CHAPTER III

EXPERIMENTAL

3.1 Instruments and Apparatus

1. Soxhlet Extraction Apparatus

2. Rotary Evaporator

   Buchi ROTAVAPOR-R with the water aspirator, EYELA
ASPIRATOR A-3S, Tokyo Rikakikai Co.,Ltd.

3. High vacuum Pump

   Gast model 0523-V103-G21DX

4. Timing Light

   Techno Test® model 136

5. Gas Chromatography - Mass Spectrometer

   Gas Chromatography model GC 8000 Series, and Mass
Spectrometer model MD 800 with Autosampler model AS 800,
Fisons Instruments

3.2 Chemicals and Materials

1. Cyclohexane

   Reagent grade ; Lab Scan

2. Standard Polycyclic Aromatic Hydrocarbons

   Polynuclear Aromatic Hydrocarbons Mixture for EPA 610 ;
Sigma-Aldrich. This mixture consists of naphthalene (1,000 μg/ml),
acenaphthylene (2,000 μg/ml), acenaphthene (1,000 μg/ml), fluorene

(200 µg/ml), phenanthrene (100 µg/ml), anthracene (100µg/ml), fluoranthene (200 µg/ml), pyrene (100 µg/ml), chrysene (100 µg/ml), benz(a)anthracene (100 µg/ml), benzo(b)fluoranthene (100 µg/ml), benzo(k)fluoranthene (100 µg/ml), benzo(a)pyrene (100 µg/ml), indeno(1,2,3-cd)pyrene (100 µg/ml), dibenz(a,h)anthracene (200 µg/ml), and benzo(ghi)perylene (200 µg/ml)

3. Dispersant Additive for Gasoline

    LZ 8195; Lubrizol

4. Glass-Microfibre Filters

    Whatman model GF/F, 90 mm diameter

5. Polyurethane Foams

    0.22 g/cm^3 density

3.3 Test Engine

The specifications of the test engine, which was inspected and maintenanced before testing, are shown in Table 3.1.

Table 3.1 Test Engine Specification

Model	Toyota Corolla (5K) 1982
Number of cylinders	4
Displacement volume (cm^3)	1,500
Fuel system	Carburetor
Emission system	Exhaust Gas Recirculation
Mileage (km)	35,664

Prior to testing, an oil filter and engine lubricant oil were changed. PTT VSH Performa lubricating oil was used throughout the study.

The test engine was run for 50 hours with the new lubricating oil before sampling commenced.

3.4 Test Fuels

The test fuels used in this study were unleaded gasoline base fuel (ULG 98), delivered from the Petroleum Authority of Thailand (PTT),and blended unleaded gasoline base fuels with a dispersant additive. The dispersant was commercially Lubrizol LZ8195 package at treat rates of 5 dosages, 300, 400, 500, 600, and 700 ppm (v/v). The test fuels were summarized in Table 3.2.

3.5 Exhaust Sampling System

Exhaust particulates and semivolatile exhaust samples from the test engine were taken from an exhaust pipe at known flow rate using a high volume vacuum pump, via a 5/8-in i.d. stainless-steel probe inserted into the exhaust pipe 10 cm from the exhaust manifold. The exhaust was passed to the cooling system and then to the sampling device which is 3-in i.d., 6-in long, stainless-steel filter holder with 5/8-in i.d., stainless-steel probe. Schematic of the exhaust sampling system is illustrated in Figure 3.1.
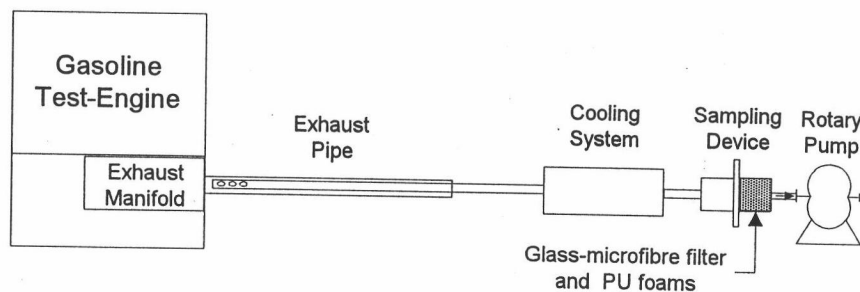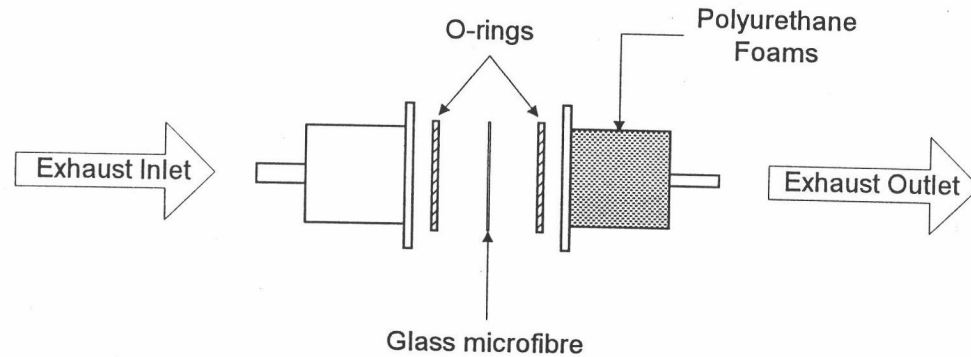

Figure 3.1 Schematic of Exhaust Sampling System

In the sampling device, a glass-microfibre filter and polyurethane foams were packed, as shown in Figure 3.2, for trapping the particulates and semi-volatile gases in the exhaust, respectively.

Figure 3.2 Schematic Sampling Device for Particulates and Semivolatile Gases Collecting

3.6 Exhaust Emission Test Procedure

3.6.1 Sample Collection

The sampling was undertaken with constant speed and no load. Five series of samples were collected at 1,000, 1,500, 2,000, 2,500, and 3,000 rpm, for each fuel.

The test engine was warmed up for 45 minutes at the start of each test and held for 10 minutes at each different engine condition to establish equilibrium before sampling. For each conditioned engine setting, a sample was collected by the sampling system as describes in Figure 3.1 for 15 minutes. The pressure of the high vacuum pump was recorded every 5 minutes for determining an exhaust flow rate. The exhaust was cooled by mean of water to ensure that semivolatile compounds were trapped on

polyurethane foams. After sampling, glass-microfibre filters and polyurethane foams were kept dark and refrigerated until the further processing.

3.6.2 Sample Extraction and Concentration

The glass-microfibre filters and polyurethane foams exposed to the exhaust were Soxhlet extracted for 12 hours with 300 ml cyclohexane and the extracts were evaporated on a rotary evaporator, at reduced pressure and at 65°C, to 5 ml. Aliquots of cyclohexane extract were refrigerated until the chromatographic analysis commenced.

3.6.3 Analysis

Gas Chromatography - Mass Spectrometry technique was employed to analyze the samples. The individual PAHs samples were seperated on DB-1HT capillary column with conditions shown in Table 3.3.

The identification of PAHs in samples derived from exhaust emissions of the test engine was performed by comparing their retention times with those of polynuclear aromatic hydrocarbons mixture of EPA 610. Also, Selected Ion Monitoring (SIM) and computerized library searching of mass chromatograms based on the Nation Bureau of Standard Library (NIST) were employed to support the identification of PAHs.

Quantitative estimations were carried out by comparing the integrated peak area of molecular ion of samples to the corresponding standard calibration curve. The results were calculated and reported in micrograms per cubic meter of exhaust sample.

Blank samples were analyzed for the quantity of contaminants from materials and equipments used in the sample collection and analysis. Each experiment was performed for 3 times.

Table 3.3 GC-MS Conditions for PAHs Analysis

GC column	DB-1HT capillary column 30 m × 0.25 mm i.d. (0.1 μm film thickness)
Carrier gas	Helium, 99.999% purity, with flow rate of 0.8 ml/min
Injector port temperature	250°C
Injector system	Splitless
Injection volume	1 μl
GC temperature program	60°C for 1 min
	increase 20°C/min to 150°C, isothermal for 3 min
	increase 8°C/min to 200°C, isothermal for 3 min
	increase 8°C/min to 310°C, isothermal for 8 min
GC-MS interface temperature	300°C
MS mode	EI$^+$ with the ionization voltage of 70 eV
MS source temperature	200°C
MS analyzer	Quadrupole
Scan range	30-320 amu at the rate of 320 amu/sec
Scan time	1 sec
Solvent delay	3.75 min

3.7 Standard and Calibration Curve Preparation

Polynuclear aromatic hydrocarbon mixture for EPA 610 was used as the standard for establishing the calibration curve. The external standard technique was employed for quantitation. The procedure is described as follows :

---

1. The standards were prepared by diluting a stock dilution of the polynuclear aromatic hydrocarbon mixture for EPA 610 or the more concentrated one with cyclohexane. The minimum of three concentrations of standard solutions were prepared. One of the external standards should have the concentration near, but above, the minimal detection limit (MDL) of the detector and the others should correspond to the expected concentration ranges of samples or should define the working of the detector. All standard solutions were kept in the refrigerator at -4°C until the analysis performed.

2. The standards were analyzed by GC-MS with the same condition employed for samples. Retention time and response peak areas of each component were recorded and the standard calibration curves were established by plotting the response peak area against the concentration of standard PAHs. All the calibration curves and their linear equations are shown in Appendix A.

The linear equations of the standard calibrations are listed below:

Standard substances	*Linear equations*	
Naphthalene	$A = (3.17 \times 10^5 \times C) - 5.86 \times 10^4$	(1)
Acenaphthylene	$A = (5.74 \times 10^5 \times C) - 1.23 \times 10^5$	(2)
Fluorene	$A = (7.05 \times 10^5 \times C) - 1.52 \times 10^5$	(3)
Phenanthrene	$A = (5.74 \times 10^5 \times C) - 1.31 \times 10^5$	(4)
Anthracene	$A = (3.38 \times 10^5 \times C) - 6.97 \times 10^4$	(5)
Fluoranthene	$A = (6.35 \times 10^5 \times C) - 1.42 \times 10^5$	(6)
Pyrene	$A = (5.19 \times 10^5 \times C) - 1.14 \times 10^5$	(7)

where

A := Response peak area

C := Concentration of PAH (μg/ml)

One or more standard solutions were used to verify the sensitivity of the detector for each set of sample injection. The response should not be different more than ±10%, or new calibration curves must be prepared.

3.8 Calculation of PAHs in Exhaust Samples

The quantity of each PAH found in the exhaust emission can be calculated by the following method.

3.8.1 Calculation of the Exhaust Volume

Volume of exhaust emission was calculated by the equation :

$$V = F \times T \tag{8}$$

where
$V :=$ Volume of exhaust emission (m^3)

$F :=$ Flow rate (m^3/hr)

$T :=$ Sampling Time (hr)

An exhaust flow rate was calculated from the performance curve of pump by the manufacturer, shown in Appendix B, which the linear equation of this curve is :

$$F = \left(-6.97 \times 10^{-3} \times P\right) + 6.49 \tag{9}$$

where
$F :=$ Flow rate of exhaust (m^3/hr)

$P :=$ Pump pressure (mbar)

From the average value of pump pressure recorded during the sampling, the flow rate of exhaust emission was calculated by using the equation (9). Thus, the volume of exhaust emission could be calculated by substituting the sampling time, T, and exhaust flow rate, F, into equation (8).

3.8.2 Calculation of PAHs quantity in exhaust samples

The concentration of each PAH in 1 µl injected sample was calculated by substitute the response peak area in the corresponding calibration curve (equation (1)-(7)). The quantity of PAH per cubic metre of exhaust was calculated by the equation

$$Q = \frac{(C \times 5)}{V} \tag{10}$$

where
$Q :=$ Quantity of PAH per 1 m^3 exhaust (µg/m^3)

$C :=$ Concentration of PAH in µl injected sample (µg/ml)

$V :=$ Volume of exhaust emission (m^3)

$5 :=$ Final 5-ml volume of extract sample before GC injection

For example, the response peak area of fluorene from gasoline base fuel at 2,000 rpm was 48,852 and the total exhaust volume (from equation (8) was 1.11 m^3. Substitute $A = 48,852$ in the linear equation of fluorene calibration curve (equation (4)).

$$A = \left(7.05 \times 10^5 \times C\right) - 1.52 \times 10^5 \tag{3}$$

$$48,852 = \left(7.05 \times 10^5 \times C\right) - 1.52 \times 10^5$$

$$C = \frac{\left(48,852 + 1.52 \times 10^5\right)}{7.05 \times 10^5} \quad = 0.28 \text{ µg/ml}$$

substitute $C = 0.28$ and $V = 1.11$ in equation (10)

$$Q = \frac{(C \times 5)}{V} \tag{10}$$

$$Q = \frac{(0.28 \times 5)}{1.11} \quad = 1.28 \text{ µg/m}^3$$

Consequently, the amount of fluorene in the exhaust emission of the test engine using gasoline base fuel at 2,000 rpm is 1.28 $\mu g/m^3$.

The quantitation of the other PAHs in exhaust emission were calulated by the same way.