CHARACTERIZATION AND QUANTIFICATION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) IN USED AND FRESH ENGINE OIL BY CHROMATOGRAPHY AND SPECTROSCOPY TECHNIQUES

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A research report submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, in partial fulfilment of the requirements for the degree of Master of Science in Engineering

Johannesburg 25 May 2015

DECLARATION

I declare that this research report is my own unaided work. It is being submitted to the Degree of Master of Science to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other University.

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(Signature of Candidate)

……..day of……..year……
day *month* *year*

ABSTRACT

Polycyclic Aromatic Hydrocarbons (PAHs), which arise from incomplete combustion during engine operation, escape the combustion chamber, leading to lubricant contamination. PAHs have been declared highly detrimental to living organisms, and thus, PAH regulation in the environment is crucial because used engine oil accumulates PAHs in high levels. Engine oil samples were collected at different car maintenance workshops around Johannesburg, where the analysis of 5 target PAHs was carried out in both fresh and used engine oil samples (different oil bands), and then subjected to Gas Chromatography- Mass Spectrometry (GC/MS) and High Performance Liquid Chromatography (HPLC). In contrast to preliminary studies reporting higher PAH values of 300+ in used engine oil, the PAH value has decreased significantly, with PAH content being 70 and 7 times more in used engine oil by HPLC and GCMS respectively due to the different capabilities of the two instruments. Fourier Transform Infrared (FTIR) revealed evidence showing the formation of PAHs, which was corroborated by the presence of a band at 1600 cm^{-1}, which is associated with a C-C stretch in a ring. In comparison to fresh oil, used oil quantitative proton Nuclear Magnetic Resonance (NMR) revealed a new intense peak at the aromatic region between 7-7.5 ppm, which may have arisen due to PAH formation. It was also observed that the PAH content was considerably lower compared to other constituents found in the oil sample. This drastic reduction in PAH concentration, may be due to the significant improvements made in lubricating (engine) oil formulations, refining processes, and engine designs.

DEDICATION

In memory of the fallen soldiers belonging to squad:

Shakoane, Khumalo, Monareng and Mashego

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NOMENCLATURE

ACEA:	Association des Constructeurs Europeans D'Automobiles
A/F:	Air/Fuel
APCI:	Atmospheric Pressure Chemical Ionization
BO:	Base Oil
DAD:	Diode Array Detection
DIY:	Do It Yourself
ECD:	Electron Capture Detector
EGR:	Exhaust Gas recirculation
EPA:	Environmental Protection Agency
FID:	Flame ionization Detector
FTIR:	Fourier Transform Infrared
GC:	Glass Chromatography
GHG:	Green House Gas
HC:	Hydrocarbons
HCCI:	Homogeneous-Charged Compression Ignited
HPLC:	High Performance Liquid Chromatography
ICE:	Internal Combustion Engine
LOD:	Limit of Detection
LOQ:	Limit of Quantification
MS:	Mass Spectrometry
NOx:	Nitrogen Oxides
PAH:	Polycyclic Aromatic Hydrocarbons
PCB:	Poly Chlorinated Biphenyls
PFI:	Port Fuel Injection
RS:	Resolution Factor
SAE:	Society of Automotive Engineers
SCSI:	Stratified Charge Spark Ignited
SFE:	Supercritical Fluid Extraction
SPE:	Solid Phase Extraction
UV:	Ultra-Violet
VI:	Viscosity Index

CHAPTER ONE

1.1 INTRODUCTION

South Africa generates about 120 million litres of used engine oil each year and about 40 million remains unaccounted for (Rose, 2010). Where does the rest go? Car repair/maintenance facilities, "Do it yourself" (D.I.Y) practices, industries such as electricity generation, smelting and mining operations, are amongst the major sources of used engine oil. In the USA the RCRA prior to banning improper use and disposal of waste oil; used oil used to be discarded inappropriately (and it still is) into the environment (Pitchel, 2014). Disposal of oil haphazardly is mainly done by facilities that have no access to proper disposal units, such as owners who change the oil from their vehicles and end up discarding it in the ground, storm sewer drains, ordinary trash, spread on gravel, in the garden, etc. (Rose, 2010).

Used engine oil is a petroleum-based product, which after engine operation (performing lubrication on the machinery parts), becomes contaminated with impurities that diminish its purpose as a lubricant. This type of waste is a huge environmental problem, not only is it insoluble and persistent but it also contains toxic constituents (PAHs) and chemicals, ultimately making used engine oil detrimental to the environment, humans, animals and plants (Pitchel, 2014). Used oil enters the soil in the following ways:

- Its application on gravel for dust control in rural areas
- Disposal in landfills
- During asphalting
- Escape/loss (on the surface pavements, streets, car parks, etc.) during engine operation

This oil remains until it is washed off either by the municipality or by rain (storm-water), transporting it into the waste pipes or nearby soil (close to the roads). It is rapidly transferred to aquatic environments through runoff. It seeps through the soil and contaminates ground water and kills plants. Ultimately the accumulation of toxic substances in the soil contaminates water and poisons animals and plants which may be consumed by humans (Blodget, 1997).

1.2 Engine Oil and Functions

Back in the 1900's, there was a lack of knowledge in the area of lubricant formulation science, leading to no technological breakthroughs or advances hence the concept of 'performance specification' did not exist. Most of the cars back then had enormous engines which were steam driven and were very slow. Refining crude at that stage was still an unknown notion because at that time crude oil products did not dominate the lubricant technology as they do presently. By the 1930's, the automobile design and technology had progressed, and advanced in the understanding of lubrication and oil refining. The engines were smaller and running much faster thus getting hotter and showing stress leading to the era of introducing additives in the engine oil to enhance performance began. In time, pressure began to mount on the engine industry and fuel economy. The engine oil had to meet certain standardized specifications (such as low emissions); engine designs became smaller and more complex but resulted in higher power output (Mitchell, 2011).

Currently, the oils are significantly improved, there are reduced greenhouse gases (GHG) and PAH emissions. The focus is being placed upon fuel consumption as it is directly proportional to the emitted CO_2 (GHG), and unfortunately other emissions apart from CO_2 have not been diminished yet. With continuous technological advancement in motor cars and engine designs, lubricants are becoming more complex and sophisticated (Rose, 2010).

Engine oil is mainly used for lubricating internal combustion engines. Lubricating oils consist of residues from atmospheric crude oil distillation further distilled under vacuum conditions, producing vacuum distillates. It has a number of functions.

- It lubricates the engine parts such as bearing, pistons, piston rings, cylinder liners, etc. and prevents wear. This is a basic function of oils, keeps moving parts separated; thicker oil films provide better wear protection. The viscosity of oils is improved from low to high by incorporating additives.
- Reduction of friction, since metal-to-metal contact is eliminated
- Corrosion prevention-degradation of oils and the presence of moisture and acids result in formation of corrosive by-products. Thus important to incorporate acid-neutralizing and anti-corrosion additives.

- Keeps components such as pistons clean to prevent sludge build-up on internal surfaces.

- It must be compatible with seals by keeping them lubricated and not cause seal deterioration which might result in leakage due to seal failure.
- Prevents foam formation which reduces lubrication of the oil.
- Cool the engine
- Reduction of combustion chamber deposits. (Pentrite, 2008)

1.3 Base Oil

In the early days, base oils (BO) used in car engines were said to be made from crude fractions of certain gravity and viscosity, suitable for operating at high speed. Different BOs obtained from different crudes, were found to have low viscosity index (VI) and higher aromatics content which neutralised their use as base oils. This led to petroleum refiners developing processes that would further upgrade the less desirable to more suitable BOs (Sequira, 1994).

BO is a by-product of refined crude oil (Figure 1.1), which acts as a basis or a precursor for lubricant formulation. It has additives incorporated into it for maximum performance, which ultimately contribute to the formation of PAHs (further discussed section 2.2).

Therefore, proper testing is required to ensure that the engines oil performance is not adversely affected by substitution of different BO. Choosing the correct BO for lubricant formulation is imperative, as it affects the sulphur content of the final formulation, consequently affecting the concentration and the additives needed for the final product, to meet the required performance or specifications (Pentrite, 2008).

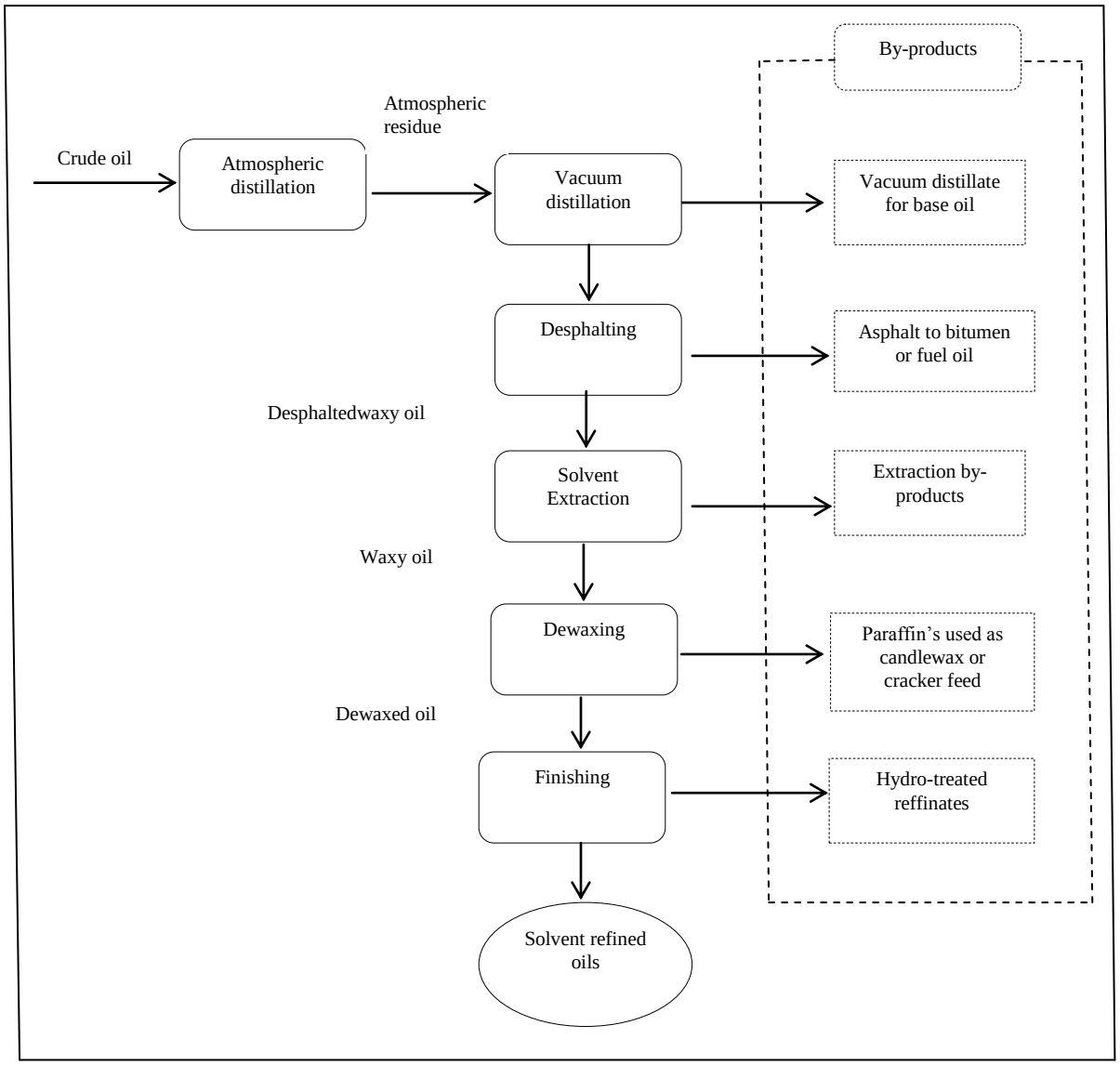


Figure 1.1: Lubricant formulation processes (Bilewski, *et. al.* 2012)

1.4 Additives

Whilst it might have been easier to use animal fat for axles on ox carts centuries ago, times are changing, modern machinery is becoming more and more advanced, engines are becoming smaller and more complex thus during the automotive-era, engine oil was least highly specialized nor standardized and therefore required frequent oil changes(Ludema, 1996). However, the same basic principle of lubrication still reigns (Rizvi, 2009). All lubricants provide a reduction in friction or a, metal-to-metal contact, but other lubricants tend to perform better than others and this is because of the materials or elements they possess or their ability to enable the machines to execute successful operations (Hervely, 2012).

Additives either impart a new property (anti-wear, anti-corrosion, suspending ability, etc.) enhance the already existing properties (pour point, viscosity index, oxidation resistance, etc.), or reduce the rate at which undesirable changes occur. In present world, machinery from car engines, gears, railroads to turbines, is expected to perform at high speed. The introduction of additives in lubricants has significantly aided in their development and performance. These agents are problem solvers (Bilewski, *et. al.* 2012). Since their dawn in the early 1930's, they have solved a variety of engine problems from corrosion, soot deposition, acidic combustion, wearing and many more. Figure 1.2 shows the three main categories of the extensively used additives (Leslie, 2003)

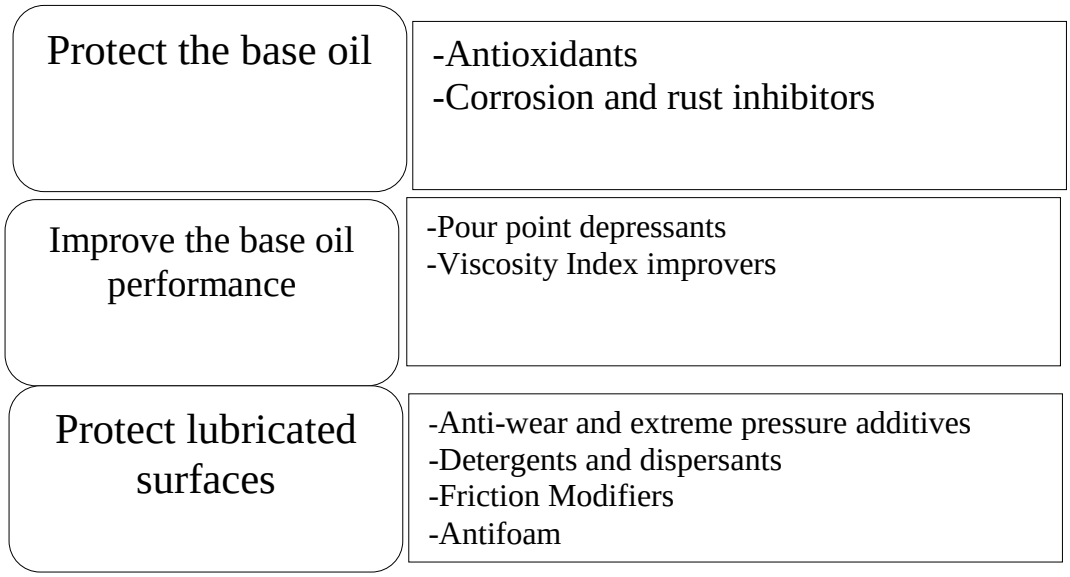


Figure 1.2: General categories of additives (Hervely, 2012)

Although additives play an important role in lubrication but they are insoluble in water and thus making it easier for its derivatives (PAHs (Polycyclic Aromatic Hydrocarbons, PCBs (Poly Chlorinated Biphenyls), dioxins, etc.) to be easily released into the environment. Since halogenated additives are considered more toxic they are absent in modern additives (Bilewski, *et. al.* 2012).

1.5 Context of the Study

In addition to the additives (VI improvers, dispersants, detergents, oxidation and rust inhibitors) and hydrocarbons already present in the formulated product, used motor oil accumulates contaminants that arise during engine operation. The main sources of these contaminants are: the degradation of additives, material leaking from the combustion chamber

to the lubricant oil, burnt oil, metal particles such as Pb, Zn, As, Cd and Ni occurring from the wearing of engine parts from lubrication, oxidation and heating during engine operation (U.S. EPA, 1984).

But what mostly characterizes used engine oil is the high concentration of PAHs. Their formation in engines is a result of incomplete combustion of organic matter, where these contaminants are fuel products that are then carried to the crankcase thus accumulating in the lubricant (Hewston, 1994). They are also found to be toxic, carcinogenic and highly detrimental to human health (U.S. EPA, 2001).

Techniques such as Gas Chromatography-Mass Spectrometry (GC-MS) have been used to successfully characterize PAHs in oil due to the fact that these organic compounds are highly lipophilic. As such, it becomes imperative to quantify and decrease the amount of PAH's in used engine oils before disposal to prevent environmental contamination and negative effects on human health. Due to used engine oils chemical composition, dispersion and impact on the environment it's considered as a health hazard.

1.6 Problem Statement

Used engine oil is characterized by high PAH content and preliminary studies have reported high PAH concentration in used engine oil compared to fresh oil by 300 times or more. Although these studies are obsolete (the first study made in the 80's and the latest in the early 2000's), they may not be a true reflection on the design of engines and the engineering of modern motor oil (Kubsh, 2013). As the years have progressed, there has been advancement and breakthroughs made in oil formulations. Engine designs have become more sophisticated as technology steadily progresses, and this can be corroborated by stringent emission legislative limits such as the euro 6, which are being put into place and have to be abided by all car and lubricant manufacturers (Mitchell, 2011). Hence, the old results might be misleading therefore new studies have to be carried out.

This study serves as an updated investigative overview that will bridge the knowledge gap between the early 2000's and now, thereby eliminating a huge discrepancy in many current engine oil and PAH studies.

1.7 Overall Aims of the Study

The main aim of the study is to compare the High Performance Liquid Chromatography (HPLC) and GC methods for PAH quantification and also compare the PAH content in used and fresh engine oil, while the objectives to achieve this aim include:

- Characterization and quantification of PAH in used engine oils around Johannesburg, which will be carried out, with the use of chromatographic techniques: HPLC and GC/MS.
- Data Validation by Spectroscopy: infrared (IR) and Nuclear magnetic Resonance (NMR).
- Quantification of PAH chemical composition in fresh and used engine oil will be carried out in parallel, in order to evaluate the issue of PAH elimination with regards to improvements in lubricating oil formulations, refining processes and improved engine designs.

CHAPTER TWO

2.1 LITERATURE REVIEW

In the auto-motive industry, engine oil is predominantly used as a lubricant which has several functions within an engine of a car. Its role includes lubrication of moving parts whilst operating at high speed and temperature. It decreases friction and prevents mechanical wearing of the parts. Components of the engine are kept clean, by keeping particles that form in cold parts of the engine in suspension. As the lubricant is thermos-stable, it is exposed to a wide range of temperatures, it cools heated parts, and it is exposed to oxidation, combustion and rust but is made to be resistant against them. To be considered as a top notch lubricant, it has to satisfy certain specifications to maintain a certain standard. The mentioned roles are made possible by incorporated additives. Continuous engine operation leads to accumulation of heavy metals and polycyclic aromatic hydrocarbons, consequently producing a hazardous waste due to the toxicity of these compounds (Audibert, 2006).

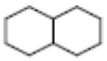
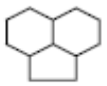
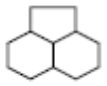
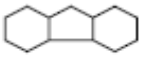
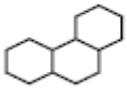
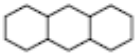
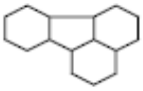
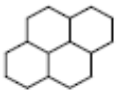
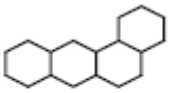
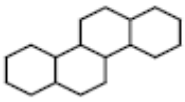
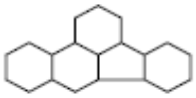
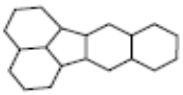
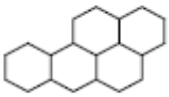
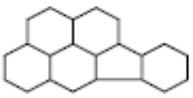
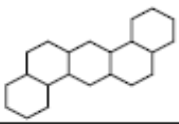
2.2 Polycyclic Aromatic Hydrocarbons (PAHs)

Petroleum (including its products) along with individual PAHs are found throughout the ecosystem in the world. They are detected in living and non-living systems, with crude oil being the major environmental source of these toxic PAHs, thus serving as a potential hazard for all organisms (Hoffman, *et. al.* 2002).

PAHs are organic compounds that have two or more aromatic rings that have been fused together. Their water solubility is said to decrease with increasing hydrophobic interactions (increasing molecular weight) therefore, they are found to be lipophilic (Messinger, 2002). These organic particles are highly persistent in soils and sediments, they bio-magnify, therefore they are highly bio-available. In addition, they are mutagenic and carcinogenic thus, making these toxic pollutants a serious environmental concern. This explains why their concentration is highly regulated in all environmental sections (land, air, and aquatic) (Joa, *et. al.* 2009).

Table 2.1 shows the defined 16 United States Environmental Protection Agency (U.S. EPA) PAHs known as primary pollutants and over 100 PAHs are found but these 16 are said to be the most toxic of them all (Messinger, 2002).

Table 2.1: The properties of the U.S. EPA PAHs (Joa, *et. al*. 2009)

PAH	Abbrevi-ation	Structure	Molecular mass, Daltons	Boiling point, °C	Vapor pressure at 25 °C, Pa	Log K_{ow}
Naphthalene $C_{10}H_8$	**NA**		128	218	10.4	3.37
Acenaphthene $C_{12}H_{10}$	**AC**		154	278	30×10^{-1}	3.92
Acenaphthylene $C_{12}H_8$	**ACN**		152	265	9.0×10^{-1}	4.00
Fluorene $C_{13}H_{10}$	**FL**		166	295	9.0×10^{-2}	4.18
Phenanthrene $C_{14}H_{10}$	**PHE**		178	339	2.0×10^{-2}	4.57
Anthracene $C_{14}H_{10}$	**AN**		178	340	1.0×10^{-3}	4.54
Fluoranthene $C_{16}H_{10}$	**FA**		202	375	1.2×10^{-3}	5.22
Pyrene $C_{16}H_{10}$	**PY**		202	360	6.0×10^{-4}	5.18
Benz[a]anthracene $C_{18}H_{12}$	**B[a]A**		228	435	2.8×10^{-5}	5.91
Chrysene $C_{18}H_{12}$	**CHR**		228	448	5.7×10^{-7}	1.65
Benzo[b]fluo-ranthene $C_{20}H_{12}$	**B[b]F**		252	481	N/A	5.80
Benzo[k]fluo-ranthene $C_{20}H_{12}$	**B[k]F**		252	481	5.2×10^{-8}	6.00
Benzo[a]pyrene $C_{20}H_{12}$	**B[a]P**		252	495	7.0×10^{-7}	6.04
Benzo[ghi]-perylene $C_{22}H_{12}$	**B[ghi]P**		276	N/A	6×10^{-8}	6.50
Indeno[1,2,3-cd]-pyrene $C_{22}H_{12}$	**IP**		276	536	N/A	6.58
Dibenz[a,h]-anthracene $C_{22}H_{14}$	**D[ah]A**		278	524	3.7×10^{-10}	6.75

K_{ow} – octanol/water partition coefficient
N/A – not available

2.2.1 Sources and PAH Formation

The formation of PAH is mainly through pyrolysis and recombination of organic molecules. At high temperatures, they are produced via incomplete combustion processes as shown in Figure 2.1.

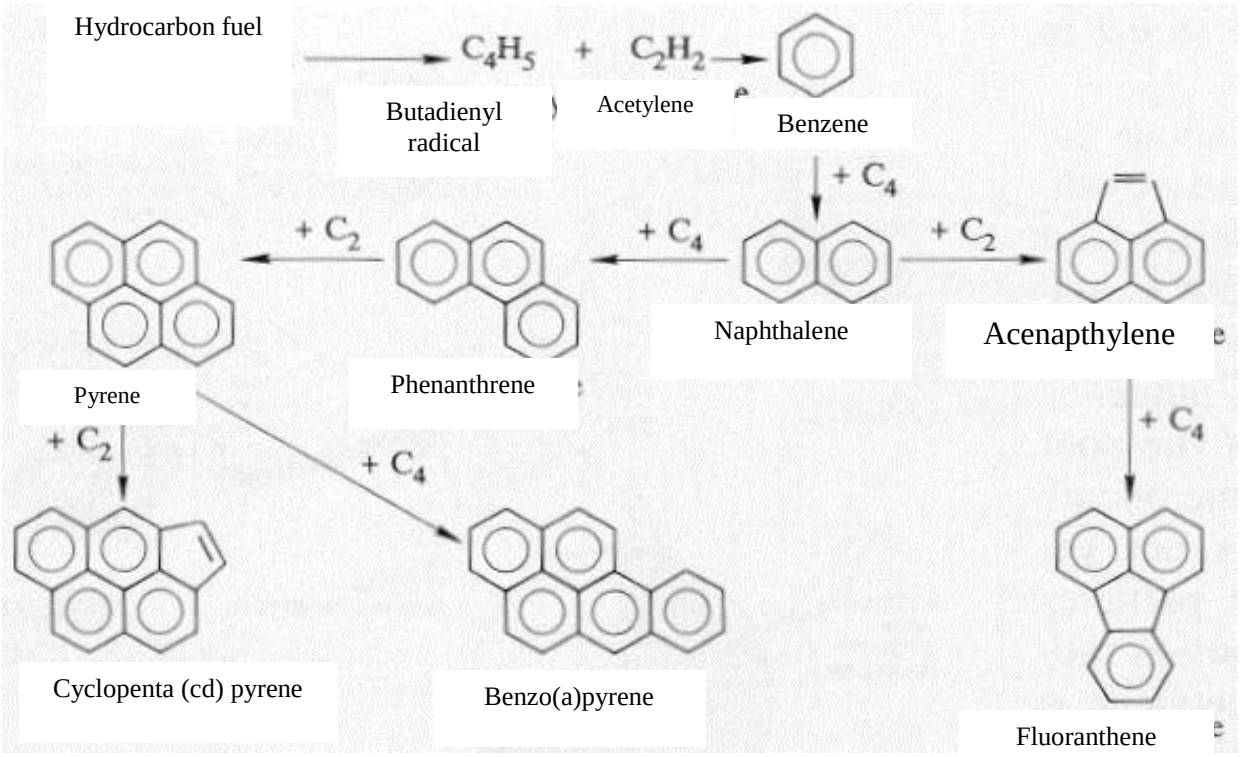


Figure 2.1: Chemical Scheme showing the formation of PAH during fuel combustion (McLoughlin, 1982)

Natural sources of PAHs are soil seeps, bacteria, fungi, grass and forest fires, volcanoes, etc. (Hoffman, *et. al.* 2002). Crude oil, power generation, combustion of fossil fuels, automobile exhaust fumes, production of coke, coal tar, asphalt, agricultural and industrial processes are all anthropogenic sources of PAHs as depicted in Figure 2.2 (Kao, *et. al.* 1985).

Without the incorporation of radical scavenger additives such as anti-oxidants, there would be a huge increase in PAH concentration, due to the formation of free radicals such as hydro peroxides and hydroperoxyls which are unstable and short-lived, as they would react with PAH precursor molecules consequentially leading to an increment in PAH content.

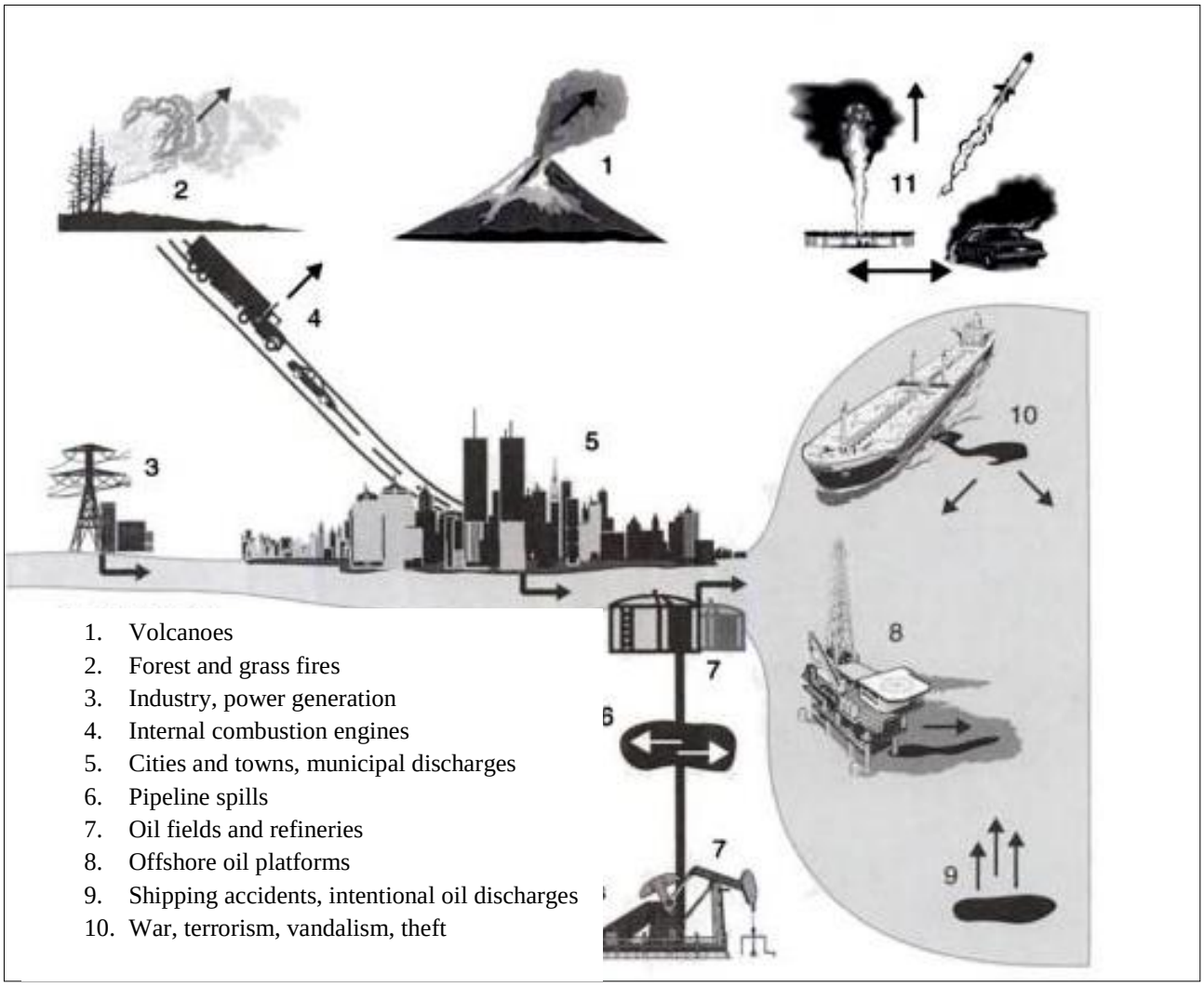


Figure2.2: Sources of PAHs and their movement (arrows) in the environmental compartments i.e. land, air and water (Hoffman, *et. al.* 2002).

2.2.2 PAHs in Used Engine Oil

In internal combustion engines (ICEs), PAHs are formed during combustion of organic compounds derived from the formulation material and additives of the lubricant oil. Literature shows that the content of PAHs in fresh and used engine oil varies considerably (Hoffman, *et. al.* 2002)

A study by Pruell and Quinn (1988), using a 1981 gasoline-powered engine showed low levels of PAHs in new lubricating oil. However, it was observed that the concentration of PAH increased rapidly with an increase in the amount of miles driven. The concentration of light PAHs components comprising of 2-3 rings, increased until ~ 4000 miles then levelled off whilst the heavy PAHs (4 and 5 rings) which are more toxic, were only detected at ~ 5800 miles, which was the longest distance driven. This study suggests that with continuous engine

operating time not only does PAH concentration increase, but there is also formation of the heavy, highly stable and most toxic PAH. PAHs consisting of 4-7 rings have been directly associated to the carcinogenic effect of used engine oil. This suggests that the accumulation of 2-3rings (lower molecular weight compounds) is rapid whilst that of 4-7 aromatic rings is slow, thus found in low quantities (Pruell and Quinn, 1988).

A similar study by Grimmer (1982), also proved that the concentration of PAH in used engine oil is 100-300^{+} times higher than that of fresh motor oil. Grimmer also showed that the concentration of dibenzo[α]-anthracene, 4-methylpyrene, fluonocenthene, benzo[α] anthrecene, were 36,49, 253 and 720 times higher respectively in used than fresh engine oil (Grimmer, *et. al.* 1982). Vazquez-Duhalt (1989) reported a staggering value of 670 times of PAH in used oil relative to fresh motor oil (Vazquez-Duhalt, 1989).

2.2.3 PAH Impact on the Ecosystem

As previously mentioned; PAHs are environmental pollutants that consist of fused aromatic rings. There is more than 100 of them but the USEPA has listed 16 of them as priority pollutants (Auer and Malissa, 1990). These components are highly hydrophobic, thus explaining their persistence and bioaccumulation in environments as they have high affinity for organics in the soil. Incomplete combustion of organic material leads to their formation. In addition to factors that have impact on used engine oil, additives also contribute to the increasing of PAH concentration, thus explaining the low levels of PAH found in fresh engine oil (Audibert, 2006). These compounds are highly carcinogenic and mutagenic due to the presence of bay regions (a four carbon pocket) formed by fused rings, therefore the higher the number of rings a PAH contains, the more carcinogenic it becomes. Waste motor oil still remains to be a major concern around the world (specifically due to the presence of PAHs), since a significant amount of it is still being discharged into the environment without the following of proper procedures (Blodgett, 1997). In the USA, it is estimated that out of the 28 million tonnes of used oil produced, ~10% is used as fuel ~ 15% is incorporated into asphalt and the remaining ~30% is discarded into the environment (Vazquez-Duhalt, 1989).

Used engine oil is a major environmental contaminant, entering the aquatic ecosystem, through runoff (Auer and Malissa, 1990). It is believed that the major pollutant in urbanized estuaries is found in used engine oil (Grimmer, *et. al.* 1982). With naphthalene, benzo[α]pyrene, fluorine and phenanthecene being the most common PAH components in

used engine oil. In Philadelphia's region storm water, used engine oil was found to be the main source of PAH whilst in rural areas PAHs enters streams from the highways (Maliney, 1993).

From 1990-1991 a study was made (Upshall, *et. al.* 1993), where sediment samples were acquired from downstream water near a highway in England. Results revealed elevated levels of trace metals such as Zn, Cd, Cu, Ni, Ca, etc. and also hydrocarbons including PAH which were all detected in used motor oil. Another noteworthy discovery made, was that there was a change in the community structure, in a sense that there was now a shift from a mixed community at the upstream to a community mainly dominated by another species. The toxicological tests carried out with sediment samples collected from up- and downstream, revealed that the downstream sediment was highly toxic due to the presence of aromatic hydrocarbons mainly PAH's in sediments (Upshall, *et. al.* 1993).

Used oil enters the soil through loss during engine operation, asphalting, application on rural roads and direct disposal on landfills. An effect of introducing waste engine oil in the soil results in a change in the total microbial community. It promotes the growth of anaerobic hydrocarbon bio-degrading microorganisms. It fills the pores of the soil hindering oxygen access (Raymond, *et. al.* 1976); in such conditions there's inhibition in growth of plants, due to the presence of heavy metals that inhibit the sulphur, carbon and phosphorus mineralization, primary production, and also the transformation of nitrogen in the nitrogen cycle (Babich and Stotkzy, 1985).

2.2.4 Mutagenicity, Carcinogenicity and Toxicity of PAHs

The following studies have been carried out to demonstrate the lubricant oil's carcinogenic and mutagenic effects

The mutagenic effect of engine oil was assayed on *Salmonella typhimurium*. It was found that the new oil showed no mutagenic effect on bacteria; however it was observed that the used engine oil was found to be highly mutagenic to bacteria (Dutcher, *et. al*. 1986). This mutagenicity of used engine oil on bacteria is a result of an increase in PAH content during engine operation specifically, the benzo[$\propto$]pyrene which increases significantly accounting for ~ 18% of the total carcinogenicity in the oil. Normally PAHs containing more than 3 rings account for about 70% of the total carcinogenicity in the crankcase oil, consisting of about 1.14% of the total oil sample (Thony, *et. al.* 1975).

Additives have the potential to increase the carcinogenicity of PAHs; examples being ditert-thiooctyl polysulphide, disulphide and ditert-thiobutyl sulphide but they show no carcinogenicity when applied without other components (Bingham and Horton, 1966). Lead-naphthalene-containing additive used in lubricant formulation has shown carcinogenetic activity, inducing tumours in 35/40 animals, with 75% found to be carcinomas (Baldwin, *et. al*. 1961). Its activity is completely dependent on base oil components, indicating that carcinogenicity of a lubricating oil is proportional to the PAH content (Gradiski, *et. al*. 1983).

A study involved applying used engine oil from gasoline powered vehicles onto the skin of mice, which induced tumours were not observed when new engine oil was applied (Saffioti and Shubik, 1963). Upon application of used oil, 0.625 mg induced 100% papilloma, 0.625 mg induced 53% carcinoma and 1.875 mg induced 64% cancerous tumours. (Grimmer, *et.* al. 1982).This suggests that the degree of exposure of mice skin to used engine oil is proportional to the severity of induced tumours. Additionally it was found that high molecular weight PAHs account for more than 70% of the total carcinogenicity in the used lubricant oil (Grimmer, *et. al*. 1982).

Birth defects by external application of used engine oil on bird eggs were tested. Exposure of ducks and quail eggs to used and fresh motor oil took place upon 48 hrs of development. Used oil was found to be toxic to the embryos of both the species relative to new oil and consequently resulted in 84% mortality in ducks and 88% in quail. Surviving births showed brain and eye defects, low haemoglobin and red blood cell concentration in hatchlings and embryos (Hoffman, *et. al*. 1982).

Toxicity is dependent upon dose, bioavailability, route of exposure and species type. The PAHs mechanism of toxicity is said to interfere with the function of the cellular membrane and the enzymes associated with it (Hoffman, *et. al*. 2002).The PAHs reactive metabolites that bind to DNA and proteins consequentially, lead to biochemical perturbations and damage which further leads to mutations, tumours and cancer cell development (Eisler, 2000).

2.3 Engine Oil Specifications

Countries around the world are becoming more and more developed. As such stringent policies are now being implemented to lower motor vehicle exhaust emissions for cleaner air quality. Car manufacturers' product's design has to be in line with the new regulations and new non-compliant vehicles cannot be sold in some parts of the world.

2.3.1 API and ACEA

There are two types of specifications; the API (American Petroleum Institute) and the ACEA (Association des Constructeurs Europeans D'Automobiles). The purpose of these specifications is to indicate oil performance and the tests it must exceed prior to being declared fit for use (Focus will be on gasoline and or light duty diesel engines). Thus, lubricant manufacturers examine and assess their products, in expectance of meeting or surpassing the requirements of the API or ACEA specifications (Mitchell, 2011).

Tables 2.3, 2.4, and 2.5 provide evidence of the significant progression of lubricants, made over the years. They also show compatibility between engine design and gasoline engine oil specifications. There has been a huge gap in performance classification between the two specifications (ACEA and API) since the late 90's. It's mainly because the European requirement for engine oils surpasses that of the US (Mitchell, 2011).

Table 2.2: API gasoline engine oil specifications, S=Petrol, 2nd letter (A, B, C, D, etc.)= order of introduction (Mitchell, 2011).

GASOLINE ENGINES		
Category	**Status**	**Service**
SM	**Current**	For all automotive engines currently in use. Introduced in 2004, SM oils are designed to provide improved oxidation resistance, improved deposit protection, better wear protection, and better low temperature performance over the life of the oil. Some SM oils may also meet the latest ILSAC specifications and/or qualify as Energy Conserving
SL	**Current**	For 2004 and older automotive engines
SJ	**Current**	For 2001 and older automotive engines
SH	**Obsolete**	For 1996 and older engines
SG	**Obsolete**	For 1993 and older engines
SF	**Obsolete**	For 1988 and older engines
SE	**Obsolete**	**CAUTION:** Not suitable for use in gasoline powered automotive engines built after 1979.
SD	**Obsolete**	**CAUTION:** Not suitable for use in gasoline-powered automotive engines built after 1971. Use in more modern engines may cause unsatisfactory performance or equipment harm
SC	**Obsolete**	**CAUTION:** Not suitable for use in gasoline-powered automotive engines built after 1967. Use in more modern engines may cause unsatisfactory performance or equipment harm.
SB	**Obsolete**	**CAUTION:** Not suitable for use in gasoline-powered automotive engines built after 1951. Use in more modern engines may cause unsatisfactory performance or equipment harm.
SA	**Obsolete**	**CAUTION:** Contains no additives. Not suitable for use in gasoline-powered automotive engines built after 1930. Use in more modern engines may cause unsatisfactory performance or equipment harm.

Table 2.3: Latest specifications with the most recent SN specification (Mitchell, 2011).

API classification	Applicable period	Properties specified
SA	Up to 1930	Mineral oils with no additives
SB	1931 - 1963	Oxidation resistance, Corrosion prevention, Wear control
SC	1964 - 1967	Based on engines tests. As for SB but with no detergents/ dispersants. Control of cocking deposits. Control of sludge
SD	1968 - 1971	As per SC but more severe tests, hence higher levels of additives
SE	1972 - 1979	AS per SD but more severe tests and higher levels of additives. Performance in stop/start operation
SF	1980 - 1988	As per SE but more severe tests and higher levels of detergency. Some suitability for diesel engines
SG	1989 - 1993	As per SF but more severe and some additional tests. Higher dispensancy. Limit on phosphorus content (0.12%) and introduction of modest shear stability test. Limits of evaporation loss, filterability, foaming and flash point (flammability).
SH	1993 - 1996	Similar to SG but with requirement that all testing be done in accord with new CMA code.
SJ	1996 - 2001	As per SH but lower evaporation loss and reduced phosphorus (0.10%). New high temperature deposit and low temperature gelation tests.
SL	2001 - 2004	As per SJ but more severe tests. May also be energy (fuel) conserving.
SM	2004 - 2010	As per SL but more severe tests. Reduced phosphorus (0.08%).
SN	2010 -	As per SM but more severe tests. Still 0.08% max phosphorus for low viscosity grades, but relaxed for higher grades.

Table 2.4: ACEA API gasoline oil specifications; A=Petrol, B=Light duty diesel engines (Mitchell, 2011).

Category	Description
A1/B1	Oils intended for use in petrol and diesel car and light commercial vehicles specifically capable of using low friction, low viscosity oils with high temperature/ high shear characteristics
A3/B3	For use in high performance petrol and diesel cars and light commercials where extended drain intervals are specified by the vehicle manufacturer and/ or for year-round use of low viscosity oils and/ or for use in severe operating conditions as defined by the vehicle manufacturer
A3/B4	For use in high performance petrol and diesel cars and light commercials where extended drain intervals are specified by the vehicle manufacturer and/ or for year-round use of low viscosity oils and/ or for use in severe operating conditions as defined by the vehicle manufacturer
A3/B5	For use in high performance petrol and diesel cars and light commercials where extended drain intervals are specified by the vehicle manufacturer and/ or for year-round use of low viscosity oils and/ or for use in severe operating conditions as For use in high performance car and light commercial petrol and diesel engines designed for low viscosity oils where extended oil change intervals are specified by the vehicle manufacturer

ACEA is a European body formed by 15 high profile manufacturers (such as Volvo, Volkswagen, BMW, Audi, etc.). These members are responsible for setting emission levels (from vehicles) and drawing-up guidelines for lubricants (Mitchell, 2011). ACEA mainly focuses on the car requirements rather than the oil. Its mandate is to have an extended drain system thus reducing oil consumption but re-cuperating overall quality of the lubricant. On the other hand API was the first group to set motor oil standards whereby, it's most recent specification is SN (launched in 2010). These specifications are set for lubricant manufacturers to test their products and submit licensing, and upon satisfying the specification criteria, the oil canisters can display the API 'donut' (Peak lubricants, 2009).

2.3.2 SAE Viscosity Specifications

In the lubricant industry, viscosity is the main feature for proper lubricant application however, other variables (temperature, speed, load, contain ability, etc.) also have to be considered. The Society of Automotive Engineers (SAE) is responsible for setting the requirements for lubricant manufacturers (Hoffman, *et. al.* 2002). It created two viscosity benchmarks SAE J300 and SAE J306 (viscosity classification for maul and axe transmission oils). The SAE J300 standard was published in 1911, a viscosity classification for engine oils

created to reflect engine oil sustainability (Sae, 2009); the different grades (mono-grades or straight grades) are flow rates measured at 100^0C (Table 2.5).

Table 2.5: SAE J300 engine oil grades for low ('W') and high temperature specifications (Sae, 2009)

SAE Viscosity Grade	**Low-Temp (^{0}C) Cracking Viscosity**	**Low-Temp (^{0}C) Pumping Viscosity, cP Max with no yield stress**	**Kinematic Viscosity (cSt) at 100^0 C Max**	**Kinematic Viscosity (cSt) at 40^0 C Max**	**High Shear Viscosity at 150^0 C Min**
0W	3250 @ -30	60000 @ - 40	3.8	-	-
5W	3500 @ -25	60001 @ - 35	3.8	-	-
10W	3500 @ -20	60002 @ - 30	4.1	-	-
15W	3500 @ -15	60003 @ - 25	5.6	-	-
20W	4500 @ -10	60004 @ - 20	5.6	-	-
25W	6000 @ -5	60005 @ - 15	9.3	-	-
20	-	-	5.6	<9.3	2.6
30	-	-	9.3	<12.5	2.9
40	-	-	12.5	<16.3	2.9*
40	-	-	12.5	<16.3	3.7**
50	-	-	16.3	<21.9	3.7
60	-	-	21.9	<26.1	3.7
* For 0W40, 5W40 and 10W40 grades **For 15W40, 20W40 and 40 grades					

In 1952 major changes occurred having to assign oil grades with ‘W’ = winter. This change came about so as, to tackle cold conditions which affected oil performance. The grades that existed were unable to meet oil specifications e.g. at low freezing conditions. An oil meeting SAE 20 specifications derived from a thick crude was found to be thicker and different from a lubricant derived from a lighter crude which performed better during cold conditions (and were also found to have different viscosity indices) (Toefer, 2014). Grades designated with a ‘W’ were meant for winter use. It then became a nuisance having to change engine oil with a change in season. Advances in the lubricant industry lead to the development of viscosity enhancer’s additives which increases the VI of lubricants enabling them to operate optimally at low and high temperature conditions, and also to meet the temperature grade specifications. Hence the introduction of multi-grade oils (Table 2.6); expensive synthetic oils which have extended life span and are said to be cleaner during engine operation.

Table 2.6: Multi-grade oil and their application (Api, 2009).

If lowest expected outdoor temperature	Typical SAE Viscosity Grades for Passenger Cars
0^0C (32^0F)	5W-20, 5W-30, 10W-30, 10W-40, 20W-50
18^0C (0^0F)	5W-20, 5W-30, 10W-30, 10W-40
Below -18^0C (0^0F)	5W-20, 5W-30

2.3.3 Recycling used engine oil by re-refining

Used oil is being recycled in many countries on a large scale basis preventing indiscriminate disposal of used oil (Rose, 2010). Refining used oil is economically feasible with regards to environment protection and conservation, energy consumption for production is lower and high quality products are independent of imported oil (Vest, 2000). It undergoes extensive processes such as distillation hydro-finishing refining process, solvent treatment distillation finishing refining process and high temperature distilling process. The aim of re-refining is to return the use engine oil to its original state. Figure 2.3 is an example of a process flow diagram, where T104 is a PAH/Solvent recovery unit.

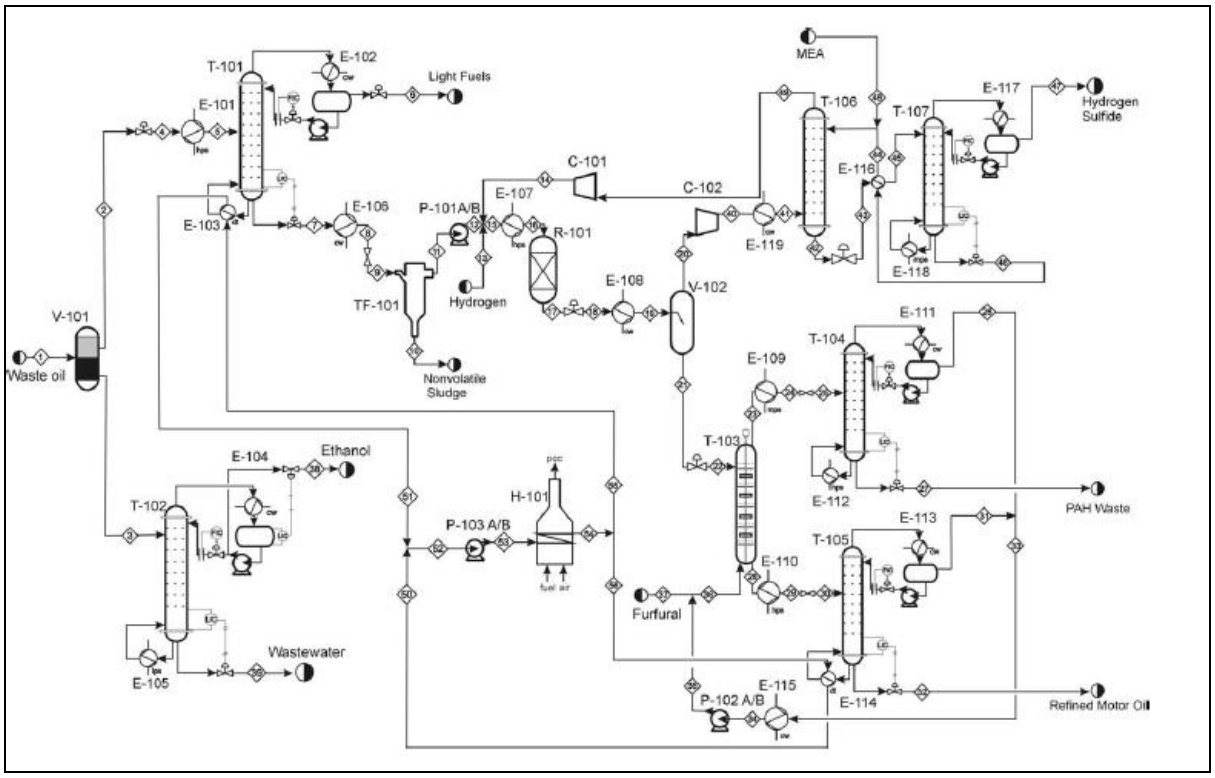


Figure 2.3: Process diagram flow of used engine oil re-refining processes (Vest, 2000)

2.4 Improvements on an Engine

Over the years car technology has steadily progressed, advancement and breakthroughs have been made in oil formulations, technical and technological developments (such as fuels, combustion processes, exhaust gas treatment, etc.) have led to a more sophisticated engine design. In recent times, studies have shown the correlation between engine advancement and PAH emission, but the focus has now directly shifted on heavy duty diesel engines, which is slightly different to gasoline-driven engines (light duty diesel engines). The stringent emission legislative limits have been put into place for car and lubricant manufacturers to be in compliance with and for the reduction of emissions (such as PAH particulates), although further developments are taking place as limits continue to become more stringent (Fiebig, *et. al*. 2014).

2.4.1 Advancement made on Combustion Systems

The majority of cars use the internal combustion engine, which consists of a cylinder with pistons, intake and exhaust valve, and spark plugs (for spark ignition engines); there are also the port fuel injection (PFI) engines. Particulates including PAH are produced during combustion processes and escape the combustion chamber through piston rings to the crankcase oil by blow-gases that are adsorbed (Fujita, *et. al.* 2007). Numerous studies have been carried out to achieve particulate (PAH/HC) emission reduction.

In 2007, a review study by Alkidas stated the combustion modes at which an engine needs to operate for reduction in PAH emissions, which were stratified-charge spark ignited (SCSI), Homogeneous-charged compression-ignited (HCCI) and Homogeneous charge spark ignited (HCSI) and can be achieved by using recent combustion advanced technologies such as spray-guided direct injection system, flexible variable-valve actuation and cylinder pressure based engine controls. The above can only be achieved in combustion systems of direct injection spark ignition (DISI) engines (Alkidas, 2007).

Wel and colleagues carried out a study using a cold exhaust gas re-circulation (EGR) by increasing the compression ratio from 8 to 11.8 in a gasoline engine where fuel injection was controlled electronically. Not only did this improve fuel economy but it also managed to reduce HC emissions by 44.99% (Wel, *et. al*. 2007).

Another study by Lin involved the usage of a plasma-enhanced combustion system which increases the content of free radicals in the intake air allowing for efficient combustion

process whereby an increase in voltage resulted in a decrease in pollutant PAH emissions (Lin, *et. al*. 2013).

2.4.2 Advanced Internal Combustion Engine (ICE)

Efficiency is linked to emissions; for example, increasing efficiency of gasoline engines means using fuels with a higher octane rating, which consequently means using higher levels of aromatics in the fuel. Whilst this might improve the efficiency it leads to high HC/PAH emissions, thus alternative approaches are being exploited for the satisfaction of both factors (Wallington, *et. al*. 2006).

Lots of effort is being dedicated to develop engines with decreased emissions and improved efficiency. The two factors are highly dependent upon sophisticated mechanical and computerized control of combustion systems, allowing the engines to operate optimally by exploiting Air/Fuel (A/F) mixtures, spark/combustion timing, etc. Innovative strategies persist in being implemented targeting specific problems such as cold start emissions which are linked to PAH emissions. Car manufacturers came up with an idea of producing volatile fuel inside an engine (hence ICE), to reduce cold start emissions, which in turn to leads to a reduction in fuel condensation on the cylinder walls which ultimately leading to reduced HC emissions (Wallington, *et. al*. 2006). This may lead to contaminated crankcase oil if there is a fault with the piston ring liners.

Crankcase emissions (Table 2.7) are those that result from incomplete combustion of fuel components that escape the combustion chamber under high pressure, past the pistons and into the crankcase and possibly the lubricant. Mitigation measures that are under consideration involve the use of new and innovative technologies that provide re-ventilation of the crankcase and help minimize these emissions and they involve:

- Hydrocarbon conversion (catalytically/ non-catalytically)
- Quantity reduction of contaminants escaping the combustion chamber by modifying the engine
- Subjecting carbon monoxide and unburnt hydrocarbon components in the exhaust port injection under oxidizing and low pressure conditions (Bhandarkar, 2013).

Table 2.7: Gasoline-driven vehicle emissions (Bhandarkar, 2013)

S.N.	Source	Amount of Emissions (%)	
		4- Stroke	2-Stroke
1	Crankcase blow by	20	Nil
2	Evaporative Emissions	20	3
3	Exhaust Emissions	60	97

2.4.3 Particulate Reduction Systems

Since its introduction in 1975 two-way catalyst (and the introduction of a three-way catalyst in 1980 as seen in Figure 2.4), has been mandatory for vehicles so as to combat toxic emission (Woodford, 2014).

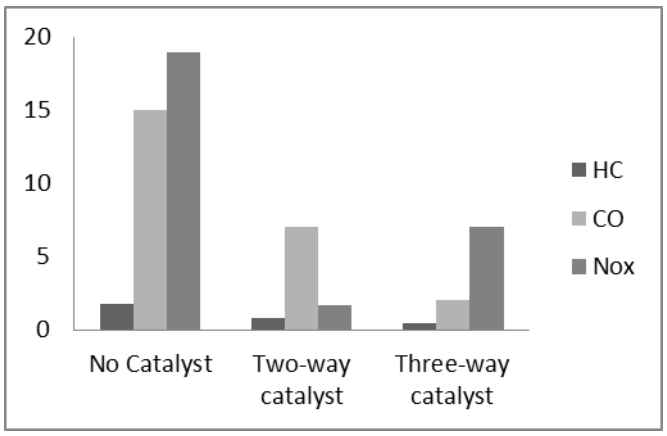


Figure 2.4: Efficiency of the different catalytic converters (Woodford, 2014)

A filtering system located between a muffler and an engine in the exhaust system, results in the reduction of PAHs (as part of HC), NOx and CO tailpipe emissions, (Hermann, 2004) so as to maintain air quality. The main function of catalytic converters is to reduce or strip-away the exhaust ability to pollute (Schobert, 2002). The three above-mentioned harmful compounds are converted into CO_2 and H_2O through oxidation and reduction mechanisms on palladium, rhodium and platinum based catalysts (Figure 2.5).

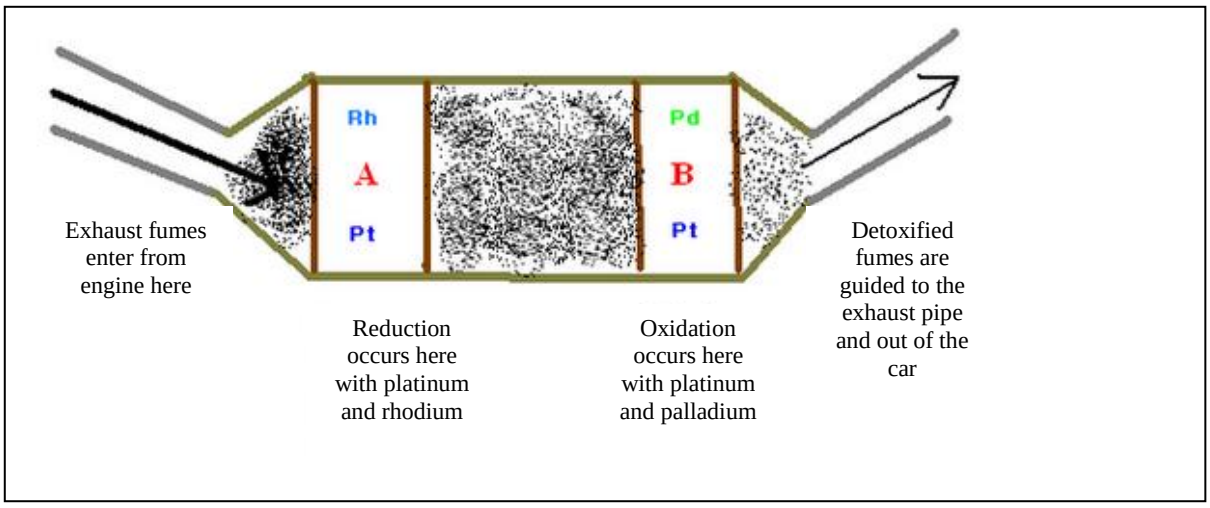


Figure 2.5: Fundamentals of a basic catalytic converter (Chemwiki, 2014)

Figure 2.6 shows the varying level of emissions at varying combustion conditions. At fuel-lean conditions, there are high concentrations of oxygen and conversely at fuel-rich conditions, there are low levels of oxygen and high levels of both CO and unburned HC's. The catalytic converters work optimally at stoichiometric combustion conditions, where the three curves intersect as shown in Figure 2.6 and Figure 2.8 shows how NOx, HC and CO are reduced and oxidised respectively(Schobert, 2002).

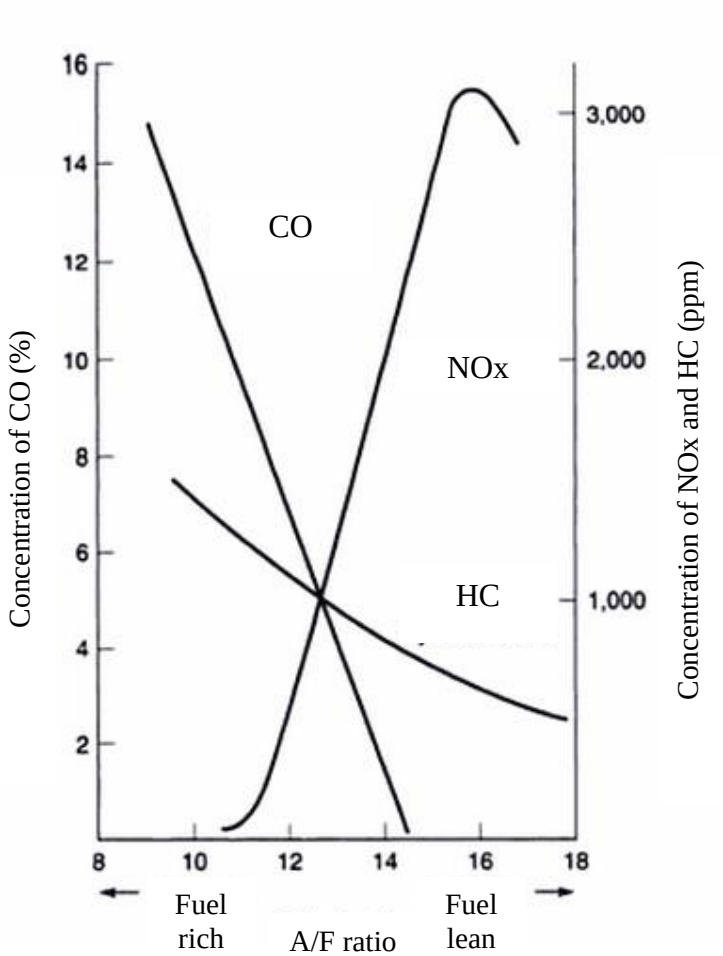


Figure 2.6: varying emission levels at varying combustion conditions (Schobert, 2002).

$$CO + 0.5\ O_2 \rightarrow CO_2$$

$$C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O$$

$$2NO_2 \rightarrow N_2 + 2O_2$$

Figure 2.7: reduction and oxidation of NOx and HC & CO respectively (Schobert, 2002)

2.4.4 After Treatment Engine System

With on-going engine advancements, fuel composition has been fine-tuned to strike a balance between power need and efficiency, whilst minimizing a particulate emission which is highly dependent upon engine operating parameters (speed, spark timing, A/F ratio and engine temperature). For successful low emissions and high efficiency it is best to optimize the complete fuel-engine after-treatment system (Wallington, *et. al*. 2006).

A study in 2010 by the California Air Resources Board, showed the influence of different exhaust after-treatment systems (coated and uncoated) on PAH emissions. It was observed that

95% of particulate PAH was reduced and (independent of the catalytic coating) but conversely gaseous PAH reduction was highly dependent on the catalytic coating and the exhaust temperature. In the absence of an exhaust after-treatment system, the emissions were several orders of magnitudes higher compared to the coated and uncoated exhaust after treatment system (CARB, 2010).

To corroborate this study, Khalek and colleagues ran a 16hour test cycle on the engine of a 2004 model in comparison to that of 2007model (with Exhaust gas recirculation (EGR) and a particulate filter). The findings showed a significant emission reduction for advanced engine technologies (Khalek, *et. al*. 2009).

2.4.5 The Future and Beyond

In the past 30 years, cars have steadily been developed with regards to efficiency and environmental sustainability. For the reduction in PAH emissions, numerous technical developments are responsible for this drastic change, with engine development being the main factor. There is now a paradigm shift from mechanical to electronically-controlled engines, permitting precise regulation of the combustion cycle along with the engine components (Kubsh, 2013). These days, advanced engine technologies include improved fuel injectors with enhanced injection pressure, which are interlinked to advanced control algorithms meant for precise or better mixtures of A/F (Air/Fuel) ratio, whilst minimizing combustion temperature. Other technologies include EGR being controlled electronically which significantly reduces NO_x emissions. Variable valve technology, upgrading piston ring liners, crankcase design and after treatment engine systems are some of the measures that are directly linked to the reduction of PAH/HC accumulation in engine oil (Fiebig, *et. al.* 2013 and Kubsh, 2013). Advance emission control technologies and advance engine technologies work cohesively and will continue to progressing.

2.5 Chromatography and PAHs

A number of chromatography methods have been established for PAH detection, although there are still problems associated with these GC (Gas Chromatography) and HPLC (High Performance Liquid Chromatography) techniques with respect to quantitative and qualitative evaluation (Schuster and Gratzfeld-Hugen, 1995). Since the 1980's, analysis of PAHs in the environment has led to a number of methods being developed (Lee, *et. al.* 1981). HPLC and GC are extensively used for PAH analysis but when comparing the two in terms of peak capacity, selectivity and sensitivity, HPLC is inferior (Dennis, *et. al*. 1983).

Traditional methods for PAH analysis includes:

1) Extraction of PAH from the entire matrix (lipids), which involves three procedures namely saponification, liquid-liquid partition and caffeine complexation.

2) Purification which removes contaminants from the extract (PAHs) through SPE (Solid Phase Extraction) silica cartridges which produces better recoveries in comparison to other column chromatography procedures (Moret, *et. al*. 1996).

3) Analytical determination involving modern techniques HPLC and GC coupled to MS (Mass spectrometry), enabling unknown PAH detection at critically low PAH concentration.

The major reason for GC being categorized as a preferential technique is due to its high resolving power, which gives a detailed compositional analysis. Whilst HPLC is a much faster technique, is able to separate isomers and is highly advantageous when it comes to separating high molecular PAH components, the GC is unable to do such because of thermal degradation occurring at high temperatures (Guillen, 1994). Table 2.8 shows some alternative methods for sample preparation and analysis that have been used.

Table 2.8: PAH Analysis in Oils using Traditional Methods (Moret and Conte, 2000)

Sample extraction	**Sample purification**	**Analytical determination**
Liquid-liquid partition with DMF-water and CE	Silica gel column + Sephadex LH-20 column	GC-MS
Liquid-liquid partition with DMF-water and CE	Silica gel column + GPC on S-X3column	GC-MS
Liquid-liquid partition with DMSO and CE	Silica gel column + TLC on solica gel	GC-FID
Liquid-liquid partition with DMF and CE	Silica gel column	GC-MS (SIM), HPLC-FL
Liquid-liquid partition with DMF and CE	SPE on silica gel cartridge (500mg)	HPLC-SF
Caffeine complexation and extraction with CE	Silica gel column + TLC on Al_2O_3-Al sheet	UV-spectroscopy fluorescence measurem
Caffeine complexation and extraction with CE	Silica gel column + HPTLC	GC-FID
Saponification and extraction with CE	Liquid-Liquid partition + silica gel column	HPLC-SF, HPLC-FL
Saponification and extraction with CE	Silica gel column	HPLC-SF, TLC, HPLC-FL, GC-MS

2.5.1 Limitations

For an analytical procedure to be deemed reliable it needs careful detailed validation and its efficiency has to be evaluated. The steps prior to analysis or characterization (sampling, sampling preparation), have to be carefully considered as they are often neglected and are often the major influencers affecting the results (Manoli and Samara, 1999).

The problem with PAH chromatography analysis is that there is not a single standard method followed. There are often too many methods being developed which give varied outcomes. The general problems that are often associated with chromatography and encountered are: sampling, sampling storage losses, efficient separation and selective techniques. Furthermore issues such as low PAH concentration levels, and complexity of samples has driven research towards improving analysis by achieving cost effective, high efficient methods and thus leading to the advancement of analytical equipment themselves(Martinez, *et. al.* 2004).

However optimization and validation of methods, for example extraction techniques such as ultrasonic, soxhlet, SFE (Supercritical Fluid Extraction), MAE (Microwave assisted extraction), etc. often involve tedious and time consuming steps that often use a lot of organic solvents, this leads to poor recoveries which are not representative of the native compounds and somehow affect the results. This explains why some studies are carried out without PAH extraction.

2.5.2 PAH Analysis by HPLC and GC studies

This section discusses studies that have been performed by employing chromatographic techniques such as GC or HPLC and investigating the PAH content in different mediums due to exposure to used engine oil and given.

A study by Rosado and Pitchel (2003) used GC/MS and spectroscopy to compare fresh and used engine oil. Results on a GC/MS spectrum revealed numerous new peaks which were more intense compared to those in fresh oil. The newly identified peaks were found to be benzene-based and naphthalene-related compounds (Rosado and Pitchel, 2003), which are found to be predominant hydrocarbon structures in the composition of used engine oil (Upshall, *et. al*. 1993) This corroborates the findings of Cotton and colleagues (1997), who detected acenaphthalenes, Naphthalene, dinaphthenoanthracenes, benzo[$\propto$]pyrene and benzo[$\propto$]anthracene in used oil samples, which were absent in fresh oil (Cotton, *et. al.* 1997).

Using the GC, Obini and colleagues (2013), determined PAHs in soils that were contaminated with used engine oil in Abaliki of Ebonyi state in Nigeria, where auto-mechanic shops are found to be disseminated all over the town and where pollution of used engine is found to be more prevalent than crude oil (Odjegba and Sadiq, 2002).This is a result of oil spillage, leakage, mishandling and haphazard disposal. Randomly collected soil samples were then homogenized into composite samples, that were screened, followed by sample extraction in a mixture of acetone: methylene chloride (50%:50%, v/v) with a sonicator. The resulting sample was then spiked with 1 ml of internal standard, and then mixed. Determination of the EPA 16 PAH's was done by using GC/FID-ECD and their findings showed that the samples had high PAH content. The samples were ran under the following conditions: 20 µl injected in GC port, He carrier gas, HP-5 cross-linked PH-ME siloxane column of 30m in length, 0.25 mm in diameter and 1µm thickness , 1.2 ml/min spit-less injection and constant flow rate. This work showed that the study-site was highly contaminated with PAH's arising from disposal of crankcase oil (Obini, *et. al*. 2013).

Another GC/MS method by Oostdijk, involves the fast separation of the 16 EPA-PAHs under the following conditions: 1 µl injection volume, He carrier gas, 2.0 ml/min; injector: 300 ^{0}C spit-less mode, 0.75 min @ 50 ml/min, column: select-PAH-column, 30 m X 0.25 mm, Temp gradient: 70 ^{0}C (0.8 min), 60 ^{0}C/min, 180 ^{0}C, 20 ^{0}C/min, 350 ^{0}C (5 min). The above optimized GC method resulted in a single run, resolving all the 16 PAH in less than 13 minutes run time (Oostdijk, 2010).

A study at the University of Sao Paulo was performed to investigate the amount of PAHs in water samples. The samples collected underwent liquid-liquid extraction then solid phase extraction prior to analysis by two different HPLC methods (HPLC-UV-diode array detection and HPLC-APCI-MS)

The findings showed that HPLC-UV-DAD gives the best Limit of Quantification (LOQ) and Limits of Detection (LOD) values due to the presence of chromosphere structures of PAH, thus making UV a very sensitive technique. However MS also showed some advantages as it gives structural information about the compound thus eliminating ambiguity in relation to the identity of structures. Unfortunately, the optimized methods of HPLC-MS or HPLC-UV showed no PAH content in the water samples collected (Titato and Lancas, 1996).

Soil and sediment samples in the vicinity of an oil refinery in India were assessed for PAH and heavy metals. Sample preparation took place firstly by extracting PAHs using the USEPA

method 3540 (EPA, 1986) and then soxhlet extraction. PAH analysis proceeded by analysing the samples for the 16 PAHs using HPLC under the following conditions: C_{18} (250 X 4 mm; 5 µm) column, UV detector at wavelength of 254 nm, mobile phase Acetonitrile: Water (70:30; v/v), flow rate of 1.5 ml/min and run time of 50min. Consequently the results showed high concentration of PAHs which was 1.20 times higher in soils than the standard value of 50 ppm by ICRCL (Tiwan, *et. al.* 2011).

2.6 PAH Reduction

There are a variety of ways of reducing PAH levels such as exposure limits, environmental PAH regulation in waste disposal containing PAHs recycling & re-refining of used engine oil etc.

An extensive method for PAH regulation in waste oil by removal of impurities involves recycling and re-refining (Durrani, *et al*, 2012). It involves techniques such as acid clay treatment, clay treatment, vacuum distillation and solvent extraction (Khan and Kamal, 2009), which has been the main attraction over the years, due to its ability to overcome a high fraction of problems associated with chemical treatment (Durrani, *et al*, 2011). The processes are described as follows:

2.6.1 Acid Clay Treatment

An obsolete process considered illegal due to the production of the hazardous acid clay, during the refining process.

- Oil filtration for water, and solid particles removal
- Addition of sulphuric acid for removal of impurities, unsaturates and ashpaltene.
- Acidic sludge by product precipitates out of the oil.
- The remaining slightly acidic oil is mixed with oil for colour improvement and mercaptan removal.
- Removal of clay by filtration from oil
- Neutralization and distillation of the oil

(Khan and Kamal, 2009).

2.6.2 Vacuum Distillation

Takes advantage of the boiling points by producing high surface area thereby facilitating extraction of various components with lube distillate being the ultimate product, (meeting the API group I base oil specifications Appendix C1) (Fitch, 2011).

2.6.3 Clay Treatment

This technique follows the vacuum distillation process. It involves either bringing the lube distillate in contact with clay in reactors or feeding lube distillate through static beds at high temperatures (removing odour, colour and small fractions of sulphur). It meets API group I but not API group II base oil specifications (Durrani, *et al*. 2011).

2.6.4 Solvent Extraction

This technique improves the quality of lube distillate obtained from vacuum distillation. It is a useful method as it removes aromatics whilst increasing the amount of saturates. A great disadvantage is that it also removes unsaturates which may affect the overall yield. Like the previously mentioned techniques, it also meets group I but not group II base oil specifications (Emam and Shoaib, 2013).

These are some of the waste oil re-refining processes that involve the reduction of PAHs (aromatics) eventually producing base oil with low PAH content prior to the addition of additives.

CHAPTER THREE

3.1 METHODOLOGY

This chapter describes the methodology employed. The HPLC and GC methods implemented in this research were adopted from the methods developed by Tiwan, *et. al*. (2011) and Odjegba and Sadiq (2002), respectively with trivial alterations for optimization. The quantification of PAH's in used engine oil involve sampling, followed by sample preparation and then analysis by HPLC-UV and GC-MS. Data validity or assurance is illustrated by the use of FTIR and ^{1}H NMR.

3.2 Standards and Reagents

Acetronitrile and N-Hexane were of HPLC grade and Naphthalene, Anthracene (99%), Phenanthrene (>=99.5%), Pyrene (98%), Benzo[α]pyrene, and Fluoroanthene (98%) in solid form, were all purchased from Sigma-Aldrich and used without further purification.

3.3 Fuel Sampling

Fresh and used engine oil samples were collected around Johannesburg (Auckland-park and Braamfontein) in June 2014. The oil samples were collected from car dealerships with in-service or maintenance & repair workshops; namely VW, Audi, Bosch and Volvo, representative of the following engine oil brands respectively: Engen, Castrol, Castrol-GTX and Engen. About 20 mL of both fresh and used oil were either sampled directly from the engine or from the used oil recycling steel canister, into the PVC sample vials and stored in ambient temperature away from UV light to prevent analyte loss and photodegradation.

3.4 Preparation of Solutions and Standards

1000 ppm stock solution of each of the five PAH (Pyrene, Fluoroanthene, Naphthalene, Anthracene, and Phenanthrene) was prepared by weighing and quantitatively transferring 0.1 g of each PAH into a 100 mL Volumetric flask and dissolved and filled up to the mark with Acetonitrile. From the 1000 ppm stock solution, 10 ppm stock solutions were prepared which contained a mixture of all the PAHs, which were in turn used to spike standard solutions ranging from 1-6 ppm for the calibration curve. The mobile phase comprised of 30% Acetonitrile & 70% Water which was further filtered through a 0.45 micron membrane filter and passed through a degasser prior to analysis. 0.5 ml of each oil sample was dissolved in 20 ml of acetonitrile.

3.5 Equipment and Instrument Conditions

3.5.1 GCMS

Samples were subjected to a high performance QP2010 Gas Chromatograph coupled to a Mass Spectrometry, equipped with a quadruple mass filter and a differential vacuum filter

Table 3.1: GCMS Analysis Conditions

GC Parameters		**MS Parameters**	
Column	Rxt-5ms (length=30 m, diameter=0.25 mm, thickness=0.25 µm)	Interface Temp	200 ^{o}C
Injection mode	Split-less	Ion source Temp	250 ^{o}C
Injection Temp	120 ^{o}C	Solvent cut time	2 min
Column Oven Temp	From 45 ^{o}C to 325 ^{o}C at 12 ^{o}C/min, hold for 10min	Scanning mode	SIM
Carrier gas	Helium	m/z	Napthtalene 128
Flow control mode	Pressure		Phenantene 178
Pressure	100 kPa		Anthracene 178
Column flow	1.74 ml/min		Fluoranthene 202
Sample injection volume	2 µl		Pyrene 202

3.5.2 HPLC

An Agilent 1200 Series HPLC equipped with a quaternary pump, variable wavelength detector and a thermostatic auto-sampler.

Table 3.2: HPLC analysis conditions

Column	**Agilent Eclipse XDB-C_{18} (150 mm, 4.6 mm, 5 µm)**
Column Temp	60 ^{o}C
Flow rate	0.8 ml/min
Injection volume	20 µl
Void volume	60%
Mobile phase	Acetronitrile: water (70:30; v/v)
Elution	Isocratic
Detecor	UV (254 nm)
Run time	40 in

3.5.3 NMR

A Bruker AVANCE 300 model was used to record quantitative ^{1}H and spectra at 75.473 MHz. TMS was used as a reference occurring at 0 ppm for ^{1}H and chemical shift values were reported against it, where the coupling constants were expressed in Hz.

3.5.4 FTIR

Used and fresh oil samples were analysed using the Bruker Tensor 27 Fourier Transform Infrared Spectrometer (FTIR) model, equipped with a diamond ATR attachment. The working range was 600-4000$cm^{-1}$and hence all signals are reported based on the wave-number scale (cm^{-1}). The samples were analysed in their own form without phase alteration and were measured by loading a drop of oil (sample) directly on the diamond cell.

CHAPTER FOUR

4.1 RESULTS AND DISCUSSION

The following section represents the acquired results from the chromatography and spectroscopy techniques employed on engine oil samples collected around Johannesburg at Volvo, VW, Bosch and Audi car dealerships with in-service maintenance workshops. It also demonstrates the comparison of PAH content between similar and different oil brands.

4.2 Separation and Detection by GCMS and HPLC

Separation of all five target PAHs was achieved by analysing the standard PAH mix in Acetonitrile, where the PAHs were simultaneously detected using both the GCMS and the HPLC. Figures 4.1 and 4.2 represent the signal response of the individual PAHs. Elution of these components depends upon the affinity between the analyte and the stationary phase (Joa, *et. al.* 2009).

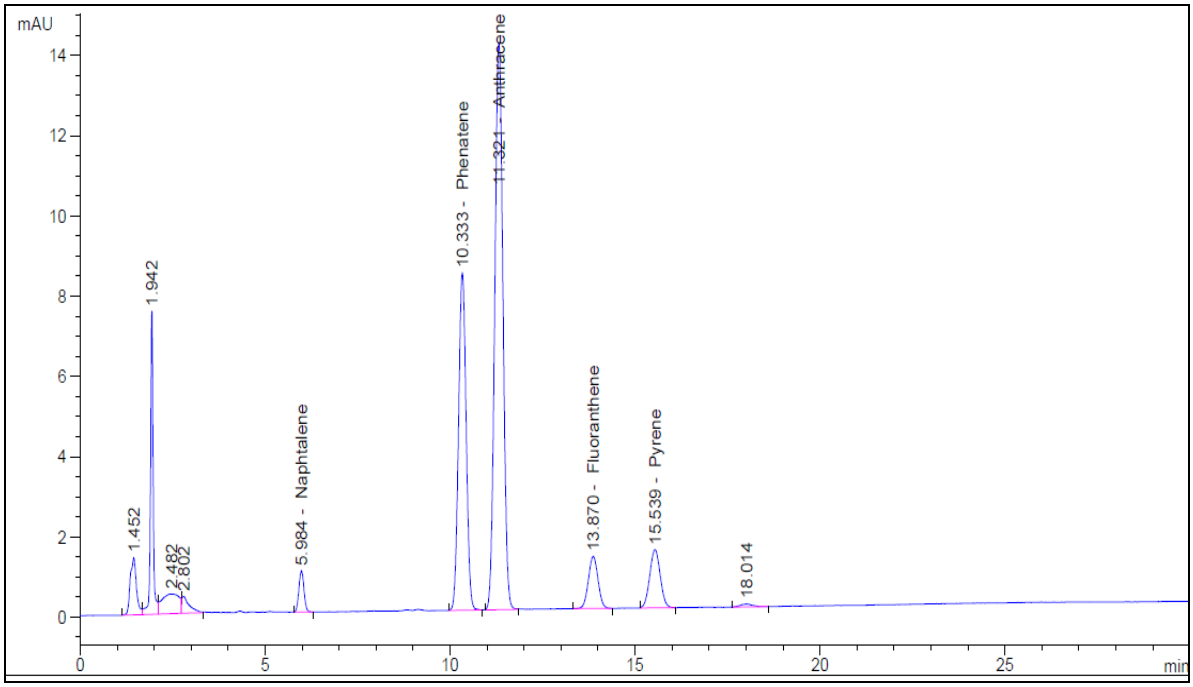


Figure 4.1: HPLC standard mixture chromatogram (absorbance vs. ret-time) showing the retention times of the individual PAH with resolution factors of 7.4, 1.2, 3 and 2 respectively.

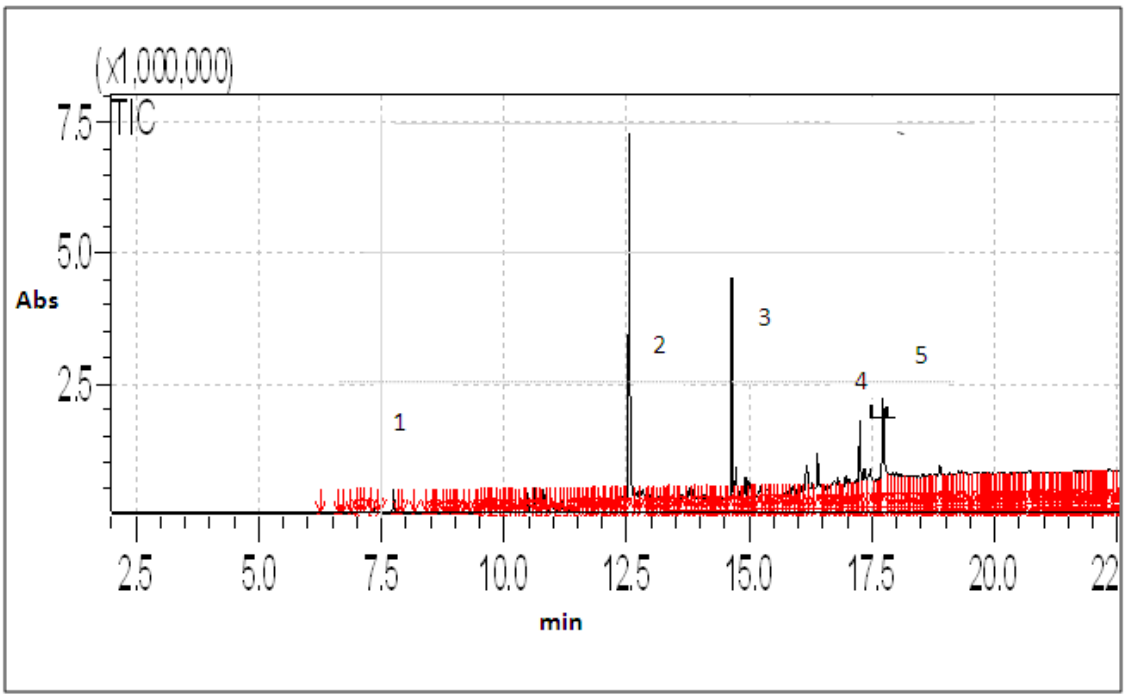


Figure 4.2: GC chromatogram illustrating the individual PAHs and their elution times.1) Napththalene, 2) Phenanthrene, 3) Anthracene, 4) Pyrene and 5) Fluorathene

On HPLC, it was believed that the order of elution of the last two PAH compounds was fluoranthene then followed by pyrene (Figure 4.1), where elution is dependent upon hydrophobic interaction with the stationary phase. But on GC/MS, it is observed that pyrene is eluted first followed by fluoranthene (Figure 4.2), which has a boiling point of 375 ^{o}C, only 15 ^{o}C higher than pyrene.

The ion chromatogram (Figure 4.3) displays only three instead of five peaks, due to the fact that both phenanthrene & anthracene weigh 178 Daltons whilst fluoranthene and pyrene weigh 202 Daltons, explaining the three peaks observed.

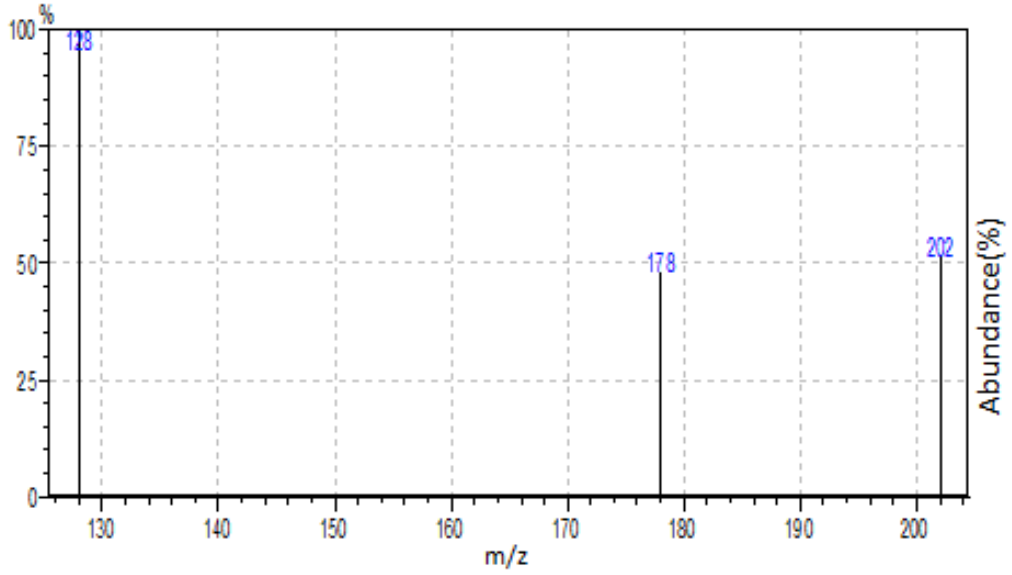


Figure 4.3: Ion chromatogram showing the m/z of the five target PAHs

4.3 HPLC and GCMS Comparison

Compared to HPLC, GCMS has the longest run time and HPLC possesses better separation of peaks than GCMS. Normally GC better separates low molecular weight PAHs but HPLC gives best resolution for high molecular weight PAHs (Chiu, *et.al*, 1997). This becomes imperative during the analysis of oil samples which contains impurities that interfere, making it difficult to identify and quantify all target PAHs, thus not all of the target PAHs were detected, subject to matrix interference as seen on Figure 4.4. Although another reason for undetected PAHs in samples as depicted on Figure 4.5, might be because they are completely absent during lubricant formulation.

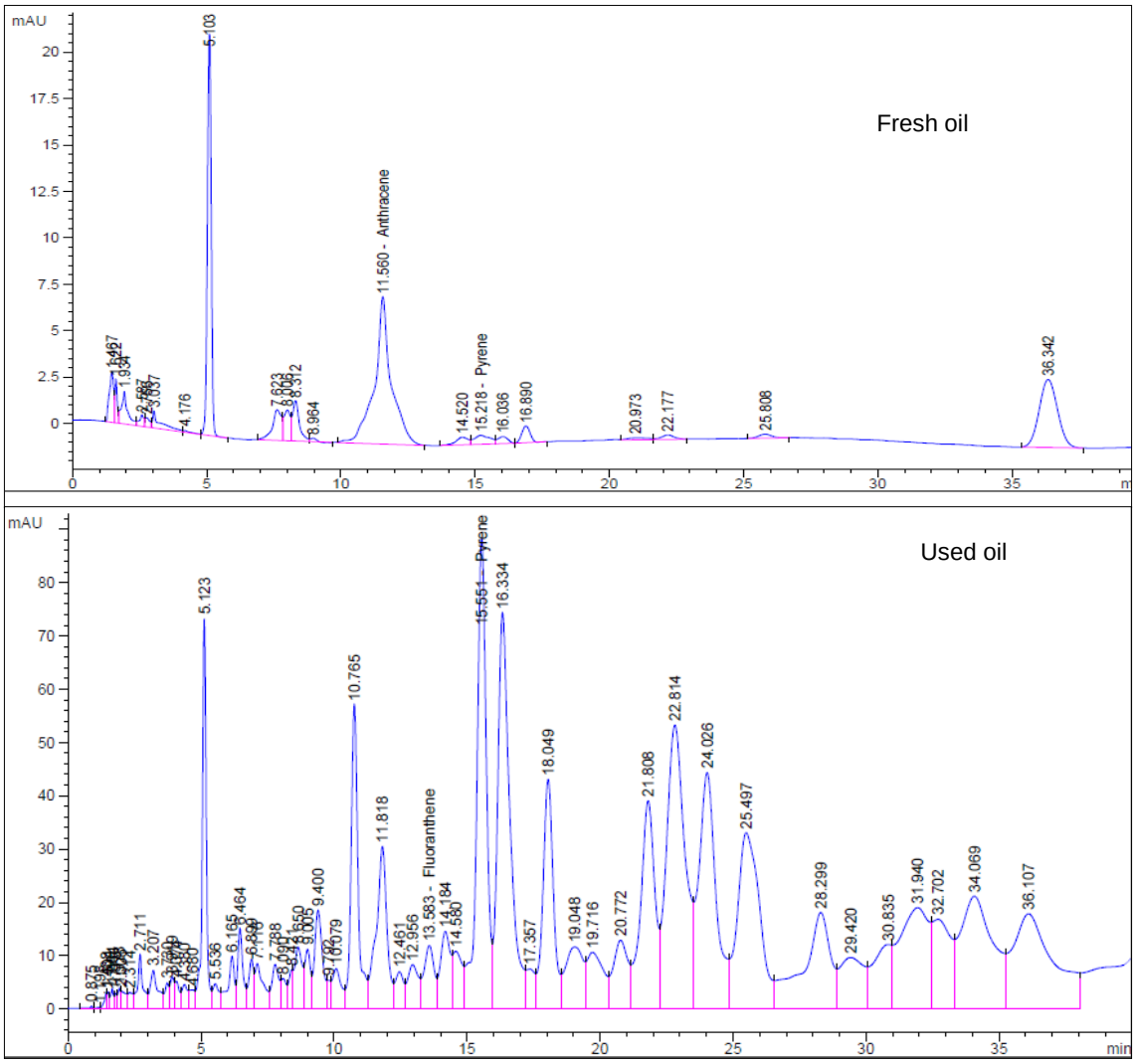


Figure 4.4: HPLC chromatogram of fresh vs. used engine oil

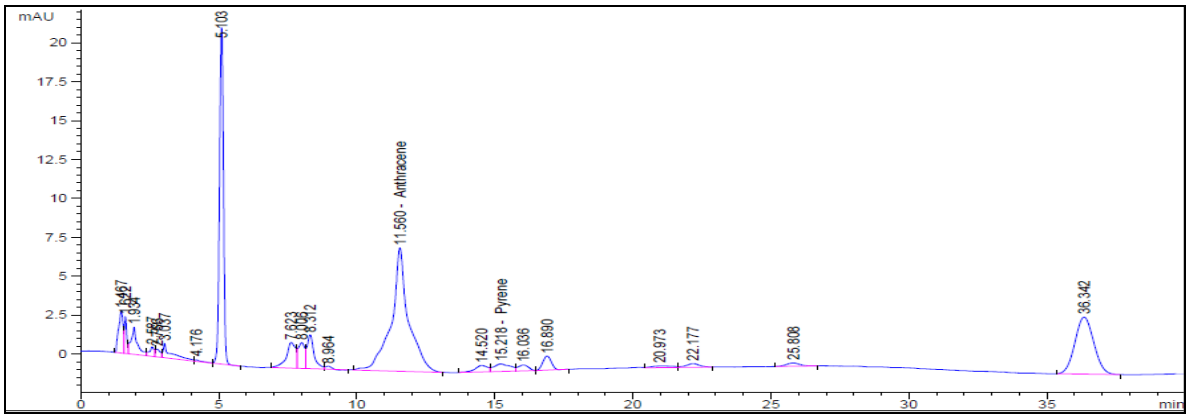


Figure 4.5: HPLC fresh engine oil chromatogram with two detectable PAHs.

The GCMS PAH profile of a fresh sample differs from that of a used oil sample. This can be seen on Figure 4.6 below, a data comparison of fresh and used engine oil sample, where the height or the intensity of the peaks is proportional to the amount of PAHs present.

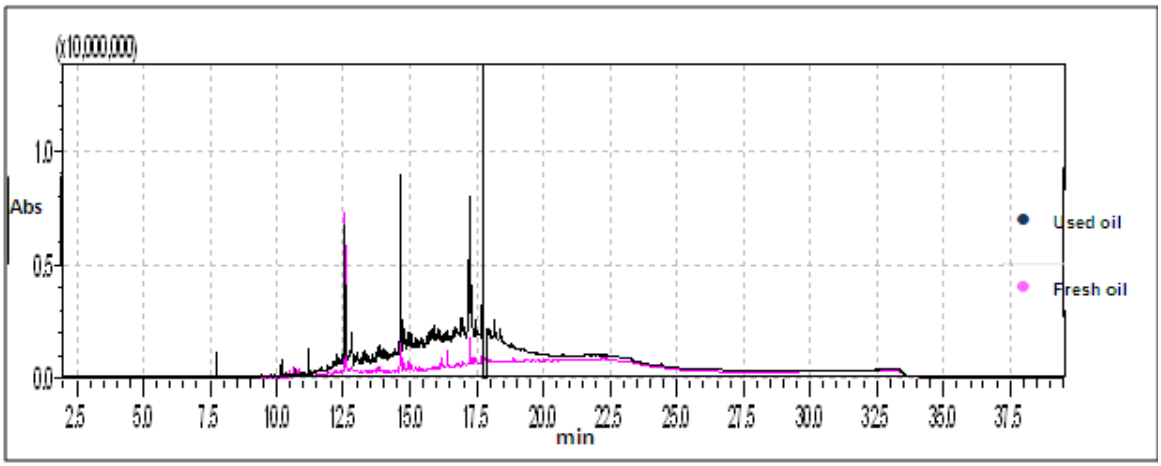


Figure 4.6: GCMS chromatogram depicting data comparison of fresh (pink) and used (black) engine oil

4.4 Quantification and Validation Parameters

The USEPA has declared both GCMS and HPLC equally valid methods to analyse PAHs (Kumar, *et al*, 2014). It can be observed that the results obtained from the two analytical methods are different as shown on (Tables 4.1 and 4.2). Not detected (nd) concentration obtained is indicative of a sample analysed consisting of a concentration below the determination limits of the analytical method used. Therefore it is vital to validate the chosen method for consistent, accurate and reliable data during analysis, and this can be further explained by various validation parameters such as Limit of detection (LOD) and Limit of quantification (LOQ).

Table 4.1: 5 target EPA PAH concentration detected by HPLC in engine oil samples

	AUDI	Amount (g/L)		VOLVO	Amount (g/L)	
PAH		**Fresh**	**Used**		**Fresh**	**Used**
Napthtalene		nd	nd		0.00632	0.0122
Phenantene		nd	nd		0.000564	0.00917
Anthracene		0.00324	nd		0.000212	0.00433
Fluoranthene		nd	0.024		nd	Nd
Pyrene		0.00135	0.156		nd	Nd
Total		0.00459	0.180		0.007091	0.0257
	VW	**Amount (g/L)**		**BOSCH**	**Amount (g/L)**	
PAH		**Fresh**	**Used**		**Fresh**	**Used**
Napthtalene		nd	0.00451		nd	0.0182
Phenantene		0.000396	0.00296		0.000106	0.00606
Anthracene		0.000517	0.00432		0.0000770	0.00390
Fluoranthene		nd	nd		nd	nd
Pyrene		nd	nd		0.000289	0.0776
Total		0.000913	0.0118		0.000471	0.106

nd (not detected)

Table 4.2: 5 target EPA PAHs concentration detected by GCMS in engine oil samples

	AUDI	Amount ppm)		VOLVO	Amount (ppm)	
PAH		**Fresh**	**Used**		**Fresh**	**Used**
Naphthalene		nd	nd		nd	nd
Phenantene		nd	nd		nd	nd
Anthracene		nd	nd		nd	nd
Fluoranthene		nd	nd		nd	13.5
Pyrene		nd	0.994		nd	2.12
Total		0	0.994		0	15.8
	VW	**Amount (ppm)**		**BOSCH**	**Amount (ppm)**	
PAH		**Fresh**	**Used**		**Fresh**	**Used**
Napthtalene		0.347	0.819		nd	nd
Phenantene		nd	3.07		nd	1.34
Anthracene		1.38	4.80		nd	1.45
Fluoranthene		0.034	5.12		nd	nd
Pyrene		0.210	2.00		nd	nd
Total		1.98	15.8		0	2.84

nd (not detected)

4.4.1 LOD and LOQ

LOD (limit of detection) is the lowest analyte concentration that can be determined at a specified confidence level, whilst LOQ (limit of quantification) is the lowest concentration quantified at a predetermined level of both accuracy and precision. Notice that any concentration that is below LOD, analysis is not feasible (Armbruste, *et al*, 1994). Therefore the main question is, which method (HPLC or GCMS) in this study is better for PAH quantification? The values of LOD and LOQ for target PAHs are reported on Table 4.3 below.

Table 4.3: The calculated validation parameters for quantification of the target PAHs

	HPLC		GCMS	
PAH	LOD (g/L)	LOQ (g/L)	LOD (ppm)	LOQ (ppm)
Naphthalene	0.000700	0.00220	0.370	1.11
Phenantene	0.000800	0.00250	0.0200	0.0500
Anthracene	0.000800	0.00260	0.0200	0.0600
Fluoranthene	0.001900	0.00580	0.00	0.0100
Pyrene	0.000700	0.00210	0.0300	0.0900

It can be seen that GCMS is the most sensitive method compared to HPLC, and this can be used for identification.

4.4.2 Linearity

PAH compounds were quantified by performing calibration curves with concentration ranging from 1 – 6 ppm, for both HPLC and GCMS. The HPLC gave good level of linearity with correlation coefficient values of 0.97-0.99, whilst GC/MS gave a poor r^2 value of 0.217 for phenanthrene.

Table 4.4: Correlation coefficient values indicating linearity of each PAH calibration curve

PAH	**r^2 -HPLC**	**r^2 –GC/MS**
Napthtalene	0.997	0.920
Phenanthrene	0.996	0.217
Anthracene	0.996	0.761
Fluoranthene	0.980	0.907
Pyrene	0.998	0.837

4.4.3 PAHs in Fresh and Used engine oil

Figures 4.7 and 4.8 compare the total concentration of the PAHs by HPLC and GC/MS respectively of the different oil samples in different car models.

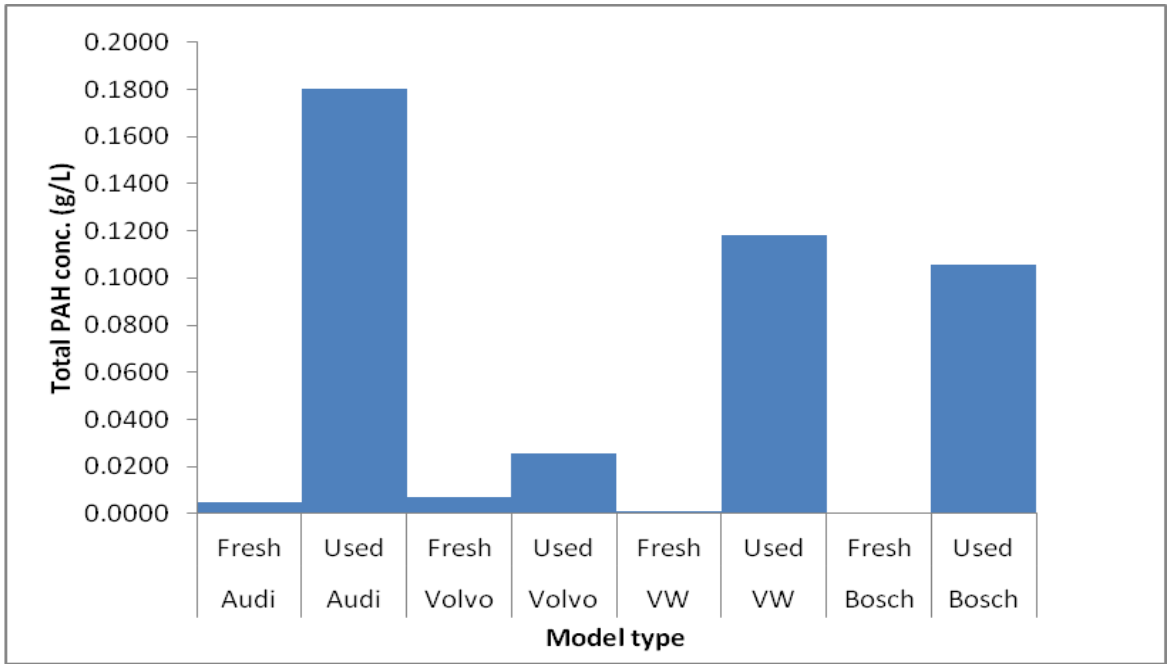


Figure 4.7: Total PAH concentrations detected in engine oil samples by HPLC

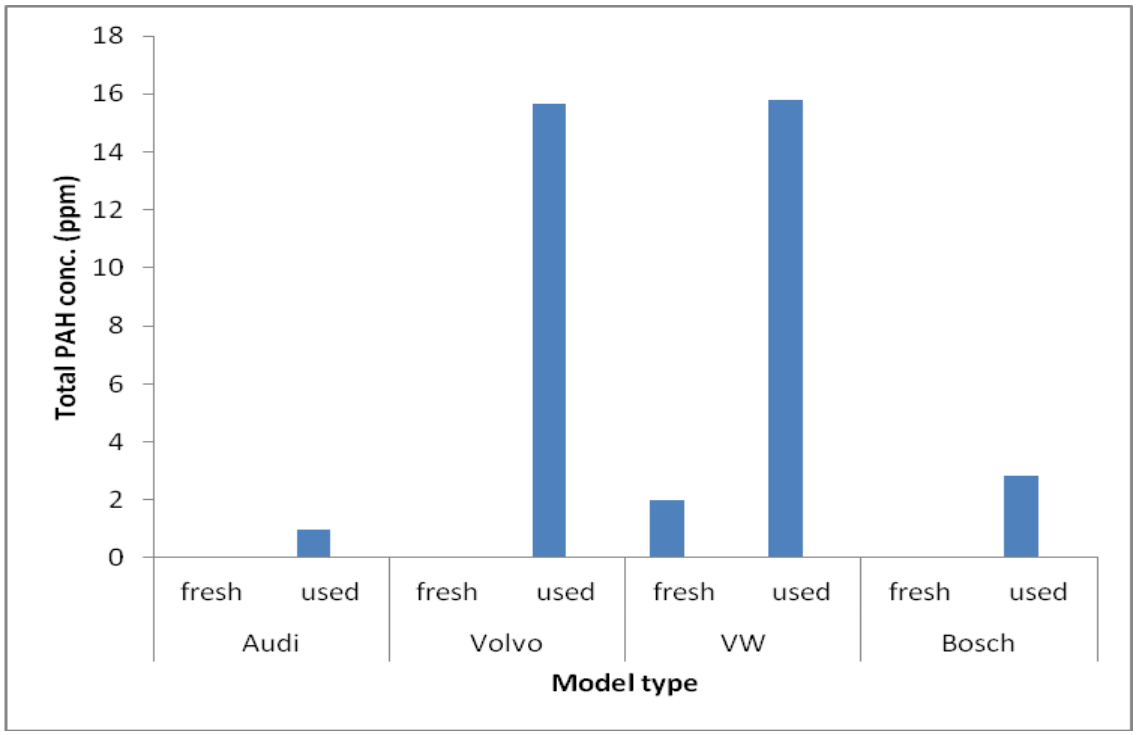


Figure 4.8: Total PAH concentration detected in engine oil samples by GCMS

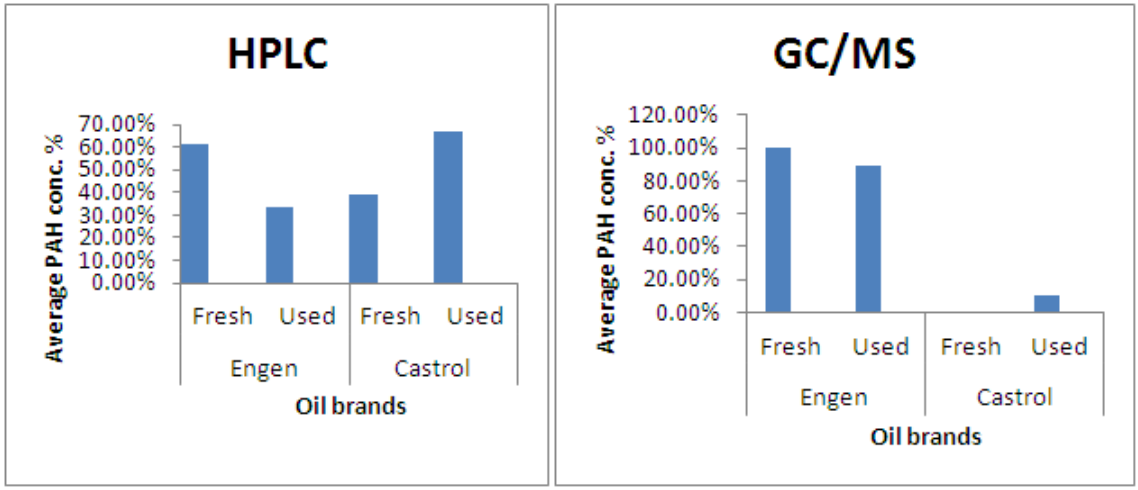


Figure 4.9: Data comparison of PAH concentration averages in Engen (Volvo, VW) and Castrol (Audi and Bosch) oil brands

Figure 4.9 compares PAH average concentration between the two oil brands, representative of the four car models, of both used and unused engine oil.

GCMS

- Engen's fresh and used oil have higher PAH content than Castrol's
- Engen's fresh oil PAH content decreases by 10% after engine operation
- no PAH concentration is found in Castrol's fresh oil and the content in Castrol's used oil is far much lower compared to Engen used oil PAH content

HPLC

- Engen fresh oil decreases by 25% after engine operation
- After engine operation, Castrol's PAH content increases by 25%
- Overall HPLC has detected more PAH particulates than HPLC

Without a noticeable trend, it is rather difficult to declare one brand superior over the other that produces reduced PAH emissions, owing to the difference in engine operation, car mileage, etc. And one would also need compositional data of base oils and additives used and the origin/source of crude oil. The Engen and Castrol lubricant manufacturers have been in the automotive industry for a very long time and are in partnership with the car manufacturers such as VW, Volvo, VW, etc. developing innovative engine technology along with liquid engineering, tailor made for the latest car engine. This is just to show that technology is constantly being pushed beyond its limits.

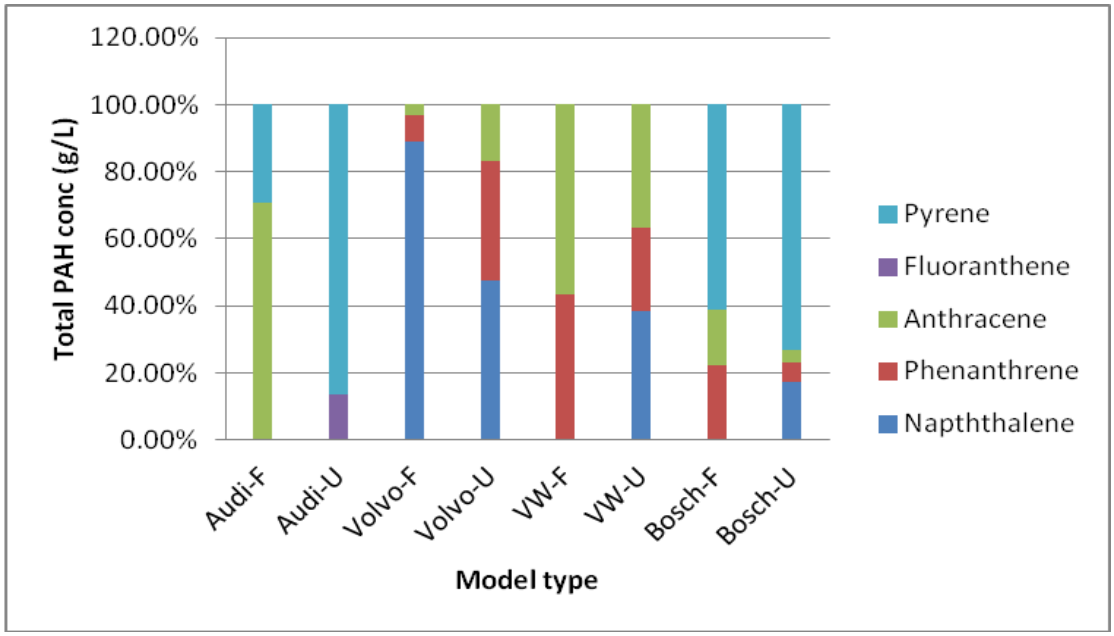


Figure 4.10: Individual PAH composition in used and fresh engine oil samples (f-fresh, u-used) by HPLC analysis

The results of the PAH content investigated in the different car models and engine oil brands represented on the above figures, show that the PAH content of used engine oil is considerably higher than that of fresh oil samples, with Audi being the highest followed by VW, Bosch then Volvo. However the individual PAH concentration contribution represented on Figure 4.10 depicts Anthracene concentration ranging from 2.99%-70.63% in all samples apart from the Audi used oil sample; Fluoranthene only showing up in one (Audi used) oil sample at 13.48%; Pyrene ranging from 29.37%-73.39% in both the Audi and Bosch oil samples (same oil brands), with phenanthrene ranging from 5.74%-43.40% in all samples except in the Audi oil samples.

A rather peculiar observation made on Figure 4.10 about PAHs such as Napthtalene, Anthracene and Phenathrene, which are found in higher quantities in fresh than in used engine oil samples. This is a resultant of the engine extreme operating conditions which alters the chemical structure, hence the chemical composition of the analytes (PAHs). For example Volvo fresh sample constitutes of 89% Naphtalene, 7.95% of Phenanthrene and 2.99% of Anthracene. Whilst Volvo used sample constitutes of 47% Naphthalene, 35.47% of Phenanthrene and 16.88% of Anthracene. At extremely high temperatures (> boiling point) disintegration and integration of molecules occur, explaining the decrease of Naphthalene and

the increase of both Phenanthrene and Anthracene in concentration from fresh to used engine oil samples.

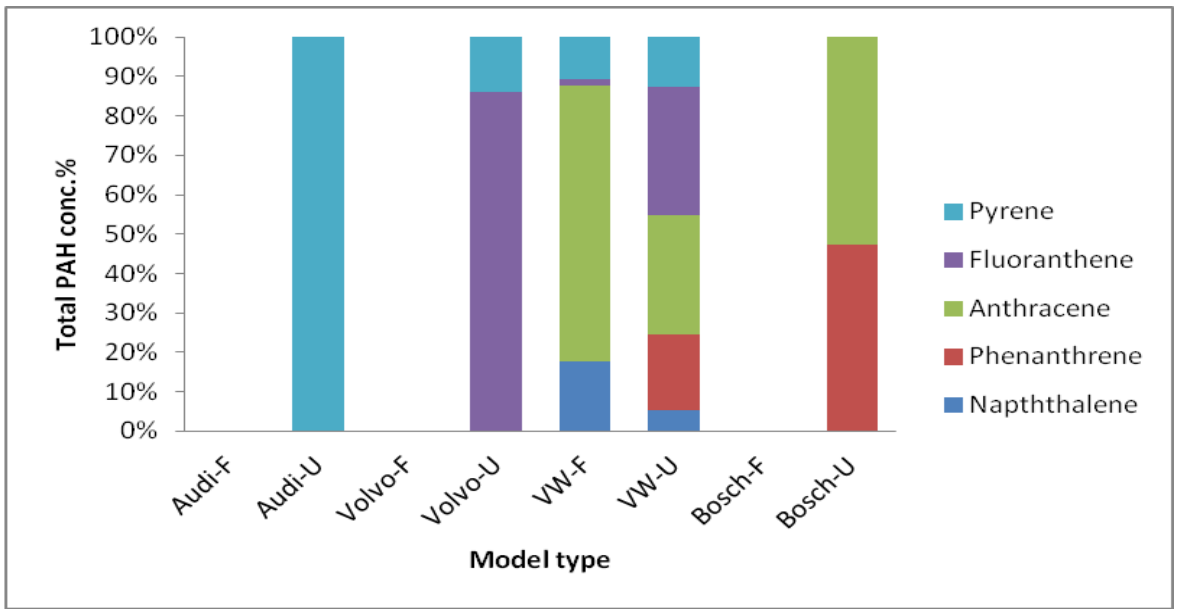


Figure 4.11: Individual PAH composition in used and fresh engine oil samples (f-fresh, u-used) by GC/MS analysis

Figure 4.11 shows that some of the PAHs are absent, which as previously mentioned, is due to the analyte concentration being lower than LOD, which consequently cannot be quantified accurately, thus is represented as undetected. PAHs were undetected in all fresh samples (with VW being the exception). Naphthalene was found to be present only in VW samples. Only Pyrene was detected in Audi used oil sample, and in the remaining samples; it is found in low concentration in fresh than used engine oil samples.

Table 4.5: PAH ratio of used engine oil to fresh engine oil

Model	**HPLC** used/fresh	**GCMS** used/fresh
Audi	39.3	0.994
Volvo	3.62	15.7
VW	12.9	8.01
Bosch	224	2.84

In this study it is found that in average PAHs in used oil is ~70 times more than in fresh oil by HPLC and ~7 times more by GCMS. As per mentioned, the differences and the limitations of the two instruments have already been clarified owing to the huge gap between these two

findings. Using results by HPLC, a declining trend can be observed on Figure 4.12, by other studies performed by Grimmer (300+), Rosado(179), including this one (70). Hence, it is evident that the value is lower than what was established in preliminary studies.

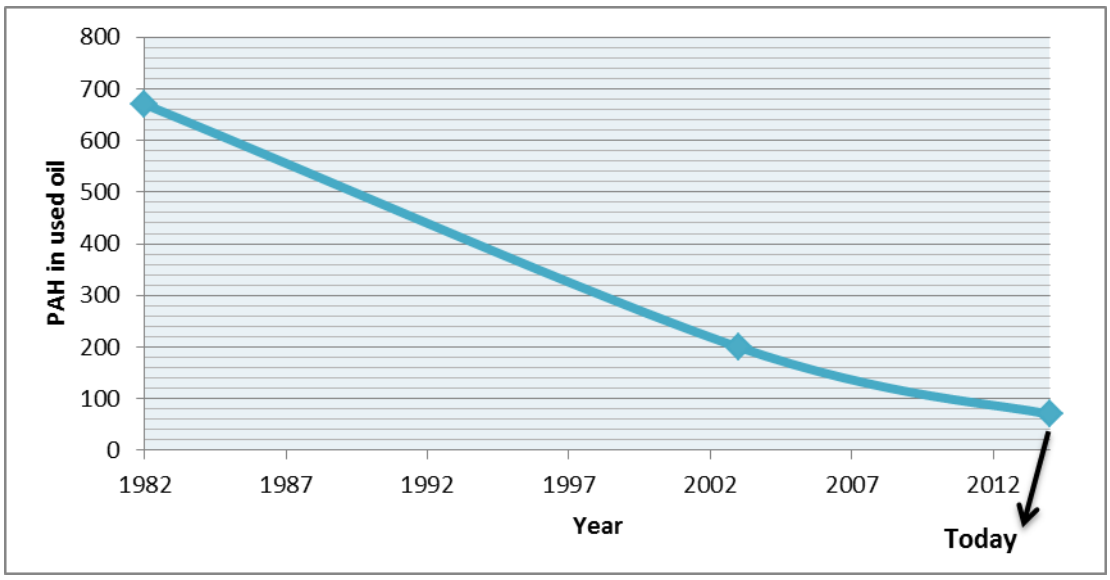


Figure 4.12: Difference in magnitude of PAHs in used oil relative to fresh engine oil

4.5 FTIR and NMR

From the obtained FTIR spectra, few notable differences were observed from fresh and used engine oil samples as seen from Figure 4.13. Major absorption bands were localized in the same regions; and are: a split sharp band occurring at 2924 and 2908 cm^{-1}, medium bands at 1465, 1379 and 723 cm^{-1}, which are a resultant of hydrocarbon mixture compounds containing short C-H chains and C-H vibrations (stretches, bends, etc.) in all oil samples.

On Figure 4.13, it is observed that new bands have occurred on the used oil sample. Although these peaks are so small and can be mistakenly ignored; but accordingly the bands occurring at 709.78 and 1624.97 cm^{-1} are due to the presence of additives (Zieba-Paulus & Koscielniak, 1999). Other bands occurring at 659, 1105.1 and 1614 cm^{-1} are enhanced in comparison to fresh oil bands, this is due to the presence of additives such as organic salts, Zn, Mg, Ca, etc. (Geach, 1996). Evidence showing the formation of PAHs in used engine oil can be corroborated by the presence of a small band occurring at 1600 cm^{-1} as seen on Figure 4.14, which is associated with C-C stretch in a ring (Dominguez-Rosado & Pitchel, 2003).

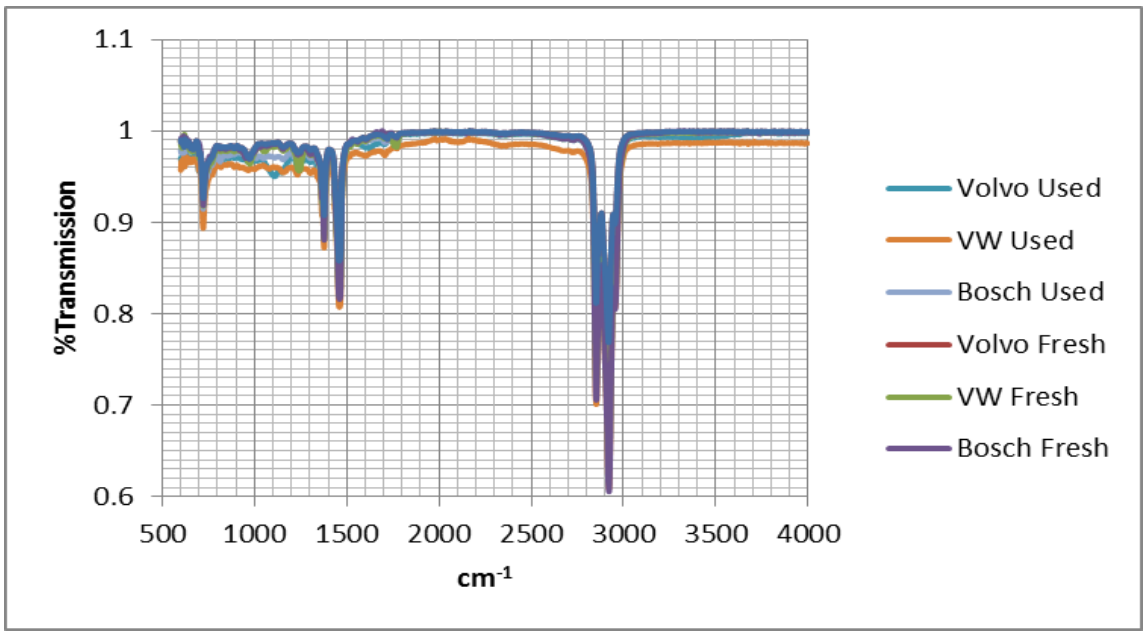


Figure 4.13: Combined FTIR spectra of both fresh and used engine oil samples

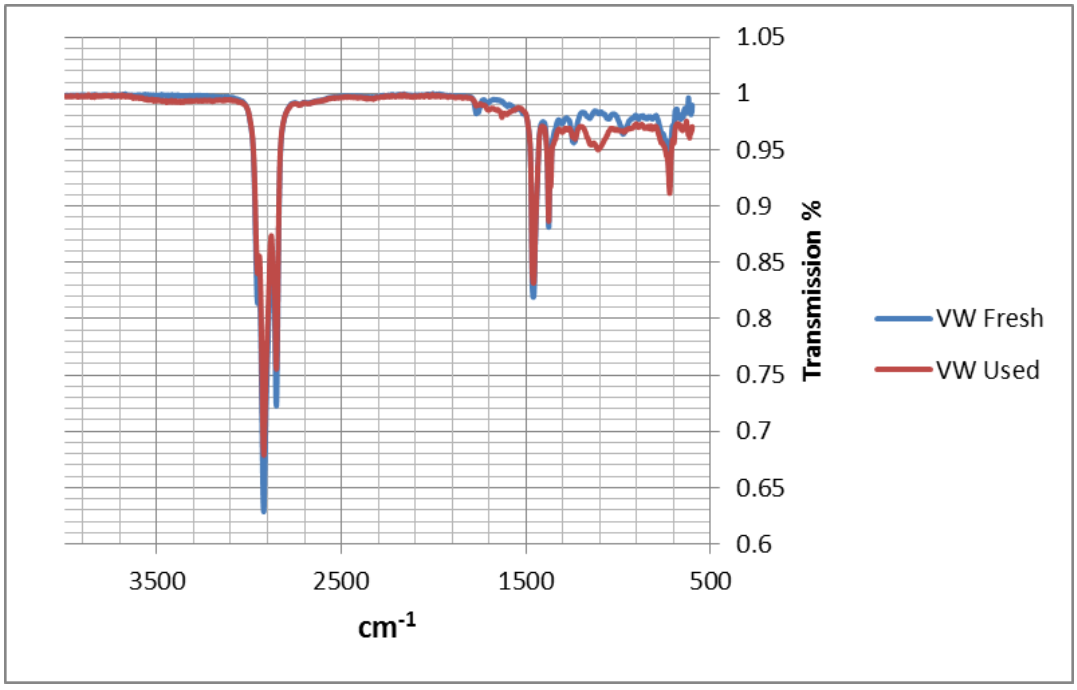


Figure 4.14: FTIR comparison between a fresh and afresh oil sample

Figure 4.15 shows the difference in proton spectra of fresh and used engine oil samples. On the used oil spectrum, a new intense signal was observed at the aromatic region between 7-7.5 ppm, which may have risen due to PAH formation, whilst the increase in intensity of other aliphatic signals from fresh to used oil, is due to the transformation of fresh oil during engine operation. A quantitative NMR is able to inform us about the quantity of compounds in the

sample, therefore when looking at the difference in content of PAHs relative to other compound signals on both the fresh and used oil sample, it is clear that PAH content is considerably lower compared to other components found in the oil sample.

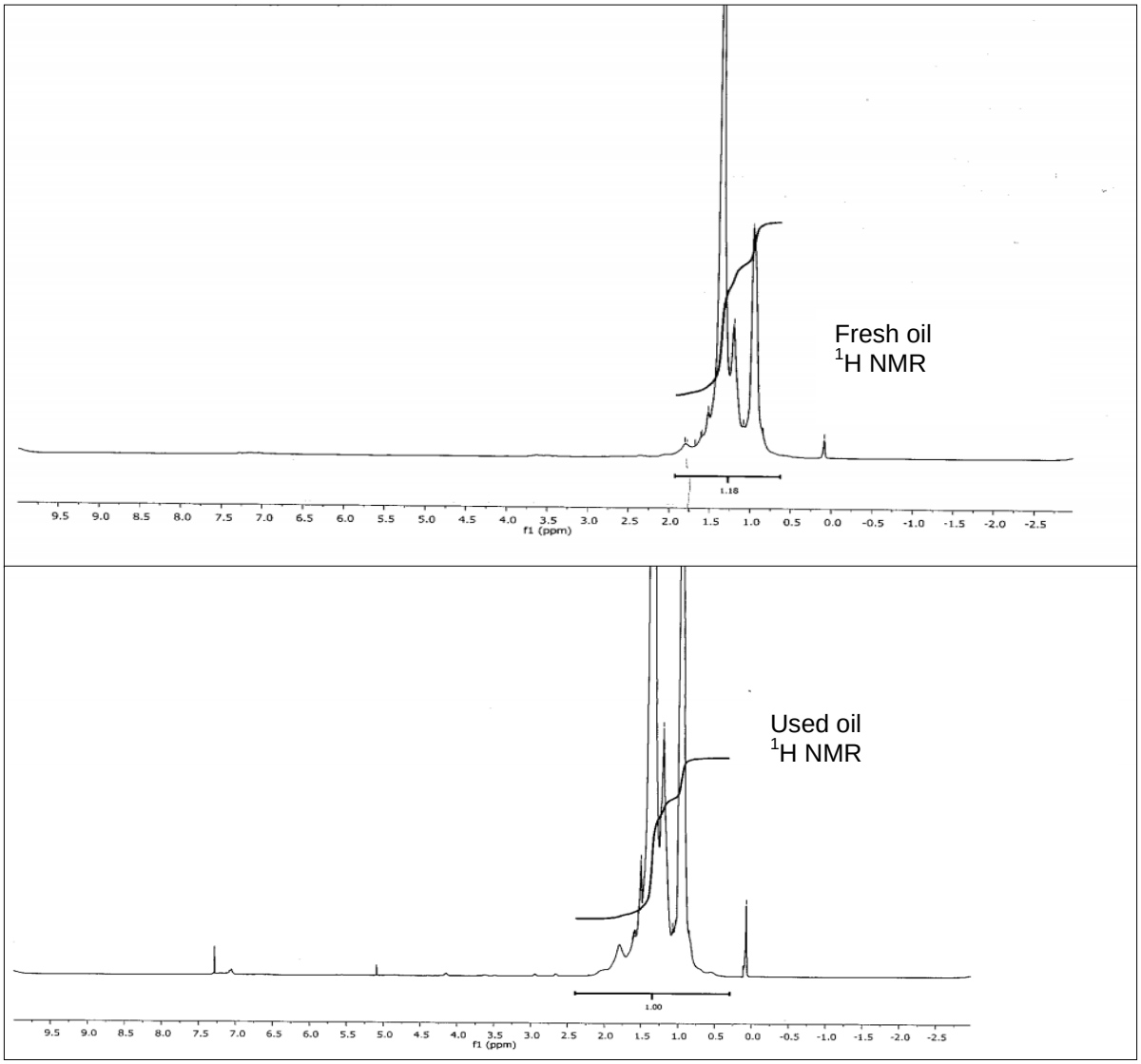


Figure 4.15: PAH proton NMR spectrum of fresh vs. used engine oil

CHAPTER FIVE

5.1 Conclusion

In this study it was found that PAHs in used engine oil still surpasses the amount found in fresh engine oil. Due to the different capabilities of the GCMS and HPLC, the total average concentration of PAH in used relative to fresh engine oil was found to be 7 and 70 times more in GCMS and HPLC respectively. In this scenario, with the validation parameters obtained, it was confirmed that HPLC is a better quantitative and GCMS a better qualitative instrument. Therefore it is evident from this study that the PAH levels in used relative to fresh engine oil has significantly decreased over the years which may be due to the highly sophisticated engine designs and top-niche oil formulations, which might have played a huge role in the staggering reduced levels, this is confirmed by the trivial PAH (aromatic) bands/signals on both the FTIR and the ^{1}H NMR. Despite the method employed, an in-depth study has to be performed to give reliable and exact amounts of the EPA 16 PAHs found in different local lubricants, in order to develop a method or a technique that will ultimately eliminate these lethal elements.

With many companies venturing in the recycling/re-refining of used motor oil business, the spread of waste oil in the environment is seen to have been decreasing. Recycling of used oil has been shown to be highly beneficial, both economically due to energy and environmental conservation, with the engine oil quality being improved, producing a less toxic product as heavy metals are extracted and stabilised into asphalt flux (waste) and PAHs are recovered during the re-refining process.

5.2 Recommendations

- Usage of additives, that are less likely to act as precursors for PAH formation during incomplete combustion processes.
- Since synthetic lubricants are designed to out-perform conventional lubricants, which lead to extended engine operation span, thus accumulating high levels of PAHs compared to conventional engine lubricants therefore appropriate measures should be taken, such as segregation of synthetics from conventional oils during recycling and re-refining processes.
- Due to the superiority of synthetic oils, they involve a blend of highly processed and highly refined mineral oils and base oils respectively, increasing energy consumption. It would be advisable to find alternative routes/ processes that use less energy or possibly shorten the process by incorporating accelerating agents.
- Due to the extensive use of synthetic engine oils, it would be advisable to incorporate biodegradable agents/additives that will enable the lubricant to be user friendly by breaking into components that can interact with environment without adverse effect or allow biodegradation by micro-organisms.
- The hydro-treatment step in solvent extraction method, needs further exploitation for complete PAH (aromatics) removal and severe lubricant quality improvement to meet group II base oil specifications
- Mimic the acid-clay re-refining treatment by using acidic agents (with similar characteristics to sulphuric acid such as acetic acid) but produces less harmless waste.

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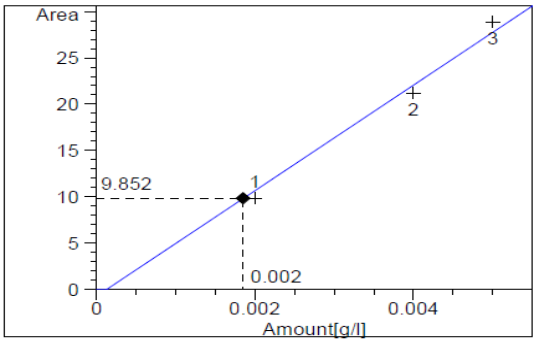
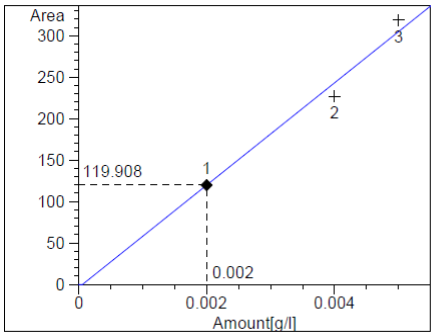
APPENDIX A
HPLC




```
Naphtalene at exp. RT: 5.987
VWD1 A, Wavelength=254 nm
Correlation:              0.99663
Residual Std. Dev.:       1.27335
Formula: y = mx + b
       m:    5699.24351
       b:      -6.96080e-1
       x: Amount
       y: Area
```

Figure A1: Naphthalene calibration curve

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Phenatene at exp. RT: 10.339
VWD1 A, Wavelength=254 nm
Correlation:              0.99586
Residual Std. Dev.:      15.30979
Formula: y = mx + b
       m:   61781.26151
       b:      -3.45173
       x: Amount
       y: Area
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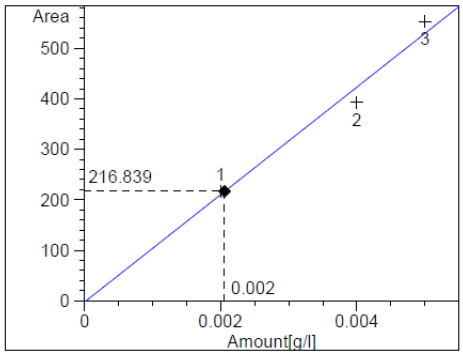
Figure A2: Phenanthrene calibration curve

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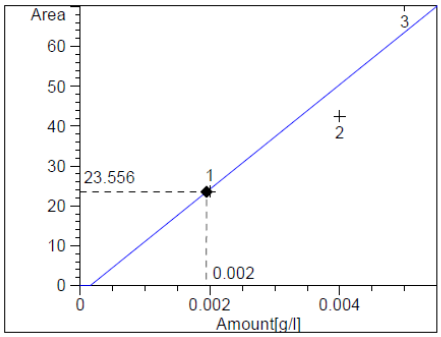
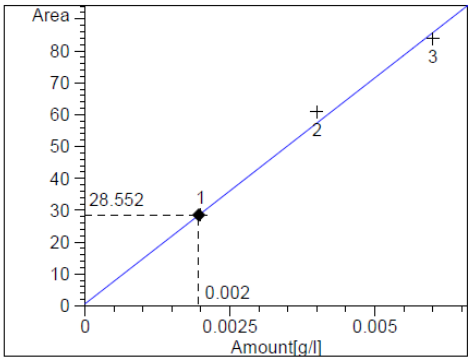
Anthracene at exp. RT: 11.327
VWD1 A, Wavelength=254 nm
Correlation:              0.99560
Residual Std. Dev.:      27.23597
Formula: y = mx + b
       m: 106594.46225
       b:      -2.47983
       x: Amount
       y: Area
```

Figure A3: Anthracene calibration curve




```
Fluoranthene at exp. RT: 13.878
VWD1 A, Wavelength=254 nm
Correlation:              0.97805
Residual Std. Dev.:       7.59693
Formula: y = mx + b
       m:   13131.88508
       b:      -2.02630
       x: Amount
       y: Area
```

Figure A4: Fluoranthene calibration curve




```
Pyrene at exp. RT: 15.547
VWD1 A, Wavelength=254 nm
Correlation:            0.99788
Residual Std. Dev.:     2.92396
Formula: y = mx + b
      m:  14186.76863
      b:      7.58239e-1
      x: Amount
      y: Area
```

Figure A5: Pyrene calibration curve

Table A1: PAH composition percentage

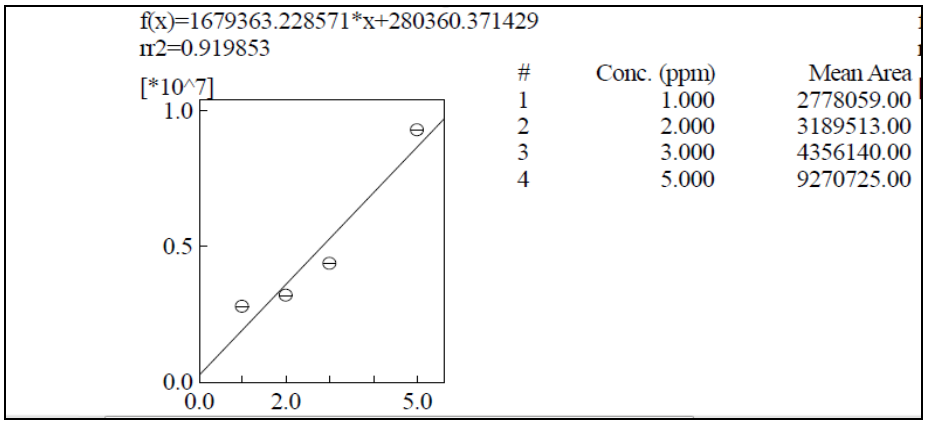
PAH	**Audi-F**	**Audi-U**	**Volvo-F**	**Volvo-U**
Napththalene	0.00%	0.00%	89.06%	47.39%
Phenanthrene	0.00%	0.00%	7.95%	35.74%
Anthracene	70.63%	0.00%	2.99%	16.88%
Fluoranthene	0.00%	13.48%	0.00%	0.00%
Pyrene	29.37%	86.52%	0.00%	0.00%
PAH	**VW-F**	**VW-U**	**Bosch-F**	**Bosch-U**
Napththalene	0.00%	38.30%	0.00%	17.18%
Phenanthrene	43.40%	25.09%	22.39%	5.74%
Anthracene	56.60%	36.61%	16.32%	3.69%
Fluoranthene	0.00%	0.00%	0.00%	0.00%
Pyrene	0.00%	0.00%	61.29%	73.39%

Table A2: Average PAH concentration

	Engen		Castrol	
	Fresh	Used	Fresh	Used
Avg PAH conc %	61.27%	33.44%	38.73%	66.56%

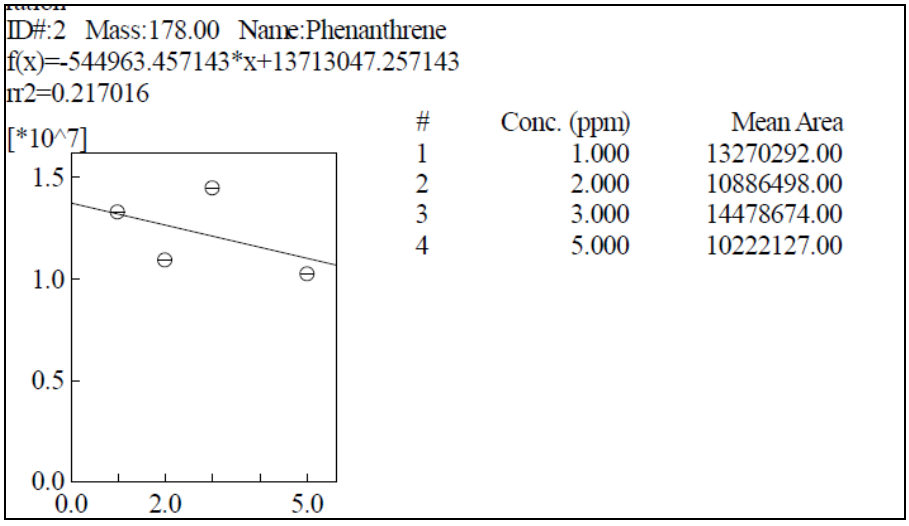
APPENDIX B

GCMS



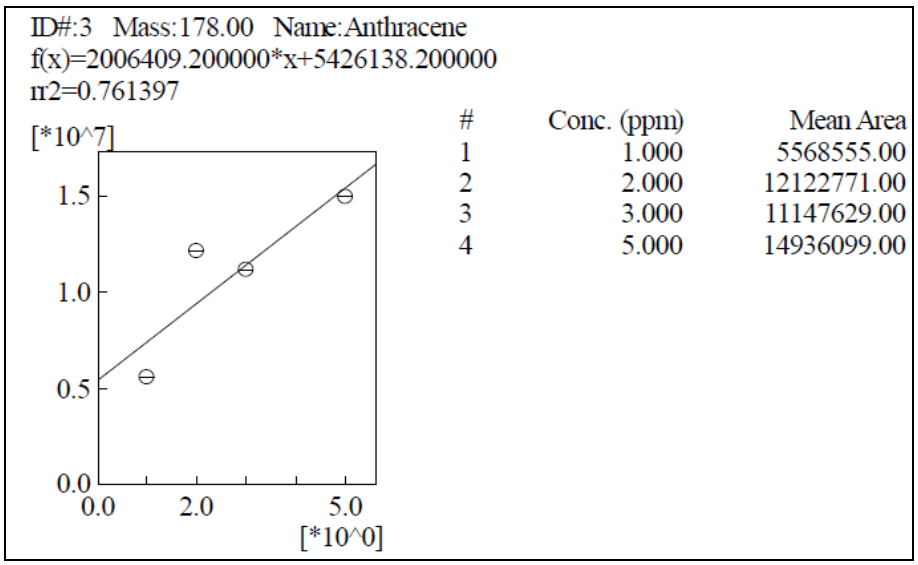
#	Conc. (ppm)	Mean Area
1	1.000	2778059.00
2	2.000	3189513.00
3	3.000	4356140.00
4	5.000	9270725.00

Figure B1: Naphthalene calibration curve



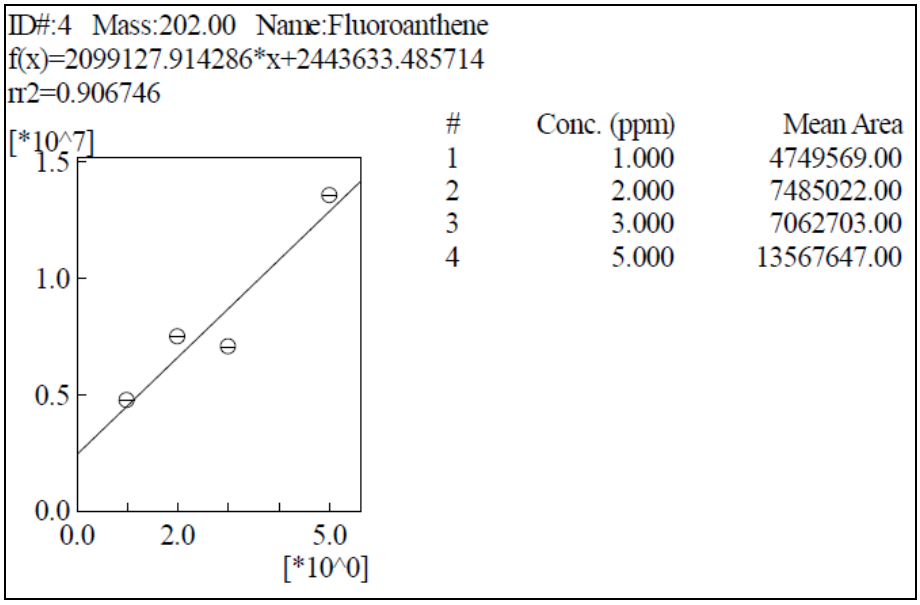
#	Conc. (ppm)	Mean Area
1	1.000	13270292.00
2	2.000	10886498.00
3	3.000	14478674.00
4	5.000	10222127.00

Figure B2: Phenanthrene calibration curve



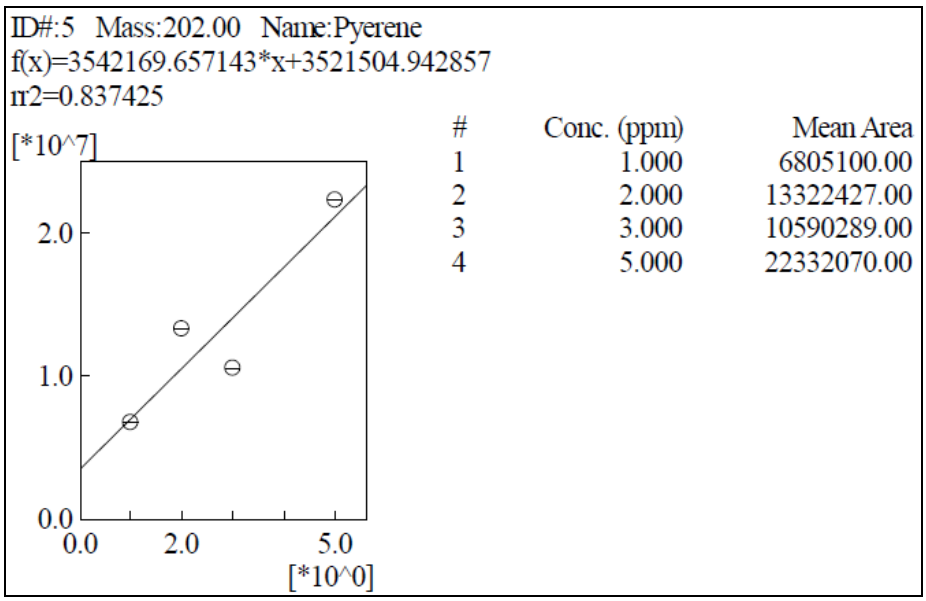
#	Conc. (ppm)	Mean Area
1	1.000	5568555.00
2	2.000	12122771.00
3	3.000	11147629.00
4	5.000	14936099.00

Figure B3: Anthracene calibration curve



#	Conc. (ppm)	Mean Area
1	1.000	4749569.00
2	2.000	7485022.00
3	3.000	7062703.00
4	5.000	13567647.00

Figure B4: Fluoranthene calibration curve



#	Conc. (ppm)	Mean Area
1	1.000	6805100.00
2	2.000	13322427.00
3	3.000	10590289.00
4	5.000	22332070.00

Figure B5: Pyrene calibration curve

Table B1: PAH composition

PAH	**Audi-F**	**Audi-U**	**Volvo-F**	**Volvo-U**
Napththalene	0.37%	0.00%	0%	0.00%
Phenanthrene	71.9%	0.00%	0%	nd
Anthracene	15.5%	0.00%	0%	0.00%
Fluoranthene	6.50%	685 %	0%	179%
Pyrene	5.74%	nd	0%	29.3%
PAH	**VW-F**	**VW-U**	**Bosch-F**	**Bosch-U**
Napththalene	38.2%	5.18%	3.61%	nd
Phenanthrene	nd	19.4%	14.7%	76.6%
Anthracene	152 %	30.4%	58.7%	85.7%
Fluoranthene	3.74%	32.4%	14.1%	nd
Pyrene	23.1%	12.7%	8.92%	0.00%

Table B2: Average PAH concentration

	Engen		Castrol	
	Fresh	Used	Fresh	Used
Avg PAH conc %	-4.73%	93.7%	105%	6.34%

APPENDIX C

Table C1: API base oil stock classification (Jaaskelainen and Majewski, 2014).

Group	**Sulphur %**	**Saturates %**	**VI**	**Manufacturing method**
I	>0.03	<90	80-119	Solvent refined
II	<0.03	>90	80-119	Hydro-processed
III	<0.03	>90	120+	Severely hydro-processed
IV	poly alpha olefins (PAOs)	-	-	Oligomerization (man-made)
V	All others (including esters)	-	-	Various
VI	Poly internal olefins (PIOs)	-	-	Oligomerization (man-made)

APPENDIX D
RESENTATIONS AND PUBLICATIONS

A. Presentations

L.N. Shakoane, A.J. Higginson and S Iyuke. Characterization and quantification of Polycyclic Aromatic Hydrocarbons (PAHs) in used and fresh engine oil by chromatography and spectroscopy techniques. Cross-Faculty postgraduate symposium 2014, 28th October. University of the Witwatersrand (South Africa). *Poster presentation*

B. Publications

- L.N. Shakoane, A.J. Higginson and S Iyuke. Characterization and quantification of Polycyclic Aromatic Hydrocarbons (PAHs) in used and fresh engine oil by chromatography and spectroscopy techniques (Submitted to International Journal of Sciences: Basic and Applied research)
- L.N. Shakoane, A.J. Higginson and S Iyuke. Characterization and quantification of Polycyclic Aromatic Hydrocarbons (PAHs) in used and fresh engine oil by chromatography and spectroscopy techniques (Submitted to Journal of Marine Pollution Bulletin)