CHAPTER I



INTRODUCTION

It is likely that diesel engines will increasingly be favoured by motorists, because of their greater fuel savings. Diesels also offer financial benefits in maintenance and resale value. The superior fuel economy is of environmental significance because of increased awareness that the products of hydrocarbon combustion, such as carbon dioxide, are involved in 'global warming'.

A major drawback of diesel combustion is the emission of fine carbonaceous particulate matter, on which organic compounds from the exhaust stream can be adsorbed and condensed. The solvent-soluble organic fraction of the particulates includes polycyclic aromatic hydrocarbons (PAHs), many of which have been shown to be genetoxic. The submicrometre particulate size enables the associated PAHs to penetrate deeply into the human respiratory system. Diesel exhaust was classified as a possible human carcinogen in 1988. Presently, legislation does not cover PAH emissions, but future control measures involving PAHs are likely to be introduced.

The PAH emissions arise in two main ways. One is by survival from a combination of fuel PAHs and lubricating oil PAHs; the other is by generation of PAHs from pyrolysis of fuel or oil components during combustion. Survival of fuel PAHs has been postulated as the dominant route [1].

1.1 Diesel Particulate Matter (PM)

Diesel particulate matter (PM), as defined by the EPA regulations and sampling procedures, is a complex aggregate of solid and liquid material. Its origin is carbonaceous particulates generated in the engine cylinder during combustion. The primary carbon particles form larger agglomerates and combine with several other, both organic and inorganic, components of diesel exhaust. Generally, components in PM from conventional diesel engines are divided into three classes as shown in Figure 1.1. The

amount of components in PM depends on fuel properties, engine design and operating parameters. The first class of components in PM is the solids fraction which is the visible smoke from diesel exhaust. This material is composed of sub-micron sized dry carbon particles, commonly known as soot, which are formed during the diesel combustion process. The second class is the soluble organic fraction (SOF), which contains heavy hydrocarbons adsorbed and condensed on the carbon particles. A portion of this material results from incomplete combustion of the fuel and the remainder is derived from engine lube oil that passes by the piston oil rings. The third class is the fraction containing sulfates and bound water. The amount of this material is directly related to the fuel sulfur content [2].

The actual composition of PM depends on the particular engine and its load and speed conditions. "Wet" particulates may contain up to 60% of the hydrocarbon fraction (SOF), while "dry" particulates are comprised mostly of dry carbon. The amount of sulfate compounds is directly related to the sulfur contents of the diesel fuel.



 Nuclei Particles
 Agglomerated Particle

 0.08 - 1 micron diameter

 Figure 1.1 Schematic composition of diesel particulate matter.

 (Duplicated from http://www.nett.ca/faq_diesel.html.)

Diesel particulates are very fine. The primary (nuclei) carbon particles have a diameter of 0.01–0.08 micron, while the agglomerated particle diameter is in the range of 0.08 to 1 micron. As such, diesel particulate matter is almost totally respirable and has a significant health impact on humans. It has been classified by several government agencies as either "human carcinogen" or "probable human carcinogen". It is also known to increase the risk of heart and respiratory diseases [3].

1.2 Polycyclic Aromatic Hydrocarbons [4, 5]

Polycyclic aromatic hydrocarbons (PAHs) are a group of condensed multiple benzenoid-ring chemicals formed during the incomplete combustion of coal, oil and gas, garbage, or other organic substances. Instead of carbon being completely oxidized to carbon dioxide, hydrocarbon fragments are generated which can interact with each other to yield complex polycyclic structures. PAHs can be man-made or occur naturally. There is no known use for most of these chemicals except for research purposes. A few of PAHs are used in medicines and to make dyes, plastics, and pesticide.

As pure chemicals, PAHs generally exist as colorless, white, or pale yellow-green solids. Most PAHs do not occur alone in the environment (including those found at hazardous waste sites), rather they are formed as mixtures of two or more PAHs. PAHs in general have high melting points and low vapor pressures, and are virtually insoluble in water. Many PAHs are often associated with or adsorbed onto particulate matter, and a large mass fraction of airborne PAHs is associated with ultrafine particles. In addition, they can occur in soil or sediment as solids [4].

Polycyclic aromatic hydrocarbons are hydrocarbons containing two or more benzene rings. Many compounds in this class are known human carcinogens. PAHs in the exhaust gas are split between gas and particulate phase. The most harmful compounds of four and five rings are present in the organic fraction of PM (SOF).

PAHs are a class of very stable organic molecules made up of only carbon and hydrogen. These molecules are flat, with each carbon having three neighboring atoms much like graphite. Although the health effects of the individual PAHs are not exactly alike, the following 16 PAHs, classified as priority pollutants by the U.S. EPA, are considered in this study. Their chemical structures are shown in Figure 1.2.

These 16 PAHs were chosen for study because (i) more information is available than on the others; (ii) they are more harmful than many or most of the others; (iii) there is a greater chance that humans will be exposed to these PAHs than to the others.



Figure 1.2 Chemical structure of selected PAHs in EPA 610.



1.3 Palm Oil

The oil palm, *Elaeis guineensis*, fruit is unusual in that it yields two distinct oils: palm kernel oil differs from the kernel and palm oil from the pulp (about 50%). Palm oil is deep orange-red by the large amount of carotene. It is used for making vegetable, margarine, soap, and the small amount is used in marking thin plate and in aluminium sheet rolling [6].

Palm oil, unlike other vegetable oils, contains equal amounts of saturated and unsaturated fatty acids. Crude palm oil is chemically composed of the following:

- 50% of saturated fatty acid (Palmitic acid and Stearic acid)
- 40% of monounsaturated fatty acid (Oleic acid)
- Vitamin "E" (Tocopherols and Tocotrienols)
- Vitamin "A" (Beta-Carotene)

Fatty acid composition of palm oil

Palm oil has saturated and unsaturated fatty acids which palmitic and oleic acids are the main component acids. More than 85% of unsaturated fatty acids are located at the 2-position of the glycerol nucleus of triglyceride composition of palm oil (Figure 1.3). Both the glyceride structure and the FFA content affect the melting and plastic properties of palm oil [6].

Figure 1.3 Chemical structure of palm oil.

Common Name	Systematic Name	Structure	Content in Palm Oil (% wt/wt)
Saturated			
Myristic acid	tetradecanoic	CH ₃ (CH ₂) ₁₂ COOH	0.6 – 1.6
Palmitic acid	hexadecanoic	CH ₃ (CH ₂) ₁₄ COOH	32 – 45
Stearic acid	octadecanoic	CH ₃ (CH ₂) ₁₆ COOH	3.7 - 5.5
Unsaturated			
Oleic acid	cis-9-	$\mathbf{C} = \mathbf{C}$	39 – 42
	octadecanoic	CH ₃ (CH ₂) ₇ (CH ₂) ₇ COOH	
Linoleic acid	cis-9,cis-12-	F 7	6 - 9
	ocdecanoic	$\begin{array}{c} H \\ CH_{3}(CH_{2})_{3} \end{array} \begin{array}{c} H \\ CH_{2} \end{array} \begin{array}{c} (CH_{2})_{7}COOH \end{array}$	

 Table 1.1 Composition of fatty acid in palm oil [6]

Objective and Scope of the Research

The principal objective of this research is to investigate the effect of palm oil methyl ester blended with diesel fuel on polycyclic aromatic hydrocarbons generated from exhaust emission of diesel engine.

In initial study, palm oil methyl ester will be prepared from crude palm oil *via* transesterification process and then blended with diesel fuel. The influence of the amount of palm oil methyl ester and engine speed on the amount of PAHs in diesel exhaust will be investigated.