

## CHAPTER II

### THEORY AND LITERATURE REVIEW

The parent monocyclic species, which contain only carbon and hydrogen, are the familiar PAHs. In addition to the PAHs, there are thousands of substituted PAHs that could have various substitute groups, such as alkyl, amino, chloro, cyano, hydroxy, oxy, or thio groups. Also there is a wide spectrum of PAHs heterocyclic derivatives that contain one or several heteroatoms such as nitrogen, oxygen, or sulfur in the aromatic structure.

The use of different names by various research groups has often led to confusion. Some investigators have referred to PAHs as *polycyclic organic compounds* (POCs), whereas others have preferred the term *polycyclic organic matter* (POM). The term *polynuclear aromatic* (PNA) *compounds* has also been frequently used. At present, no one term has achieved universal acceptance[5].

#### **Significance of PAHs in Air Pollution[3,5]**

It is generally accepted that PAHs are produced from 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 temperature. 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 micro-particles which then agglomerate to form larger particles. In general, the PAHs remain in the gas phase at temperature above 150 °C but rapidly condense onto fly-ash particles below that temperature. At typical ambient temperature, PAHs exist primarily in the particle phase.

### Vapor Pressure and Temperature

The extent to which a particular PAH molecule will exist in the gas phase or in the particle phase is determined by the vapor pressure of the compound and ambient temperature. A first approximation for urban air particulate matter, is that compounds with vapor pressures in excess of  $1 \times 10^{-5}$  kPa should occur predominately in the gas phase, whereas those with vapor pressure below  $1 \times 10^{-9}$  kPa should exist exclusively in the particle phase. For clean air aerosols, the corresponding vapor pressure were  $1 \times 10^{-6}$  and  $1 \times 10^{-10}$  kPa. Any compound with a vapor pressures between these upper and lower limits would be expected to occur in both the vapor and particulate phase.

### Particle Size Distribution

Many studies have shown that the PAHs are associated primarily with particles less than 3  $\mu\text{m}$  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 associate with particles between 0.075 and 0.26  $\mu\text{m}$  and 30% was associated with particles between 0.26 and 2.0  $\mu\text{m}$

Submicron particles, in the absence of wet deposition, have atmospheric residence lifetimes of between 100 and 1000 h, whereas particles, in the 1-10  $\mu\text{m}$  size range should have an atmospheric lifetime 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 PAH may travel great distances before being removed from the atmosphere.

Table 2.1. Half-Life of PAHs (in hours) under Simulated Sunlight

PAH	Simulated Sunlight
Anthracene	0.20
Benz[a]anthracene	4.20
Dibenz[a,h]anthracene	9.60
Dibenz[a,c]anthracene	9.20
Pyrene	4.20
Benzo[a]pyrene	5.30
Benzo[e]pyrene	21.10
Benzo[b]fluoranthene	8.70
Benzo[k]fluoranthene	14.10

The nature of photodecomposition suggested that, where PAH existed on particles in a multilayered deposition, the surface layer which was exposed to the atmosphere would react very rapidly, exhibiting the reaction rate in Table 2.1, while the subsurface PAHs would remain essentially protected from oxidation reaction.

## **Diesel Fuel and Diesel Engine[4,6,7]**

Diesel -type engines are well known for being highly durable and fuel efficient. Because of this durability and fuel efficiency, diesel-type engines have long been used in heavy-duty vehicles, such as trucks, buses and locomotives.

Diesel fuel can be made from any number of components that are produced in an oil refinery. The American Society for Testing and Materials (ASTM) has set specifications for diesel fuels. Some states, including California, have adopted those specifications as legal requirements.

Diesel engines rely on compression for ignition of the fuel. The source of ignition energy is the high temperature, high pressure air present in the combustion chamber towards the end of the compression stroke. To achieve these high temperatures and pressures, diesel engines typically have far higher compression ratios than do gasoline engines.

Upon injection into the combustion chamber, fuel must quickly mix with air to form a flammable mixture and the mixture must ignite. Since there is normally no additional means for ignition ( such as the spark plug in gasoline engine ), the fuel must self-ignite, a process called "autoignition". This process takes time and is influenced greatly by the engine combustion system and by fuel properties.

Diesel engines use the heat developed by compressing a charge of air to ignite the fuel injected into the engine cylinder after the air is compressed. More specifically, in the engine, the air is first compressed, the fuel is injected in to the cylinder; as fuel contacts the heated air, it vaporizes and finally begins to burn as the self-ignition temperature is reached. Additional fuel is injected during the compression stroke and this fuel burns almost instantaneously, once the initial flame has been established.



A period of time elapses between the beginning of fuel injection and the appearance of a flame in the cylinder. This period is commonly called “ignition delay” and is a major factor in regard to the performance of a diesel fuel. If ignition delay is too long, the fuel will accumulate in the cylinder until it reached ignition conditions and then will burn rapidly, causing a sudden pressure increase which may result in engine knocking. Too long an ignition delay may result in a smoky exhaust, a decrease in engine efficiency, and possibly dilution of the crank case oil. A reduction in ignition delay can be obtained by varying the chemical nature of the injected fuel. Straight-chain paraffinic hydrocarbon give the least ignition delay, while branched-chain paraffins and cyclic (including aromatic) hydrocarbons tend to have poorer ignition characteristics. Aromatic hydrocarbons are relatively compact and unreactive molecules compared to the other prime constituents of diesel fuel.

### Cetane Number

n-hexadecane (“cetane”) has long been used as a standard reference material for determining the ignition quality of commercial diesel fuels. A scale called “cetane number” has been devised for ranking the relative ignition delay characteristics of a given diesel fuel. The cetane number of an unknown fuel is determined by comparing its ignition delay in a standard test engine with reference fuels which are prepared by blending cetane (assigned a rating of 100) and 2,2,4,4,6,8,8-heptamethylnonane (assigned a rating 15) until a reference fuel is found to have the same ignition delay characteristics as the unknown fuel, the cetane number is obtained by the equation:

$$\text{EQU Cetane No} = (\text{Vol \% Cetane}) + [15 (\text{Vol \% Heptamethylnonane})]$$

In general, large stationary engines which run at fairly constant speeds and loads have the lowest cetane number requirements (e.g. 30 to 45), while smaller motor vehicle diesel engines have the highest requirements (e.g. 40 to 55) for obtaining optimum performance.

One of the more important difficulties that arises through the use of diesel engines is the problem of starting the engine when it is cold. Fuels with high cetane numbers have the advantage of giving relatively easy starting at low temperatures. Additionally, fuels with high cetane numbers reduce destructive combustion knock, provide more efficient combustion and smooth engine operation, lower maximum cylinder pressures, and reduce carbon deposits on cylinder heads.

### **Volatility**

The distillation characteristics of the fuel describe its volatility. A properly designed fuel has the optimum proportion of low-boiling components for easy cold starting and fast warm-up and heavier components, which provide power and fuel economy when the engine reaches the operating temperature. Either too high or too low volatility may promote smoking, carbon deposits, and oil dilution due to the effect on fuel injection and vaporization in the combustion chamber. The 10, 50, and 90 percent points and the final boiling point are the principal volatility control. Diesel engine in automotive, agricultural, and construction service use fuel with a final boiling point approaching 371 °C (700 °F). Urban use generally use a fuel with a lower boiling point to minimize exhaust smoke and odor. Detroit Diesel specifies a 228 °C (550 °F) maximum end point for its engines in city bus service.

## Viscosity

The viscosity of the fuel affects atomization and fuel delivery rate. The viscosity of diesel fuel is normally specified at 38°C (100 °F ). Fuels for medium-speed and high-speed engines generally lie in the range from 1.4 to 4.3 centistokes viscosity at 38°C (100 °F ). The lubricating properties of some low-viscosity, low pour winter fuels can be improved by the addition of 1 percent crankcase oils or lubricity additives. This is important where injection pump and injectors depend on fuel oil for lubrication and the fuel oil viscosity is below 1.3 centistokes at 38°C (100 °F ).

Fuels with viscosities over 6 centistokes at 38°C (100 °F ) are limited to use in slow-speed engines and may require preheating for injection.

## Pour Points and Cloud Points

Before the pour point of a fuel is attained, the fuel will become cloudy due to the formation of wax crystals. This usually occurs some 5°C to 8°C (10 °F to 15 °F ) above the pour point and is referred to as the cloud point. Wax crystals may begin to plug fuel filters when the fuel temperature drops to the cloud point. How critical this is in winter operation depends on the design of the fuel system with regard to fuel line bore, freedom from bends, size and location of filters, and degree of warm fuel recirculation as well as the amount and kind of wax crystals.

Additives known as *flow improvers* are being used successfully to improve the fuel fluidity at low temperatures. Flow improvers modify wax crystal growth so that the wax, which forms at low temperature, will pass through the fine (typically 10 to 20 microns) fuel filter screens. The addition of

typically 0.1 percent flow improver can result in satisfactory fuel flow at  $-9^{\circ}\text{C}$  ( $15^{\circ}\text{F}$ ) colder temperatures than possible with either untreated fuel.

### **Heat Value**

The heat value of fuel is a general indication of how much power the fuel will provide when burned. This is obtained by burning the oil in a special device known as a calorimeter. With such equipment, a measured quantity of fuel is burned and the amount of heat carefully measured in BTUs per pound of fuel.

### **Flash Point**

The flash point is determined by heating the fuel in a small enclosed chamber and allowing the vapors to ignite when a small flame is passed over the surface of the liquid. The temperature of the fuel at this point is the flash point. The flash point of a diesel fuel has no relation to its performance in an engine nor to its autoignition qualities. It does provide a useful check on suspected contaminants such as gasoline present that can lower the flash point of the fuel very markedly.

Shipping, storage, and handling regulations are based on minimum flash point categories.

### **Sulphur Content**

Sulphur in diesel fuel can cause combustion chamber deposits, exhaust system corrosion, and wear on pistons, rings and cylinders, particularly at low

water-jacket temperatures. Sulphur tolerance by an engine is dependent on the type of engine and the type of service.

A fuel sulphur content above 0.4 percent is generally considered as medium or high whereas fuel sulphur content below 0.4 percent is considered low. Summer grades of commercially available diesel fuel are commonly in the 0.2 to 0.5 percent sulphur range. Winter grades often have less than 0.2 percent sulphur. Some slow- or medium-speed engines in stationary service are designed to operate on heavy fuels, which have sulphur contents up to 1.25 percent or even higher.

Diesel-engine crankcase oils are formulated to combat various level of fuel sulphur content. It is important to use the manufacturers, recommended crankcase oil quality and oil change intervals, which often relate to the sulphur level of the fuel as well as to other service conditions.

Most diesel fuels are low in sulphur content; by using the manufacturers, recommended crankcase oil quality, and oil change intervals, there should be no concern with the effects of fuel sulphur.

### **Mass Spectrometry of PAHs[5,9]**

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 PAHs.

### Electron-Impact Ionization.[5]

The electron-impact mass spectra of PAHs are usually quite simple. Because of the extensive electron delocalization, molecular ions in these spectra are very 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.

In general, in the mass spectra of all PAHs, the molecular ion is always 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 2.1. The mass spectra of the five different methyl phenanthrene isomers and of the three different 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  $m/z$  165. The other ion of significant intensity in the mass spectrum is the doubly charged molecular ion at  $m/z$  96.

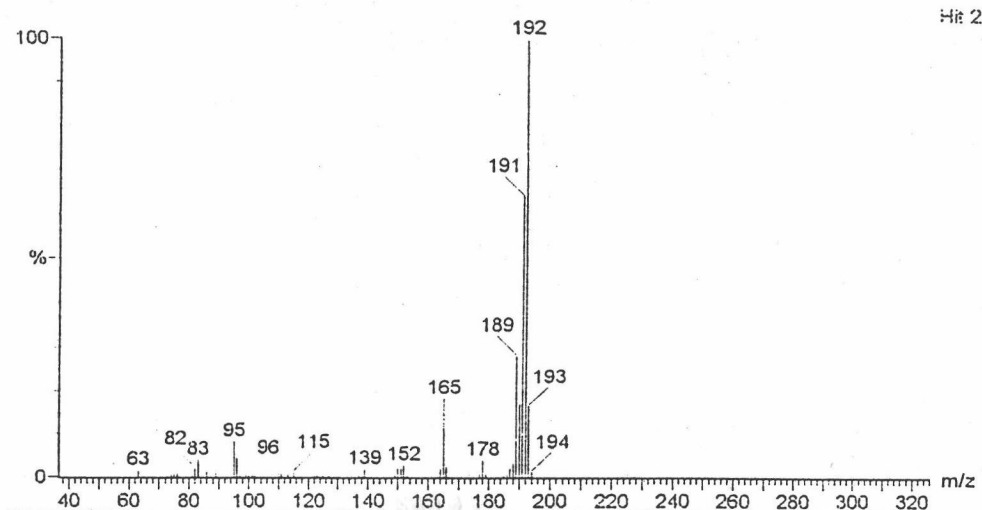


Figure 2.1 Mass Spectrum of 1-Methylphenanthrene

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; (see structure I in Figure 2.2) 9-Methylphenanthrene would give a fused-ring tropylium ion in which the seven-membered ring is in the middle; see structure II in Figure 2.2. A similar argument holds for 1- and 2-methylanthracene, which would give a tropylium ion of type II, 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 between the structures of the four tropylium ions (I-IV) given in Figure 2.2 by electron-impact MS. It remains to be seen whether MS/MS techniques can make this distinction.

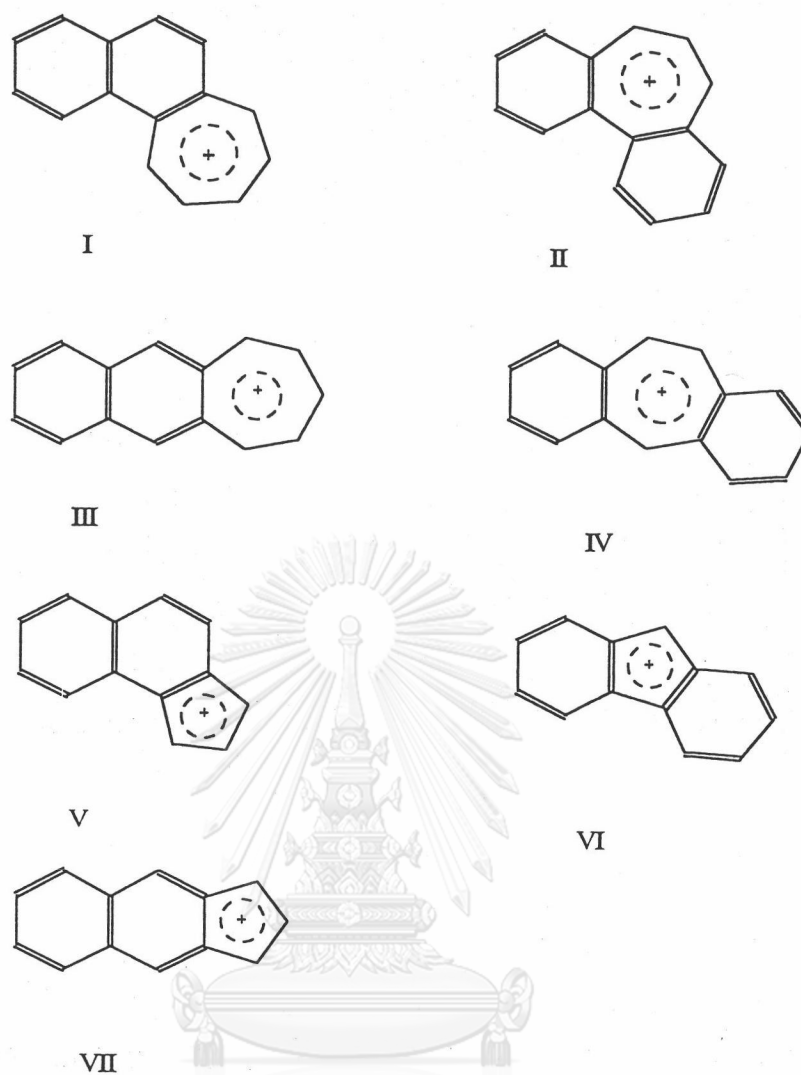


Figure 2.2 Possible Structures of the  $m/z$  191(I to IV) and  $m/z$  165 (V to VII) Ions in the Electron Impact Spectra of Phenanthrene and Anthracene-related Compounds

The ion at  $m/z$  165 occurs in most of the spectra of anthracene- and phenanthrene-based compounds. This ion presumably has one of the three structures given in Figure 2.2 (see structures V-VII). The exact structure of this ion depends on which of the four fused-ring tropylium ions it came from, although a rearrangement into the most stable form is possible. If this



rearrangement take place, it is quite likely that the structure of  $m/z$  165 is a fluorene ion (see structure VI in Figure 2.2).

### Literature Review

In recent years, diesel fuel composition, particularly the aromatic and sulphur contents, has received considerable attention from legislative authorities and the research community. One question of major importance continues to be: what is the effect of the fuel aromatic content on exhaust emission? Numerous investigators have addressed this problem in the past, but rarely with clear-cut conclusions.

A change in the aromatic content of a diesel fuel can affect the exhaust emissions in complex manner. The reason for this is that the aromatics content affects a number of physical and chemical properties of the fuel which have significant influence on the combustion process. Such fuel properties include the chemical structure, cetane number, density, viscosity and boiling range. With regard to the chemical structure of the fuel, it has been shown that, at least in continuous diffusion flames, the molecular structure of pure hydrocarbon compounds, particularly the hydrogen/carbon ratio, plays a significant role in soot formation[4].

One major problem that has faced investigators over the years is rooted in the fact that the aromatic content effects so many aspects of engine operation. For example, in addition to the effects on the combustion chemistry, the timing of the combustion process relative to the piston motion and the air-fuel mixing process are effected. In particular, the balance between the amounts of fuel burnt in the premixed and diffusion modes is altered.

Motor vehicles account for the majority of PAH emissions in urban area. In general exhaust emissions of PAH from mobile sources originate by

three distinct mechanisms; (I) synthesis from simple molecules in the fuel, particularly from aromatic compounds, (ii) storage in engine deposits and subsequent emission of PAH already in the fuel and (iii) pyrolysis of lubricant. The emission rate of PAH from vehicle exhaust are dependent upon a large number of factors including; engine type, operating conditions and composition of both fuel and lubricating oil[1].

The effect of engine type is largely determined by the design of the combustion system, the fuel/air mixture, the temperature within the combustion chamber and the manufacturing quality. It has been established that different vehicles operated under the same conditions with the same fuel can emit significantly different amounts of PAH[3].

The main engine operating parameters that affect exhaust PAH content are engine load, air to fuel ratio and engine coolant temperature. The latter was found that only slightly influence PAH emissions, indicating that wall temperature of the combustion chamber *per se* is not the main cause of the high PAH emission from cold-started engines[3].

#### **Low Emission Diesel Fuel[6]**

The aromatic hydrocarbon content of fuel has been the main focus of concern directed at the composition of fuels, since benzene and its derivatives, such as ethyl benzene and xylene were better precursors for PAH formation than benzene itself.

Through the years, many types of additives have been prepared to raise the cetane number of diesel fuels. Such additives usually contain nitrogen or sulfur, both of which are known cetane improvers under certain circumstances. The most popular additives, for example, appear to be hexyl or octyl nitrate. However, these additives are highly combustible, as are most of the organic nitrogen- or sulfur- containing additives commonly used. Further, the nitrogen-

containing compounds can add to an engine's  $\text{NO}_x$  emission, which contribute to photochemical reactions known to cause smog formation, as well as formation of nitric acid, a factor in acid rain. The sulfur-containing compounds contribute to  $\text{SO}_x$  formation which can contaminate the lube oil by forming sulfuric acid which breaks down various antiwear additives found in the oil. Also,  $\text{SO}_x$  emissions contribute to the formation of particulate matter in the form of sulfates which must be emitted from jet exhaust.

The potential for process options are certain distillate processes, which employ methanol as a feedstock, and several hydroprocessing options which use hydrogen and a catalyst to reduce the aromatic hydrocarbon content.

Higher concentration of fuel aromatics, beyond their effect on cetane number, also appear to cause small increases in particulate and oxide of nitrogen emission. In general, aromatic hydrocarbons have a higher flame temperature relative to the other prominent components of diesel fuel.

This higher temperature may, by itself, lead to higher oxide of nitrogen formation.

The state of California has defined a diesel fuel containing an extremely low level of aromatic compounds for adoption by fuel suppliers for sale in the State, hereinafter referred to as "California LAD". While California LAD may have advantages in the form of lower exhaust emissions relative to diesel fuel produced and sold today, the production cost impact upon refiners who must adopt processes to produce California LAD is enormous.

The proposed California regulation requires a minimum of 10% aromatics content in vehicular diesel fuel starting on Oct. 1, 1993. Compliance with the low aromatic rule could require major investments in California refineries. Refiners have the potentially less costly option of producing a higher aromatic diesel fuel if they can demonstrate equivalent emissions relative to a 10% aromatic reference fuel.

Lowering the aromatics content of fuel from the current levels of well over 30% to those below 10% requires major capital investment and operating cost for severe hydrotreating processes in most California refineries. This is a severe financial burden during a period in which very large capital funds are needed to make the many changes required for producing reformulated gasoline and for complying with a range of other environmental regulations. The California Air Resources Board has allowed fuel producers the option of producing a less costly alternative fuel with a higher aromatics content, if equivalent emissions can be demonstrated.

Conventional diesel fuels are distillates with a boiling range of about 149 °C to 371 °C ( +300 °F to +700 °F), obtained by the distillation of crude oil. They are predominately straight-run fractions that contain the greatest amount of normal paraffins and naphthenes, and the least amount of isoparaffins and aromatics. Normal paraffins and naphthenes have superior diesel ignition qualities, but they have the disadvantages of higher pour points than isoparaffins and aromatics.

### **Sampling System[9,10,11,12,13]**

There are two major sampling systems for determination of PAHs in exhaust emission, the dilution tunnel and the total exhaust solvent stripping apparatus (TESSA).

Exhaust particulate emissions were collected while a production car equipped with a 5.7 L diesel engine was driven on an electric chassis dynamometer. The entire exhaust was transferred via a 1.5-m-long stainless steel tailpipe extension to a 0.3-m-diameter dilution tunnel, where it was mixed with prefiltered air. The tunnel is assembled in sections joined with O-ring seals and is fabricated of

clear polyacrylate, except for the short entrance and transition sections. An annular ring in the entrance section of the tunnel, coincident with the discharge end of the tailpipe extension, creates additional turbulence that promotes mixing of the exhaust gas and dilution air. The total flow rate in the tunnel is controllable over the range 19 to 34 m<sup>3</sup>/min by means of a variable sheave pulley on the fan drive. In the experiments described here, the flow rate was 19 m<sup>3</sup>/min.

During a test, two filter samples were collected simultaneously at the sampling section. The probes for the filter assemblies were 3.0 cm-I.D. stainless steel, sized for isokinetic sampling at a 0.170 m<sup>3</sup>/min sampling rate and 19 m<sup>3</sup>/min flow in the dilution tunnel. Because the sampling rate was varied in some experiments, the sampling was not always isokinetic, but departures from isokinetic flow are assumed to be inconsequential in view of the submicrometer size of the diesel particulates. The filters were 102 mm-diameter Dexiglas glass-fiber filters which are efficient for collecting particles of all sizes (efficiency  $\geq 99.7\%$  at 0.3  $\mu\text{m}$ ), free from extractable material and stable for thermal analysis. They must be stored at constant temperature and humidity to ensure constant weight.

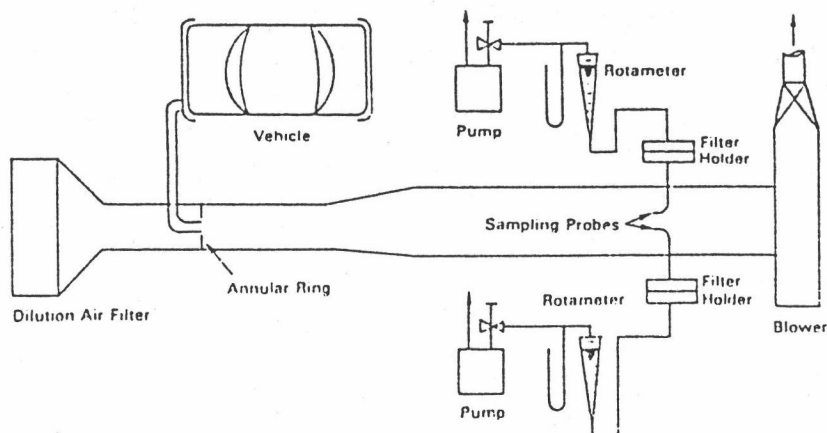


Figure 2.3 Schematic of the Particulate Sampling System

The TESSA system consists of a vertical stainless steel tower (~1.5x0.3 m) connected by a short (50 cm) heated transfer line to the engine. The tower comprises two sections. Collection of the exhaust organics occurs in the lower section, which is filled with graded glass tubing to maximize the area of contact between solvent and exhaust gases. The upper section is used to cool the exhaust effluent and contains a series of cooling baffles. The exhaust is sampled using a pressure-controlled countercurrent flow of solvent (dichloromethane-methanol 1:1) which strips the organic species from the exhaust gases as they enter the apparatus. The exhaust sample is collected in large flask at the base of the tower.

### Formation and Emission of PAHs in Diesel Exhaust

At the Volkswagen research test facility, the fuel blends were tested 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 (PAHs) to be expected, and the odor of diesel exhaust gases likely to be reduced by alcohol fuels as well. Particulates, PAHs and aldehydes were measured in a dilution tunnel, the sample taking process being illustrated in figure 2.4.

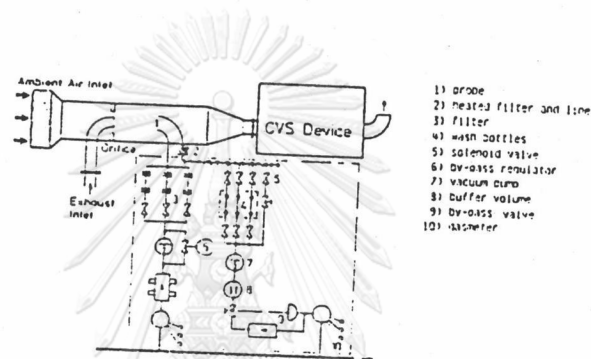


Figure 2.4 Sampling System Schematic

A comparison of the emission of PAHs show (Figure 2.5) shows that 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 shows that, compared 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. However alcohol-diesel fuel blends will emit more aldehydes because of the oxygenates in the blend[10].



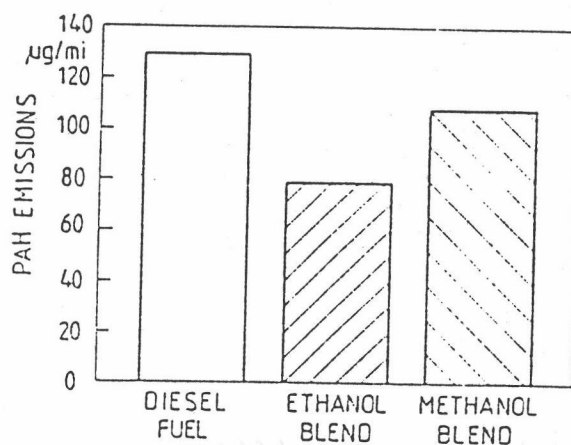


Figure 2.5 Total PAH Emissions

In 1984, Obuchi, *et al* reported techniques for the determination of PAHs in the dichloromethane extracts of diesel exhaust particulate matter and diesel fuel oils, using a reversed-phase preparation column (Sep-Pak C<sub>18</sub>).

In their study, PAHs extracted into dichloromethane, together with aliphatic hydrocarbons were successfully determined by reversed-phase HPLC. This was by conducting a series of clean-up procedures, during which the solvent was changed from dichloromethane to acetonitrile and insoluble matter and aliphatic hydrocarbons were eliminated by using a preparation column, in order not to effect the performance of the HPLC column. The recoveries of PAHs were more than 97% and the detection limit of benzo(a)pyrene was 0.15 ppb in dichloromethane or 1 ng in 30 mg of particulate matter[14].

In 1991, Westerholm, *et al* studied three different sampling techniques, i.e; cryocondensation and two adsorbents XAD-2 for collection of the semivolatile phase together with a particulate filter situated upstream. The cryogenic technique was the least efficient type and the PUF technique gave the



highest recovery of polycyclic aromatic hydrocarbons (PAHs) and mutagenic activity. The amount of PAHs, mainly three-ringed PAHs, emitted in the semivolatile phase was approximately 3 times higher than that emitted in the particulate phase. Emissions of PAHs in the particulate phase are presented in Table 2.2[15].

Table 2.2 Emission of Particulate-Associated PAHs ( $\mu\text{g}/\text{km}$ )<sup>a</sup>

PAHs	mv	SD
2-methylfluorene	<0.04	
phenanthrene	29	48
anthracene	3.3	13
3-methylphenanthrene	30	27
2-methylanthracene	40	24
4-+9-methylphenanthrene	48	21
1-methylphenanthrene	41	20
fluorene	17	11
pyrene	11	14
benzo[a]fluorene	2.4	32
2-methylpyrene	2.0	19
1-methylpyrene	0.75	35
benzo[ghi]fluoranthene	1.5	19
cyclopenta[cd]pyrene	0.18	30
benz[a]anthracene	0.47	54
chrysene/triphenylene	2.8	18
benzo[b and k]fluoranthene	0.29	31
benzo[e]pyrene	0.15	28
benzo[a]pyrene	<0.06	
perylene	<0.01	
indeno[1,2,3-cd]fluoranthene	<0.09	
indeno[1,2,3-cd]pyrene	<0.04	
picene	0.01	
benzo[ghi]perylene	<0.13	
coronene	<0.01	
SUM of PAH(25)	<230	22

<sup>a</sup> n = 6, mean value (mv) +/- standard deviation (SD) (%)

In 1993, Williams and Taylor studied the aromatization of tyre pyrolysis oil to yield polycyclic aromatic hydrocarbons. Shredded scrap automotive tyres were pyrolysed in a static batch reactor in a stream of nitrogen. The products were passed directly to a second heated reactor, where secondary reactions of the pyrolysis vapours occurred. The condensed tyre pyrolysis oil, after secondary reaction, was analyzed for the content of PAHs. The concentration of PAHs were found to increase with increasing secondary reactions involving the aromatization of olefinic compounds.

Diels-Alder mechanisms were proposed in. When the tyre oils were subjected to secondary cracking reactions in a post-pyrolysis reactor heated to higher temperatures the concentration of individual PAH and total PAHs increased as the temperature was increased[16].

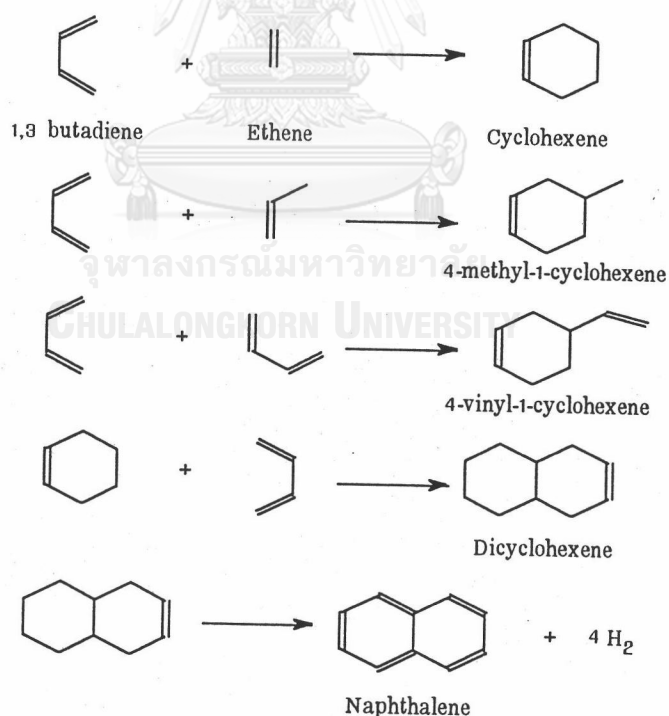


Figure 2.6 Formation of PAH in Pyrolysis Tyre Oil

In 1994, Westerholm and Li applied a multivariable statistical approach to fuel-related PAHs emission from heavy-duty diesel vehicles by using principal component analysis (PCA). It was used to investigate the relationship between fuel parameters and PAHs content. Linear regression analysis, and partial least-squares regression to latent structures (PLS) were used to study the correlation of PAH in fuels and PAHs in exhaust emissions. A linear relationship was determined between fuel PAHs input and emissions of PAHs. In the combustion process, more than 99% of fuel-related PAHs are decomposed. In the exhaust emission, the ratio of uncombusted fuel related to the sum of PAHs varies from about 1% to 80% depending on the fuel. PAHs are also formed in the combustion process. By the selection of diesel qualities with low PAHs content ( $< 4\text{mg/L}$  sum of PAHs), the PAH exhaust emission can be reduced by up to approximately 80% as compared to diesel fuel with PAHs contents larger than  $1\text{g/L}$  (sum of PAHs). By reducing fuels PAHs contents in commercially available diesel fuel, the emission of PAHs to the environment will be reduced[14].

In 1995, Tancell, *et al* studied the survival of PAHs during diesel combustion by the application of a radiotracer technique to investigate the source of PAHs in diesel exhaust emissions. Survivals of these PAHs 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. The relationship observed in the current experiment suggests that for these PAHs 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 survival of exhaust PAHs during diesel combustion. Using this relationship, it should be possible to predict the extent of PAHs survival in diesel emissions from a knowledge of the PAHs composition of the fuel[19].

In 1995, Collier, *et al* studied polycyclic compound profiles from a light-duty direct-injection diesel engine. The exhaust from the engine was sampled for PAHs at three constant speeds and five load settings for each speed, using a total-exhaust solvent-stripping apparatus. Exhaust samples were analysed for 3-and 4-ring PAHs and dibenzothiophene by GC-MS in electron-impact mode. The PAHs recoveries (percent of fuel PAHs) were highest at low loads and progressively declined with increasing load as shown in Figure 2.7.

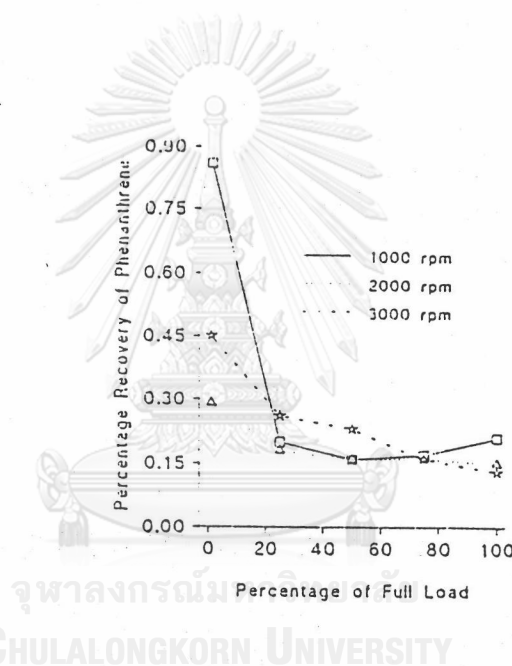


Figure 2.7 Effect of Engine Speed and Load on Percentage Recovery of Phenanthrene

The recovery of all PAHs converged at high load, indicating survival of fuel PAHs unchanged. A greater range of PAHs recoveries was found at low load. The increased range of recoveries at high speed may be due either to pyrosynthetic contributions or to a range of combustion efficiencies of individual PAHs structures[12].

In 1995, Nikanjam, *et al* studied a low emission diesel fuel with prescribed levels of aromatics and cetane number which, resulted in lower emissions than the California Reference diesel fuel[6].

In 1996, Sjogren, *et al* studied particulate and gaseous exhaust emission phases from running 10 diesel fuels. Principle components analysis (PAC) was applied for the statistical exploration of the obtained data. In addition relationships between chemical and physical parameters of fuels to the exhaust emissions were derived using partial least squares (PLS) regression. The PAC clearly indicates that emission of PAHs, particulates, and sulfates are the most descriptive exhaust emission factors. These exhaust emissions can, as shown from the PLS analysis, be much reduced by a decrease of aromatics, PAHs and sulfur in the fuels[17].