocouple. Soot contaminated oil was used with 2.5% and 5%.

Tests were also conducted with virgin oil. Tests were run for 20 minutes which is equivalent of 340,000 meters of contact with the disk.

The morphology, elemental composition and structure of the wear scars were assessed. The most common tribological mechanism of wear by soot

contaminated oil is abrasion. But microscopy of the wear scars was conducted to see whether any other effects were present.

As has been discussed in the literature review in chapter 3, biodiesel can lead to increased wear of components in the engine. In order to investigate the effects of soot on wear this chapter presents the results of tests with soot in oil against steel.

The soot generated with different diesel and biodiesel blends has also been characterized using TEM. The aim of the tests was to measure progressive wear over an extended period of time and determine wear rates and wear coefficients of the material in presence of different percentages soot contaminated oil.

5.1 Wear Results

The SZX optical microscope was used for taking images from the wear area on each samples and measuring the length and the average width of wear area.

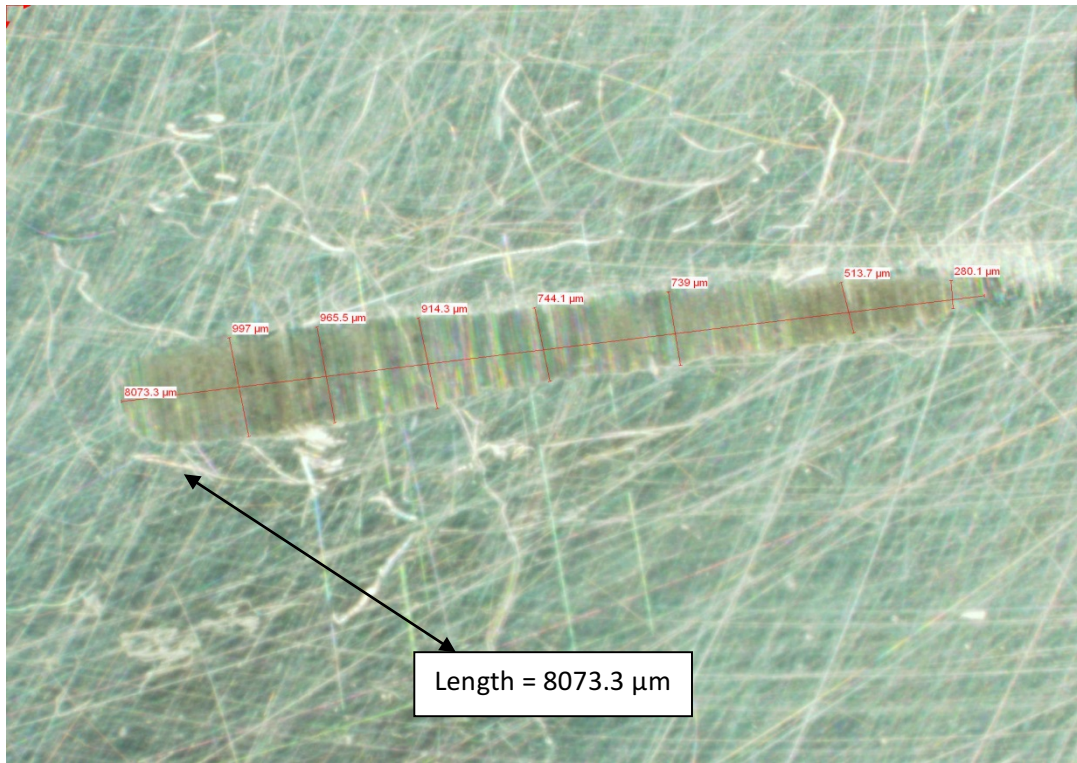


Figure 5.1. Wear image of sample 1

Figure 5.1 shows a wear scar created from a test with 5% soot contaminated oil. The scar is just over 8 mm in length which is the same as the width of the cast iron disk counterface.

For a disk on flat the expected contact is a line contact. The wear scar is not completely symmetrical with the left being slightly wider than the right. This implies the loading on the rig was not completely symmetrical. Despite many efforts to improve this, this was the best result that was obtained. 7 measurements of the scar width were obtained and these were arranged to calculate the wear volume.

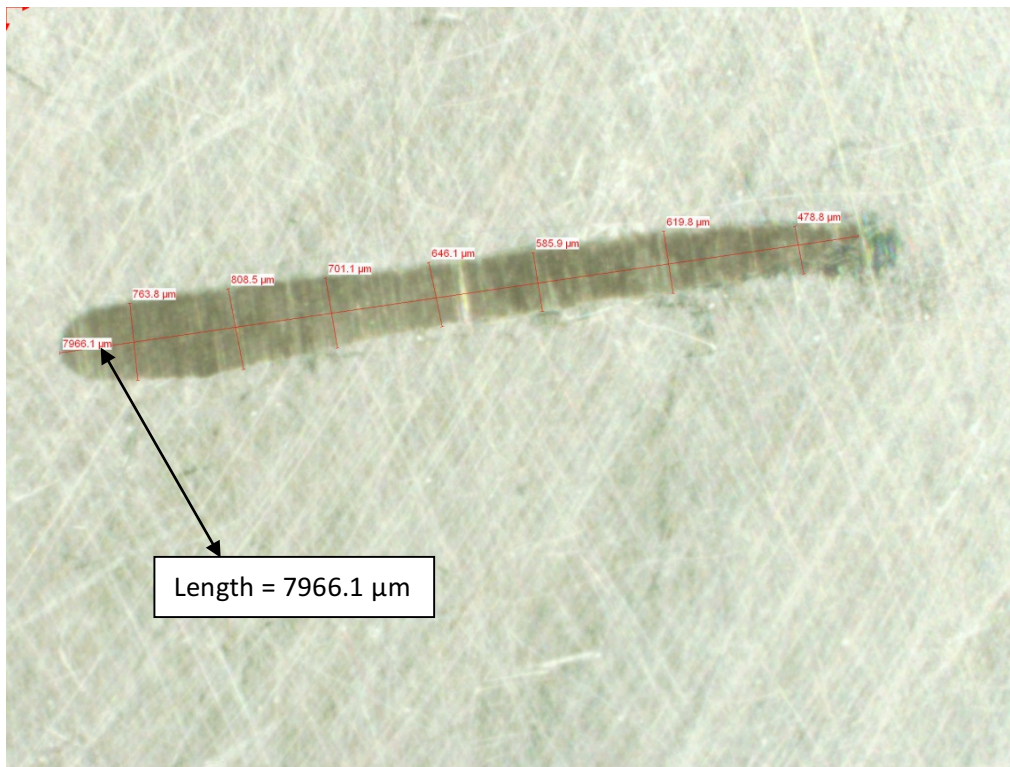


Figure 5.2 Wear image of sample 2.

Figure 5.2 shows the wear scar for the test with 2.5% soot contaminated oil. This scar length is less than the previous scar at 7.97 mm. The width of the scar is also less than for the oil containing 5% soot.

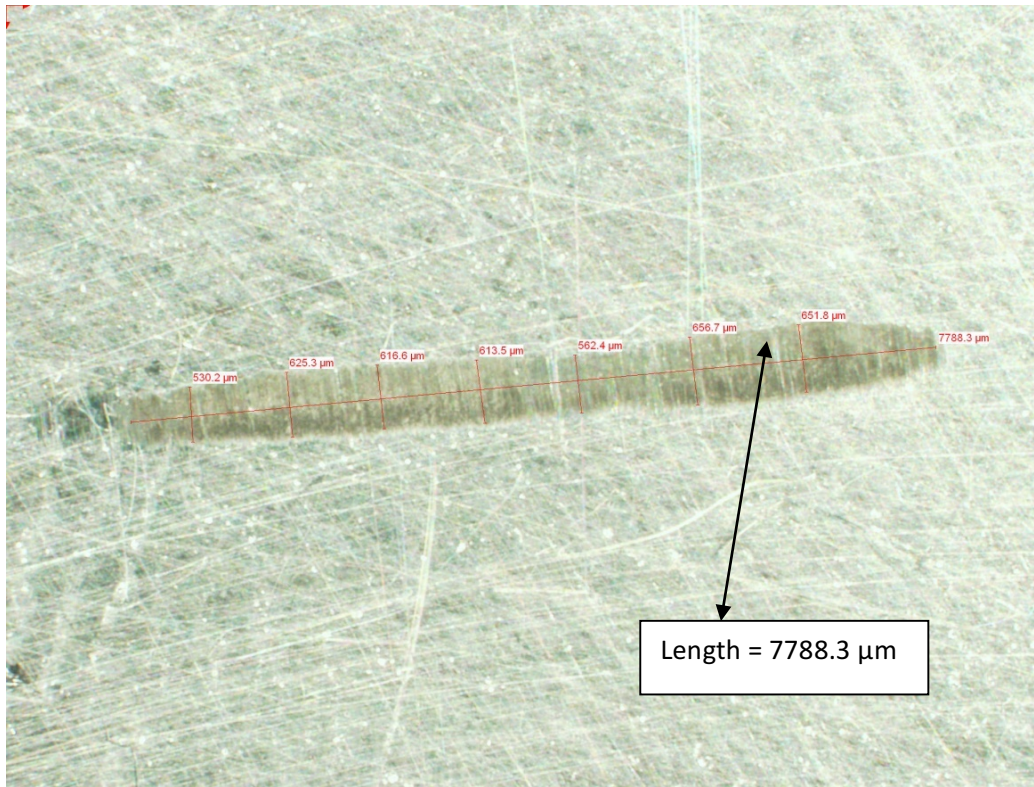


Figure 5.3 Wear image of sample 3

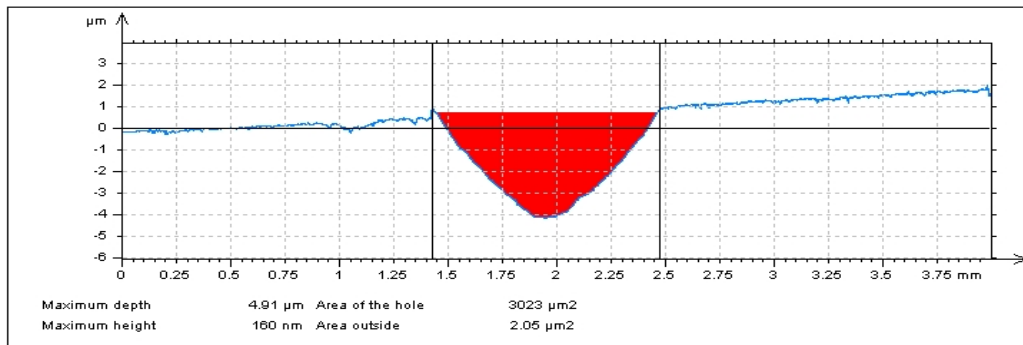
Figure 5.3 shows the equivalent scar for the virgin oil which is slightly under 8mm less long and less wide.

5.1.1 Profilometry Results

Wear areas and the total average wear volumes were assessed using profilometry.

A profilometer scan was taken at five different points across the wear scars and the area of wear scar was obtained from the software. Figure 5.4 shows a typical profilometer scan.

a



b

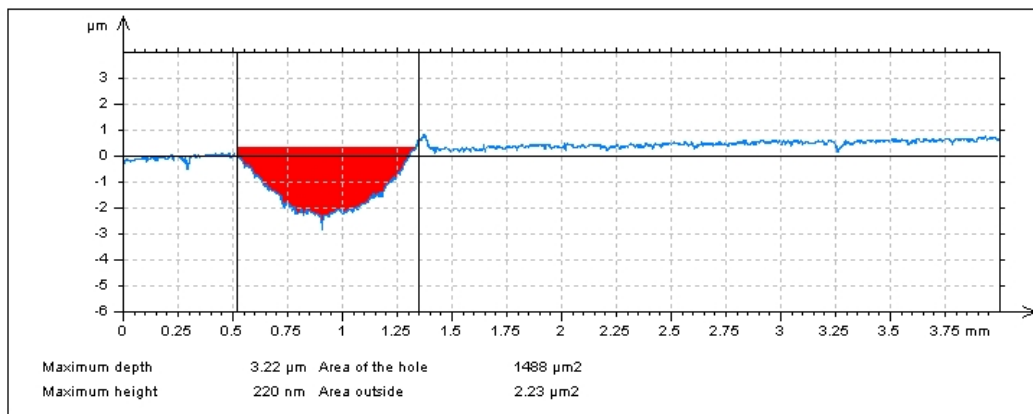


Figure 5.4 – (a) output of the first point across the wear scar for sample one with 5% soot contaminated oil. (b) Output of the first point across the wear scar for sample two with 2.5% soot contaminated oil.

Table 5.1 shows the areas measured for three different samples.

Measurement Number	Sample 1 5%	Sample 2 2.5%	Sample 3 Virgin
1	3023 μm^2	1488 μm^2	308 μm^2
2	3134 μm^2	1224 μm^2	269 μm^2
3	2751 μm^2	1374 μm^2	268 μm^2
4	2766 μm^2	1012 μm^2	390 μm^2
5	1631 μm^2	774 μm^2	596 μm^2
6	N/A	442 μm^2	N/A
Average area	2661 μm^2	1052 μm^2	366 μm^2
Standard Deviation	598.9	393.5	137.7

Table 5.1 Area of the hole measurements from five profilometer scans across the wear scars for wear from 5% soot contaminated oil, 2.5% soot contaminated oil and virgin oil.

The wear areas were then converted to wear volumes by multiplying the average area under the hole from table 1 by the track length and the results are shown in table 2.

% Soot	Area	Length	Volume
0	366 μm^2	7788 μm	0.003 mm^3
2.5	1052 μm^2	7966 μm	0.008 mm^3
5.0	2661 μm^2	8073 μm	0.021 mm^3

Table. 5.2. Wear volumes from average area under the hole and wear track length measurements.

The wear volumes as a % of soot are shown in figure 5.5 which shows that there is a significant increase in wear volume as the % of soot in the oil increases.

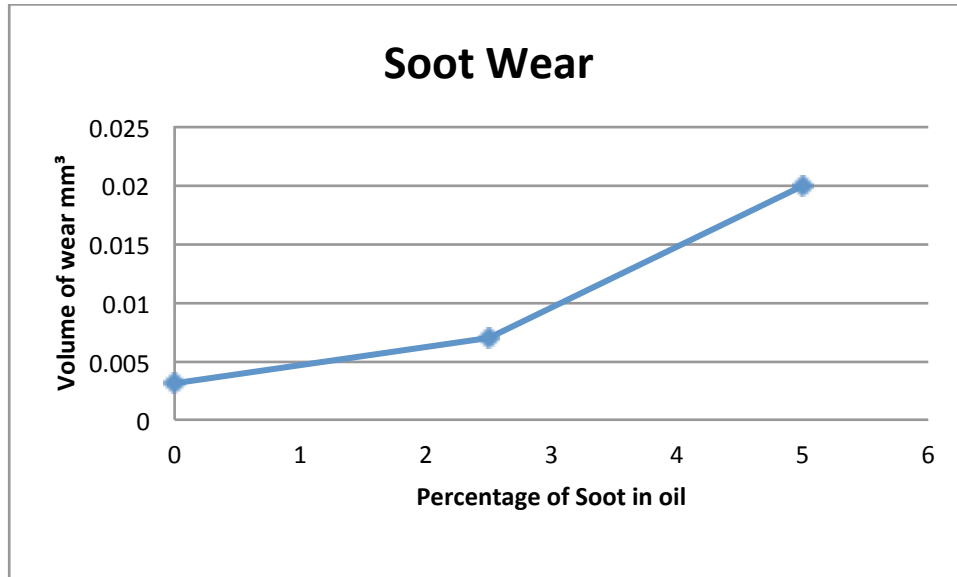


Figure 5.5 – Results of soot contaminated oil wear

5.1.2 - SEM & Optical Microscope Imaging of Samples

5.1.2.1 SEM Analysis

Figure 5.6 shows; a) an optical micrograph and b) c) and d) SEM micrographs of the wear scars obtained for the sample 1 run with oil with 5% soot. In a) it can be seen that there is a dark wear scar with what appear to be lighter grooves in the micrograph. The SEM images are all secondary electron images. The profilometry in table 5.2 showed that the wear scars created a groove on the surface of the steel tappet but the SEM images and optical microscope images also show that there appears

to be a transfer layer that is present. b) shows the patch of transferred material c) and d) show the two edges of the groove.

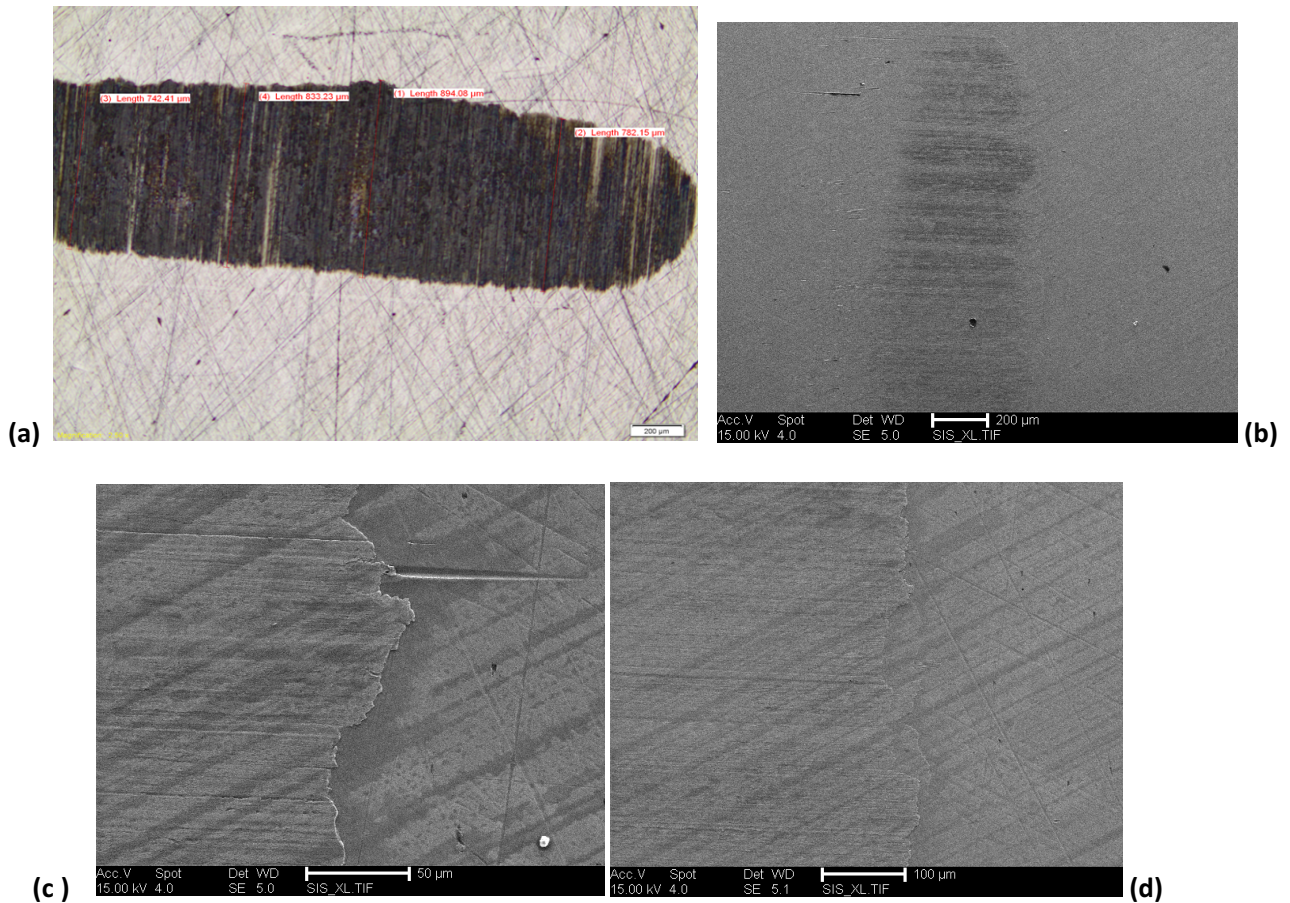


Figure 5.6 - Sample 1: Type of Oil; Castrol Q556, Flushing Oil - 400 CC Oil, 20 gr soot (5%).

Figure 5.7 shows; a) an optical micrograph, b) and c) SEM micrographs of the wear scars obtained for the sample 2 tested with oil with 2.5% soot. In a) it can be seen that there is a dark wear scar with what appear to be lighter grooves in the micrograph. The SEM images are all secondary electron images. The profilometry in table 5.2 showed that the wear scars created a groove on the surface of the steel tappet but the SEM images and optical microscope images also show that there appears to be a transfer layer that is present. b) shows the patch of transferred material c) shows the edge of the groove.

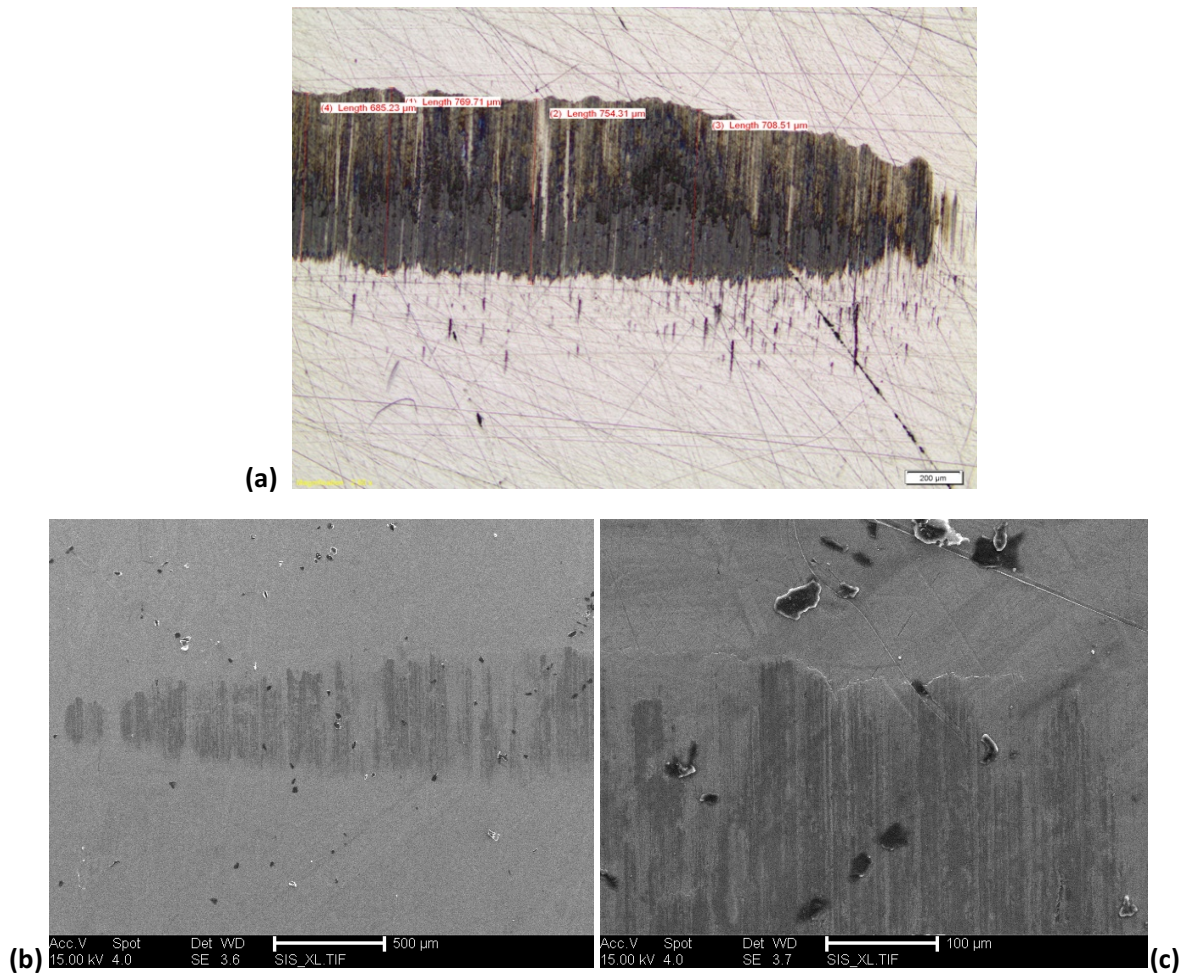


Figure 5.7 - Sample 2: Type of Oil: Castrol Q556, Flashing Oil, 400 CC Oil, 10 gr soot (2.5%).

Figure 5.8 shows; a) an optical micrograph, b) and c) SEM micrographs of the wear scars obtained for the sample 3 tested with virgin oil. In a) it can be seen that there is a dark wear scar with what appear to be lighter grooves in the micrograph. The SEM images are all secondary electron images. The profilometry in table 5.2 showed that the wear scars created a groove on the surface of the steel tappet but the SEM images and optical microscope images also show that there appears to be a transfer layer that is present. b) shows the patch of transferred material c) shows the edge of the groove.

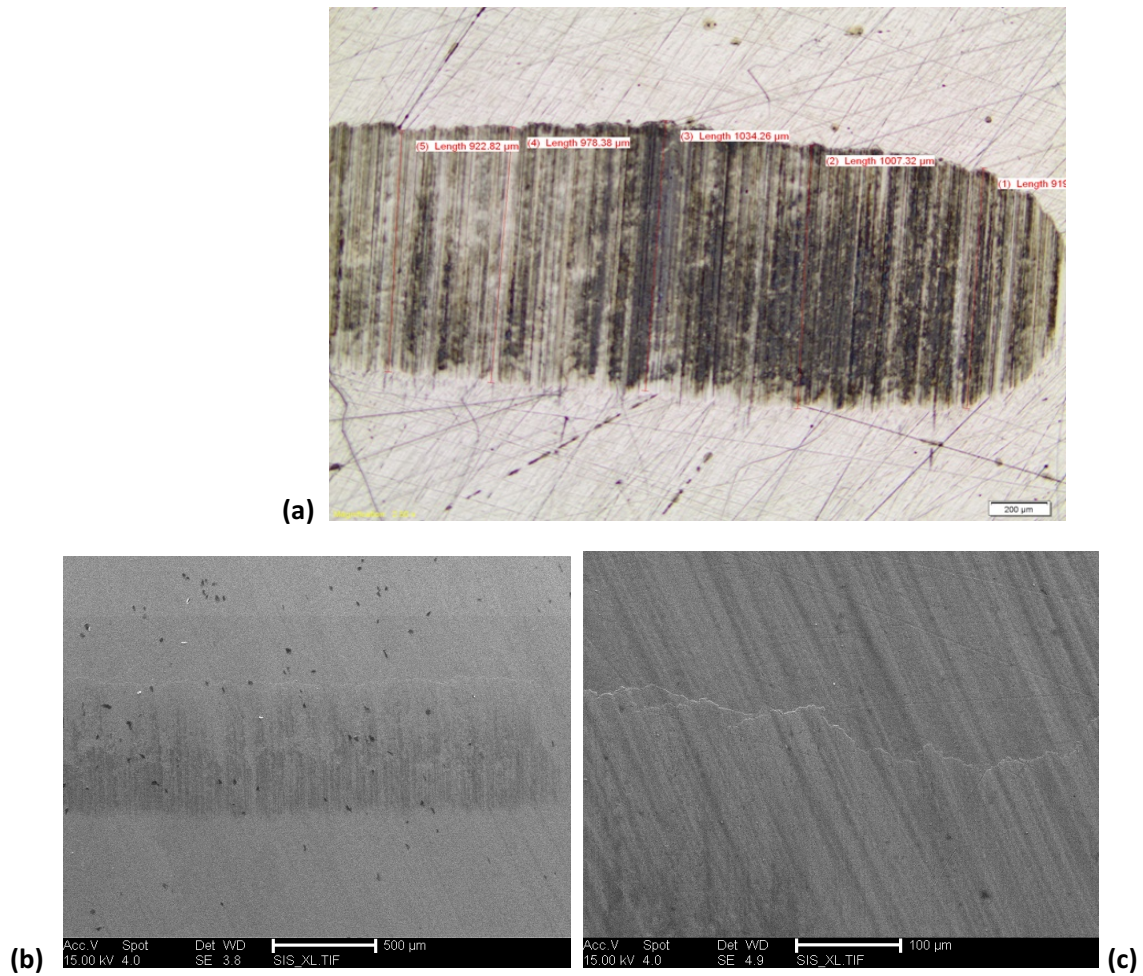


Figure 5.8 - Sample 3: Type of Oil: Castrol Q556, Flushing Oil, 400 CC Oil, No soot (Pure Oil)

SEM was used to investigate the surface morphology of each sample after wear tests. Following the SEM analysis which appeared to show a transfer layer, EDX analysis was used to determine the composition of the layer.

5.1.3 EDX Analysis

EDX analysis was used to determine the elemental composition of the worn surface layer for the samples. Different voltages were applied during the EDX analysing for recognizing the amount of the carbon in different

depth of the wear area. For each sample EDX analysis was repeated for a 10 minute acquisition time at the voltages 2 kV, 5 kV, 10 kV and 15 kV. The results are shown in the following pages.

Figures 5.9 to 5.17 show the EDX analysis for the different samples.

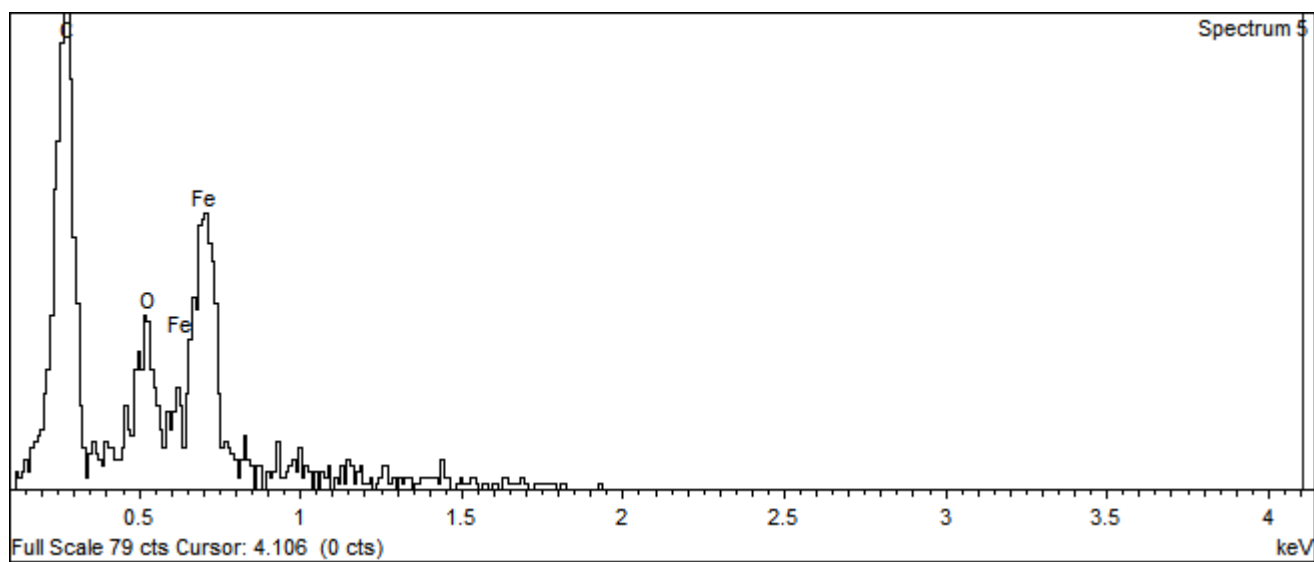
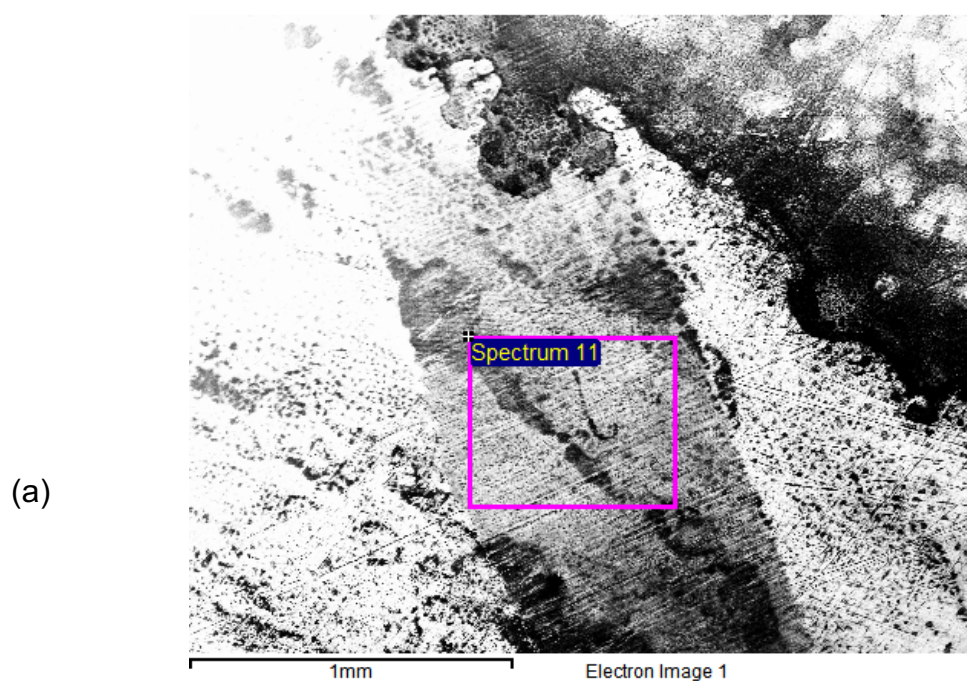
Figures 5.9 to 5.11 show the analysis at 2, 5 and 10 kV for sample 1.

Figures 5.12 to 5.14 show the analysis at 2, 5 and 10 kV for sample 2.

Figures 5.15 to 5.17 show the analysis at 2, 5 and 10 kV for sample 3.

In each case, the EDX spectra were acquired for 10 minute to allow sufficient energy for the analysis to be acquired.

EDX Sample 1, 2 kV, 10 Min



(b)

Figure 5.9- (a) spectrum sample one, 2 kV. (b) EDX sample one, soot contaminated oil 5%, 2 kV, 10 Min.

EDX Sample 1, 5 kV, 10 Min

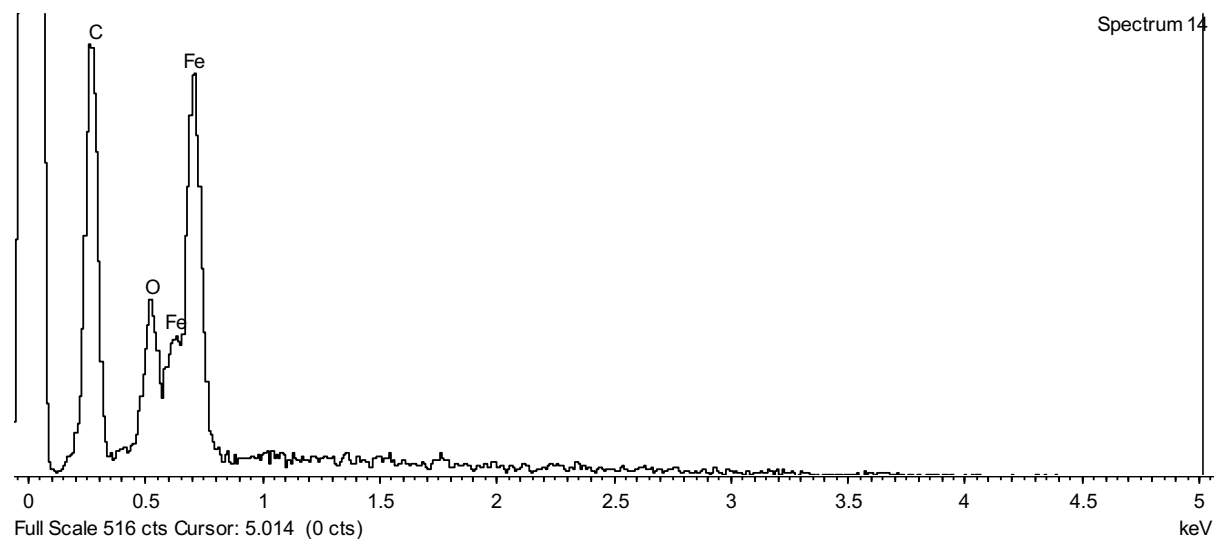
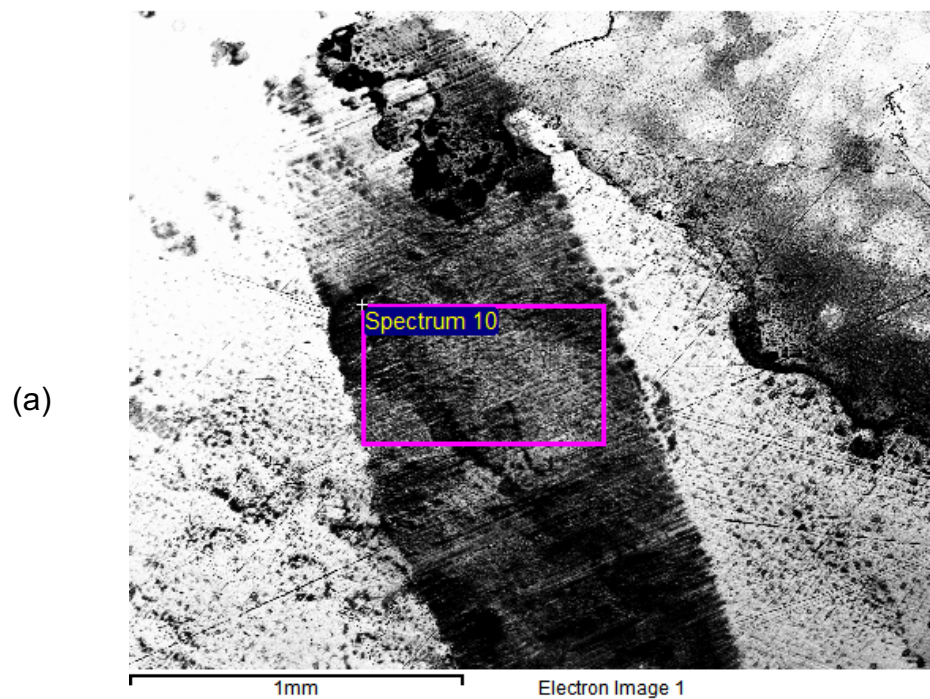
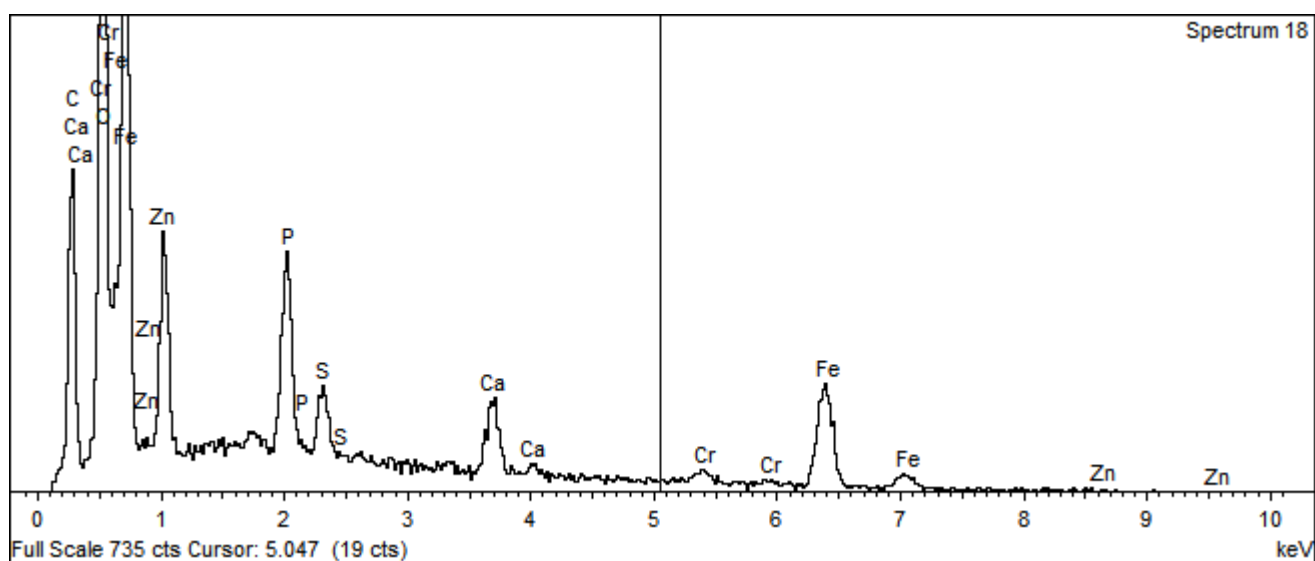
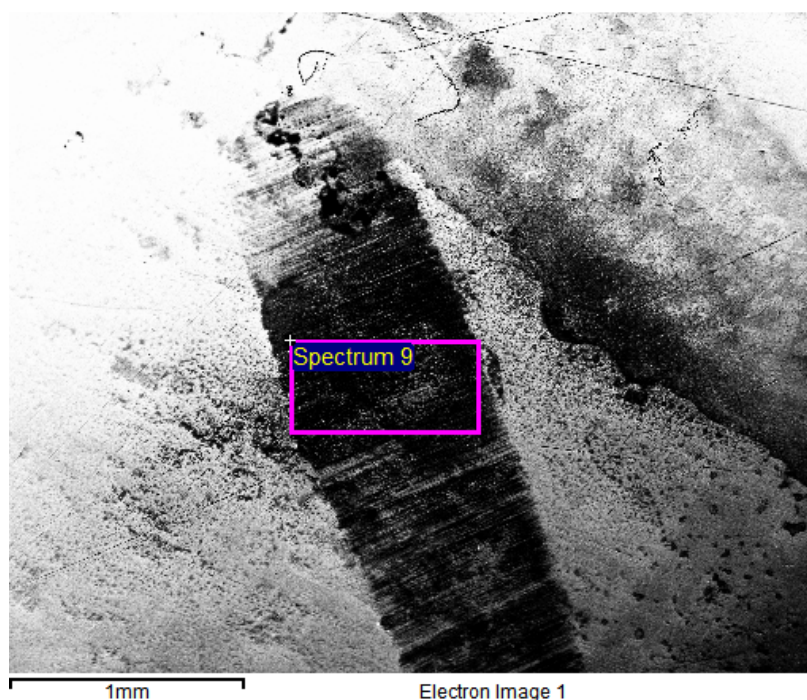


Figure 5.10 – (a) Spectrum sample one, 5 kV. (b) EDX sample one, soot contaminated oil 5%, 5 kV, 10 Min.

EDX Sample 1, 10 kV, 10 Min

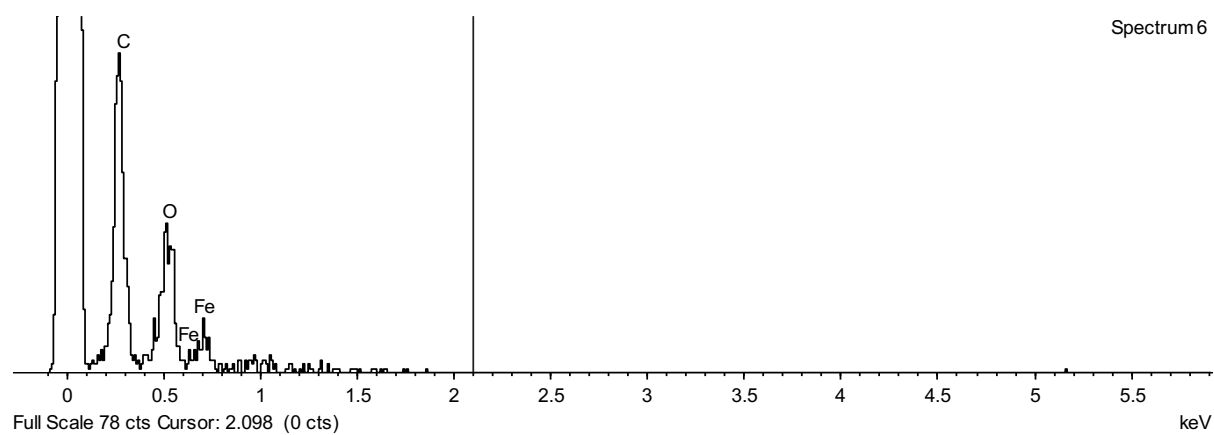
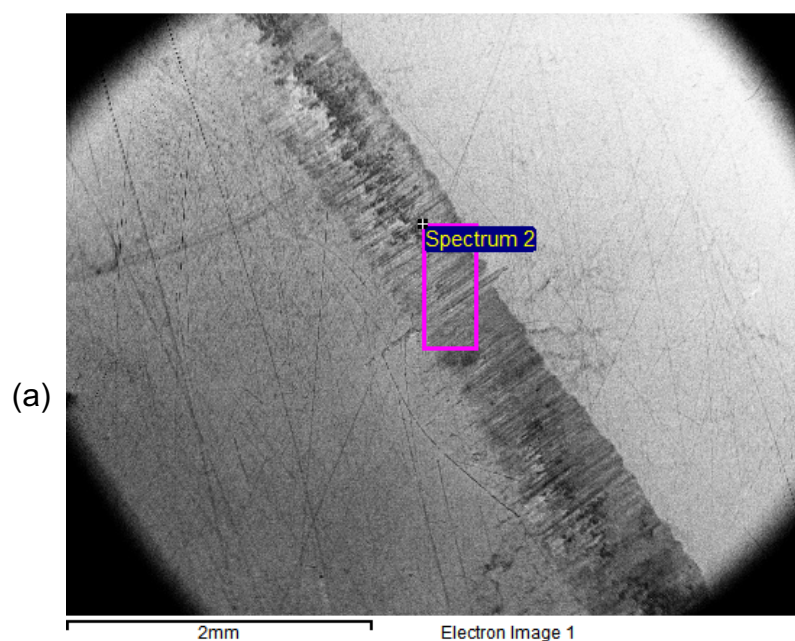
(a)



(b)

Figure 5.11 – (a) spectrum sample one, 10 kV. (b) EDX sample one, soot contaminated oil 5%, 10 kV, 10 Min.

EDX Sample 2, 2kV, 10 Min



(b)

Figure 5.12 – (a) spectrum sample two, 2 kV. (b) EDX sample two, soot contaminated oil 2.5%, 2 kV, 10 Min

EDX Sample 2, 5kV, 10 Min

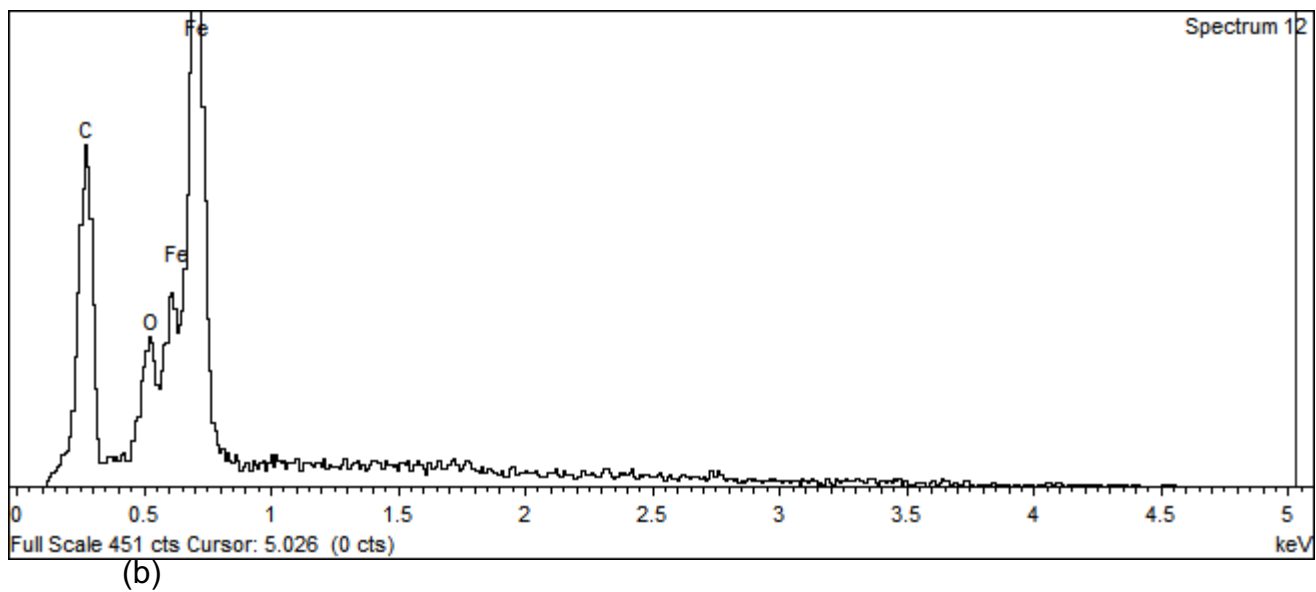
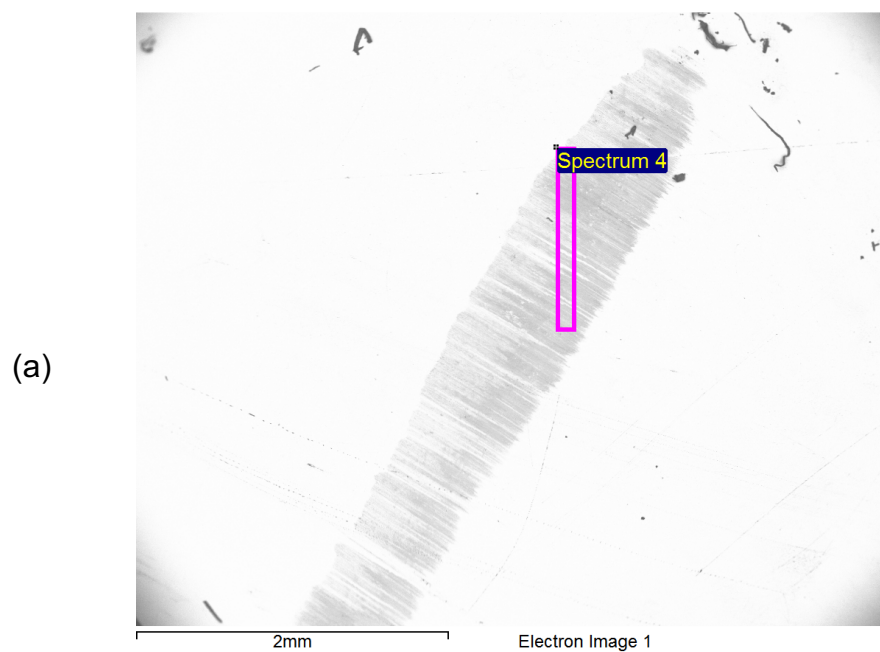
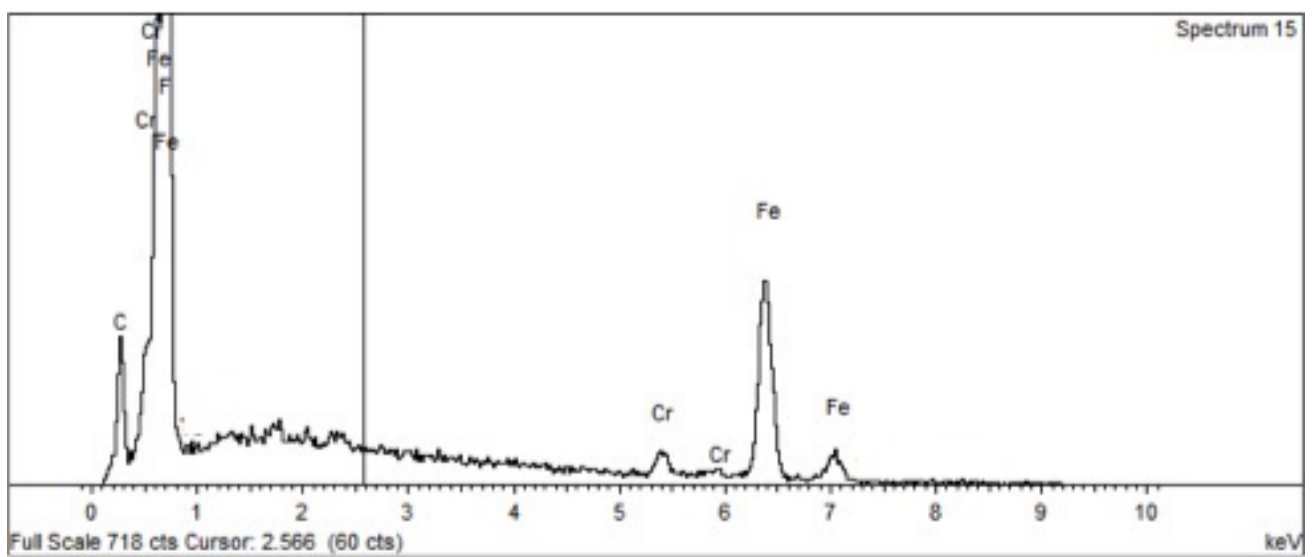
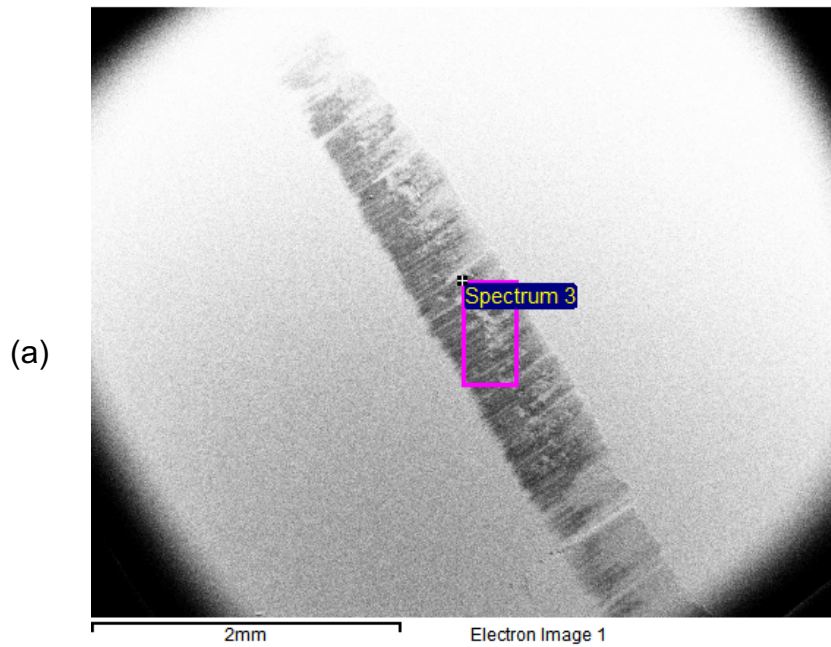


Figure 5.13 – (a) spectrum sample two, 5 kV. (b) EDX sample two, soot contaminated oil 2.5%, 5 kV, 10 Min.

EDX Sample 2, 10 kV, 10 Min

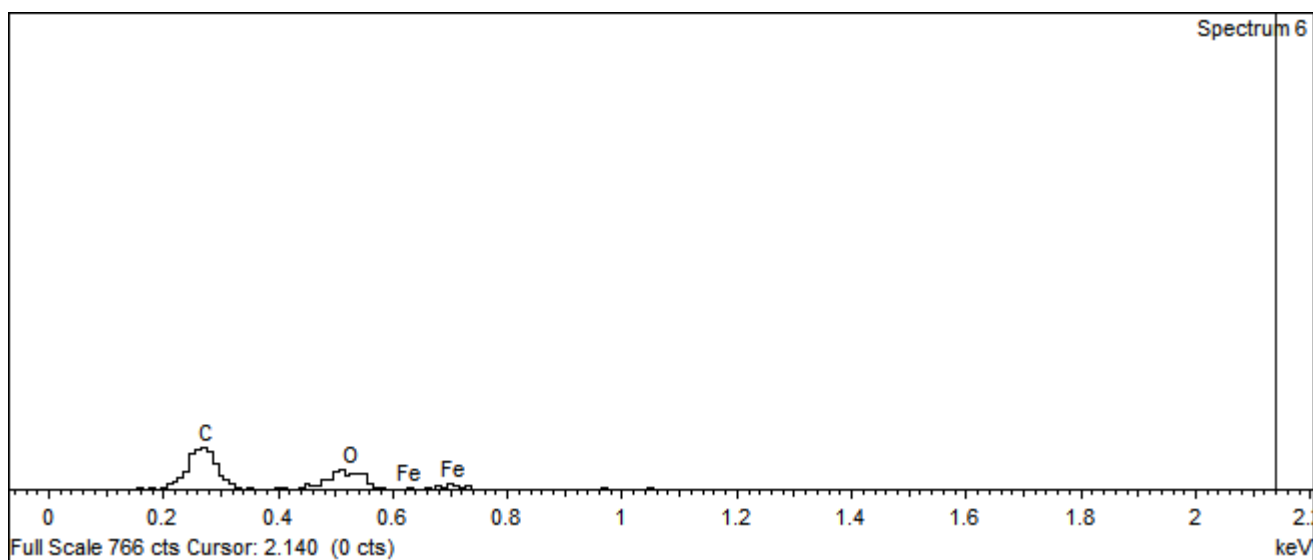
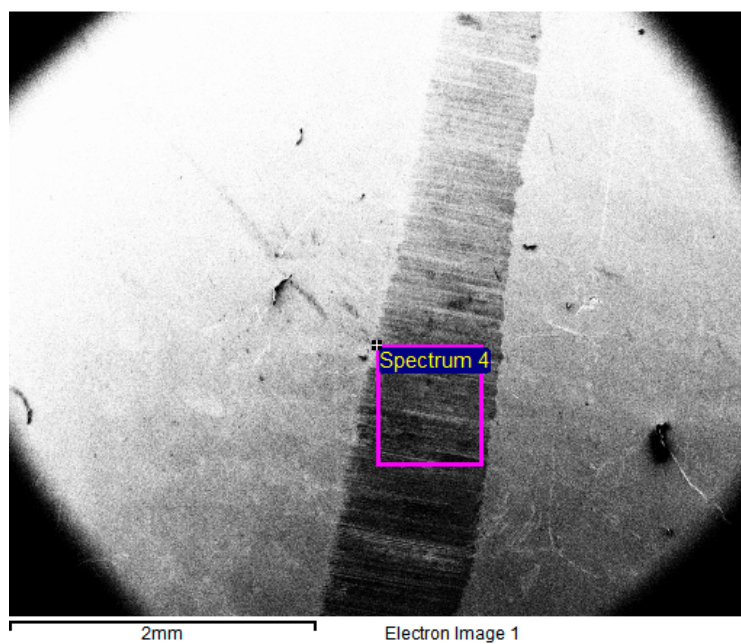


(b)

Figure 5.14 – (a) spectrum sample two, 10 kV. (b) EDX sample two, soot contaminated oil 2.5%, 10 kV, 10 Min.

EDX Sample 3, 2kV, 10 Min

(a)

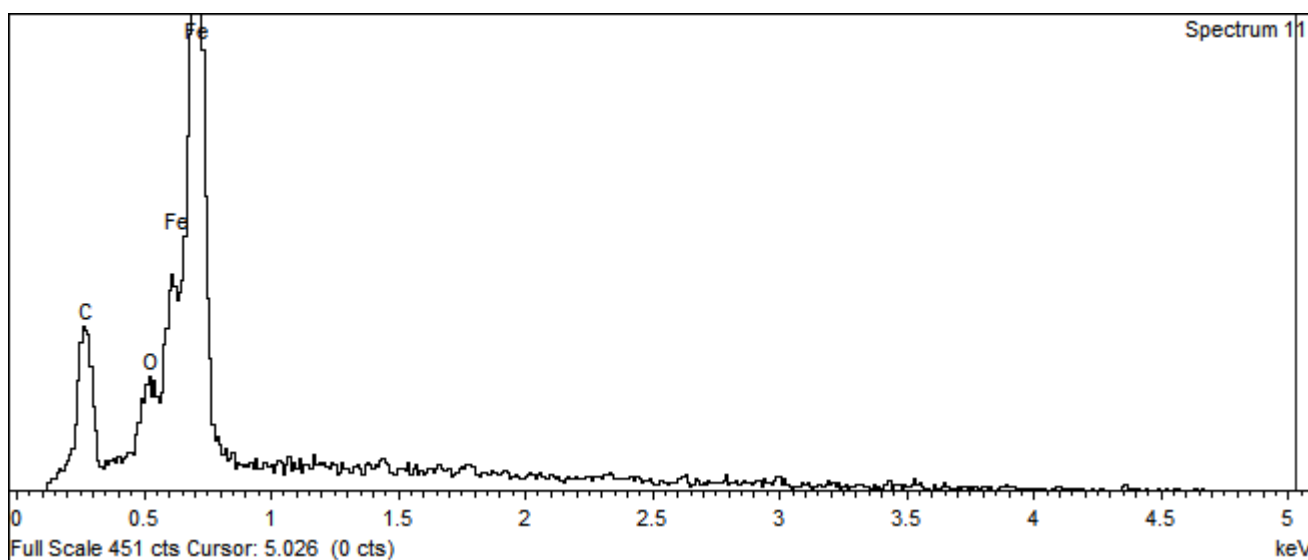
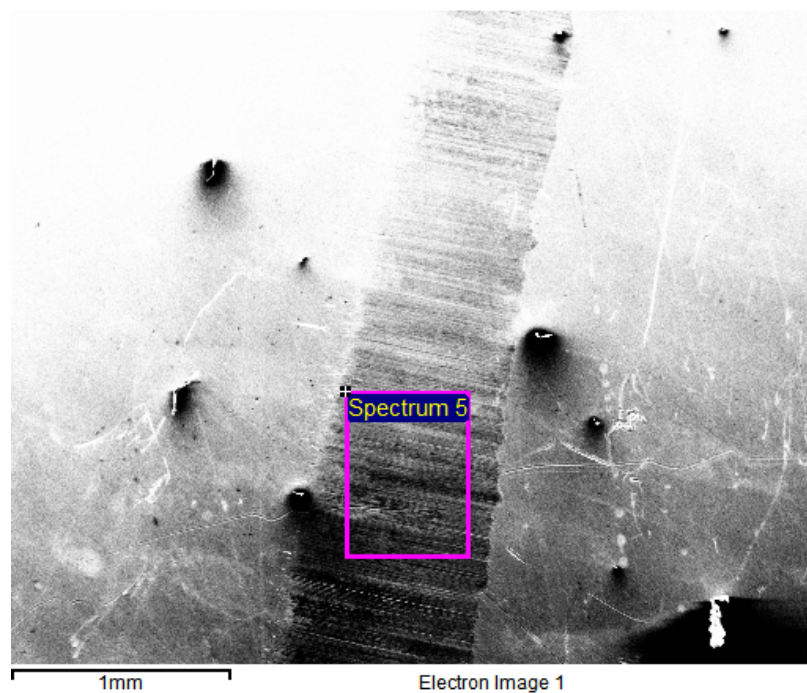


(b)

Figure 5.15 – (a) spectrum sample three, 2 kV. (b) EDX sample two, virgin oil, 2 kV, 10 Min.

EDX Sample 3, 5kV, 10 Min

(a)

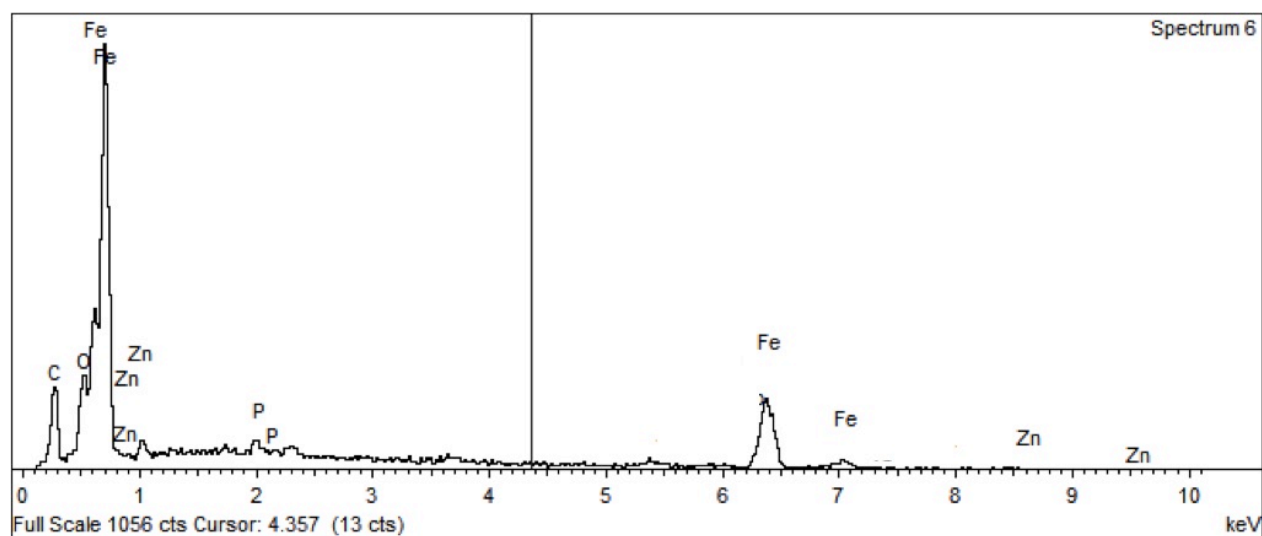
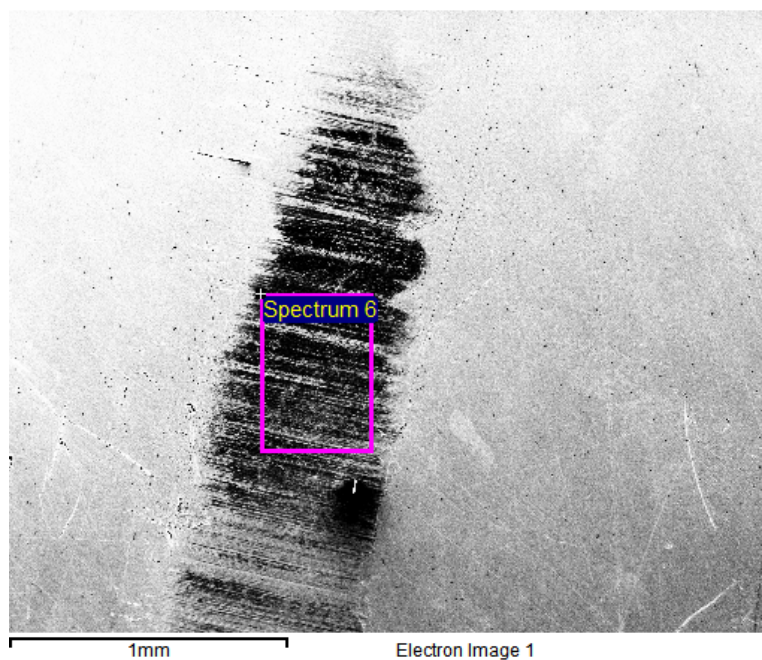


(b)

Figure 5.16 – (a) spectrum sample three, 5 kV. (b) EDX sample three, virgin oil, 5 kV, 10 Min.

EDX sample 3, 10 kV, 10 Min

(a)



(b)

Figure 5.17 – (a) spectrum sample three, 10 kV, 10 Min. (b) EDX sample three, virgin oil, 10 kV, 10 Min.

5.1.3.1 EDX Results

For studying the effect of soot (Carbon) appearance in the increasing of the wear on samples, EDX analysis has been conducted for three samples with soot contaminated oil 5%w, 2.5%w and the clean oil at different voltages such as; 2 kV, 5 kV and 10 kV. Tables 5.3 to 5.5 show the weight% of Carbon, Fe and Ca elements on the samples 1, 2 and 3 with different voltages.

EDX Sample 1, Soot contaminated oil 5%.

Voltage	Weight % C	Weight % Fe	Weight % Ca
2 kV	16.68	18.30	0.00
5 kV	6.6	24.51	4.08
10 kV	4.59	35.12	3.48

Table 5.3: The weight % of the Carbon in different voltages for sample one.

EDX Sample 2, Soot contaminated oil 2.5%.

Voltage	Weight % C	Weight % Fe	Weight % Ca
2 kV	7.49	47.49	0.00
5 kV	1.47	39.28	4.17
10 kV	2.82	36.59	3.45

Table 5.4: The weight % of the Carbon in different voltages for sample two.

EDX Sample 3, Clean Oil

Voltage	Weight % C	Weight % Fe	Weight % Ca
2 kV	3.77	66.99	0.00
5 kV	1.59	61.86	1.20
10 kV	1.45	44.19	4.08

Table 5.5: The weight % of the Carbon in different voltages for sample three.

Table 5.3 is clearly shows that the amount of carbon at 2 kV is 16 %w. The amount of carbon is sharply decreased to 6.6%w and 4.5 %w by increasing the voltage to 5 kV and 10kV. It is the same processes for two other samples with 2.5%w soot contaminated oil and the clean oil.

The results of these three tables clearly prove that the soot particles are gathered on the surface of the samples, where the oil was applied during the tests.

It should be noted that the quantitative analysis of light elements is not completely accurate and therefore the values in table 5.3 - 5.5 are indicative only but the results show that the amount of carbon debris transferred to the sample surfaces is considerably greater for the 5% soot contaminated oil.

5.2 Microscopy of Soot Particles

This section discusses the size and morphology of diesel particle soot and compares this to the soot generated by pure biodiesel (B100), 20% blend of biodiesel and diesel (B20) and pure diesel.

Soot particles derived from B100, B20 and diesel fuel were produced using a diesel engine type Petter PJ2, developing 18 HP when running at 1800 rpm, coupled to a Hamworthy two-stage air compressor (as described in Chapter 4). The engine was run at full load for a period of time, after which the soot particles were collected directly from inside of the soot catcher fitted to the exhaust.

To prepare the soot for the TEM analysis, a grid was used to hold the sample for analysis, but it is crucial that the soot is layered onto the grid as uniformly as possible and, most importantly, not too thickly. This is essential to ensure that the sample is electron transparent.

For ideal TEM analysis of the soot particles it is required that the collected material on the grid is in the range of picograms. In order to achieve this, the sample grids were prepared by placing them at the top of a vertical tube, through which a flow of pressurised air was passed. Soot placed in the lower part of the tube was rendered airborne when the air flow began and caused a fine powder of the soot to be caught on the TEM sample grids. The soot samples caught on the grids were analysed using a high resolution electron microscope (JEOL TEM-3010), operated at 200 keV using a LaB₆ filament. The magnification range used was between 5 and 1,000,000.

Figure 5.18 shows typical TEM micrographs for diesel, B20 and B100. From the microscope, it can be seen that all the soot particles examined were approximately spherical.

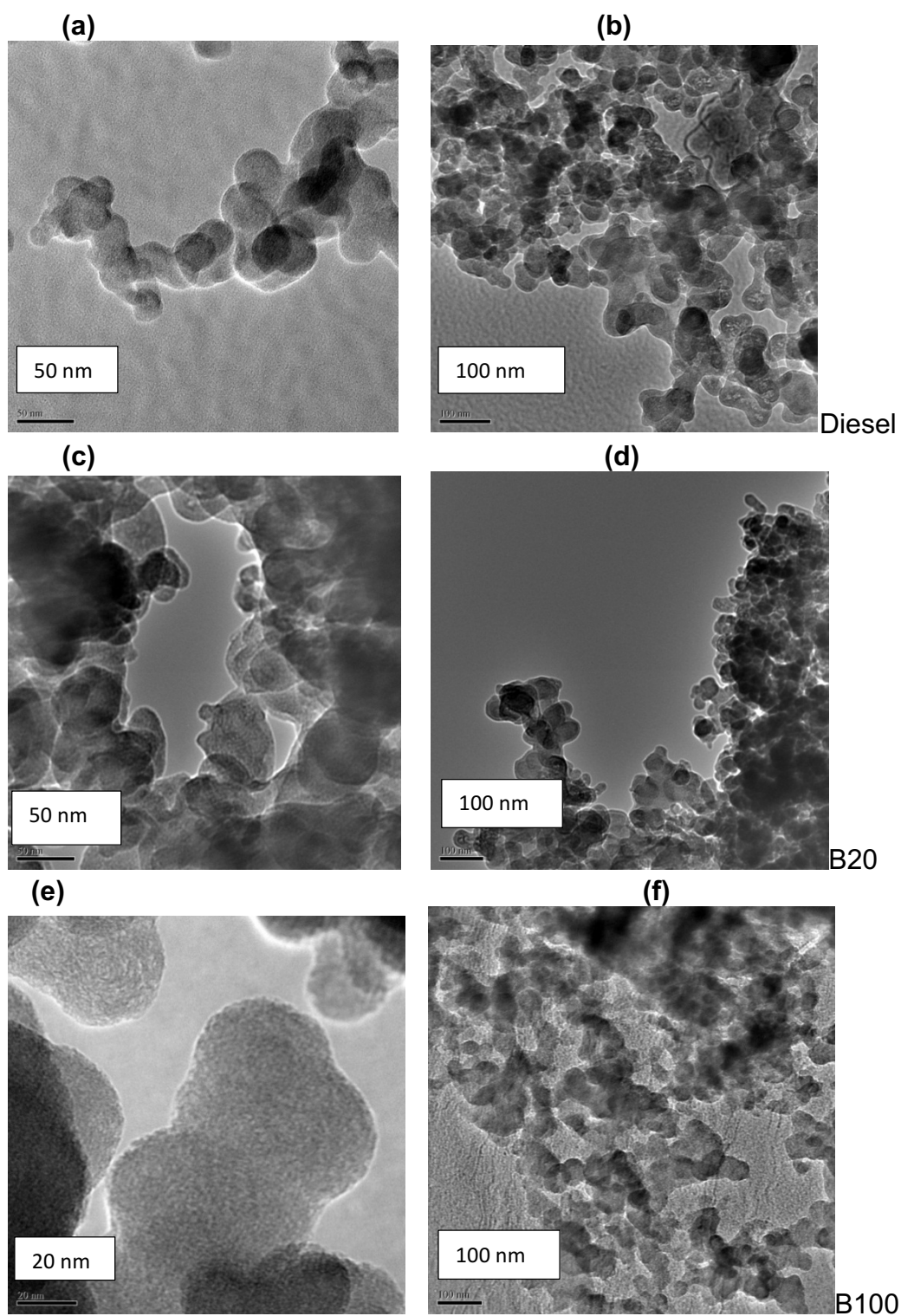


Figure 5.18 shows typical TEM micrographs for the (a) & (b) diesel, (c) & (d) B20 and (e) & (f) B100 particles.

It can be seen in these pictures that the soot particles ranged in size. The particles are all approximately spherical, although some have agglomerated. These agglomerates consist of small units known as primary soot particles. They should be ideally spherical, but appear in most cases irregularly shaped. Agglomeration occurs when individual or primary soot particles stick together to form large groups of primary particles. Changing the fuel blends used caused the formation of soot agglomerates with different size and shape. The degree of particle density per aggregate was significantly increased when pure diesel was used and finding electron transparent areas on the TEM grid was more challenging. TEM images of soot from burning B100 fuel showed aggregates of less than 1 μm in length and composed of as many as 25 particles. The single particles are approximately spherical and have a nearly uniform diameter. It is well established that the small diameter single particles tend to be present in the higher blends of biodiesel. The single or precursor particles have an average diameter of 40 nm. The diameter of a population of approximately 20 primary particles was measured to determine the mean primary particle diameter. Several micrographs were collected from the surface of the grids. Figure 5.19 shows the soot particles size produced from different biodiesel blends.

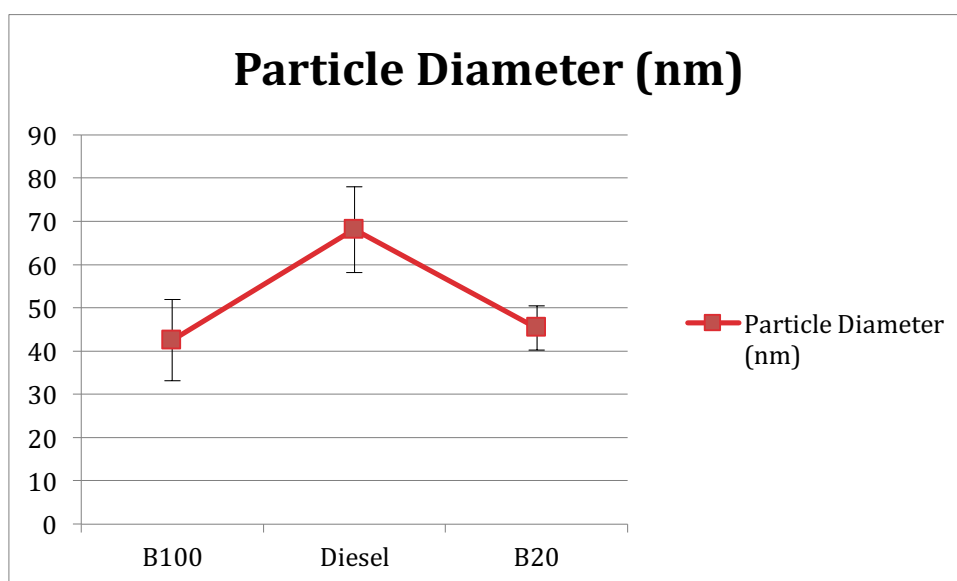


Figure 5.19 – Average soot particles diameters for different fuels.

The soot particles in all the samples tended to agglomerate which makes detailed analysis difficult.

However, for each sample a number of un-agglomerated particles could be found.

The diameter of these particles was determined by fitting a circle to the particle using Image J software. Approximately 20 particles were analysed for each sample.

The average diameter is shown in figure 5.19 which shows the mean particle diameter and error bars of +/- the standard deviation.

It can be seen from the figure that the average diameter of the pure diesel soot is approximately 70 nm whereas for the B20 and B100, the mean diameter was approximately 40 nm.

The biodiesels therefore generate finer distributions of soot particles. It is interesting that for the B20, which was approximately 20% biodiesel and

80% diesel, the soot particles produced are still very fine as compared to the pure diesel.

Figures 5.20 to 5.24 are TEM images, which are showing the soot particles shapes and agglomerations, which are produced from different biodiesel blends.

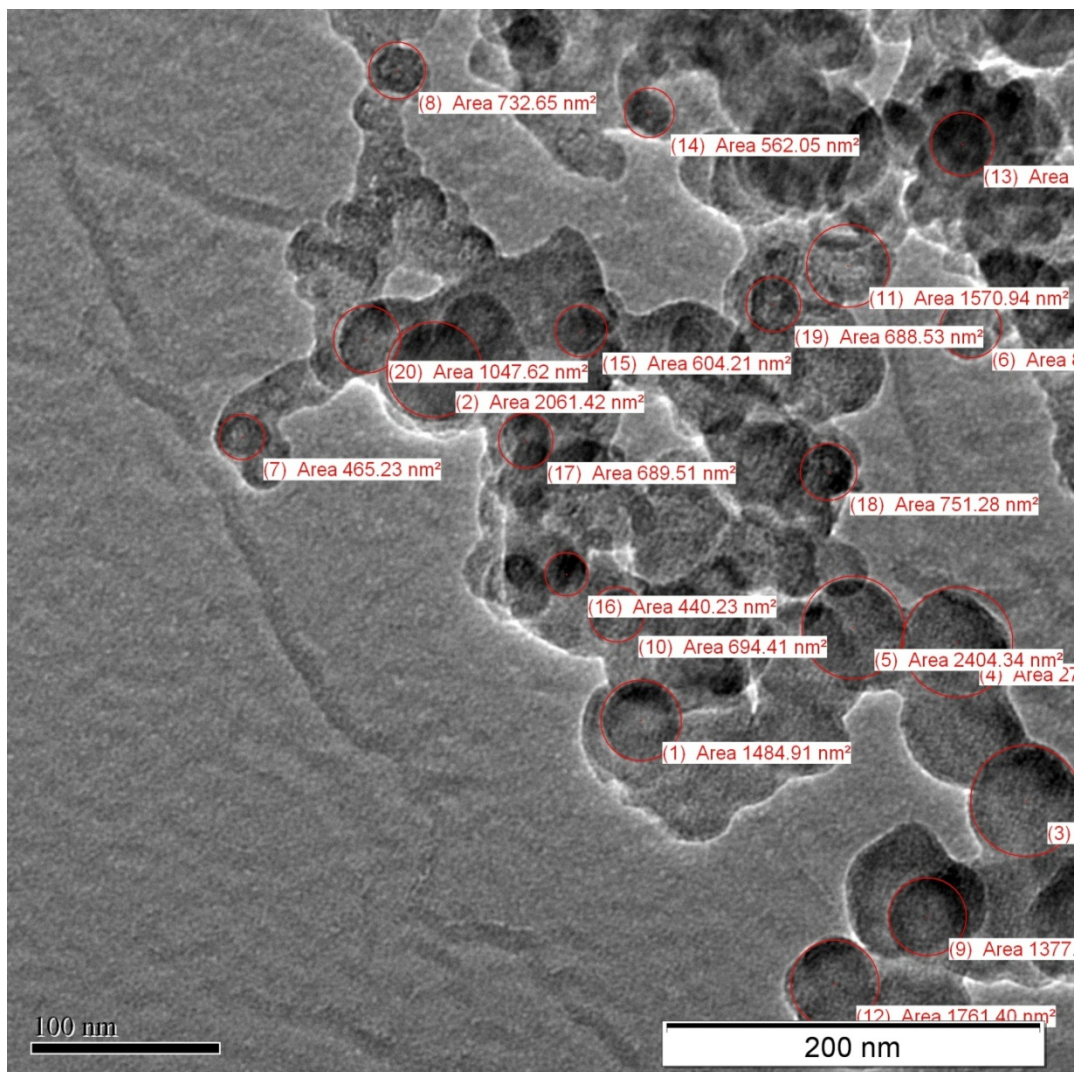


Figure 5.20 – TEM image for sieved soot particles of B20 by 53 Mic sieve.

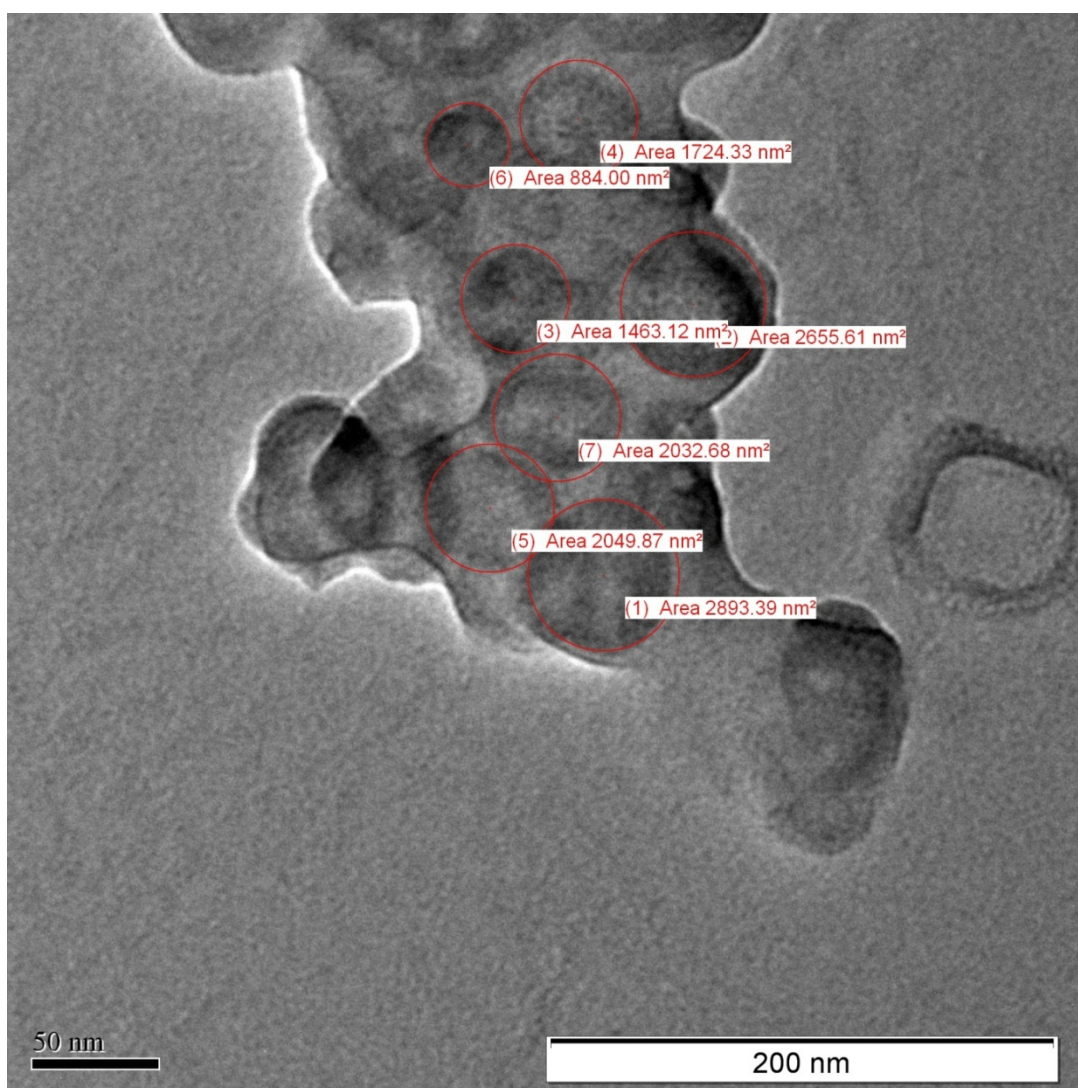


Figure 5.21 – TEM image for sieved soot particles of B100 by 53 Mic sieve.

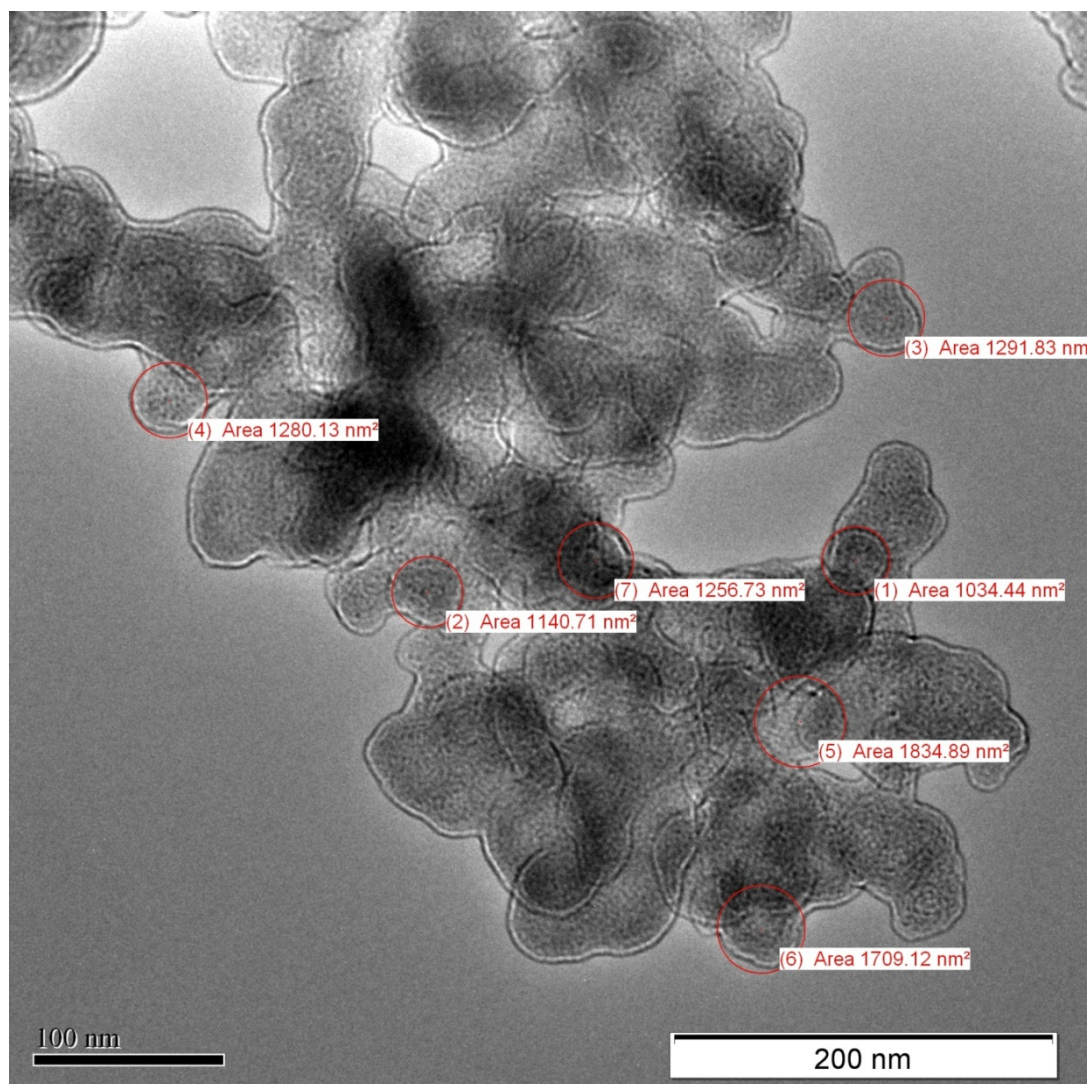


Figure 5.22 – TEM image for sieved soot particles of B100 by 200 Mic sieve.

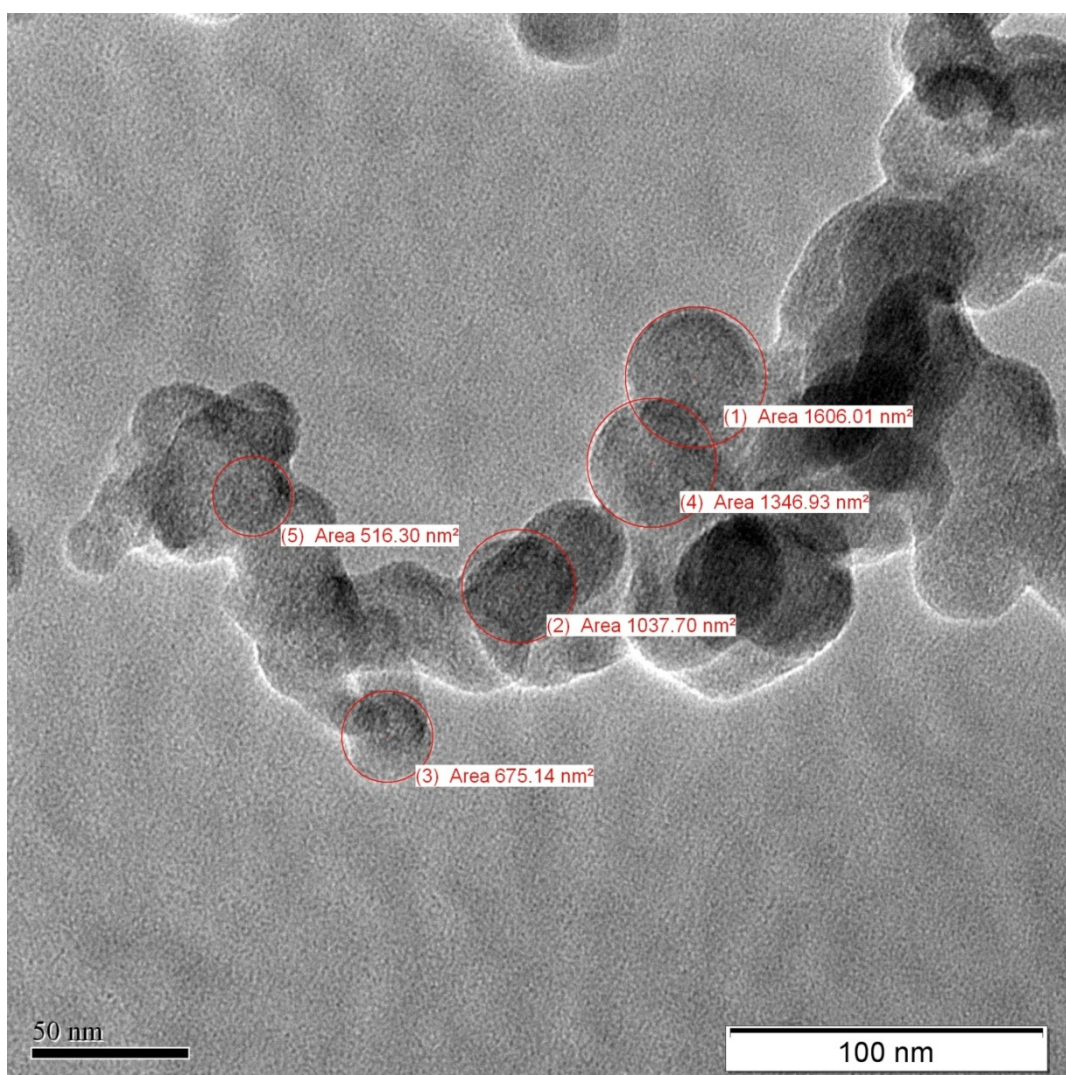


Figure 5.23 – TEM image for sieved soot particles of Diesel by 53 Mic sieve.

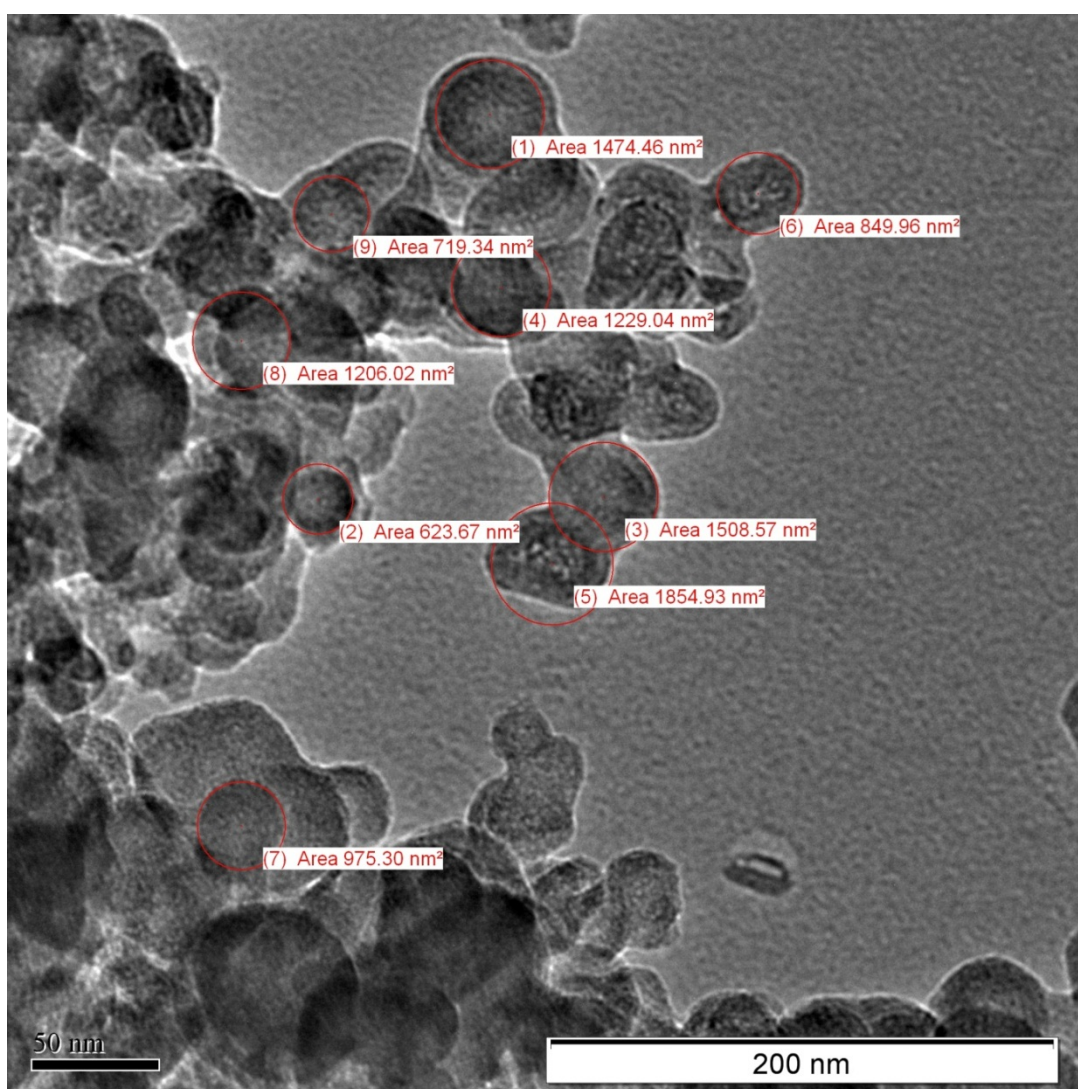


Figure 5.24 – TEM image for sieved soot particles of Diesel by 200 Mic sieve.

In this chapter, soot particulate was characterized in terms of size, distribution and shape of the agglomerates. Nanoparticle tracking analysis was employed for the measurement of soot agglomerates size from the soot contaminated oils. Meanwhile, soot samples were drawn from the exhaust manifold and prepared for transmission electron microscopy (TEM) by using special grids. TEM allows measuring the particle shape

and size of soot agglomerated as well as the characteristics of individual particles.

However, TEM imaging of soot contaminated oils is more challenging. The soot particles were found to be spherical in shape with some irregularities, although some amorphous layers were also clearly visible. Lubricant oil is a contaminant for the electron microscope and leads to instability under the electron beam which made the analysis challenging.

Although only a small proportion of the soot formed in the combustion chamber transfers to the engine oil, it contributes to the lubricant degradation. This is certainly a new challenge for the modern engines as soot contaminated oil raises concerns upon wear and engine durability.

It is well established that oil thickening has a complex dependence on soot. Various investigators have shown that diesel soot contaminated in oil increases engine wear rates.

Soot agglomerates extracted from an indirect injection stationary diesel engine slow speed have been characterised for the first time, with the aim of assessing size, distribution and shape.

The following chapter will discuss the corrosion behavior of different biodiesel blends and the virgin diesel fuel in contacts of the 3 major metallic alloys, which are widely used in diesel engine components and specially are the components which are in direct contact with the engine fuel.

CHAPTER 6

6. Corrosion

6.1 An investigation of the corrosion behaviour of biodiesel B100 on metallic materials

The corrosive characteristics of biodiesel compared to diesel fuel is an important factor when investigating the performance of different engine components, such as a fuel injection system, that are in long-term contact with biodiesel. In this chapter, the corrosion behaviour of biodiesel when in contact with five different metallic alloys including: copper, brass, Al1050, Al7075 and mild steel, is investigated.

The aim of this chapter is to describe the experimental investigation of the corrosion behaviours of above metals in contact with biodiesel B100 to investigate the effects of these metals on the biodiesel degradation process, and also the physical and chemical changes in biodiesel.

These metals have been selected for the tests because they are widely used in different engine components, for example: the production of fuel injection parts such as fuel pump, injectors, fuel filters and fuel delivery valves, and also in some piston assemblies. All of these parts, with their different metallic structures, result in different chemical interactions and degradation when in contact with biodiesel.

The biodiesel B100 used in this study was supplied by Biofuel Refineries Ltd, Buckinghamshire, England. Fuel analyses have been prepared by Oil Check Laboratory Services Ltd, Doncaster, South Yorkshire.

6.2 Immersion experiments

The behaviour of B100 over a period of 270 hours exposed to coupons of Al 1050 series Alloy, Al 7075 alloy, mild steel, 70:30 brass and copper. The coupons were polished to 6 μm diamond finish, washed with methylated spirit, dried, and weighed. The Al1050 series alloy was not polished as it was too soft. Temperature was maintained at 25, 80, 90, 100, 110 and 120 °C. At each temperature, a control B100 with no immersion was also studied, hereafter referred to as “blank”. The B100 in each experiment was sampled at 48, 100, 150, 200 and 270 h and examined by GCMS for composition. Time was limited to 270 h by availability of space. The experimental set up for each experiment is shown in figure 6.1. At the end of the experiment each coupon was washed with methylated spirits and dried thoroughly before weighing and calculating mass loss. The morphology of the coupons was examined using SEM/EDX (FEI Quanta 650).

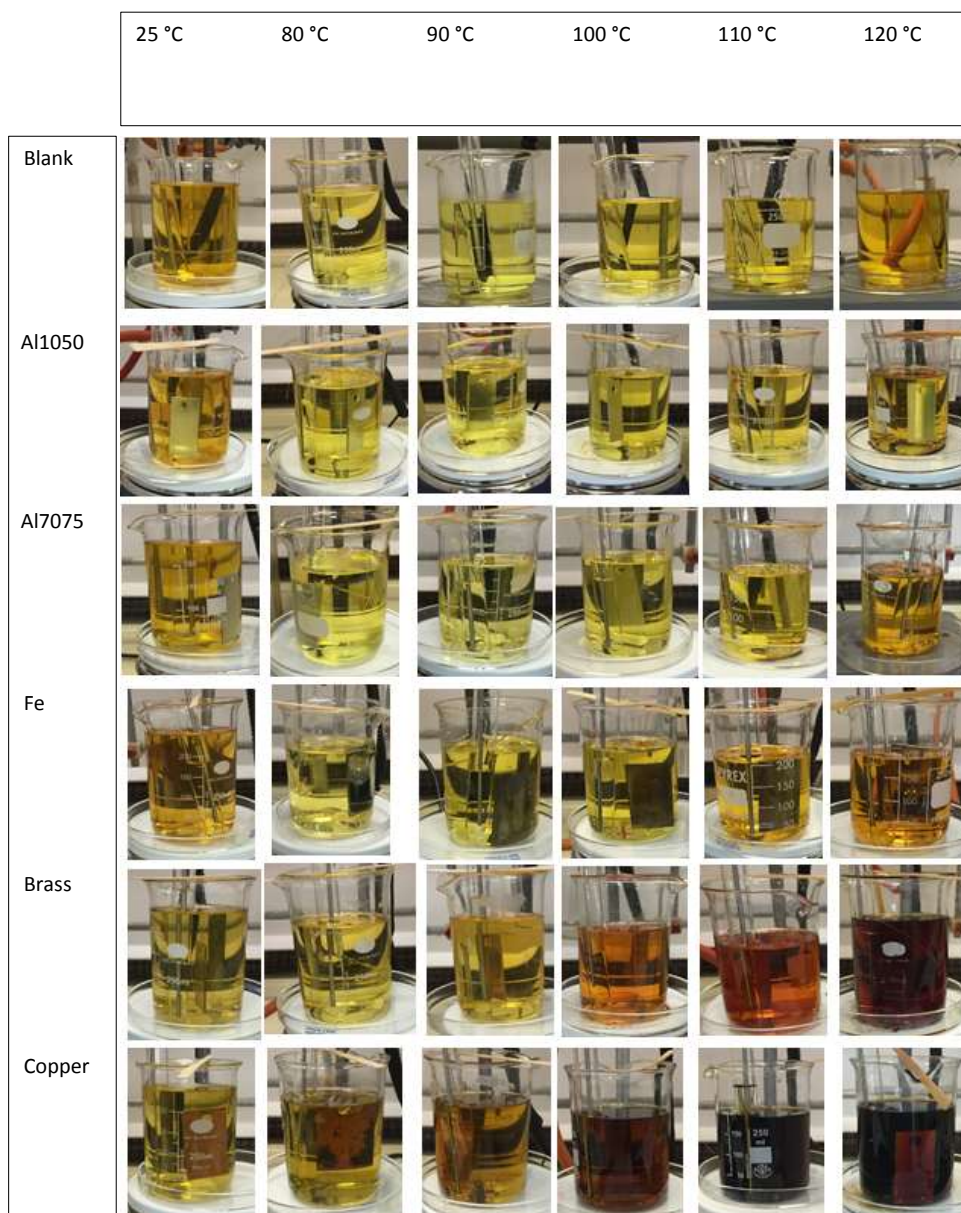


Figure 6.1. Composite image showing photographs of all experiments after 270 hours.

6.2.1 GC/MS

The B100 was sampled at intervals as indicated previously and analysed using GC/MS (Perkin-Elmer Turbomass GCMS). Two dilutions were used: 0.5% in CCl₄ to see the major components of the B100 and a 5% dilution in CCl₄ – which allowed identification of trace components. This is normal practice when there is a great discrepancy in concentration between reactants and products. The more dilute solution is used to separate the more concentrated reactants on the column but the products are too dilute and give a weak signal making identification very difficult. At the less dilute solution the reactants are too concentrated and do not separate properly, making identification impossible, however, the products of any reaction are in sufficient concentration to enable partial identification at least. CCl₄ is used for its excellent ability as a solvent. Given the relatively short time of the experiments, any reaction products were likely to be low in concentration, necessitating this dual dilution approach.

6.2.2 SEM/EDX

All metal coupons were dried at 50 °C for 100 h before examination in FEI Quanta 650 Scanning Electron Microscope. Images were recorded in SE mode at 100x, 1000x and 5000x magnification. In addition, any sites of particular interest were also subjected to further examination. Secondary electron imaging at low (2 kV) and high (20 kV) accelerating voltage, EDX and dot mapping, were employed to examine corrosion products and surface morphology.

6.2.3 ICP

At the end of the experiments, the B100 was sampled and analysed by ICP. Data for metal ion concentration, total acid number (TAN), viscosity and corrosion rates were recorded.

6.3 Results

Figure 6.1 shows photographs of all samples after 270h exposure. There is an obvious colour change at higher temperature for all samples and this is affected by the presence and type of metal. Al1050 and Al7075 show a slight darkening at 120 °C as does the control blank sample. With Fe the darkening begins at 110 °C and is more pronounced at 120 °C. With brass, the change to a darker colour is seen from 90 °C onwards and with Cu, all temperatures exhibited a noticeable colour change.

GCMS 0.5% dilution – traces are given in figure 6.2.a-b. Figure 6.2a shows the trace for unreacted biodiesel at 25 °C for 270h compared to traces for all metal coupons under similar conditions. Figure 6.2.b shows the trace for unreacted biodiesel at 120 °C and 25 °C for 270h compared to traces for all metal coupons under 120 °C conditions.

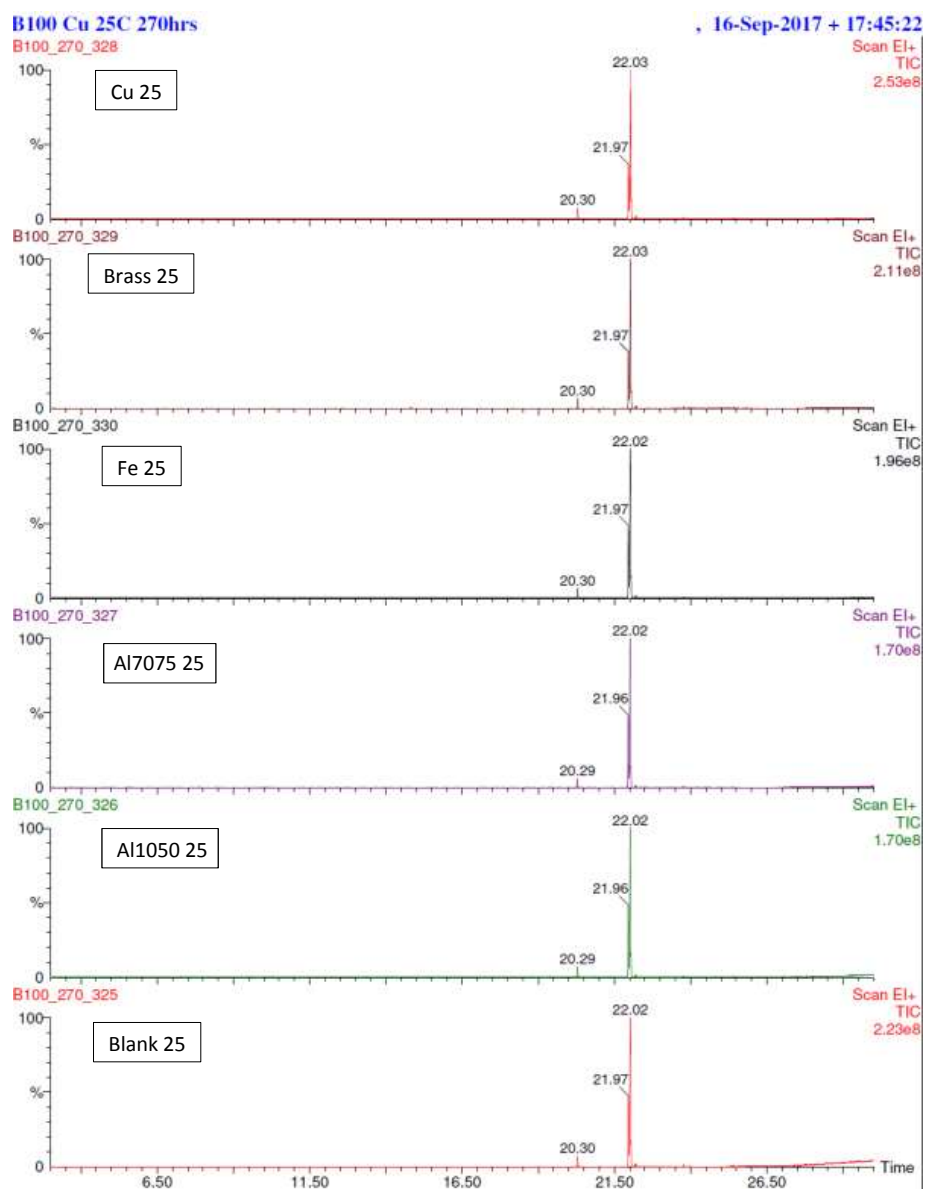


Figure 6.2.a GC-MS traces for all samples at 25 °C for 270 hours, 0.5% dilution, showing main components.

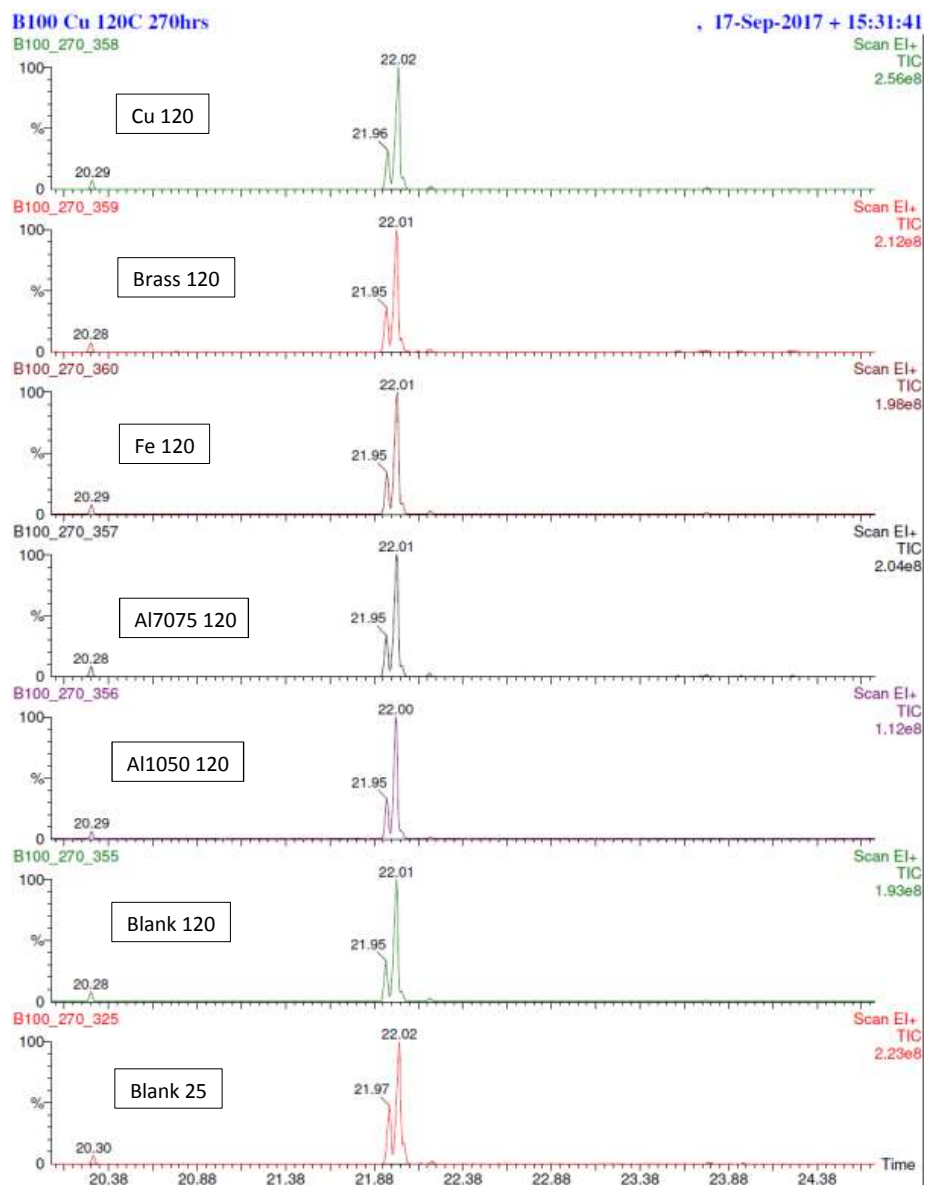


Figure 6.2.b GC-MS traces for all samples at 120 °C for 270 hours, 0.5% dilution, showing main components.

The unreacted biodiesel shows 4 main components. These were identified using the NIST database software as 16.0, 18.2, 18.1 and 18.0 methyl esters as shown in Table 6.1. The relative quantities of these constituents were calculated for B100 from relative chromatogram areas as is standard practice for GC/MS.

Table 6.1 Four Main Components of B100 Biodiesel

Time / minutes		Formula	Name	Relative fraction / %
20.30	16.0	C ₁₇ H ₃₄ O ₂	Hexadecanoic acid methyl ester	4
21.97	18.2	C ₁₉ H ₃₄ O ₂	9,12 Octadecenoic acid (Z,Z) methyl ester	29
22.03	18.1	C ₁₉ H ₃₆ O ₂	9 Octadecenoic acid (Z) methyl ester	66
22.06	18.0	C ₁₉ H ₃₈ O ₂	Octadecanoic acid methyl ester	1

The samples were weighed before and after exposure and these results are recorded in Table 6.2.

Table 6.2 Mass (grams) of Coupons Before and After B100 Exposure Tests at Different Temperatures

	25 °C	80 °C	90 °C	100 °C	110 °C	120 °C
Al1050 start	3.8661	3.8093	3.9730	3.8622	3.8719	3.8169
Al1050 end	3.8661	3.8093	3.9730	3.8622	3.8719	3.8168

Al7075 start	4.1851	4.3898	4.6084	4.1332	4.2795	3.7379
Al7075 end	4.1851	4.3898	4.6084	4.1332	4.2795	3.7378
Mild Steel start	22.9898	23.9934	23.4669	23.4799	23.1454	22.7522
Mild Steel end	22.9898	23.9934	23.4667	23.4799	23.1454	22.7522
brass start	19.4908	19.2119	19.5705	19.7595	19.9998	18.4541
brass end	19.4902	19.2118	19.5701	19.7589	19.9939	18.4500
Cu start	13.7443	15.0791	13.2769	13.0400	13.3520	13.2858
Cu end	13.7363	15.0703	13.2576	13.0065	13.3222	13.2840

Cu showed the greatest extent of reaction by weight loss and visible colour changes. Therefore to determine the extent of greatest change of starting materials the 4 main constituents were calculated relative to each other for 4 of the B100 baths. These were blank 25 °C, blank 120 °C, Cu 25 °C and Cu 120 °C. All other systems were deemed to fall within these extremes.

Graphs of the relative correlations of 16.0, 18.2, 18.1 and 18.2 were plotted and are show in figure 6.3.

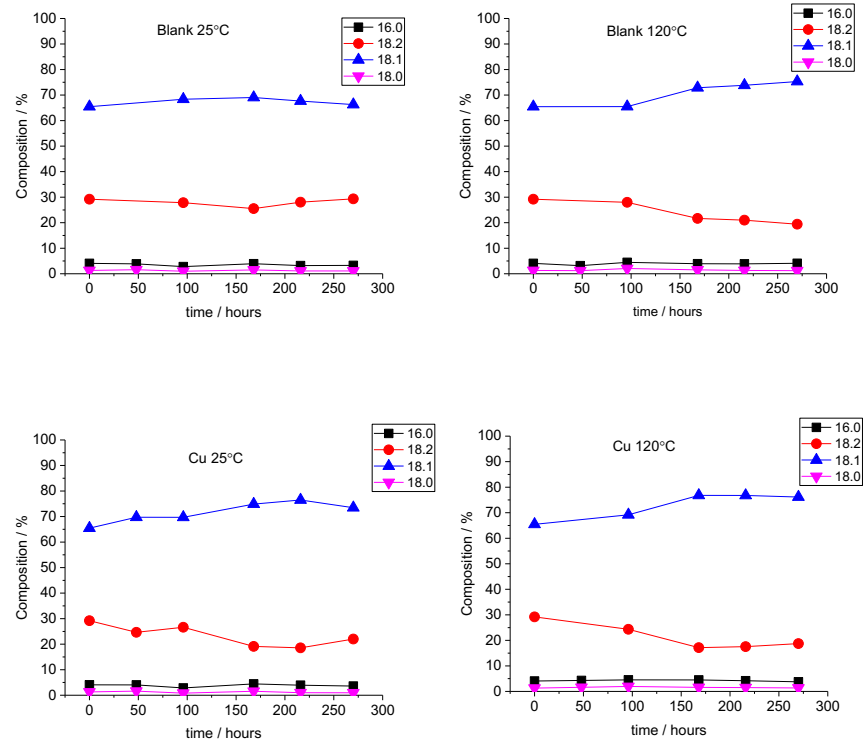


Figure 6.3. Plots of 4 main components of B100 composition with time for Blank and Copper exposure tests at 25 and 120 °C.

At 25 °C the Blank control B100 is not exposed to any metal, only the atmosphere and the concentration of each component remains constant throughout. At 120 °C there is a slight decrease in the level of 18.2 relative to other components with the B100 exposed only to the atmosphere. With Cu at 25 °C and 120 °C there is a notable decrease in the level of 18.2 compared to other components. At 120 °C with Cu the 18.2 drops from ~30% to ~20%.

To examine the products of the reaction in the B100, it was necessary to perform GC/MS at a more concentrated solution of 5% with CCl₄.

The samples at 120 °C and 270 h showed greatest extent of reaction - for clarity the GCMS for Blank 25 °C, and blank, Al1050, Al7075, Fe, brass and Cu at 120 °C are shown in figure 6.4.a.

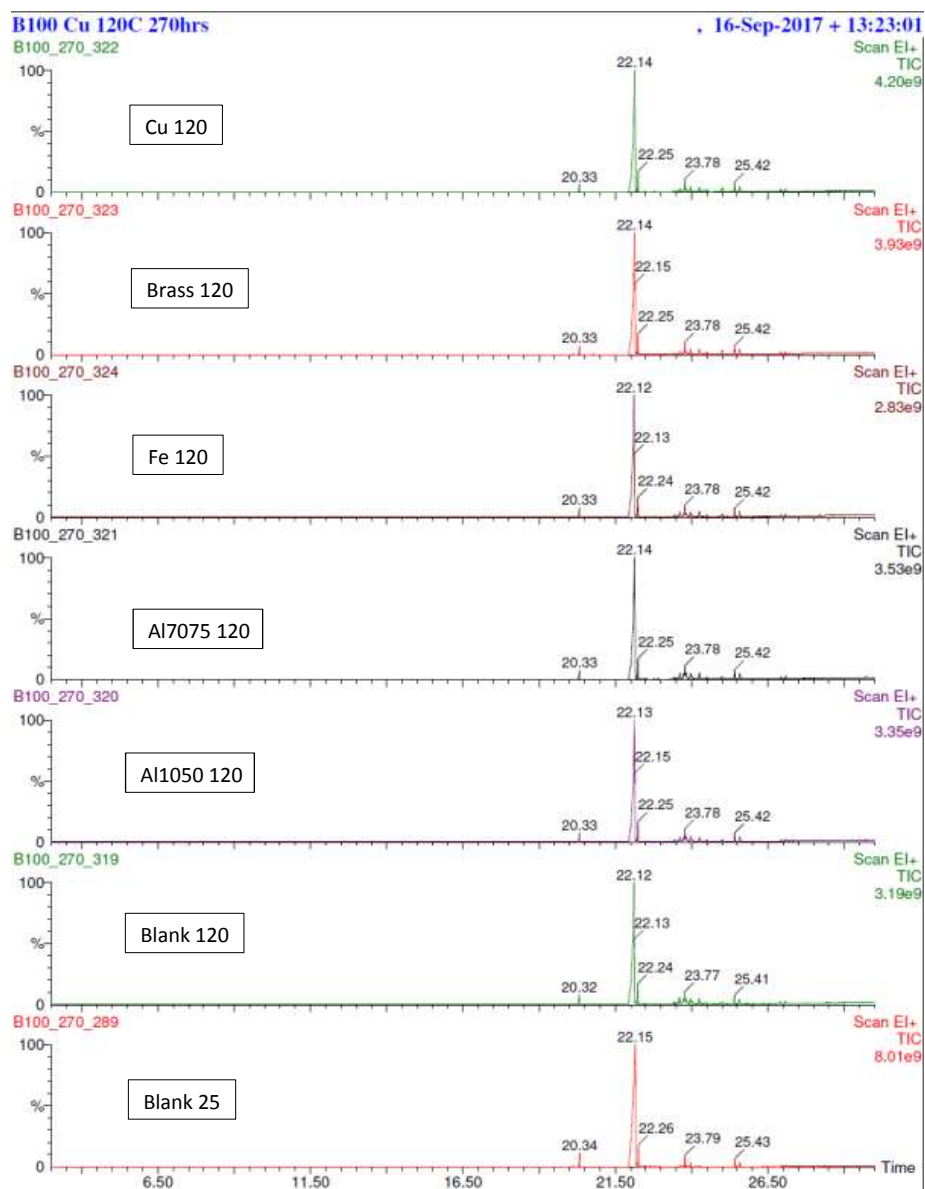


Figure 6.4.a GC-MS traces for all samples at 120 °C for 270 hours, 5% dilution, showing main components.

It is of note that the peaks for 18.2 and 18.1 become merged at this concentration, necessitating the 0.5% dilution. The benefits of this concentration are visible after 23 minutes where a cluster of new peaks are visible after exposure tests up to 26 minutes.

To examine the minor constituents of all samples each was examined at 5% concentration. Since the highest temperature gave the most change, the trace composition of each metallic type at 120 °C is examined in the regions avoiding the main 16.0, 18.2, 18.1 and 18.0 peaks since these dwarf all other components which are less than 1%.

Figure 6.4.b shows the trace from 0-20 minutes for blank 25 °C, blank, Al1050, Al7075, Fe, brass and Cu at 120 °C. Figure 6.4.c shows the trace from 20.4-22 minutes for blank 25 °C, blank, Al1050, Al7075, Fe, brass and Cu at 120 °C. Figure 4d) shows the trace from 23-26 minutes for blank 25 °C, blank, Al1050, Al7075, Fe, brass and Cu at 120 °C.

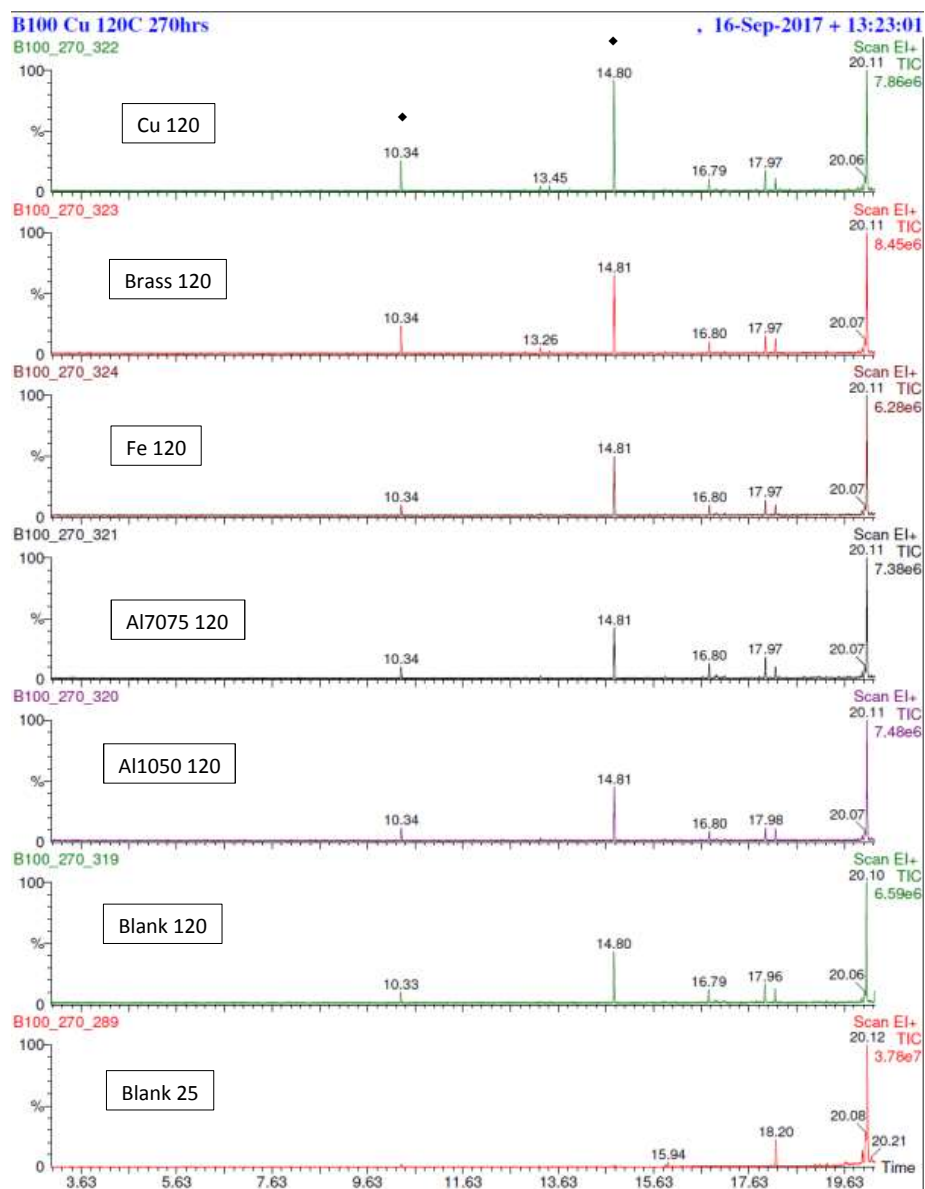


Figure 6.4.b GC-MS traces for all samples at 120 °C for 270 hours, 5% dilution, showing close up of 0-20 minute region.

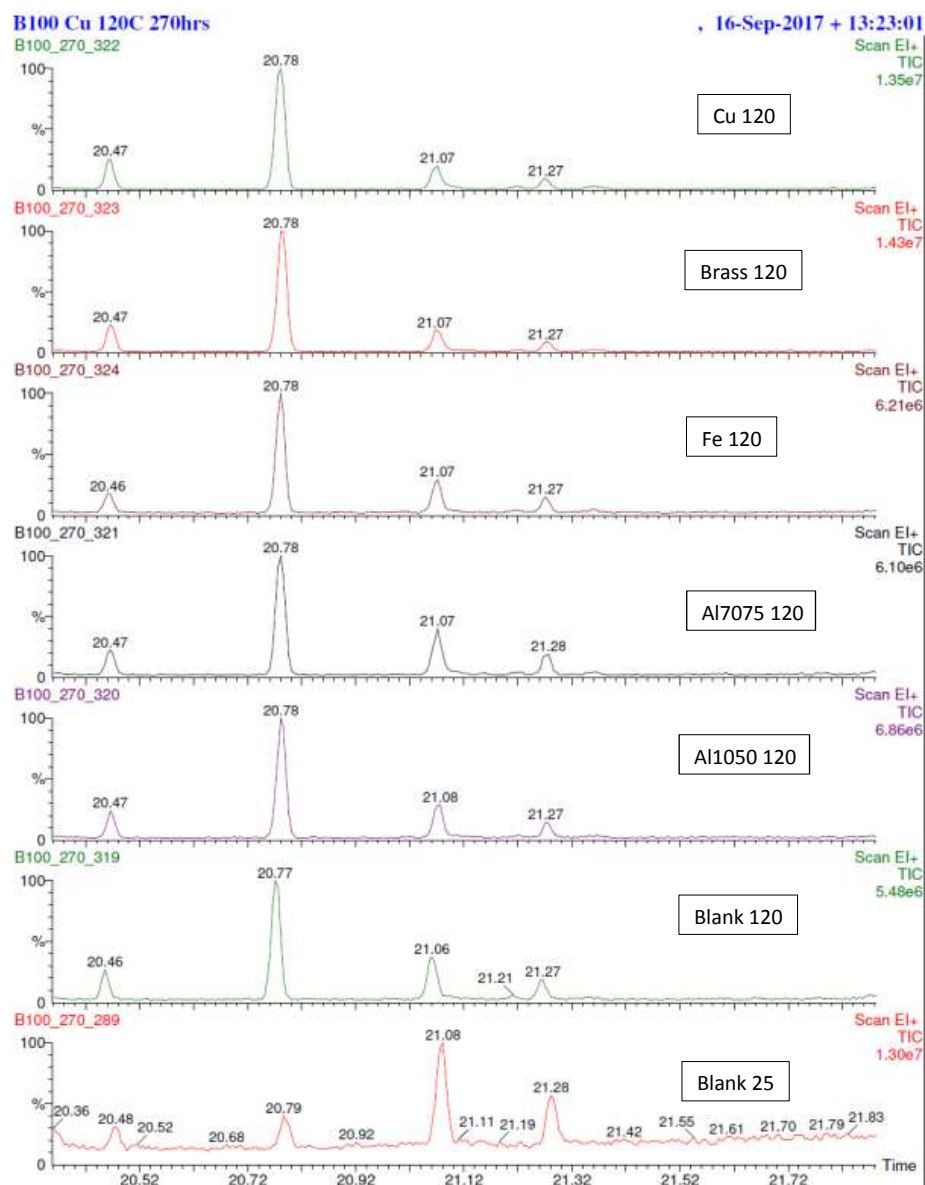


Figure 6.4.c GC-MS traces for all samples at 120 °C for 270 hours, 5% dilution, showing close up of 20-22 minute region.

In the 0-20 min region, the blank 25 °C sample shows peaks at 15.94, 18.2 and 20.12 minutes. All other samples at 120 °C showed more peaks in this region. Peak intensities were smaller for blank, Al1050, Al7075 and Fe samples, however for brass and Cu the peak intensities at 10.34 minutes and 14.8 minutes increased and small peaks were observed at 13.45 and 13.26 minutes.

The GCMS traces at 120 °C are all similar, however brass and Cu samples showed increased peak height at 10.34, 14.81, 24.95 and 25.02 minutes. See figures 6.4.b and 6.4.d. There is a decrease in intensity of the peak at ~24 min for brass and Cu. See Figure 6.4.d. Figure 6.4.e shows the 23-26 minute region for the blank samples at all temperatures, after 270 hours. Extra peaks are found for samples at 80-120 °C. Figure 6.4.f shows the 23-26 minute region for Al1050. No extra peaks are seen at 25 °C but they are visible at 80-120 °C. Figure 6.4.g shows the 23-26 minute region for Al7075. No extra peaks are seen at 25 °C but they are visible at 80-120 °C. Figure 6.4.h shows the 23-26 minute region for mild steel. No extra peaks are seen at 25 °C but they are visible at 80-120 °C. Figure 6.4.i shows the 23-26 minute region for brass. Extra peaks are observable at all temperatures compared to B100 at 25 °C. Figure 6.4.j shows the 23-26 minute region for Cu. Extra peaks are observable at all temperatures compared to B100 at 25 °C.

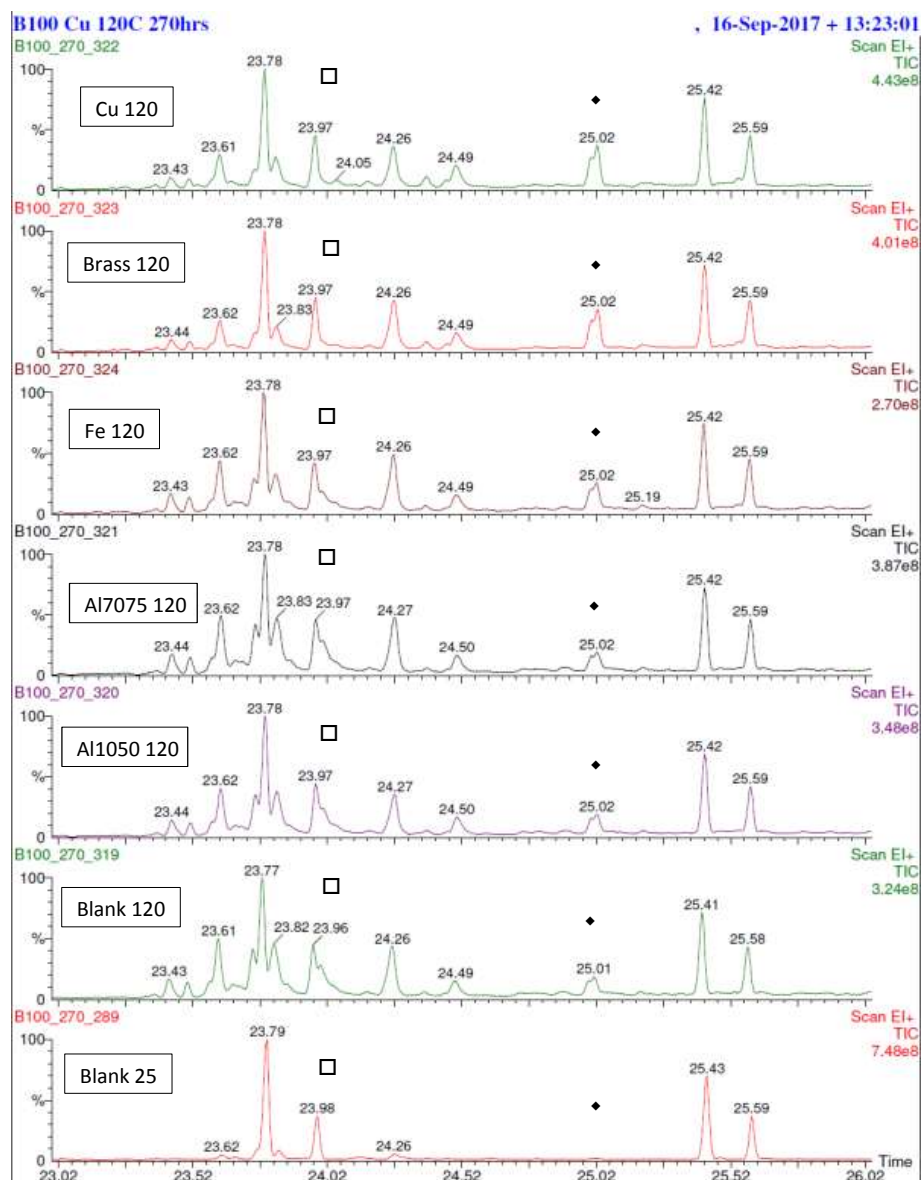


Figure 6.4.d GC-MS traces for all samples at 120 °C for 270 hours, 5% dilution, showing close up of 23-26 minute region.

♦ = doublet at ~ 25 min furyl group and propenyl group.

□ = shoulder at ~24 min could be a diol.

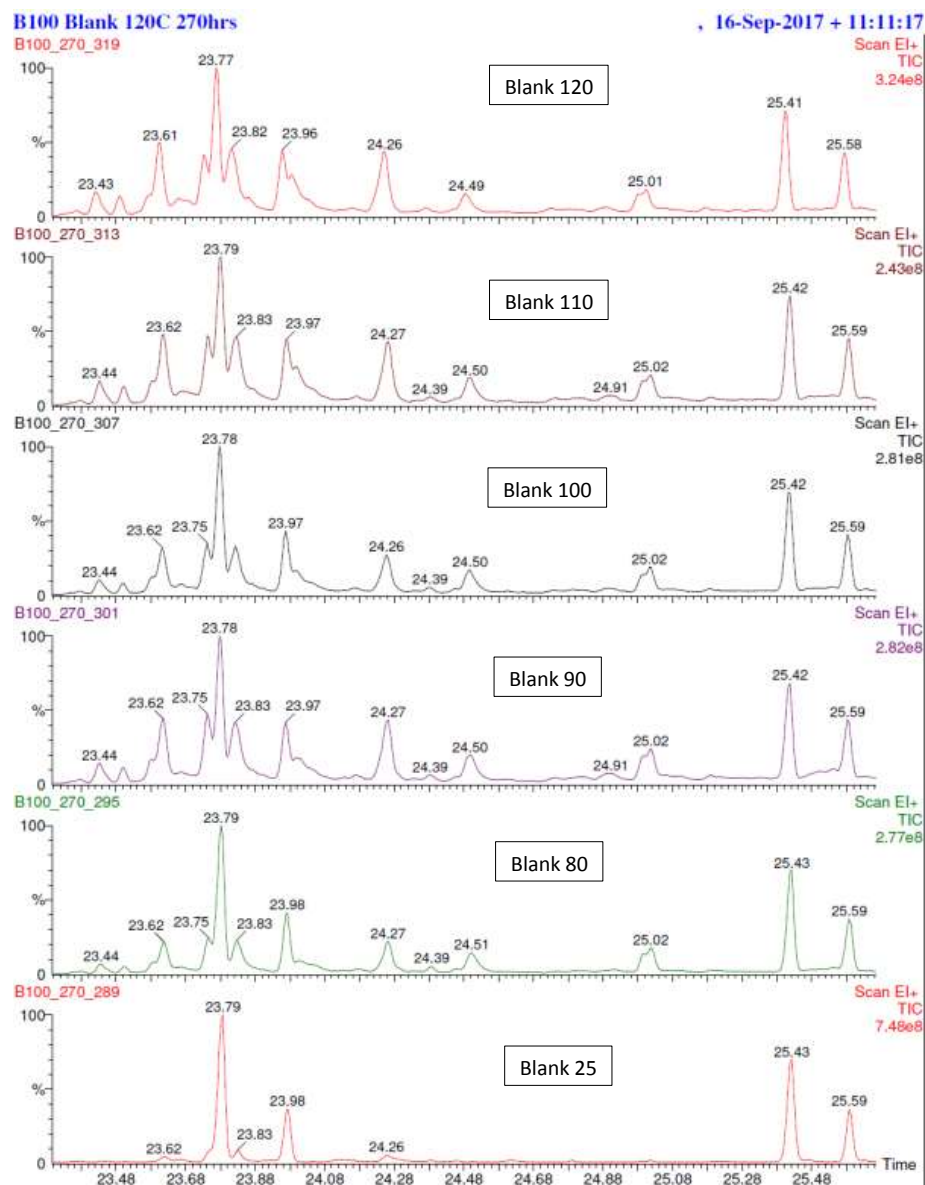


Figure 6.4.e GC-MS traces for Blank control experiments 25- 120 °C for 270 hours, 5% dilution, showing close up of 23-26 minute region.

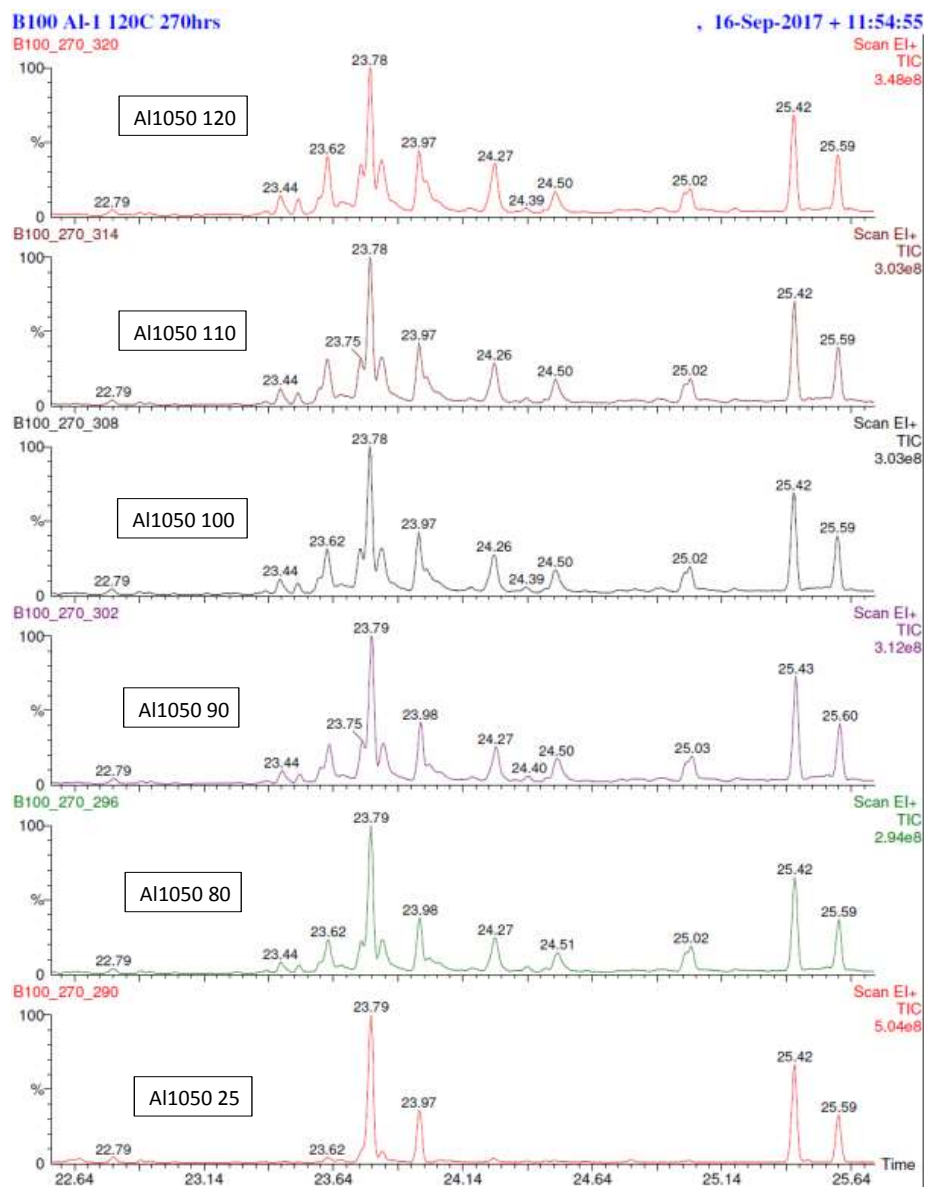


Figure 6.4.f GC-MS traces for Al1050 experiments 25- 120 °C for 270 hours, 5% dilution, showing close up of 23-26 minute region.

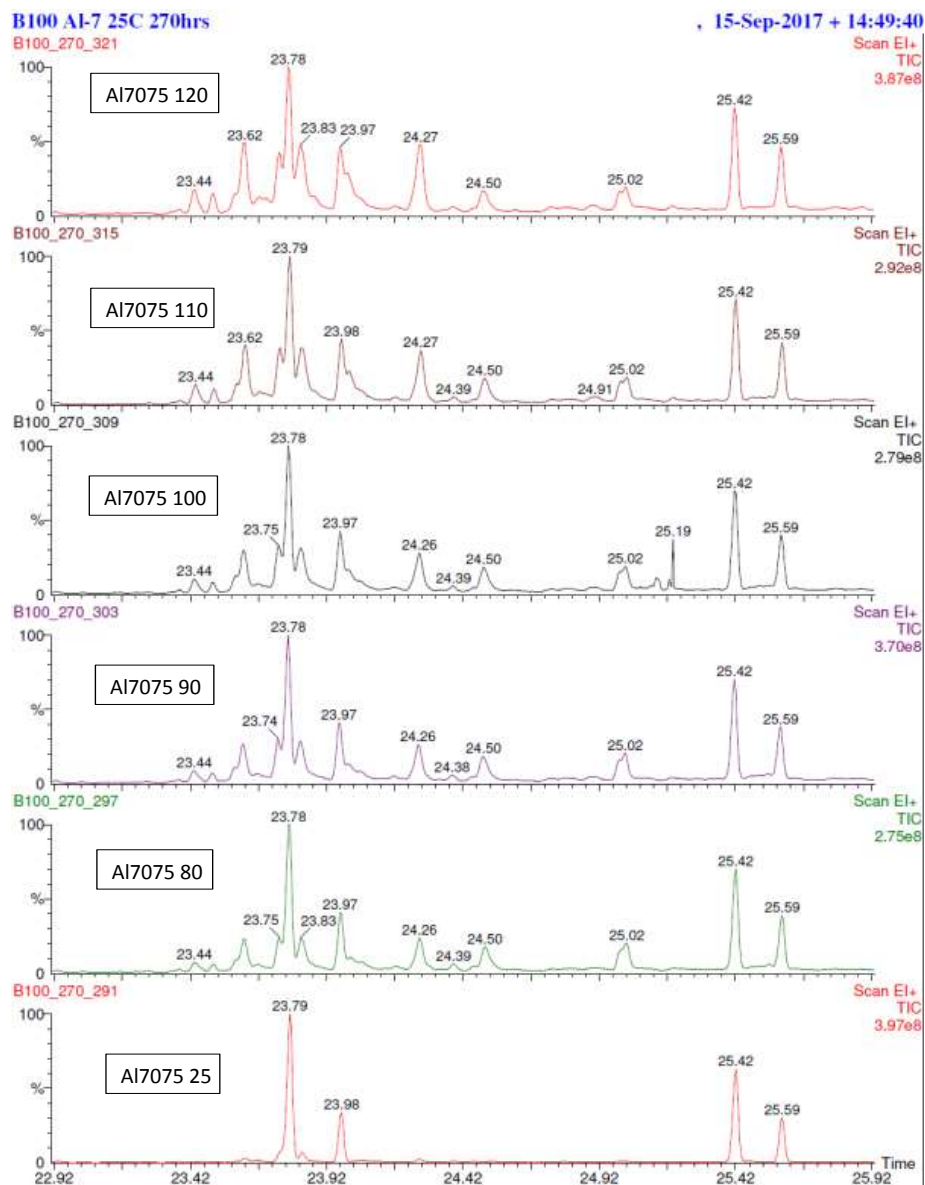


Figure 6.4.g GC-MS traces for Al7075 experiments 25- 120 °C for 270 hours, 5% dilution, showing close up of 23-26 minute region.

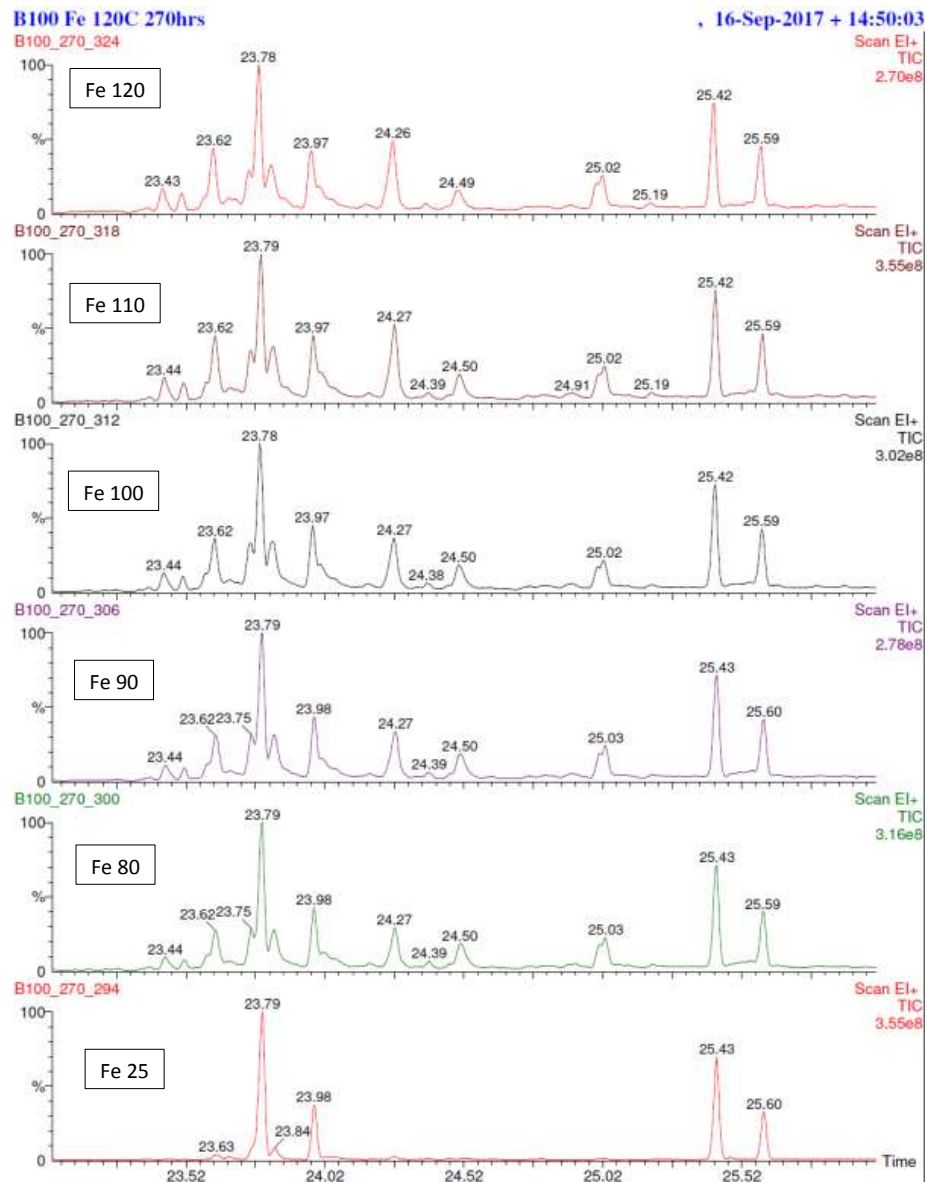


Figure 6.4.h GC-MS traces for steel experiments 25- 120 °C for 270 hours, 5% dilution, showing close up of 23-26 minute region.

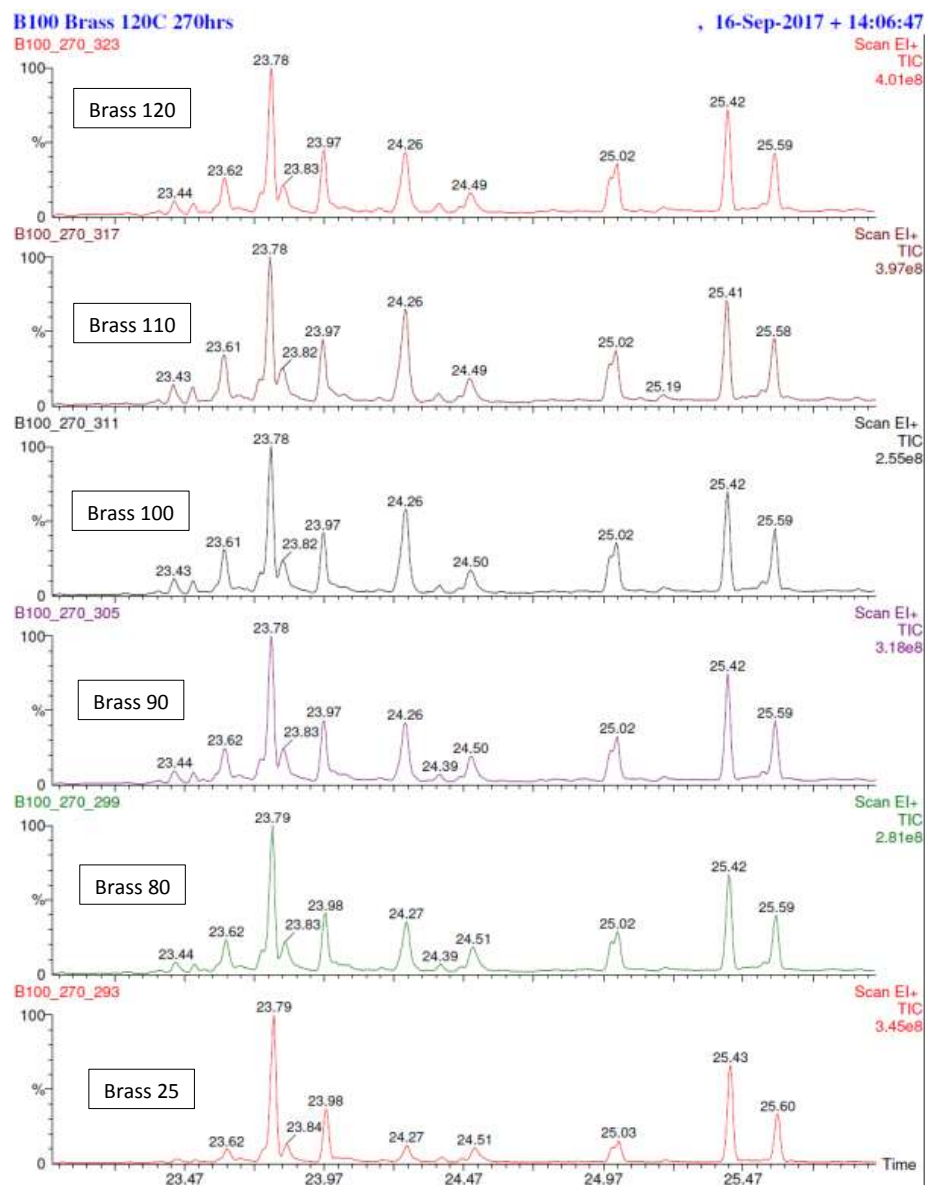


Figure 6.4.i GC-MS traces for Brass experiments 25- 120 °C for 270 hours, 5% dilution, showing close up of 23-26 minute region.

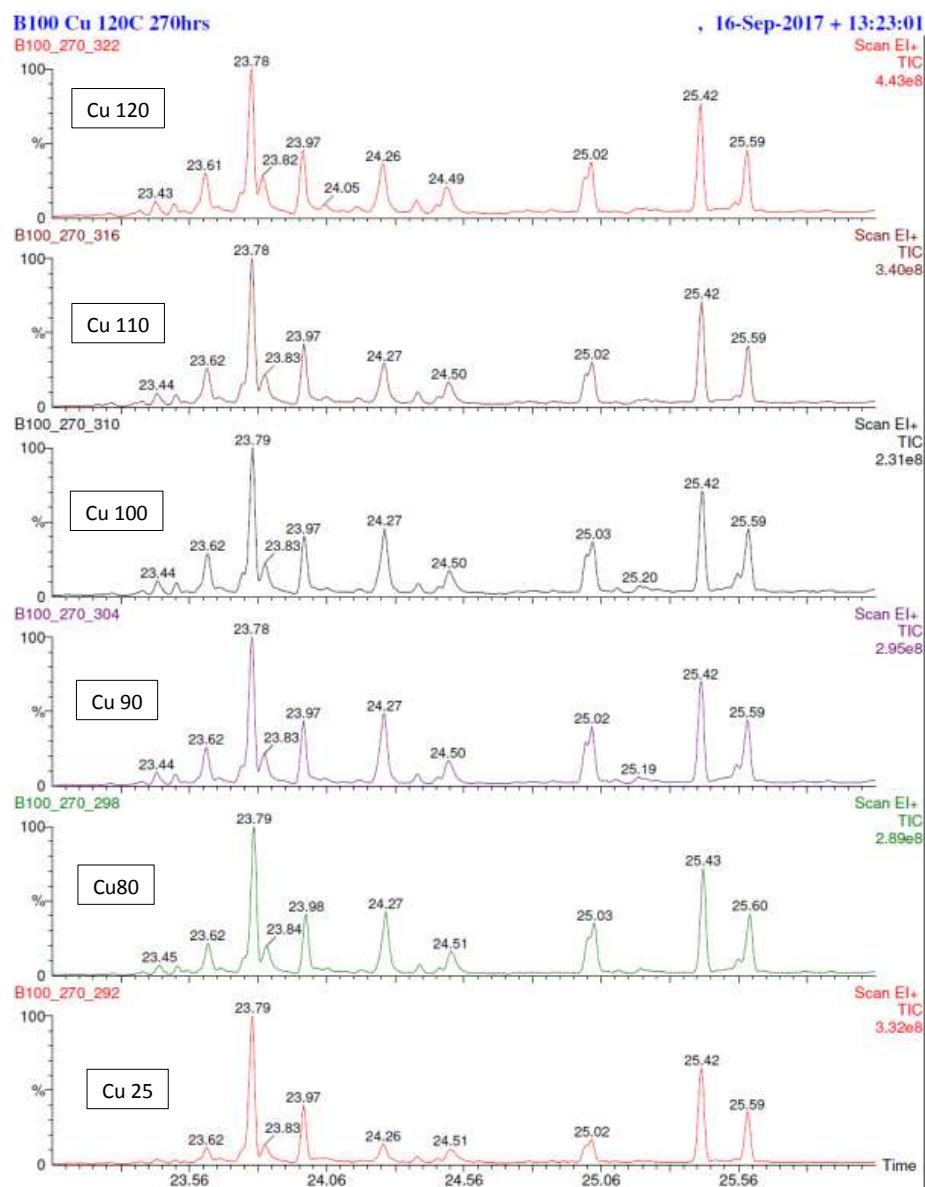


Figure 6.4.j GC-MS traces for steel experiments 25- 120 °C for 270 hours, 5% dilution, showing close up of 23-26 minute region.

The peaks are of very low intensity, which makes identification by NIST software very problematic. This has been attempted for figures 6.4.b, c and d, and results are presented in Table 6.3. This table has been produced by combining information from both 0.5% dilution (bold) and 5% dilution of B100 exposed to Cu at 120 °C after 270 h. The reason for this is given earlier; at 5% dilution the reaction products are in high enough quantity to attempt identification but the main components do not separate. At 0.5% dilution the main components separate enough to allow identification.

Table 6.3 Assignment of peaks present in GC/MS

0-20 minutes figure 6.4.b		
Peak 0-20 time/min	Present for	Assignment
10.34	blank, Al1, Al7, Fe, brass, Cu 120 °C	Octanoic acid methyl ester
13.26	brass, Cu 120 °C	?
13.45	brass, Cu 120 °C	?
14.80	blank, Al1, Al7, Fe, brass, Cu 120 °C	Oxanonanoic acid
15.94	blank 25 °C	?
16.80	blank, Al1, Al7, Fe, brass, Cu 120 °C	?
17.97	blank, Al1, Al7, Fe, brass, Cu 120 °C	?
18.20	All	C14-0, Methyl tetradecanoate
20.08	All	?
20.12	All	16-1, Hexadecenoic acid methyl ester C ₁₇ H ₃₀ O ₂

20.21	All	?
20.32	All	16-0, Hexadecanoic acid methyl ester C₁₇H₃₂O₂
20-22 minutes figure 6.4.c		
20.46	All	?
20.78	All	?
21.08	All	?
21.28	All	?
21.291	All	18-2
21.971	All	18-1
22.25	All	18.0
22-26 minutes, figure 6.4.d		
22.79	All	?
23.43	All except blank 25 °C	?
23.61	All	methyl 9,10 epoxyoctadecanoate
23.78	All	C ₂₀ H ₃₈ O ₂ cis-11-eicosanioc acid methyl ester
23.82	All	C ₂₃ H ₄₂ O ₂ methyl 13, 16, docosadienoate
23.97	All	C ₂₁ H ₄₂ O ₂ eicosanioc acid methyl ester
23.987 * shoulder	(All Al7, Fe, blank) 120. Not 25 °C, not Cu, brass	C ₁₉ H ₃₈ O ₄ <i>Octadecanoic acid 9, 10 dihydroxy methyl ester</i>
24.26	All except blank 25 °C	methyl 5, 9, octadecadienoate

24.50	All except blank 25 °C	Methyl cis 6, trans 8, cis 12 <i>octadecatrienoate</i>
24.95	All except blank 25 °C	C ₁₉ H ₃₂ O ₃ 8 (5 hexyl, -2-furyl) octanoate
25.02	All except blank 25 °C	C ₂₀ H ₃₆ O ₂ methyl 2 octylcyclopropene 1-octanoate
25.42	All	C ₂₃ H ₄₄ O ₂ Docosenoic acid methyl ester
25.59	All	C ₂₃ H ₄₆ O ₂ Docosanoic acid methyl ester

6.3.1 Corrosion Rate

Corrosion rates in m yr^{-1} were calculated from ICP and mass loss results. Plots of the corrosion rate vs temperature are shown in figures 6.5.a-e. The Cu and brass samples show increased mass loss with increasing temperature and increased metal content of the bath. The correlation is very strong for Cu, whereas the ICP results for brass tend to be lower than the total mass loss recorded but there is still good correlation. The Fe sample showed a slight positive mass gain, and the ICP results showed no Fe in solution. Both Al1050 and Al7075 showed a small mass loss, and therefore increased corrosive rate at higher temperatures, however in both cases ICP results showed no Al in solution for Al1050 and no Al Mg Zn Cu in solution for Al7075.

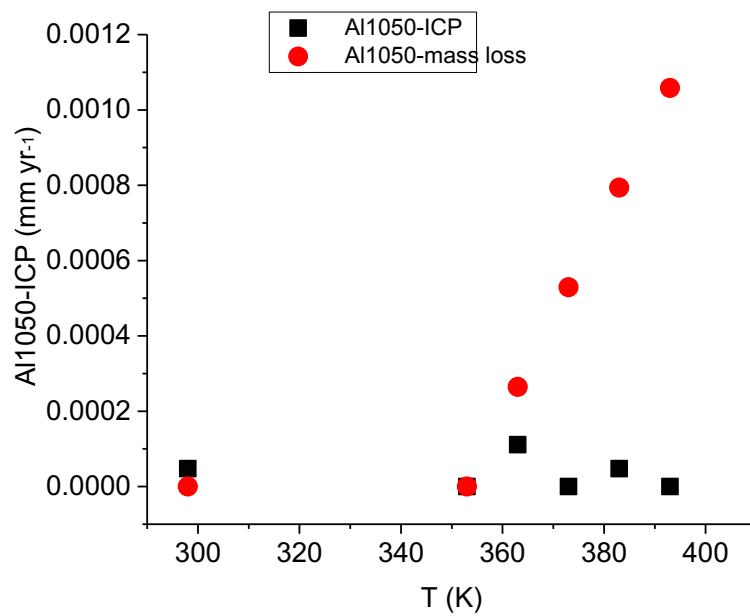


Figure 6.5.a Corrosion rate Al1050 series samples exposed to B100 at different temperatures determined by weighing of metal coupons (red circle) and mass of metal in solution by ICP (black squares), at end of 270 hours

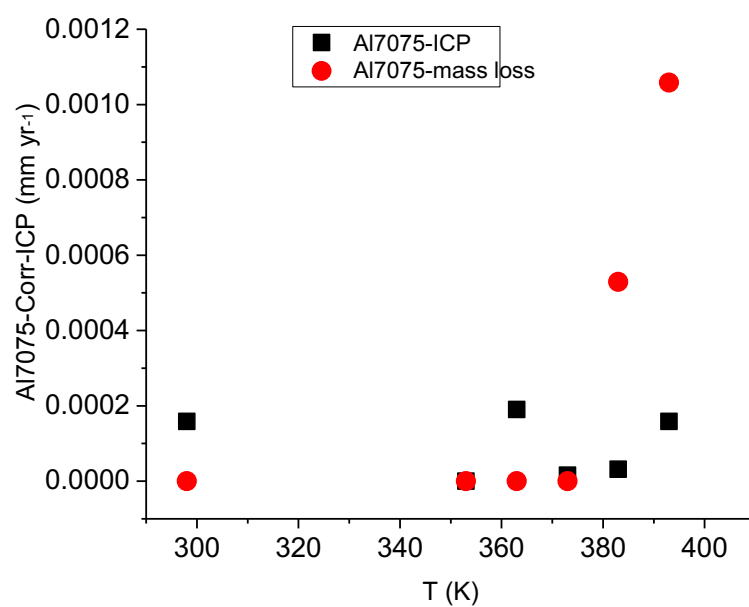


Figure 6.5.b Corrosion rate Al7075 samples exposed to B100 at different temperatures determined by weighing of metal coupons (red circle) and mass of metal in solution by ICP (black squares), at end of 270 hours

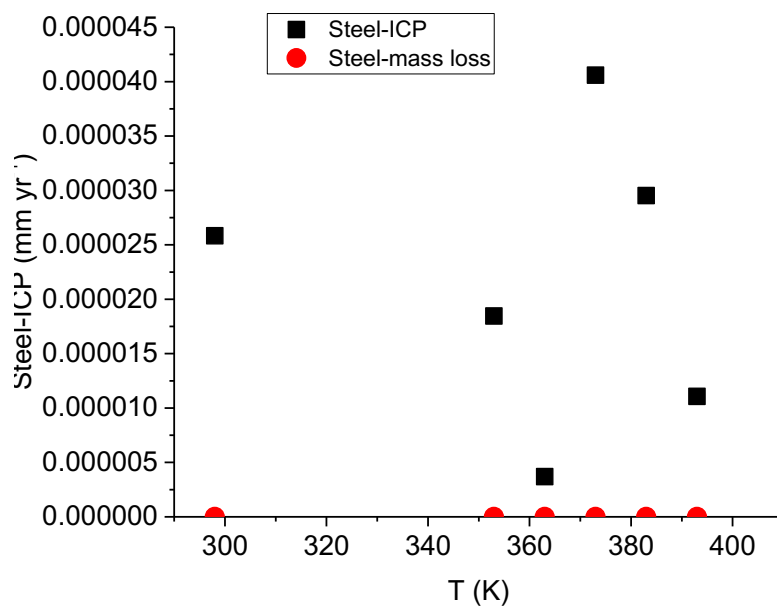


Figure 6.5.c Corrosion rate mild steel samples exposed to B100 at different temperatures determined by weighing of metal coupons (red circle) and mass of metal in solution by ICP (black squares), at end of 270 hours

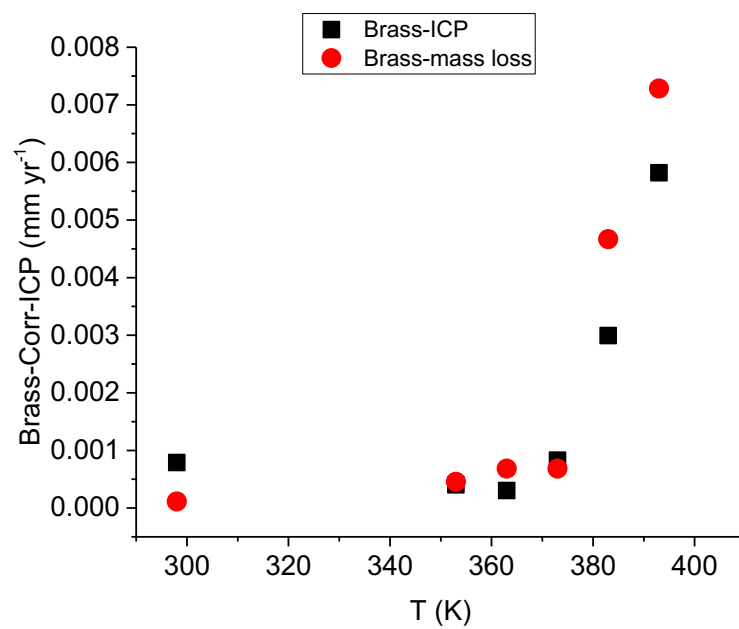


Figure 6.5.d Corrosion rate Brass samples exposed to B100 at different temperatures determined by weighing of metal coupons (red circle) and mass of metal in solution by ICP (black squares), at end of 270 hours

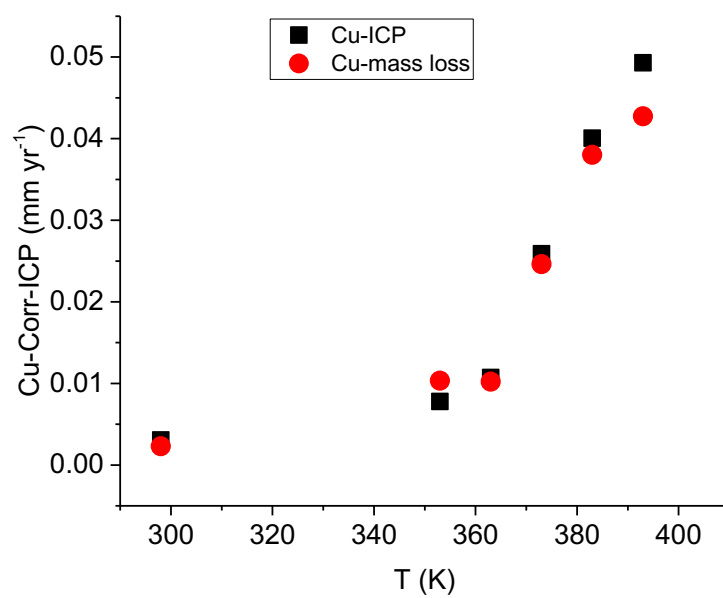


Figure 6.5.e Corrosion rate Cu samples exposed to B100 at different temperatures determined by weighing of metal coupons (red circle) and mass of metal in solution by ICP (black squares), at end of 270 hours.

By calculating the absolute rates in units of $\text{mol m}^{-2} \text{s}^{-1}$, it was possible to plot Arrhenius plots for all samples except mild steel according to:

$$\ln k = \ln A - \frac{E_A}{RT}$$

These plots are shown in figure 6.6.a-d. Since no mass loss was recordable for mild steel by weighing or ICP, no Arrhenius plot was produced.

Table 6.4 gives the slope and EA derived from Arrhenius plots in figures 4a-d by mass loss and ICP measurements.

Table 6.4 Activation Energy for corrosion of different metals measured by mass loss and ICP

Method	Slope	$E_A/\text{kJ mol}^{-1}$
Cu-ICP	-6965	-57.9
Cu-mass	-5763	-47.9
brass-ICP	-10492	-87.2
brass-mass	-10276	-85.4
Al7-ICP	-16814	-139.8
Al7-mass	-10433	-86.7
Al1-mass	-6539	-54.4

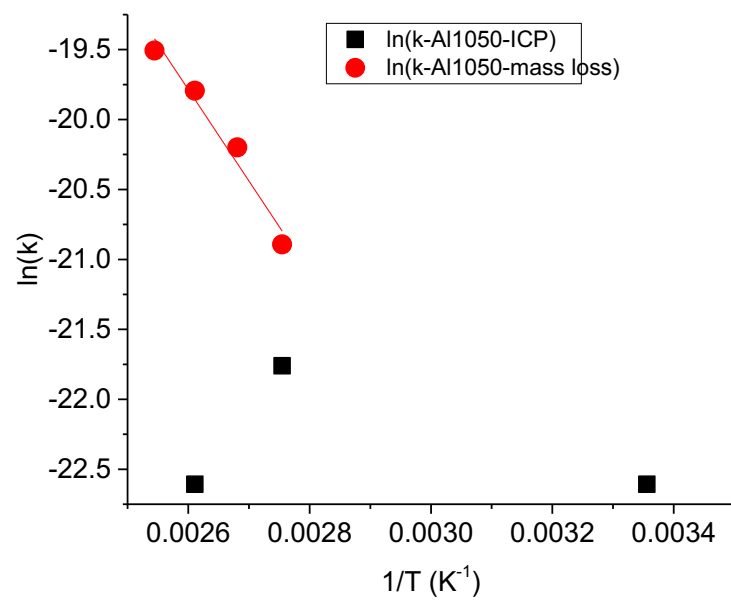


Figure 6.6.a Arrhenius plot for Al1050 series alloy

Note that k is in $\text{moles m}^{-2} \text{s}^{-1}$ because I was thinking like a chemist.

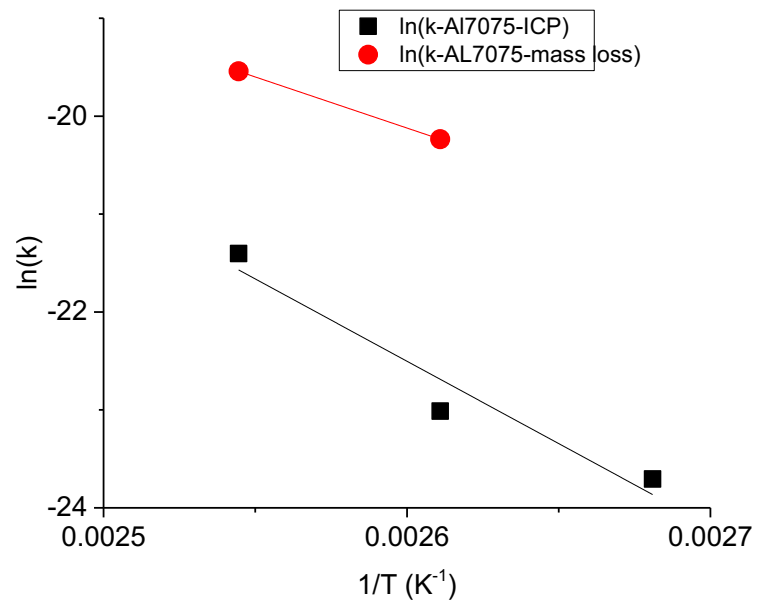


Figure 6.6.b Arrhenius plot for Al7075 series alloy

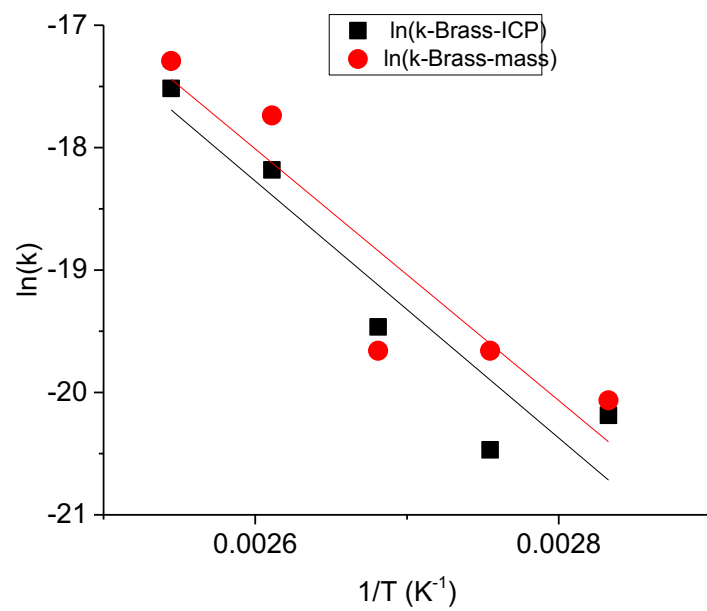


Figure 6.6.c Arrhenius plot for Brass

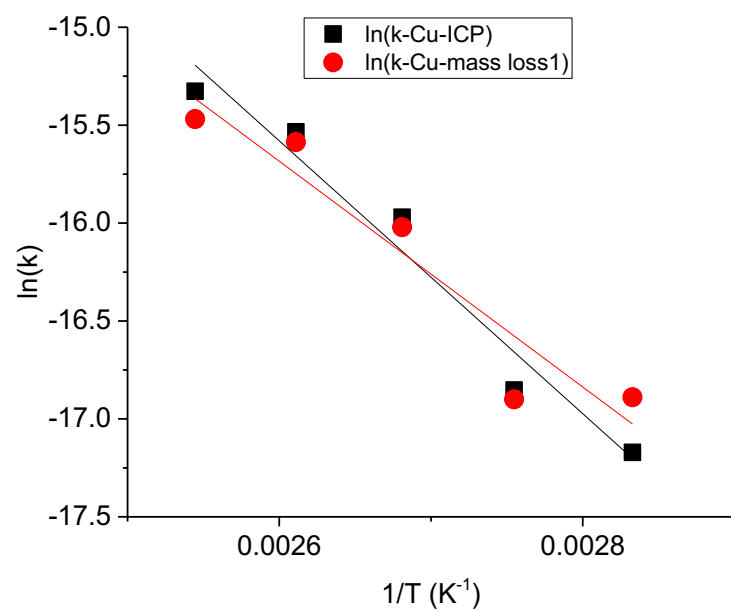


Figure 6.6.d Arrhenius plot for Copper

6.3.2 Scanning Electron Microscopy, SEM

Secondary electron images of Al1050 alloy are shown in figure 6.7.a-f. There are few signs of reaction however, EDX showed oxygen at the surface of all samples above 25°C. Pits are also observable in samples 90°C and above and an example of one is shown in figure 6.7.g along with EDX maps showing the presence of O and C in the corrosion products.

Figure 6.8.a-f shows SEM images for Al7075 at all temperatures. All corrosion proceeds via pitting.

Figure 6.9.a-f shows SEM images for mild steel at all temperatures. There are few signs of reaction however infrequent pits were observed and one is shown in figure 6.9.g for the mild steel sample at 90°C. Again, elemental mapping revealed the presence of O and C in the corrosion products.

SEM images in SE mode of brass are shown in figure 6.10.a-f. At 110°C there is a noticeable increase in pits visible. The majority of brass 120°C sample appeared as in 6.9.f, however there was a smaller region which exhibited increasing pit density and this is depicted in figure 6.10.g.

Figure 6.11.a-f SEM images of Cu from 25-120°C, in SE mode. At 120°C the sample is uniformly corroded. At 25-100 °C the samples are etched and crystals are visible as well as localised pit formation. At 110°C a region of significant pitting occurred as can be seen in figure 6.10.g.

Figure 6.11.h is a composite image moving from etched to a single large pit observed for Cu at 100°C. Elemental mapping revealed that pits in all Cu samples were filled with corrosion products, which contained significant amounts of O and C.

Figure 1 displays six SEM images (a-f) showing the surface morphology of the epoxy resin matrix. The images are arranged in a 3x2 grid. Each image includes a 20 μm scale bar and technical data at the bottom. The data for each image is as follows:

- (a) HV: 20.50 kV, Spot: 4.0, WFM: 83.0 mm, WD: 10.6 mm, mag: 5,000 x, det: ETD, mode: SE, 20 μm
- (b) HV: 20.50 kV, Spot: 4.0, WFM: 83.0 mm, WD: 10.7 mm, mag: 5,000 x, det: ETD, mode: SE, 20 μm
- (c) HV: 20.50 kV, Spot: 4.0, WFM: 83.0 mm, WD: 10.8 mm, mag: 5,000 x, det: ETD, mode: SE, 20 μm
- (d) HV: 20.50 kV, Spot: 4.0, WFM: 83.0 mm, WD: 10.1 mm, mag: 5,000 x, det: ETD, mode: SE, 20 μm
- (e) HV: 20.50 kV, Spot: 4.0, WFM: 83.0 mm, WD: 10.8 mm, mag: 5,000 x, det: ETD, mode: SE, 20 μm
- (f) HV: 20.50 kV, Spot: 4.0, WFM: 83.0 mm, WD: 10.8 mm, mag: 5,000 x, det: ETD, mode: SE, 20 μm

204

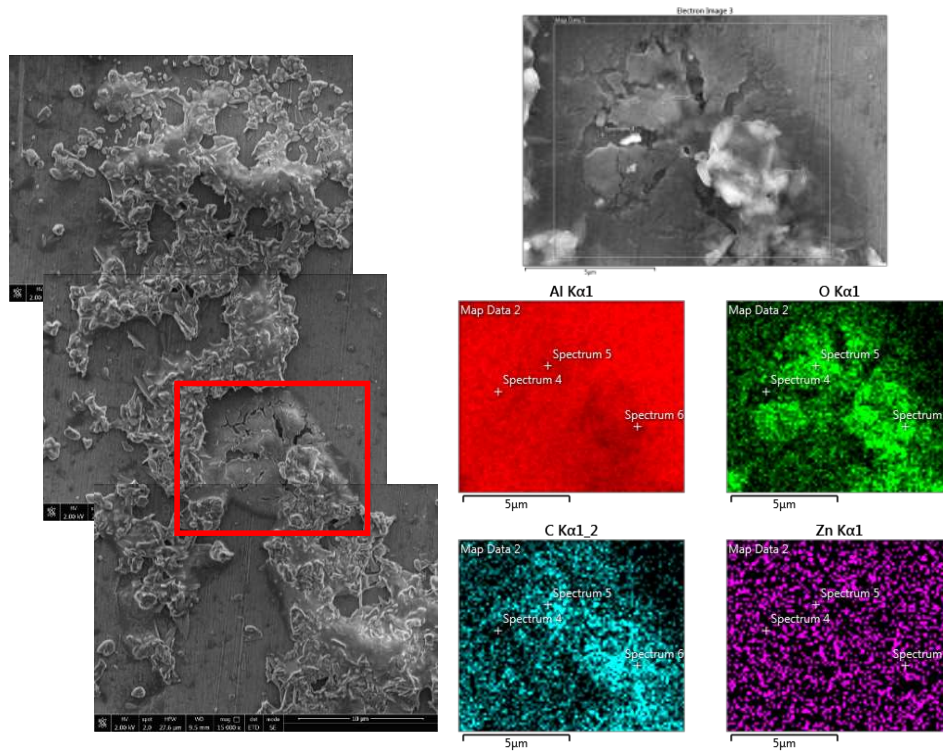


Figure 6.7.g Pit in Al1050 sample at 90 °C with EDX element mapping.

SEM

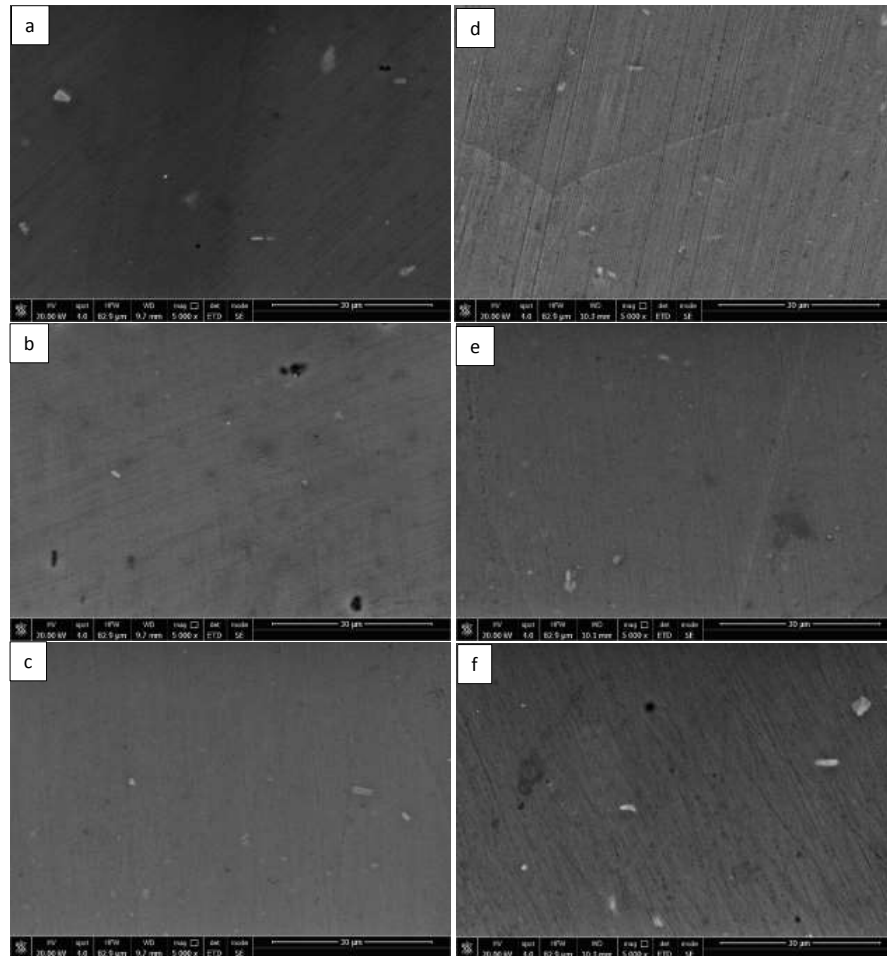


Figure 6.8 SEM images in SE mode for Al17075 series alloy after 270 h at temperatures of: a) 25 °C, b) 80 °C, c) 90 °C, d) 100 °C, e) 110 °C, f) 120 °C

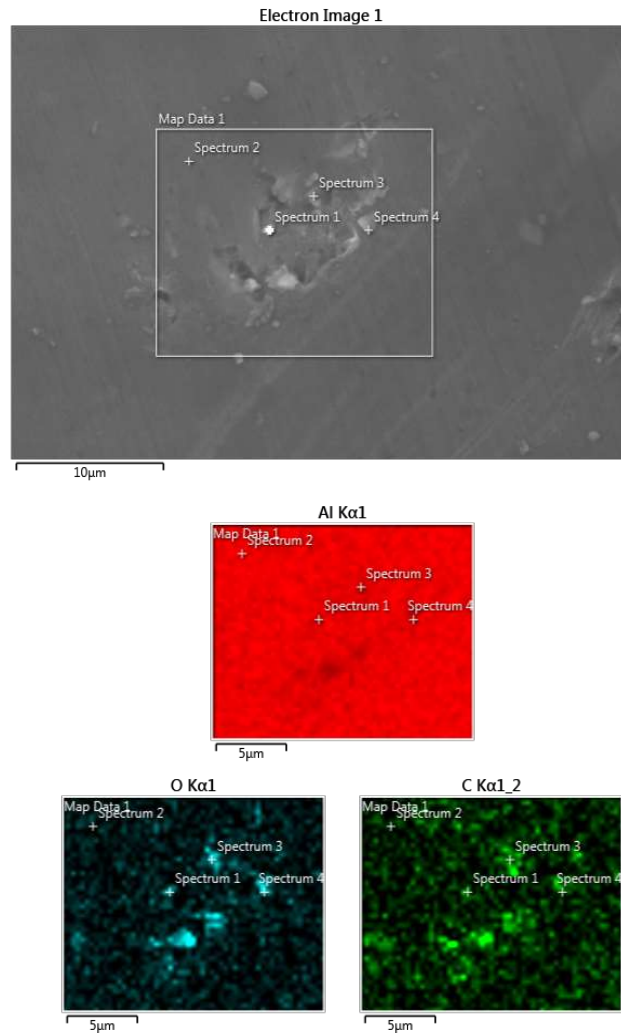


Figure 6.8.g Pit in Al17075 sample at 110 °C with EDX element mapping.

SEM

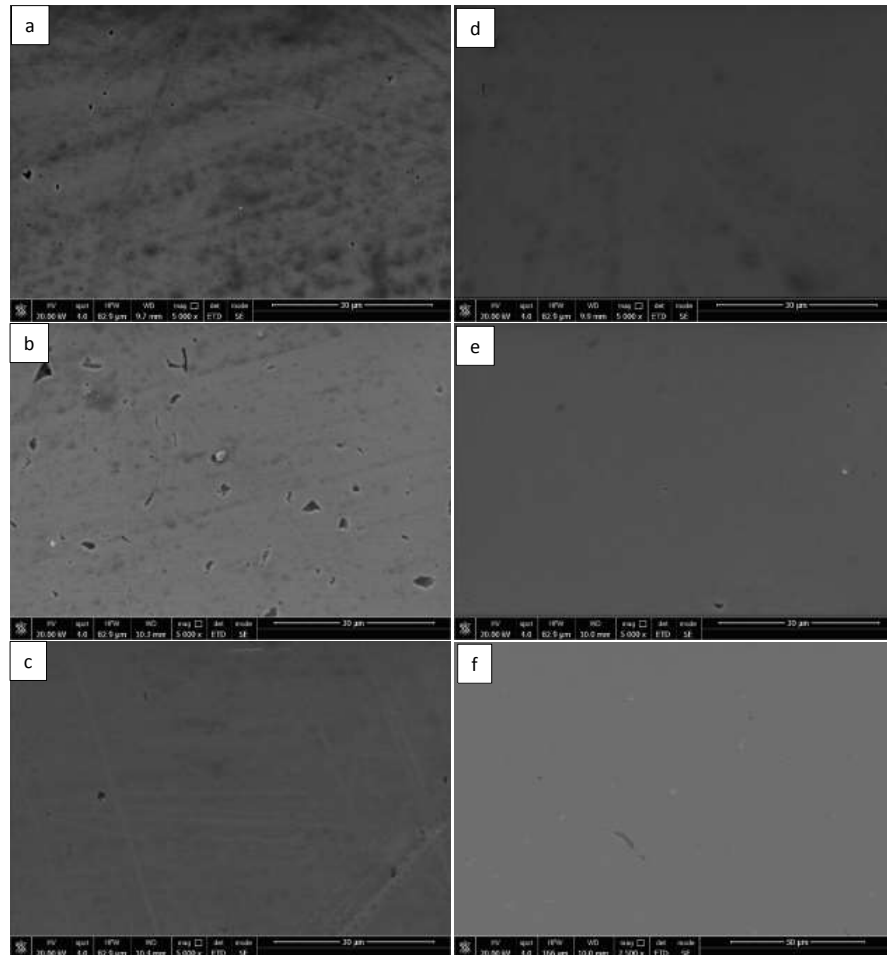


Figure 6.9 SEM images in SE mode for Steel after 270 h at temperatures of: a) 25 °C, b) 80 °C, c) 90 °C, d) 100 °C, e) 110 °C, f) 120 °C

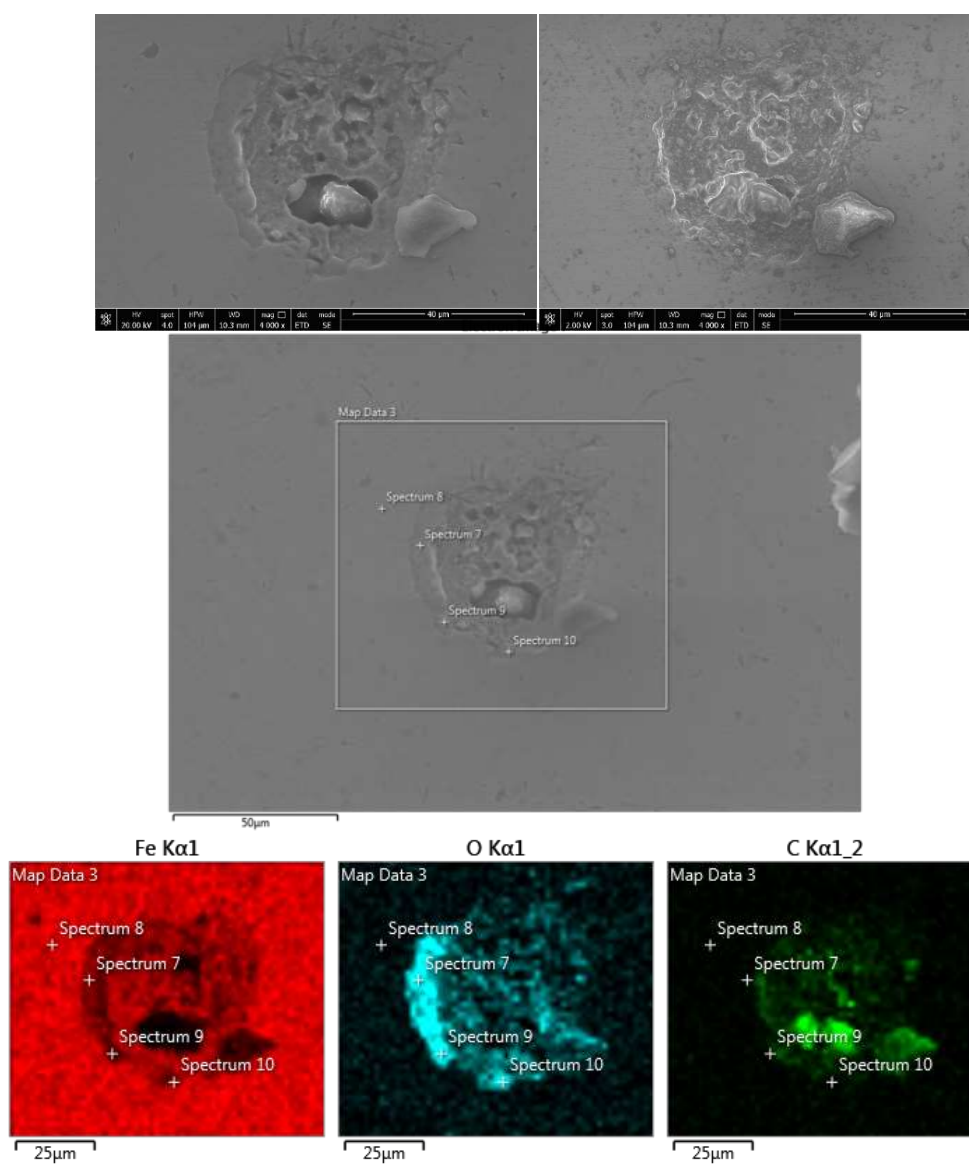


Figure 6.9.g 20 kV and 2 kV accelerating voltage images and elemental mapping for pit observed for Fe at 90°C

SEM

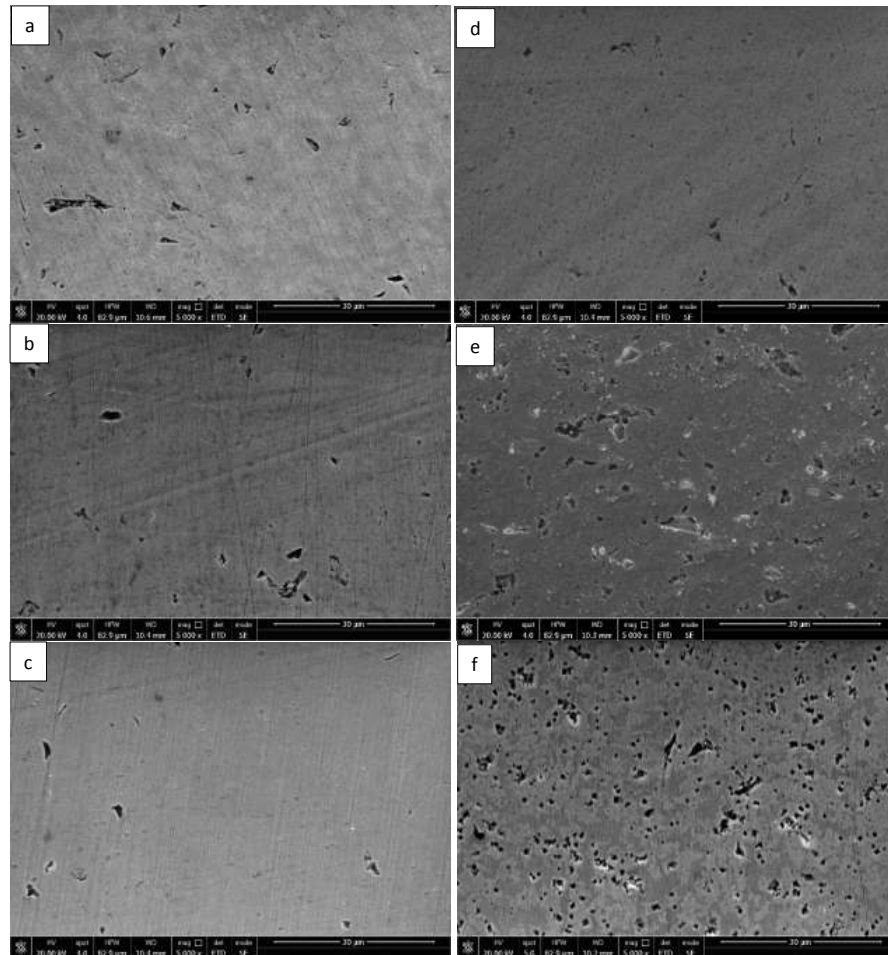


Figure 6.10 SEM images in SE mode for Brass after 270 h at temperatures of: a) 25 °C, b) 80 °C, c) 90 °C, d) 100 °C, e) 110 °C, f) 120 °C

Figure 1 consists of six SEM images (a-f) showing the surface morphology of a membrane at different stages of cycling. Each image includes a 30 µm scale bar and technical parameters at the bottom.

- (a)** 11/7/2012, 20.00 kV, 5.0, 62.9 µm, 10.1 mm, 5.000 x, ETO, SE, 30 µm
- (b)** 11/7/2012, 20.00 kV, 5.0, 62.9 µm, 10.1 mm, 5.000 x, ETO, SE, 30 µm
- (c)** 11/7/2012, 20.00 kV, 5.0, 62.9 µm, 10.1 mm, 5.000 x, ETO, SE, 30 µm
- (d)** 11/7/2012, 20.00 kV, 5.0, 62.9 µm, 10.1 mm, 5.000 x, ETO, SE, 30 µm
- (e)** 11/7/2012, 20.00 kV, 5.0, 62.9 µm, 10.1 mm, 5.000 x, ETO, SE, 30 µm
- (f)** 11/7/2012, 20.00 kV, 5.0, 62.9 µm, 10.1 mm, 5.000 x, ETO, SE, 30 µm

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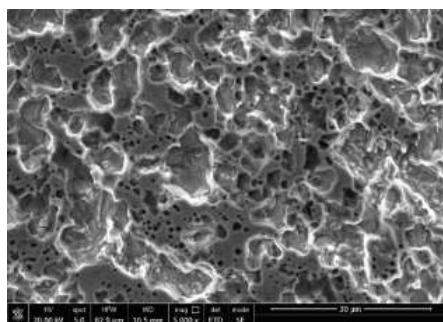


Figure 6.11.g SEM image in SE mode for Copper after 270 h at 110 °C. More pitted region

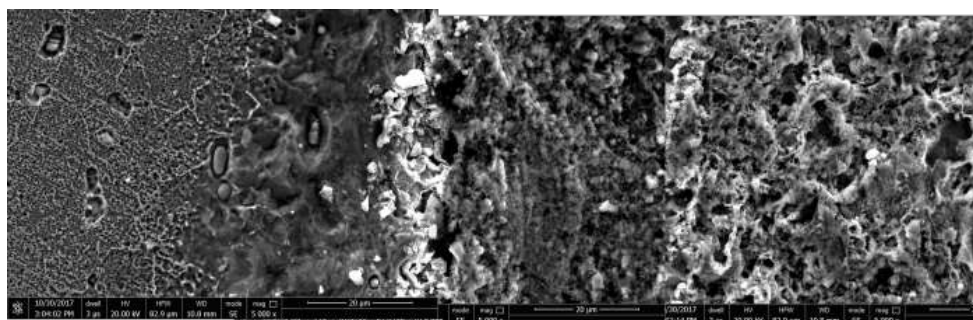


Figure 6.11.h SEM images in SE mode for Copper after 270 h at 100 °C. Edge of large pit

6.4. Discussion

The exposure experiments showed a range of related behaviours across the different metals and temperatures studied. The most obvious change is in the colour of the B100 as shown in Figure 6.1. It is clear that elevated temperature has an effect with the B100 turning from a pale yellow colour towards brown at 120 °C for the blank control experiment. There might be a slight darkening at 110 °C. The Al1050 and Al7075 samples showed similar colour changes to the blank samples. With mild steel, the colour change was more pronounced and the change at 110 and 120 °C is clearly observable. With brass and more so with Cu coupons the colour change is dramatic and observable at all temperatures. It is notable that the B100 appeared to darken slightly at 25 °C for all samples including the control.

GCMS were performed for all exposure tests periodically throughout the experiments. The B100 consists of 4 main components and these are shown outlined in bold in Table 6.3. They are identified confidently as methyl esters of 16.0, 18.2, 18.1 and 18.0. There are other minor constituents at <1% of total composition which are of similar chemistry to the main constituents but varying only in the number of carbon atoms in the chain. They can be assumed to behave in a similar fashion to the main constituents but are in such low concentration that any reaction products were unobservable. Figure 6.3 plots the relative concentration of the 4 main components of B100 measured at different times throughout the exposure test. At 25 °C with no metal coupon present the relative concentration of all components remains constant. This is confirmed in figure 6.2.a, figure 6.4.a-e. At elevated temperatures the relative concentrations of the 4 main components changes with time.

The plot for blank B100 sample at 120 °C in figure 6.3 shows that the amount of 18.2 decreases relative to other constituents from ~30% to ~20% after 270 hours.

There is a commensurate rise in the amount of 18.1. In the presence of Cu at 25 and 120 °C a similar effect is observed with loss of 18.2 to ~20% at 25 °C and to < 20% at 120 °C. All other samples showed similar behaviours. Blank, Al1050, Al7075 and mild steel all showed no change in concentration at 25 °C, but all other experiments showed some loss of 18.2 relative to other constituents with time. Of these, Cu at 120 °C showed the greatest loss of 18.2 hence its relevance in figure 6.3 where it acts as a demonstration of extreme behaviour.

Figure 6.4a-j shows GCMS for various samples at 5% concentration. The products of the chemical reactions of the four main components were found to be present in low concentrations and hence these are best observed and identified by performing GCMS on more concentrated solutions at 5%.

These solutions are too concentrated for analysing the main components which are not separated properly as seen in Figure 6.4.a at 22.15 minutes. Table 6.3 shows the position and assignment of all peaks observed in the exposure experiments. The reaction products were observed to fall into two main categories; reaction products due to chain scission reactions and reaction to oxidation processes occurring at unsaturated bonds in the hydrocarbon chain. These reactions occur naturally for B100 samples at 80-120 °C showing the inherent oxidative instability of this fuel. According to Neff, *et al* [73], 18.2 is 50 times more oxidisable than 18.1, hence it is reasonable to concentrate purely on 18.2 as the primary reactant in all processes hereafter.

Products formed by chain scission are lighter than the starting materials and will exit the column more rapidly. Products of chain scission reactions are given in table 6.3 in the 0-20 minute region, which is seen in close up in Figure 6.4.b. It is notable that the peaks at 10.34 and 14.80 minutes in brass and Cu are considerably increased in intensity and these have been assigned as octanoic acid methyl ester and oxanonanoic acid respectively.

Hence, chain scission reactions incorporating oxidation are considerably accelerated in the presence of Cu and brass compared to other metals studied. The peaks in this region are in very low concentration and are very difficult to identify confidently using the NIST software package. From 20-22 minutes all samples except blank, Al1050 and Al7075 showed a similar pattern of behaviour with increased peak height at 20.77 minutes and decreased peak height at 21.06 minutes compared to unreacted B100. Figure 6.4.c shows the change in relative peak heights for all samples at 120 °C and 270 hours compared to the blank sample at 25 °C. These peaks proved impossible to identify as they are only present in very low concentrations in all cases making identification challenging.

The highest concentrations of reaction products are observable between 3 and 26 minutes. In this region, all reacting samples show a similar pattern of peaks with few exceptions. This behaviour is clear in figure 6.4a) at 5% dilution for all samples at 120 °C and 270h.

These are compared against the blank 25 °C control which does not show any of these extra peaks. The 23-26 minute region is examined more closely in figure 6.4.d. The peaks are tentatively assigned using NIST software in Table 6.3. The 23-26 minute region shows the most changes for all samples examined by GCMS and the concentration of these extra peaks is seen to increase in intensity with increasing temperature for all experimental conditions as seen in figures 6.4.e-j). blank, Al1050 and Al7075 and mild steel do not show these peaks in the 23-26 minute region

at 25°C and only show trace starting materials identified as methyl esters of: 20.1 at 23.79 minutes, 20.0 at 23.98 minutes, 22.1 at 25.42 minutes and 22.0 at 5.6 minutes. For all other sample/temperature combinations there are a series of peaks which are difficult to assign due to their low concentrations however, wherever this is possible they are all seen to be oxidation products of double bonds.

Given that 18.2 is the most reactive species present by a significant margin it is likely that these are all products of oxidation processes occurring to 18.2. Bouaid and Martinez [74] showed the propensity for 18.2 to undergo oxidation type reactions via an auto oxidative reaction initiated by a radical process removing the H at the bis-allylic position. Once this position has been radicalised it reacts readily with oxygen and forms peroxide. From this point a range of reaction pathways are possible producing a range of products seen in the 23-26 minute region which are all conceivable as products of radical oxidation at the bis allyl position.

It is notable that for blank, Al1050 and Al7075 experiments at any given temperature the relative concentrations of oxidative products all show similar relative concentrations, indicating that the metal coupon plays little part in the reactions. With mild steel however, there is a decrease in the peak area of the shoulder at ~24 minutes ascribed to octadecanoic acid 9, 10 dihydroxy methyl ester, and an increase in the area of the doublet observed at 24.95-25.02 minutes assigned as furyl and cyclopropenyl groups as illustrated on figure 6.12.a-b.

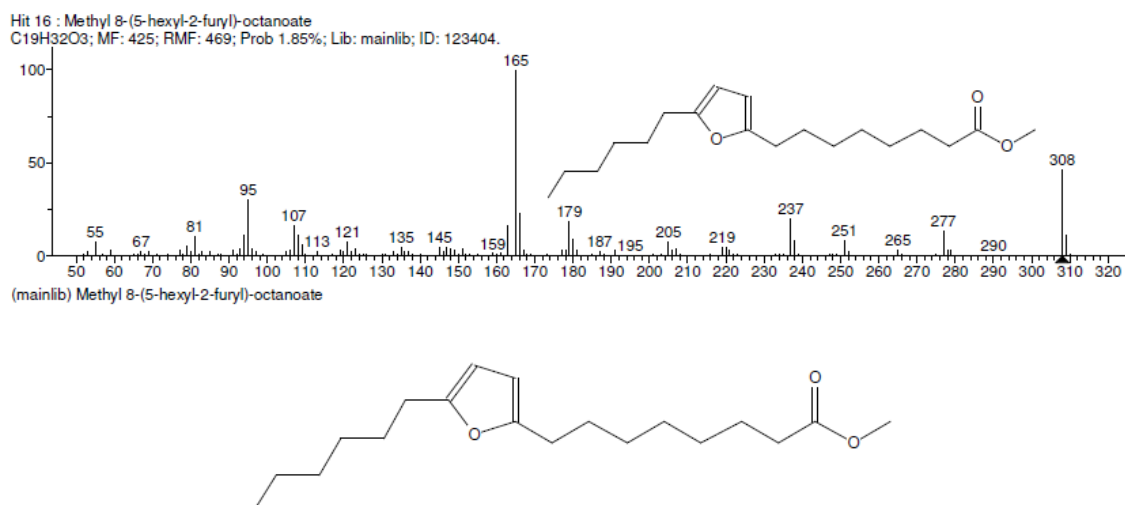


Figure 6.12.a. furyl illustration.

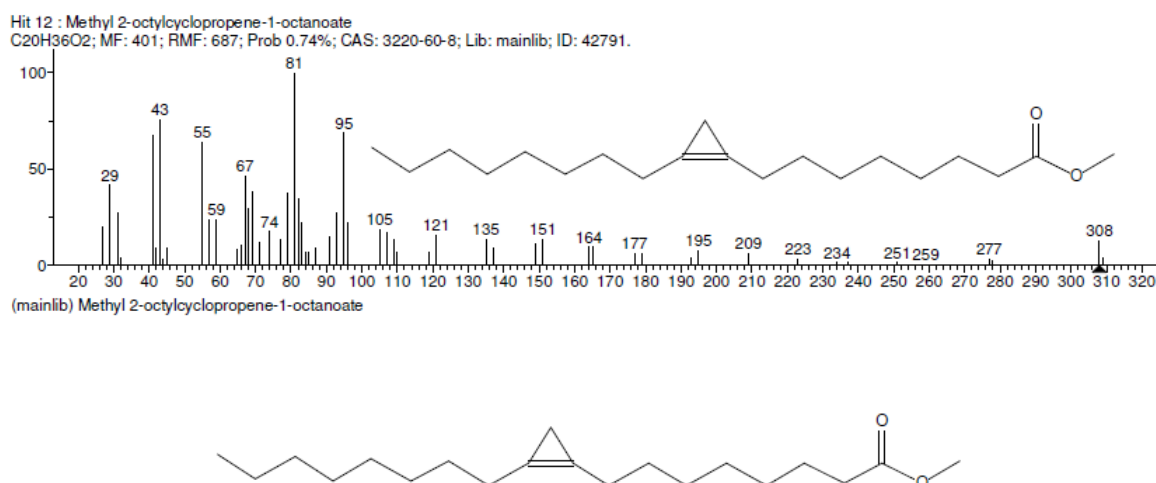


Figure 6.12.b. Propenyl illustration.

These effects are even more pronounced in the presence of brass and Cu and this is observable in figure 6.4.d. It is likely that in the presence of Fe, brass and Cu, cyclisation reactions are promoted which either consume the dihydroxy species or prevent it from forming.

6.4.1. Total Acid Number

Total acid number is a measure of the free fatty acid concentration of the B100 formed by hydrolysis of the methyl esters. Figure 6.13 shows the variation of TAN for each series of experiments at each temperature.

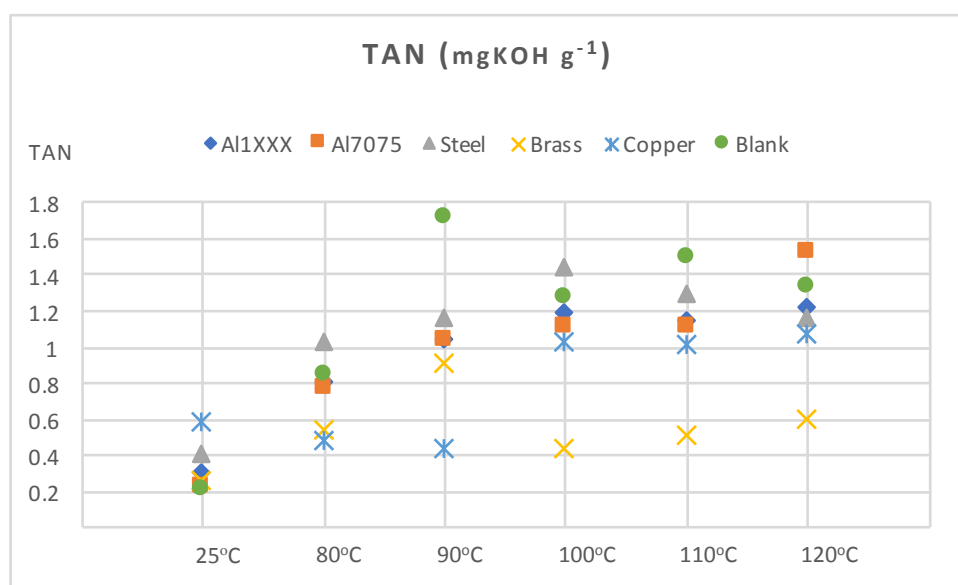


Figure 6.13. Total Acid Number changes of B100 at different temperatures and in contact with different metallic coupons.

For the blank, Al1050 and Al7075 samples the TAN behaves in a similar fashion, increasing from 0.2 mg KOH g⁻¹ at 25 °C to ~ 1.2 mg KOH g⁻¹ at 120 °C. In the presence of steel follows a similar pattern up to ~100 °C but thereafter it decreases and for the Cu coupons the TAN is decreased for all samples > 25 °C relative to the blank at similar temperatures. This is indicative of reaction between the acid and Fe brass and Cu. The temperatures for reduced TAN in brass and Cu correspond well with the observed onset of pitting in those samples.

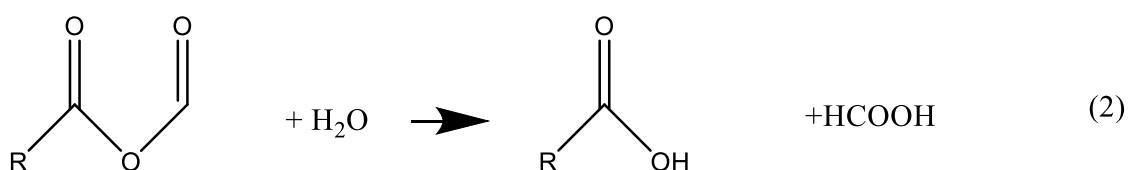
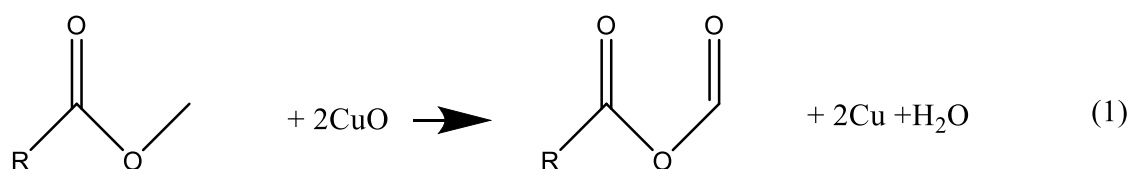
The change in colour of the B100 is coincident with the increased mass loss, ICP analysis and GCMS results observed after 270 h. For Cu and brass samples, figures 6.10 and 6.11 show significant evidence of chemical reaction in SEM images. For brass, pitting is evident at 100 °C and extensive above this temperature.

The corrosion rate calculated by mass loss and ICP for brass undergoes a notable increase beginning at 100 °C as seen in figure 6.5.d. Corrosion rates calculated from mass loss and ICP data are presented in figures 6.5.a-e. For both Al1050 and Al7075 the ICP showed no Al in B100 solution however mass loss indicated a small amount of material loss at elevated temperatures. This discrepancy may be explained by insolubility of reaction products and hence they are not observed in ICP.

SEM studies on both Al1050 and Al7075 alloys showed evidence of small, localised and infrequent pits e.g. Figure 6.7.g shows a pit in Al1050 at 90 °C. The corrosion products on the surface contain C, O and Al and are consistent with slat formation with fatty acids. With Fe coupons, ICP produced no significant Fe in solution at any temperature, and mass loss as all very small, and slightly positive, i.e. all mild steel samples gained slightly in mass during exposure to B100. Hence the corrosion rate reported was zero by mass method in figure 6.5.c. SEM studies of mild steel samples showed more isolated pits, which also contain C and O, by elemental mapping.

An example of an Fe pit is seen in figure 6.10.g at 90 °C. Again, the reaction products are ascribed to insoluble fatty acid formation hence the slight increase in mass for all Fe samples. For brass, pitting reactions are visible from 100 °C and upwards. In all cases C and O are present in the reaction products, which fill these pits. For Cu, pitting occurs at all temperatures and a large pit was observed at 100 °C (figure 6.11.h) filled with reaction products rich in C and O.

In fact, corrosion products rich in C and O were observed for all Cu samples across the surface but in higher amounts in the pits. At 110 and 120 °C, pitting no longer dominates for Cu, and a more uniform corrosion reaction occurs across the whole surface. This implies that any copper oxide passivation layers are entirely unstable at these temperatures with respect to reaction with methyl esters to form the acid and formic acid according to:



However, the Cu samples showed a much reduced TAN and there is no evidence of free acid or formic acid in the GCMS, so it is reasonable to assume that any acid formed will be in the vicinity of the copper metal where it reacts readily to form formic acid and fatty acid salts which have been observed in SEM by EDX. The mass loss for Cu matched closely with the ICP results indicating solubility of Cu salts in B100. Other researchers [75-77] have already shown that Cu is a strong catalyst for double bond oxidation reactions, even at 25 °C and can form allylic alcohols and epoxy groups, both of which have been detected in GCMS.

The corrosion rates determined at different temperatures were compared to those obtained by other researchers under appropriate conditions. Hu et al [78] obtained a corrosion rate of 0.023 mm yr^{-1} for Cu exposed to biodiesel at 43°C for 60 days, and 0.018 mm y^{-1} and 0.003 mm y^{-1} for mild steel and Al respectively. This is considerably higher than our observed results, however a reason for this may be found in the work of Fazal et al [79] who exposed palm diesel to Cu and mild steel at RT for 20, 40 and 60 days. The corrosion rate after 20 days was 0.0115 mm y^{-1} for Cu and 0.0013 mm y^{-1} for mild steel, however, after 40 days these had increased to 0.0239 mm y^{-1} and 0.0017 mm y^{-1} respectively. This increase in corrosion rate with time is explained by pitting behaviour. The initial stages of an experiment are dominated by pit initiation and the latter stages by pit growth, which is faster than initiation.

Given that experiments in the current work were limited to 270 h by availability of space, it is unsurprising that our corrosion rates are somewhat slower than those published for longer experiments.

6.5 Conclusion

Brass and copper are highly reactive towards B100 and both showed significant corrosion compared to the lower reactivity metals; mild steel Al7075 and Al1050 alloys. For brass the reaction proceeds via a pitting mechanism at all temperatures and produces a reaction product rich in C and O which is identified as metal salts of fatty acids. With Cu pitting occurs at low temperature but at higher temperatures a uniform corrosion mechanism dominates and the oxide layer is completely unstable. The reactivity of these metals is supported by the decreased TAN observed for them indicating reaction between free acid and either metal or metal oxide.

For the lower reactivity metals all showed a tendency to pit and produce fatty acid salts with a greater tendency to behave like this at higher temperatures.

The reaction products from all samples were identified by GC/MS. Without a metal sample present the B100 underwent auto oxidation and the most reactive species present was shown to be 18.2. With Al1050 and Al7075 present the reaction products were similar to the blank control experiment indicating very little interaction of these metals with the oxidative process. However, with mild steel present it is possible to see evidence of cyclisation of oxidised reaction products and this behaviour is promoted by the presence of Cu and brass metal coupons.

By mass loss and ICP it has been possible to calculate rates of corrosion over a range of temperature which has not been accomplished on such a wide scale before. This sizeable and robust body of work is a significant contribution of data to the knowledge.

The colour changes observed in biodiesel samples as a result of their contact with brass, copper and steel at temperatures higher than 80 °C. These changes in colour and brightness are related to the presence of metal species in the fuel composition. The colour changes in fuels are the result of producing different copper fatty acid salts, or zinc fatty acid salts in fuels. There is no evidence for Al, or Fe in B100 from ICP results and it is concluded that if formed, as indicated by abundance for C and O at pit sites, then these salts are insoluble.

Activation energies were calculated for Al1050, Al7075, brass and Cu samples, however the data for Al1050 and Al7075 must be treated with scepticism as the mass loss was at the limit of detectability on the balance used. The brass and copper values are more reliable. It should be noted that these values will be strongly affected by the corrosion process which

undergoes an initial initiation of pitting process followed by a propagation process. In the case of copper at high temperature the propagation process avoids any pitting at all and proceeds via uniform corrosion. The propagation process is faster than the initiation step and this is reflected in the lower corrosion rates reported in this work compared to other similar studies over longer timescales.

CHAPTER 7

7. Discussion

7.1 The use of biodiesel

Biodiesel, produced from renewable and what could be regarded as domestic sources, represents a more sustainable source of energy and will therefore play an increasingly significant role in providing the energy requirements for future transport needs. Research over the last decade has focused on the performance of biodiesel fuelled engines and their emissions. The results of this, however, have often been inconsistent for a number of reasons. These include the different types of engines used, each with operational or manufacturing differences inherent in designs from multiple manufacturers, as well as non-standard operating conditions and cycles. In addition, biodiesel manufactured from different raw material, as well as the source of reference fossil diesel, would also affect the results.

At the moment, the future of biodiesel and biofuels is uncertain. Additional research and development of biodiesel feedstocks is needed. Whilst the economic viability as a replacement or supplement to existing fossil diesel seems certain, there is a genuine need to address the problems associated with bio-fouling and bio-contamination of these fuels and their blends. Therefore, understanding the problems associated with biodiesel is paramount if its use is to become more widespread.

Biodiesel has chemical characteristics that are distinct from that of fossil diesel. It is therefore expected that they will interact differently with the numerous types of material found in modern engine systems. Compositional differences of biodiesel derived from different feed stocks

complicate the situation. A great variety of raw materials have been investigated as sources of biofuels and much effort has been done to the development of new methods for production together with improvements to the traditional methods.

In relation to this, the use of new oilseed species as biodiesel feedstock will have an economic impact as small, local producers will be able to contribute to biodiesel production. Also, the special characteristics of these biodiesels may improve the physio-chemical properties (e.g. acidity, oxidation stability, viscosity, etc.) of other biodiesels by appropriate blending.

From previous research, it was concluded that the use of biodiesel helps reduce carbon deposits in an engine and also reduces the wear of the key components when compared with fossil diesel. This is attributed to reduced soot formation, which is consistent with the reduced Particulate Matter (PM) emissions when biodiesel is used as an engine fuel, together with the inherent lubricity of biodiesel.

The PM emissions are lower, when compared with fossil diesel, due to the higher oxygen content of the biodiesel and lower content of aromatic compounds. It is also accepted that Carbon Monoxide (CO) emissions are reduced when using biodiesel, again due to the higher oxygen content and the lower carbon to hydrogen ratio when compared to fossil diesel.

The conclusion is, therefore, that biodiesel, especially when used as a blend and even as only a small percentage of the volume, could replace pure fossil diesel to help control air pollution and release the pressure on natural resources without significantly losing engine power and economy.

7.2 Soot and engine wear

This thesis has reviewed the issues associated with soot-contaminated lubricants and the associated engine wear problem. In contrast to previous research, it has been shown essentially that, with lower biodiesel blends and fossil diesel fuel, soot production increases dramatically. The primary soot particles of approximately 50nm diameter are either transported away from the engine via the exhaust system or absorbed within the engine lubricant. When absorbed by the lubricant, the soot particles tend to agglomerate into clumps of an approximate mean diameter of 300nm. If Exhaust Gas Recirculation (EGR), a technique used to reduce NO_x emissions, is fitted to the engine, then a proportion of the exhaust gasses is reintroduced into the engine, increasing the soot loading to the lubricant.

Soot contaminated lubricant has been shown to produce significant amounts of engine wear. The main mechanism of soot related wear is through abrasion, but when the level of soot content in the lubricant increases, starvation of lubricant to the metal-metal contact surfaces can occur, leading to increased wear. High concentrations of soot can increase acidity levels in the engine and in areas where high temperatures and volatile gases coexist, such as the piston, corrosion may also occur.

The biggest influence on soot particles size distribution

can be seen when EGR is used. Generally, soot particles from the nucleation mode agglomerate to form larger size aggregates in the accumulation mode. The influence of EGR or indeed injection timing on the soot emissions causes an increase in the concentration of soot particles agglomerating in the accumulation mode.

Soot contaminated lubricants have been shown to increase the wear of many engine components. The valve train of an engine has proven to be

the most seriously affected because of the thin oil-film experienced on many of its reciprocating contacts. The film thicknesses produced in such contacts have been shown to be less than the diameter of the soot agglomerations contained within the lubricant.

Engine valve trains have been shown to be the most susceptible to soot-related wear because the inherent design for that type of motion (generally reciprocating) creates interrupted oil films and low lubricant flow rates. The effect of soot contamination around the piston has also proven to create significant wear. In this latter situation, the reciprocating motion in that region of the engine is more effective in creating oil films so abrasive wear occurs to a lesser degree, but, owing to the extreme temperatures, volatile gases and the presence of oxygen, corrosive wear is more likely to occur.

Soot contamination also affects the properties of oil, in particular by leading to an increase in its viscosity. This in turn increases contact friction (the lubricant film shears less readily), leading to a reduction in engine efficiency, an increase in fuel consumption and therefore emissions.

7.3 Testing for soot-related engine wear

For fully understanding the amount of wear caused by soot contaminated oil increasing of engine component wear and more importantly, the wear mechanisms that cause the wear, various tests have been performed in this work. Although full-scale engine testing is preferred because of the more realistic results achieved, bench test data displayed significant similarities, allowing cost-effective and reliable testing to be carried out to gain an understanding of an extremely difficult issue with its many influencing factors. Each type of test provides more information to add to the increasing knowledge on the subject.

A reduction of soot produced within the combustion process can be achieved through development of currently available diesel fuels and through the introduction of synthetic diesel fuels where greater control of the component chemicals can be made during the production process. Biofuels have been reported as naturally producing less combustion soot than diesel fuels but in the engine tests in this thesis a greater quantity of soot was produced used the biodiesel blends than pure diesel.

Testing with contaminated lubricants provides many complex challenges. One main issue relates to the actual dispersion of particles within the test lubricant. Practically, it is known that in any mixture of contaminated oil there is a significant amount of residue in the bottom of the receptacle containing the mixture. In many cases, further analysis is required to assess the contamination level in the actual sample used rather than the bulk test mixture.

As previously mentioned, when the levels of soot contamination have increased, the amount of wear occurring has also increased as a result of contact starvation of lubricant. This wear reduces engine efficiency, causing an increased amount of fuel to be burnt with an attendant increase in emissions.

The main parameters to be considered when creating a test standard for investigating soot wear include;

- the contaminated oil mixture,
- test specimen preparation,
- test method and procedure,
- wear analysis.

When considering the contaminated oil mixture itself, the elements used to make it are important. The lubricant selected should depend on the aims of the test e.g. base oil, used to demonstrate wear that occurs when there are no anti-wear additives present, require a dispersant to suspend the

test particles. A formulated oil should be used to test the wear resistance of new lubricant properties and for comparison between different finished products. Turning to the soot, ideally, soot extracted from an operational engine mixed into a fresh test lubricant is the best soot simulant, however, the variability of the particles so collected compromise repeatability of tests. Standard sized manufactured carbon black particles could also be considered as an alternative to soot but do not fully replicate wear created using soot particles.

The duration of the wear tests should be long enough to produce wear data that are unaffected by a running-in period, but short enough to be a practical laboratory test (ideally in terms of minutes and not hours). Current analysis techniques using wear scar imaging (using visual and scanning electron microscopy) and surface profilometry can provide extremely useful information from quite short term tests.

Testing has shown that the presence of soot in a lubricant does not affect the properties of that lubricant's anti-wear additives. Instead, abrasive wear, caused by the soot particles starving rotating or reciprocating metal surfaces of their lubricant film, is the major wear mechanism occurring with soot-related engine wear.

The simple test rig devised for this thesis to try to understand the wear created by soot contaminated lubricants proved successful within its limits and demonstrated the effects of soot entrained within lubricating oil.

7.4 Biodiesel and Metallic corrosion

Metallic corrosion is a recognised problem in the storage of biodiesel and also when used within diesel engines. As a result, continued investigation and research in this field is essential. For instance, monitoring of trace metals in biodiesel shows how these might affect biodiesel oxidation.

When reviewing the action of biodiesel on the two main metal groups consisting of ferrous and nonferrous alloys, the ferrous alloys are more resistant to corrosion. Within the non-ferrous alloy group, copper alloys are the most vulnerable owing to the way in which copper oxides reacts directly with fatty acid esters. Aluminium alloys show resistance to corrosion due to the passivating oxide layer, however this eventually breaks down via pitting.

The presence of impurities and water increases the corrosion tendency of biodiesel. In addition, the corrosiveness of a biodiesel blend increases as the fraction of biodiesel present increases and also the extent of its natural oxidation.

Metallic components in engines may be susceptible to corrosion and/or contact damage from friction and wear. The biodiesel corrosion experiments in this thesis show that biodiesel leads to greater corrosion than diesel alone. Copper components are particularly susceptible to corrosion from biodiesel.

There are concerns that the currently used indicators of corrosiveness of biodiesel e.g. copper strip corrosion and Total Acid Number (TAN) value, prescribed by current differing standards are not effective enough. The corrosive nature of biodiesel under a wide spectrum of compositional, environmental and operating variables should be investigated.

As for the tribological degradation of metallic components in biodiesel, short term laboratory studies have shown that biodiesel offers beneficial properties in terms of lower wear and friction. However, oxidation of the biodiesel and higher test temperatures adversely affect its tribological properties.

CHAPTER 8

8. Conclusions and Future Work

The conclusions from the experimental work presented in this thesis are:

- Soot particles in lubricant lead to greater wear occurring than soot free oil.
- The greater the proportion of soot in the oil the higher the wear rate.
- Engine tests showed that biodiesel blends generated greater quantities of soot than diesel alone.
- Brass and copper both showed more corrosion than mild steel, Al 7075 and Al1050 when in contact with biodiesel B100. While biodiesel B100 should have more technical advantages than fossil diesel fuel, the tests show that biodiesel in fact instigates a higher corrosion rate, which is sharply increased by the presence of free water and free fatty acid.
- Pitting corrosion was found on Al1050, Al7075 and mild steel at elevated temperatures $> 80\text{ }^{\circ}\text{C}$. Pitting was observed on brass at all temperatures. Pitting was observed on copper at low temperatures and uniform corrosion was observed above $100\text{ }^{\circ}\text{C}$.
- The different surface corrosion rates occur with different metals in contact with biodiesel as the results of changes in the amount of dissolved oxygen in the biodiesel. Fully understanding the corrosion process is complicated owing to the number of factors affecting it including changes in Total Acid Number (TAN) values, increasing free water, oxidation, presence of metallic species, and changes in biodiesel components.
- Activation energies were calculated from corrosion rates calculated by ICP and mass loss results. These showed increased activation

energy for Al1050, Al7075 and brass compared to copper which was the lowest. The increased activation energy is associated with formation of insoluble fatty acid salts indicated by SEM/EDX and lack of metal species in solution by ICP.

In order to further understand how biodiesel influences corrosion and wear in engine applications further research is required to:

- Investigate the influence of water content, especially in the presence of metal contaminations at trace levels, as well as glycerin and glyceride content on deposit formation are necessary to gain full insight into the biodiesel corrosion mechanisms;
- determine the main mechanisms occurring during thermal degradation of biodiesel. Due to the variety of fatty acid chains and remaining hydro carbons present in diesel fuels the thermal degradation probably consists of a wide range of mechanisms resulting in complex deposits;
- understand how biodiesel production can be optimised to produce biodiesel with long term stability at engine operating temperatures;
- understand how soot formation from biodiesel blends can be controlled.
- Investigate the effect of copper fatty acid salts on other metals e.g. do exchange reactions occur leading to chemical attack.

It is clear that in certain applications, biodiesel remains the most practical solution to providing energy (for example for long distance heavy duty vehicles) for automotive applications and clearly further research in understanding how biodiesel can be optimised will provide valuable contributions to reducing NO_x and CO₂ emissions that reduce the damaging environmental effects from transport. Biofuels will be a key constituent of future strategies to provide environmental benefits.

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