

CHAPTER II

THEORETICAL AND LITERATURE REVIEW

The diesel combustion process[3-4]

Compression ignition

In any combustion process, there are at least three basic requirements;

- (1) Formation of a mixture of fuel and air
- (2) ignition of the fuel-air mixture
- (3) completion of combustion of the fuel-mixture

In the Diesel engine, these requirements are met as indicated diagrammatically in Fig. 2.1. Combustion in the diesel engine is achieved by compression ignition. Rapid compression of air within the cylinders generates the heat required to ignite the fuel as it is injected. The combustion cycle, as illustrated in Fig 2.2, can be considered in several phases. These include ignition delay, an initial phase which follows compression, when in-cylinder pressures have been considerably increased, temperatures in excess of 500°C achieved and fuel injected. This phase comprises both a physical delay attributed to fuel atomization, vaporization and mixing, plus a chemical delay during which the reactions of combustion proceed only slowly. This is followed by rapid combustion, a phase in which the fuel-air mix prepared during the delay phase ignites in uncontrolled combustion. The rate and effect of combustion

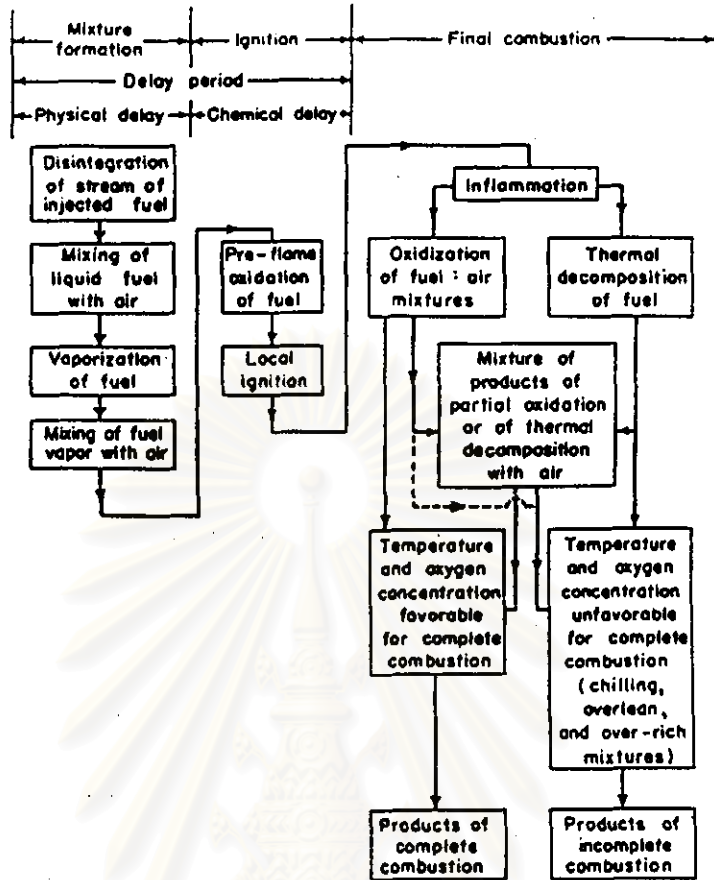


Figure 2.1 Outline of combustion process in the Diesel engine.

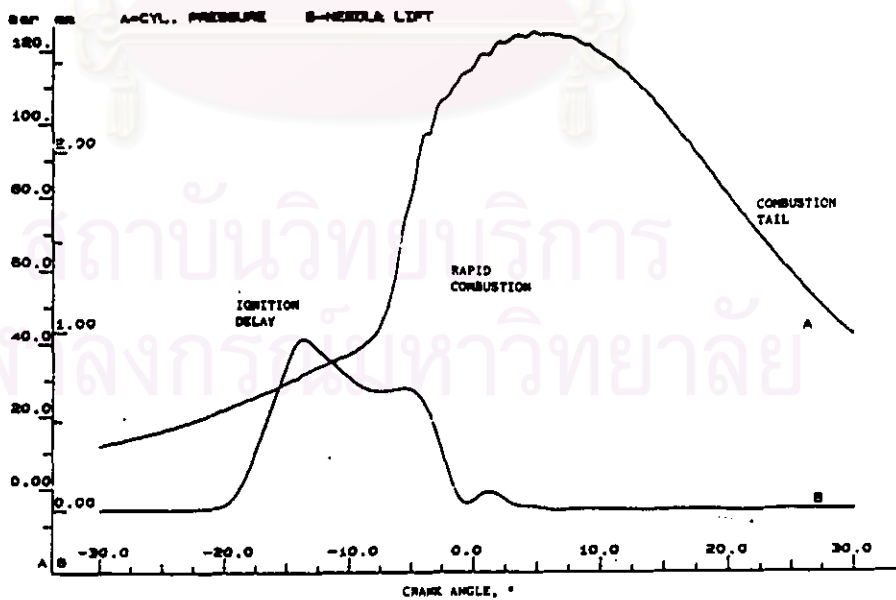


Figure 2.2 Diesel engine combustion cycle.

in this second phase is therefore very dependent upon the length of ignition delay and quantity of fuel introduced during the delay period.

Subsequent combustion is then, to some extent, regulated by the rate of fuel injection as well as by mixing and diffusion processes. The major controlling factor is, however, the need for the fuel to find oxygen. Ultimately, a combustion tail can be considered to exist, and this is the phase after all fuel has been injected when combustion continues at a reducing rate until all fuel and oxygen have been consumed.

Engine design

The diesel engine must achieve compression temperatures and pressures which are adequate to enable starting from cold and to give acceptable smooth combustion when running . In high-speed automotive diesel engines this is obtained by the use of compression ratios of between 12:1 and 23:1, depending on cylinder size, combustion system and whether the engine is turbocharged, It is the typically high compression ratio of the diesel engine which dictates the need for its general mechanical robustness and also leads to its high indicated efficiency characteristics.

After compression ratio, the main factors affecting combustion in the diesel engine are combustion chamber design and fuel injection characteristics. The time from start of fuel injection to end of combustion is very small, and during this a fuel-air mixture has to be formed which will ignite within a reasonable delay period. Good mixing of fuel and air is essential and adequate oxygen has to be available for combustion to be completed early in the expansion stroke.

In general, two combustion chamber forms are principally used in automotive diesel engine applications. These are the direct injection system as illustrated in Fig 2.3 and the pre-chamber, indirect injection system shown in Fig. 2.4 .

With the deep bowl direct injection system the required fuel-air mixing is achieved by direct injection of fuel into an open cylinder into which air has

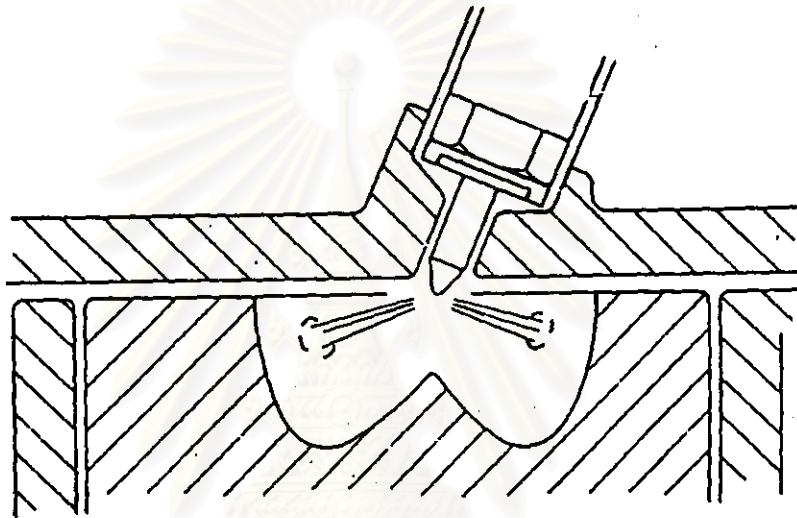


Figure 2.3 Direct injection combustion system.



Figure 2.4 Indirect injection combustion system.

been introduced with a high degree of rotational movement. The air movement is initiated during the induction stroke by correctly sited and shaped inlet ports which causes the air to swirl in the cylinder. The swirl continues as the piston rises during compression.

In contrast, in the pre-chamber indirect injection system air is forced into a pre-chamber during the compression stroke. Fuel is injected into the turbulent air, and because the chamber is not particularly sensitive to atomization, pintle-type nozzles are often used. After ignition the pressure in the chamber forces the burning mixture through a narrow passage or passages into the cylinder, where it mixes with air to complete combustion.

Fuel requirements

A principal requirement of fuels for high-speed diesel engines is good ignition quality. Fuels of poor ignition quality can lead to extended ignition delay and result in the phenomenon of 'diesel knock'. Excess fuel is injected into the combustion chamber during the delay period and in combustion causes more rapid and greater rises in cylinder pressure. This results in increased engine stress and noise together with possible losses in power and fuel economy. Changes in the ignition quality of fuels can result in rougher engine running, particularly at light loads, and can also have effects on engine exhaust emissions. In addition, in extreme circumstances the ability of a diesel engine to fire and run will be linked to the ignition quality of available fuels.

The almost universally accepted measure of the ignition quality of diesel fuels is cetane number. As shown in Fig. 2.5, the self-ignition

characteristics of hydrocarbons vary markedly with both boiling point and chemical structure.

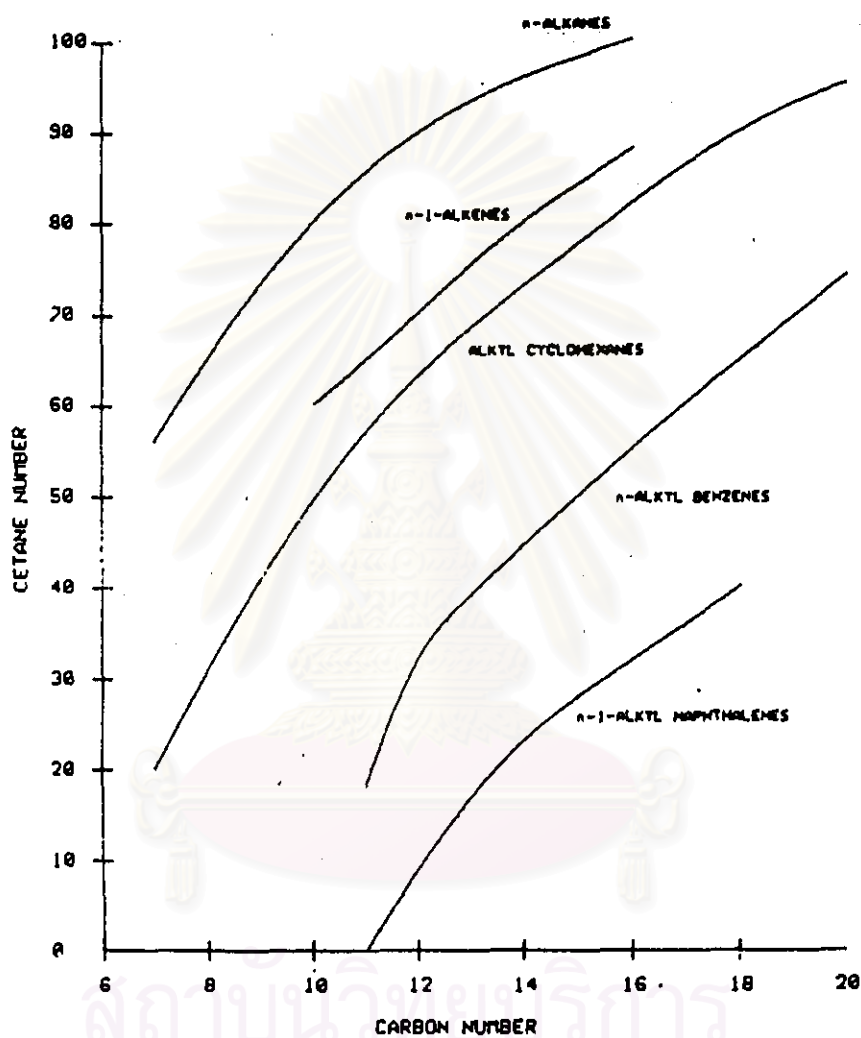


Figure 2.5 Cetane number of pure hydrocarbons.

Traditionally, a distillate fraction from crude oil within the 180-370 °C boiling range has been used as diesel fuel. For the majority of crude oils this fraction contains a high proportion of paraffinic hydrocarbons and is of excellent ignition quality. The increased use of cracked components in diesel

fuel blending is, however, leading to a general lowering of diesel fuel ignition quality. The aromatic hydrocarbons present in these components have a particularly poor ignition quality.

The physical characteristics of a diesel fuel are vitally important with respect to the production of a fuel suitable for commercial use. Ignition quality is of prime importance when considering combustion, but other properties such as volatility, viscosity, hydrocarbon composition and stability cannot be overlooked if optimum engine performance is to be achieved.

Fate in air of PAC [5-8]

The term polycyclic aromatic compound (PACs) refers to all of the members of the polycyclic aromatic hydrocarbons (PAHs) and to their alkyl-, amino-, oxygen-, halogen, and nitro-substituted derivatives, as well as to the nitrogen and sulfur heteroatom analogues of the PAHs.

In the atmosphere PACs are associated with particulate matter, especially soot. The emission of PACs to the atmosphere is of concern, principally because many of the compounds are known carcinogens and/or mutagens. During their migration through the environment, the PACs may be transformed, by interaction with oxidants and sunlight, into products which, in some cases, are much more mutagenic than the compounds from which they were derived.

Formation and Emission of PACs

It is generally accepted that PAHs are produced in combustion sources through the condensation of ethylenic radicals in the gas phase to form

the larger polycyclic compounds, and there is some evidence to show that the alkylated PAHs are formed more readily at lower pyrolysis temperatures than at high temperatures. During the incomplete combustion of organic fuel, the formation of oxygenated and nitrated PAHs may also occur.

When the stack gas cools, the gaseous PAHs condense to form microparticles which then agglomerate to form larger particles. In general, the PAHs remain in the gas phase at temperatures above 150 °C but rapidly condense onto fly-ash particles below that temperature. At typical ambient temperatures, PAHs exist primarily in the particle phase.

Vapor Pressure and Temperature

The extent to which a particular PAC molecule will exist in the gas phase or the particle phase is determined by the vapor pressure of the compound and the ambient temperature. A first approximation for urban air particulate matter, that compounds with vapor pressure in excess of 1×10^{-5} kPa should occur predominantly in the gas phase, whereas those with vapor pressures below 1×10^{-9} kPa should exist exclusively in the particle phase. For clean air aerosols, the corresponding vapor pressures between these upper and lower limits would be expected to occur in both the vapor and particulate phases.

Particle Size Distribution

Many studies have shown that the PAHs are associated primarily with particles less than 3 μm in aerodynamic mean diameter. A bimodal distribution of PAH in the air of Rio de Janeiro particulate matter in which 60

% of BaP in the particulate matter was associated with particles between 0.075 and 0.26 μm , and 30% was associated with particles between 0.26 and 2.0 μm .

Submicron particles, in the absence of wet deposition, have atmospheric residence lifetimes of between 100 and 1000 h, whereas particles in the 1-10 μm size range should have atmospheric lifetimes of 10-100 h. In the absence of wet deposition, therefore, the long atmospheric residence times of the submicron particles suggest that the particle-bound PAC may travel great distances before being removed from the atmosphere.

Sampling of PAHs

The standard method of sampling particulate carbon from a diesel engine involves cooling and diluting the exhaust with air before passing a sample through a filter. This method (EPA dilution tunnel) was devised to mimic the natural dilution and cooling of exhaust as it leaves the tailpipe. After combustion in the engine, particulate carbon scavenges organic components from the vapour phase. These include the PAC which may originate from unburned fuel and lubricating oil or from pyrosynthetic reactions involving the incomplete combustion of the diesel fuel. The PAC that is adsorbed onto particulate carbon is sampled by the filter and may be extracted, usually using a Soxhlet extraction technique, into solvents to produce a soluble organic fraction (SOF)[5]. Particulate-associated PAH emission samples were taken in dilution exhaust with Teflon-coated glass fiber filters (Pallflex T60A20) or Whatman glass fibre GF/F grade filter. However, the filter will not efficiently sample those hydrocarbons and PAH which have remained in the vapour phase. Downstream of the filter, semivolatile PAH compound were trapped on

polyurethane foam plug (PUF). However, the filter will not efficiently sample those hydrocarbons and PAC which have remained in the vapour phase.

The filter method suffers from the disadvantage that artifacts may be formed on the carbon particles as the diluted exhaust continues to pass through the filter. This is especially true when mutagenicity tests are undertaken because a relatively prolonged exposure time may be needed to obtain the sufficient weight of sample that these kinds of bio-assays require. A method which overcomes this objection involves the use of a stainless-steel tower placed immediately after the engine in which the exhaust passes countercurrent to a solvent stream. The solvent rapidly cools and strips the exhaust of all hydrocarbons which are not gaseous at standard temperatures and pressures and including any PAC present, before these can adsorb onto the carbon particles. Figure 2.6 shows a schematic representation of the total exhaust solvent scrubbing apparatus (TESSA).

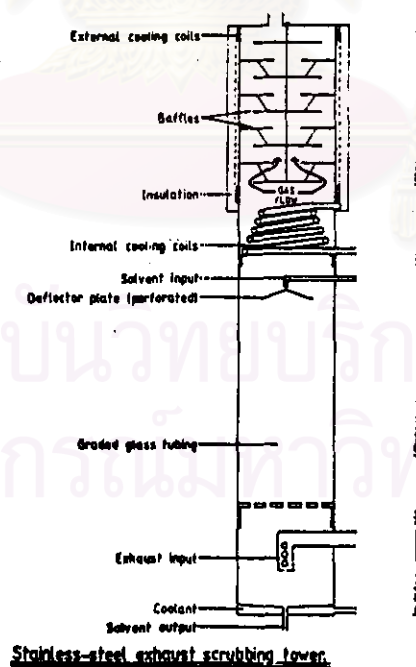


Figure 2.6 Schematic representation of the total exhaust solvent scrubbing apparatus.

Analysis PAHs from exhaust emission

The SOF from the EPA dilution tunnel of the tower extracted fraction (TES) may be taken and the exhaust hydrocarbons isolated by a simple chromatographic column method or by a high-performance liquid chromatography (HPLC) method in which any PAH is separated into ring sizes. Qualitative and quantitative analysis of PAH in each fraction is obtained by high-resolution gas chromatography (HRGC) and gas chromatography-mass spectrometry (GC-MS) or by HPLC with fluorescence and UV-diode array detection.

Mass spectrometry of PAHs

Mass spectrometry (MS) has been used for the analysis of polycyclic aromatic hydrocarbons (PAHs) since 1951. This early realization that MS was an ideal tool for the analysis of these compounds stemmed from the clear spectra that they produced. Since 1951, there have been hundreds of papers reporting on the use of MS for the qualitative and quantitative analysis of PAHsp.

Electron-Impact Ionization

The electron-impact mass spectra of PACs are usually quite simple. Because of the extensive electron delocalization of these molecules, the molecular ions in these spectra are vary intense and fragment ions are small. Because of this lack of fragmentation, it is usually impossible to distinguish among isomers using electron-impact MS alone. Thus, distinguishing among

isomers has driven research on the mass spectra of PACs. The paragraphs that follow discuss the electron-impact mass spectra of a series of a series of PACs that are derivatives of phenanthrene and anthracene. The reader should remember that the features observed in the spectra of these relatively small PACs are also observed in the spectra of other, larger PACs. As an intellectual convenience, this discussion will focus on this one series.

The mass spectrum of phenanthrene (see Figure 2.7) is almost identical to that of anthracene. Both spectra are observed; the loss H_2 predominates. Because of the intensity of the molecular ion, the doubly charged molecular ion at m/z 89 is of medium intensity. The only other fragment ions are at m/z 152, due to a loss of C_2H_2 from the molecular ion, and a doubly charged version of that ion at m/z 76. Note that the abundances of the singly and doubly charged ($M - C_2H_2$) ions are about the same. The relative abundances of the doubly charged molecular ions are a strong function of the size of the aromatic system.

In general, in the mass spectra of all PAHs, the molecular ion is the most intense peak. Loss of two hydrogens is frequently the second most intense peak. The doubly charged molecular ion is of medium intensity, and both singly and doubly charged ($M - C_2H_2$) ions are present. Furthermore, without gas chromatographic retention data or other supplementary data, it is impossible to distinguish among isomeric compounds.

The mass spectra of alkylated PAHs are also dominated by molecular ions and fused-ring tropylium ions. For example, the electron-impact mass spectrum of 1-methylphenanthrene is shown in Figure 2.8 The mass spectra of the five different methylphenanthrene isomers and of the three different

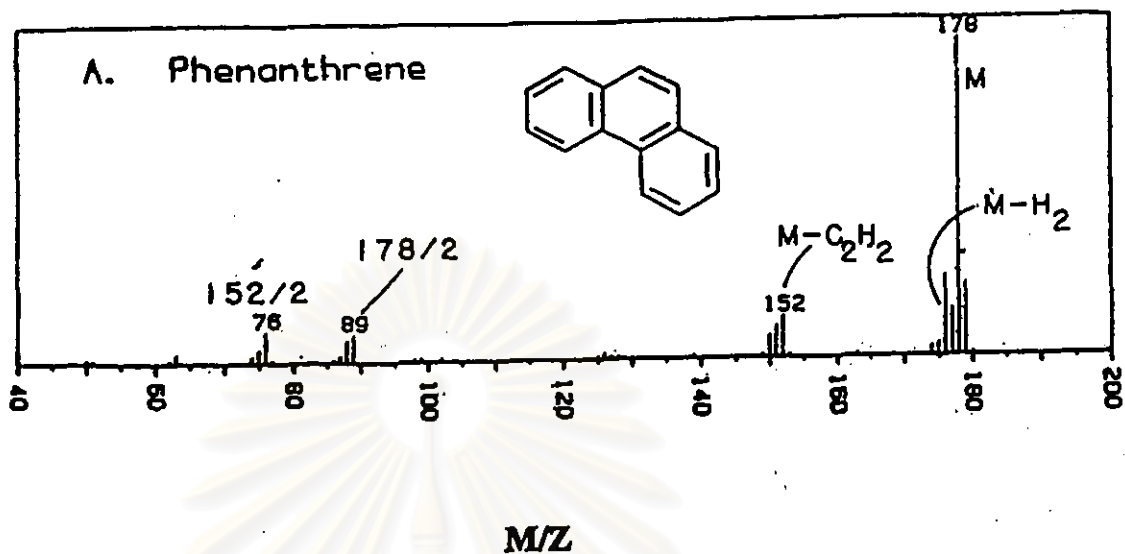


Figure 2.7 Electron-impact mass spectrum of phenanthrene.

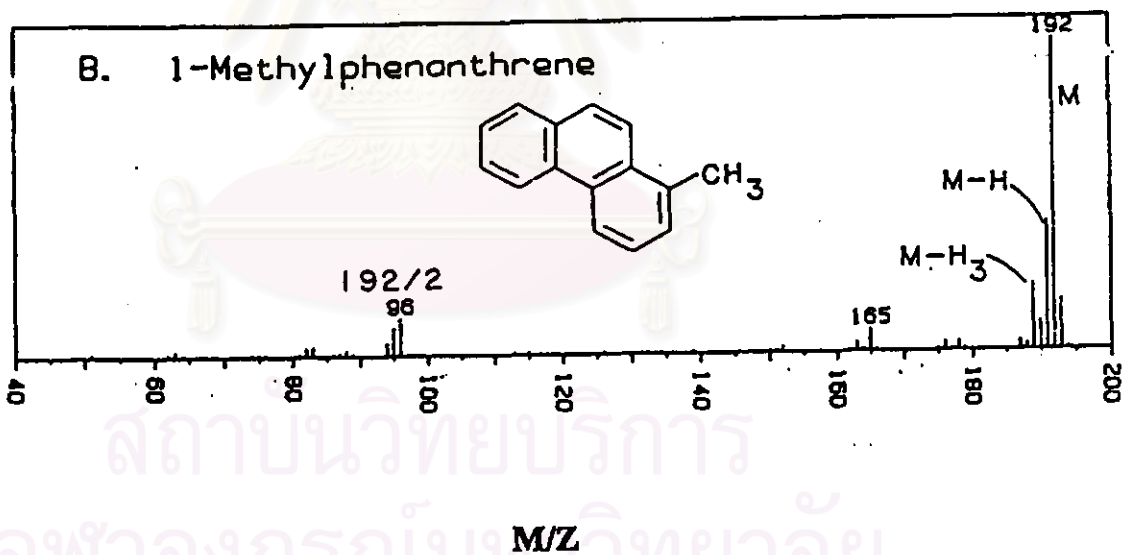


Figure 2.8 Electron-impact mass spectrum of 1-Methylphenanthrene.

methylanthracene isomers all resemble one another. Note the intense molecular ion at m/z 192 and the intense $(M-H)^+$ ion at m/z 191. This latter ion may result from the expansion of the ring to incorporate the methyl carbon. The rest of the

mass spectrum is similar to that of a PAH with a molecular formula of $C_{15}H_{11}$. For example, the fused-ring tropylium ion at m/z 191 loses two hydrogens to give an ion of medium intensity at m/z 189; the m/z 191 ion can also lose a C_2H_2 group to give the ion a m/z 165. The other ion of significant intensity in the mass spectrum is the doubly charged molecular ion at m/z 96.

The structure of the fused-ring tropylium ion is probably different, depending on where the methyl group was attached. For example, 1-,2-,3-, and 4-methylphenanthrene would all give a fused-ring tropylium ion with the seven-membered ring at the end; (structure I in Figure 2.9). 9-Methylphenanthrene would give a fused-ring tropylium ion in which the seven-membered ring is in the middle; (structure II in Figure 2.9). A similar argument holds for 1- and 2-methylanthracene, which would give a tropylium ion of type III, whereas 9-methylanthracene would give a tropylium ion of type IV. It is significant that the spectra of all of these methyl-substituted compounds are identical to one another. Clearly, it is not possible to distinguish among the structures of the four tropylium ions (I-IV) given in Figure 2.9 by electron-impact MS. It remains to be seen whether MS/MS techniques can make this distinction.

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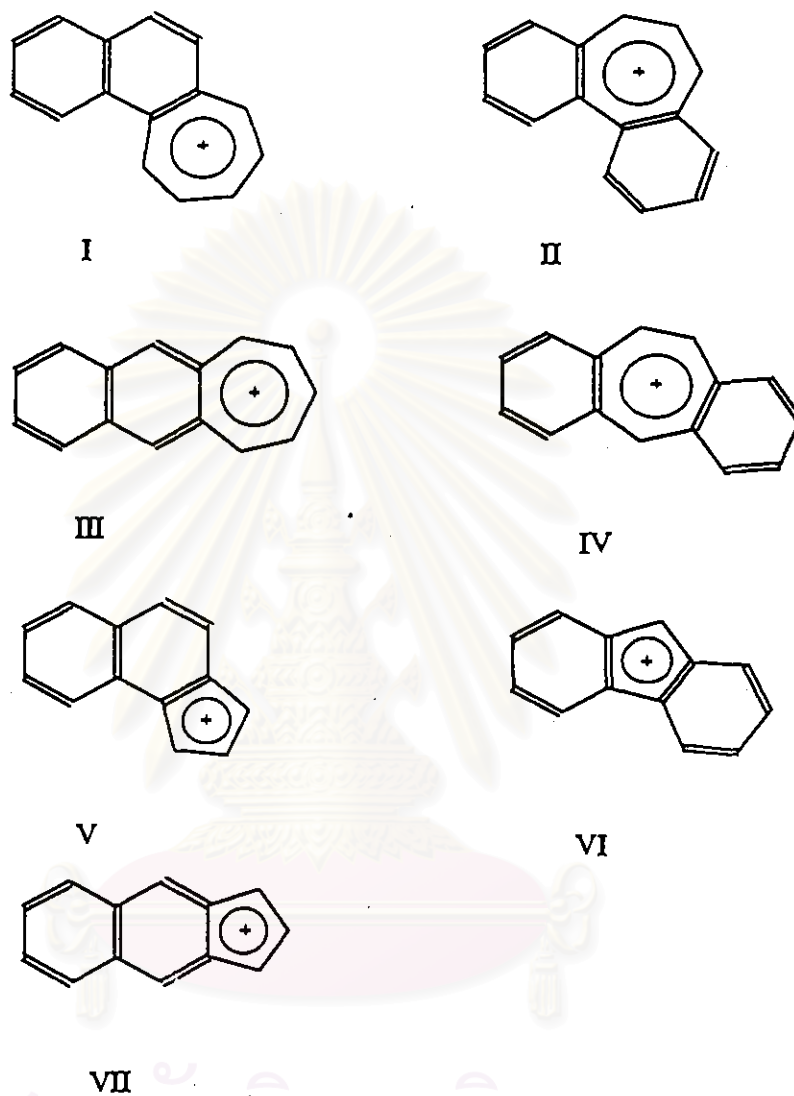


Figure 2.9 Possible structures of the m/z 191 (I to IV) and m/z 165 (V to VII) ions in the electron impact of phenanthrene- and anthracene-related compounds.

Oxygenated Compound [9-10]

The use of oxygenates to produce cleaner burning diesel fuels was initially considered over fifty years ago. Since that time, the addition of numerous oxygenated compounds to diesel fuel has been reported. Low molecular weight alcohols such as ethanol and t-butyl alcohol have been reported to reduce emission.

Pentanol

Pentanol (amyl alcohols), $C_5H_{11}OH$, Mr 88.15, are saturated aliphatic C_5 -alcohols. The eight structural pentanol isomers are often named by common names in addition to the systematic IUPAC nomenclature (see Table 2.1). Four of the pentanol isomers are primary alcohols, three are secondary alcohols, and 2-methyl-2-butanol is a tertiary alcohol.

Fusel oil has been mentioned previously as a mixture of alcohols that is a by-product of carbohydrate fermentations which were intended to produce ethanol. The composition of this mixture will vary depending on the starting raw materials, but the chief components are usually isoamyl and active alcohols, with lesser amounts of isobutyl alcohol and 1-propanol. After suitable chemical treatment and distillation, a refined amyl alcohol is obtained with a composition of about 85% isoamyl and 15 % active amyl alcohol.

Table 2.1. Pentanol isomers

Formula	Systematic name	Common name
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	1-pentanol	n-amyl alcohol
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$	2-pentanol	sec-amyl alcohol
$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$	3-pentanol	
$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$	2-methyl-1-butanol	active primary amyl alcohol
$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$	3-methyl-1-butanol	isoamyl alcohol
$\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)(\text{OH})\text{CH}_3$	2-methyl-2-butanol	tert-amyl alcohol
$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}(\text{OH})\text{CH}_3$	3-methyl-2-butanol	sec-isoamyl alcohol
$\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{OH}$	2,2-dimethyl-1-propanol	neopentyl alcohol

Table 2.2 Physical properties of 3-Methyl-1-butanol (isoamyl alcohol)

mp, °C	-117.2
bp, °C	130.5
Density, g/cm ³	0.812
Refractive index n_D^{20}	1.4078
Flash point, °C	44
Ignition temperature, °C	365
Viscosity, mPa.s	3.86 (23.8 °C)
Specific heat at 20 °C, Jg ⁻¹ K ⁻¹	2.28
Heat of vaporization, J/g	441
Vapor pressure at 20 °C, kPa	0.27
Solubility in H ₂ O at 20 °C, wt%	2.5
Expansion coefficient	0.00090

Pentanols are found mainly in fruit, honey, tea, cheese, and alcoholic beverages. They were first discovered in fusel oils and were side products in the fermentation of starch-containing materials.

Literature review

In 1984, Weidmann tested reference blends for performance, exhaust emissions and fuel economy. The use of alcohol blends in Diesel engines is likely to be advantageous in environmental terms, with a noticeable reduction in the emission of smoke and polycyclic aromatic hydrocarbons (PAH) to be expected, and the odor of Diesel exhaust gases likely to be reduced by alcohol fuels as well.

Fuel blends consisting of alcohol and Diesel fuel are not as easy to produce as gasoline-alcohol blends, since alcohols are more polar and refuse to blend well to Diesel fuels. The fact that Diesel fuels contain only a small amount of aromatics is also disadvantageous. This being so, a solubilizer has to be used to ensure a stable mixture, i.e. a solution or a micro-emulsion

Particulates, polycyclic aromatic hydrocarbons (PAH) and aldehydes were measured in a dilution tunnel the sample-taking process being illustrated in Fig. 2.10.

A comparison of the emission of polycyclic aromatic hydrocarbons is shown in Figure 2.11. Blended fuels produce noticeably smaller quantities of these substances than unblended Diesel fuel, the reduction being especially obvious in the emissions of substances which are biologically highly active. Comparing the measurements of B(a)P emissions, shown in Figure 2.12, to unblended Diesel fuel, the methanol-Diesel blend produced 50% less and the ethanol-Diesel blend as much as almost 75% less of these substances[11].

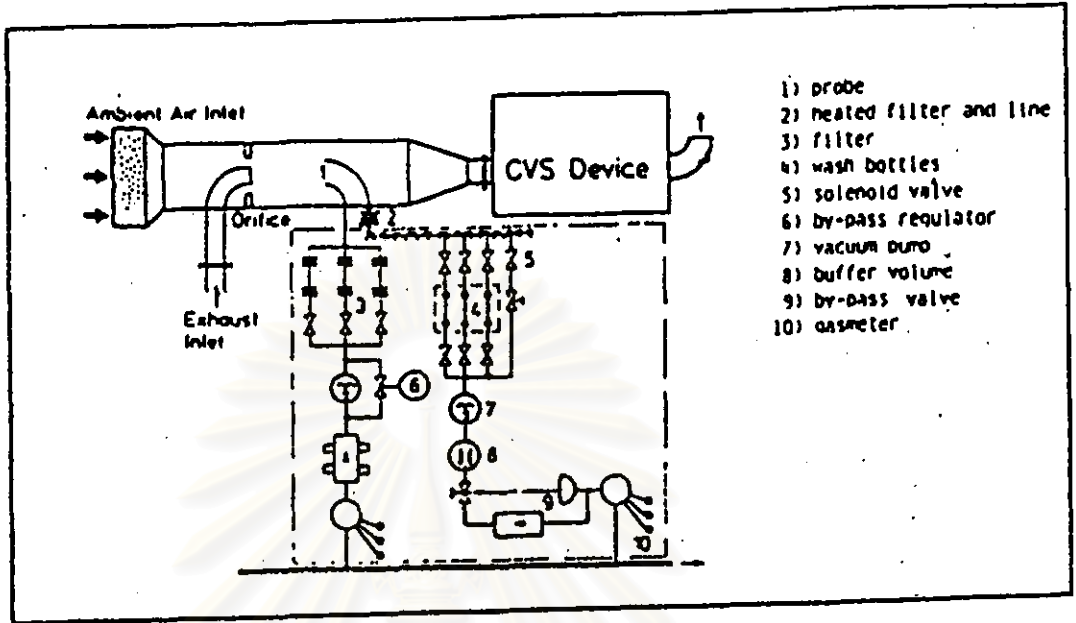


Figure 2.10 Sampling system schematic

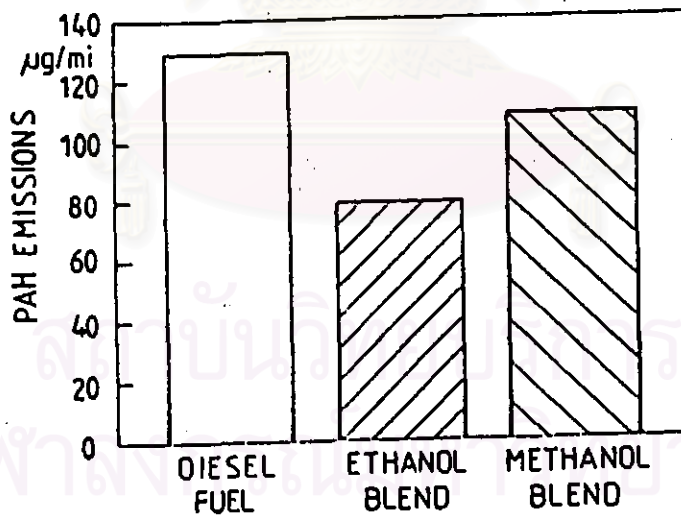


Figure 2.11 Total PAH emission

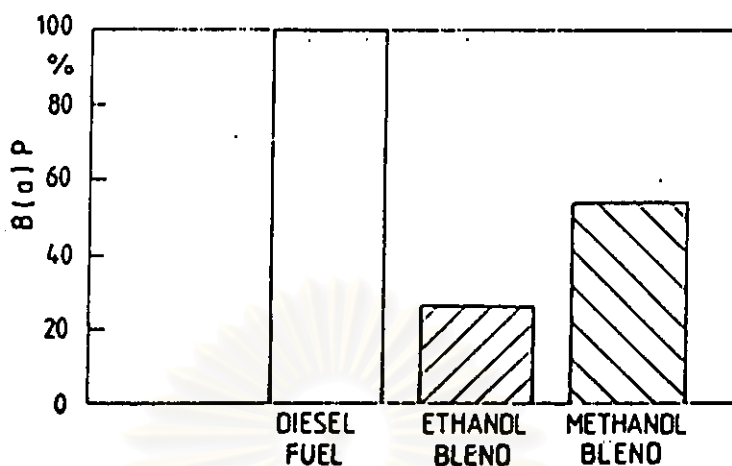


Figure 2.12 B(a)P emissions

In 1986, Williams and co-workers studied the relationship between polycyclic aromatic compounds in diesel fuels and exhaust particulates. The polynuclear aromatic compound fractions (PAC), separated by column chromatography from five diesel fuels, a gas oil and a sample of kerosene, were analysed by capillary column gas chromatography with simultaneous parallel triple detection. The principal polynuclear aromatic hydrocarbons of the fuels were naphthalene, fluorene and phenanthrene and their alkyl derivatives; mutagenic compounds were present in significant concentrations. The principal polynuclear aromatic nitrogen and sulphur compounds of diesel fuel are carbazole and dibenzothiophene and their alkyl derivatives. The PAC of diesel exhaust particulates are similar to those of the fuel, and follow the overall trend of particulate emission engine load. The 2 to 4-ring PAC in the exhaust are primarily unburnt fuel components. Between 0.2 and 1.0 wt% of these fuel PAC survive the combustion process and comprise a significant concentration of mutagenic compounds in the particulate[12].

In 1989, Williams and co-workers studied the role of unburned fuel in diesel particulate emissions. The relationship between diesel fuel composition and that of the solvent organic fraction of diesel particulates was investigated for an old DI Petter engine and a modern DI Perkins engine. Polycyclic aromatic compounds (PAC) were identified using high-resolution capillary column chromatography with a parallel triple detector system for polycyclic aromatic hydrocarbons (PAH), nitrogen-containing PAH, and sulphur-containing PAH. Identification of the PAC using retention indexes was confirmed using an ion trap detector, which was also used to quantify the low concentration (< 1 ppm) benzo[a]pyrene. It was conclusively shown for both engines that the bulk of the particulate solvent organic fraction, including the PAH fraction, was unburned fuel. However, there was some evidence that high molecular weight five-ring PAH may have an in-cylinder formation contribution, and it is postulated that this could be due to pyrolysis of lower molecular weight unburned fuel PAH. The contribution of lubricating oil to the particulate PAC discussed, and evidence is presented that shows the unburned fuel PAC accumulates in the lubricating oil and thus contributes to the particulate PAC via the large lubricating oil component of the particulate PAC[13].

In 1989, Tadashi Murayama reported the effect of fuel properties on diesel engine exhaust particulate formation. Exhaust particulates in diesel engines are affected by fuel properties, especially the aromatic hydrocarbon content and distillation properties, but the reasons for this are not clear. The process of particulate formation has been reported to start with a thermal cracking of the fuel to lower boiling point hydrocarbons followed by condensation polymerization and production of benzene ring compounds ; the formation of particulate takes place via polycyclic aromatic hydrocarbons. The

fuel properties affect diesel engine particulates because the thermal cracking and condensation polymerization of various fuels are different. This report investigated the thermal cracking and condensation polymerization processes of various fuels with different molecular structure and carbon number in a nitrogen atmosphere using a thermal cracking apparatus. The following results were obtained : (1) Paraffin and aromatic fuels display different thermal cracking and condensation polymerization processes. (2) The paraffin fuels are thermally cracked to form lower boiling point hydrocarbons, and the particulate was then formed via the polycyclic aromatic hydrocarbons. However, the benzene rings of the aromatic fuels are not thermally cracked to form polycyclic aromatic hydrocarbons[14].

In the same year, Barbella and co-workers studied the effect of fuel aromaticity on diesel emission. The effect of the fuel aromatic content on soot and heavy hydrocarbon emission from a single-cylinder direct injection diesel engine burning a pure paraffinic fuel (*n*-tetradecane), a tetradecane-toluene mixture (70-30 vol%) and two diesel oils with different aromatic content was investigated. All experiments used various air-fuel ratios with constant engine speed and injection timing advance. The detailed chemical analysis of exhaust heavy hydrocarbons in terms of mass percentage of paraffins, monoaromatics, polyaromatics and polar compounds, and the gas chromatogram-mass spectrum of each hydrocarbon class have been compared with the original fuel analyses in order to discriminate between the unburned fuel compounds and the combustion-formed products. The soot emission rate has been found to be independent of the fuel aromatic content, but the fuel affects the quality and quantity of heavy hydrocarbon emission. Low amounts of heavy hydrocarbons, mainly partially oxidized compounds, are emitted from tetradecane combustion,

whereas diesel fuel oils produced high emissions of heavy hydrocarbons, mainly unburned fuel compounds. This is particularly evident at high air-fuel ratios and can be attributed to the longer ignition delay and lower volatility of the diesel fuel oils with respect to tetradecane. However, higher emissions of heavy hydrocarbons have been found for tetradecane-toluene diesel combustion compared with tetradecane combustion, even though the addition of toluene to tetradecane did not modified the ignition delay of the fuel. Furthermore the addition of toluene reduced only the oxidation of the fuel paraffin, which survived the combustion process, as is shown by the quantitative determination of unburned tetradecane emitted in the two cases. These findings seem to indicate that toluene and, in general, the presence of aromatic compounds in the fuel, inhibit the paraffin oxidation, leading to high emissions of heavy hydrocarbons (PAH). Tetradecane and tetradecane-toluene diesel combustion indicated that these compounds are combustion-formed products, but unburned fuel PAH are the main components of PAH emitted by the diesel fuel oil[15].

Liotta studied the effect of oxygenated fuels on emission from a modern heavy-duty diesel engine. The effects on engine emissions resulting from the addition of oxygenated additives to the fuel, have been investigated using a low emissions, Detroit Diesel Corporation (DDC) Series 60 engine. The oxygenates evaluated were selected on a combined basis of their fuel blending properties and potential costs. Oxygenates of varying molecular structures were selected for evaluation. The test results show that particulate emissions are directly related to the concentration of oxygen in the fuel. The particulate reductions are accompanied by small increases in NO_x emissions. In general, the addition of an oxygenate to the fuel reduces carbon monoxide and hydrocarbon emission.



Non-regulated aldehyde and ketone emission are also reduced with the addition of an oxygenate[2].

Collier and co-workers; studied polycyclic aromatic compound profiles from a light-duty direct-injection diesel engine. The exhaust from a direct-injection light-duty diesel engine was sampled for polycyclic aromatic compounds (PAC) at three constant speeds and at five load setting for each speed, using a total-exhaust solvent-stripping apparatus. Exhaust samples were analysed for 3- and 4- ring polycyclic aromatic hydrocarbon (PAH) and dibenzothiophene by g.c.-m.s. in electron-impact mode. The PAC recoveries (percent of fuel PAC) were highest at low loads and progressively declined with increasing load. At 1000 revmin⁻¹ the averaged recoveries of four (fluorene, dibenzothiophene, phenanthrene and pyrene) decreased from 0.95% at low load to 0.2% at full load, the recoveries of all PAC unchanged, a greater range of PAC recoveries was found at low loads, e.g. the recovery of pyrene at 1% of full load was significantly higher than that of other PAC. At 3000 revmin⁻¹ the combustion efficiencies were greater and average PAC recovery decreased from 0.47% at low load to 0.13% at full load. The range of PAC recoveries at low load was greater at higher speeds . The difference between the percentage recoveries of dibenzothiophene and fluorene on the one hand and their monomethyl derivatives on the other was also most marked at high speed and low loads. The increased range of recoveries at high speed may be due either to pyrosynthetic contributions or to a range of combustion efficiencies of individual PAC structures[16].

Tancell, studied the survival of polycyclic aromatic hydrocarbons during diesel combustion by the application of a radiotracer technique to investigate

the sources of polycyclic aromatic hydrocarbons (PAH) in diesel exhaust emissions. In separate experiments, C-14-radiolabeled naphthalene, 2-methylnaphthalene (2-MeNp), fluorene, pyrene, and benzo[a]pyrene (B[a]P) were each added to diesel fuel, which was combusted in a 2-L direct injection Perkins Prima diesel engine. Exhaust samples were collected using a novel exhaust gas sampling device designed for sampling organic species in automobile exhaust emissions. Survivals for these PAH were 0.87% for fluorene, 0.54% for 2-MeNp, 0.47% for naphthalene, 0.17% for pyrene, and 0.04% for B[a]P. A linear relationship was observed between the extent to which individual PAH survived combustion and the energy level of the lowest unoccupied molecular orbital (LUMO) of the molecule. LUMO energy levels for each molecule were calculated from Huckel molecular orbital theory. The relationship observed in the current experiment suggests that, for these PAH and under steady-state engine conditions, it is the chemical kinetics of reactions occurring in the combustion chamber as opposed to thermodynamic stabilities that determine the extent of PAH survival during diesel combustion. Using this relationship, it should be possible to predict the extent of PAH survival in diesel emissions from a knowledge of the PAH composition of the fuel[17].

Tencell and co-workers studied diesel combustion of an alkylated polycyclic aromatic hydrocarbon. The combustion of the alkylated PAH in a direct-injection diesel engine was investigated using a low-aromatic diesel fuel spiked with 2- and 3-ethylphenanthrene. Exhaust samples were collected using a total exhaust solvent stripping apparatus (TESSA). The 2- and 3-ethylphenanthrene were recovered in yields of 0.3 and 0.35 wt% respectively. The major product from the combustion of ethylphenanthrene was shown to be vinylphenanthrene, produced in a yield of 0.01wt% of the total added

ethylphenanthrene. Although there was no increase in the emission of phenanthrene or other PAH, a statistically significant increase in the emission of 3-methylphenanthrene was observed. These results suggest that for these isomers, under the engine conditions used, no significant dealkylation occurs. The results fit a model based on Dewar reactivity indices, which predicts the extent to which alkyl PAH isomers are dealkylated under pyrolysis conditions[18].

In 1996, Septhum reported the effect of cetane improver on polycyclic aromatic hydrocarbons in diesel exhaust. The effect of cetane improver on the quantity and quantity of polycyclic aromatic hydrocarbons in diesel exhaust was studied by operating the diesel engine coupled with a dynamometer for laboratory tests at different loads and speeds of engine. PAHs in the particulate phase and the semivolatile phase from the diesel exhaust were collected by glass fiber filter and polyurethane foam, respectively. Then they were extracted by soxhlet extraction and analysed by gas chromatograph-mass spectrometer. PAHs found in diesel exhaust were naphthalene, methylnaphthalene, dimethylnaphthalene, acenaphthene, phenanthrene, methylphenanthrene, fluoranthene and pyrene. The result of addition of cetane improvers, 2-ethylhexyl nitrate and di-t-butyl peroxide, could reduce PAHs in diesel exhaust. For the engine load test, it was found that the amount of PAHs in diesel exhaust was lowest at 50% load and highest at 80% load. For the engine speed test, it was found that the amount of PAHs in diesel exhaust at the engine speed of 2500 rpm was slightly higher than at engine speeds of 1500 and 3500 rpm[19].