

## CHAPTER III

# EXPERIMENTAL

### 3.1 Instrumental and Apparatus

The Soxhlet extraction apparatus was utilized for extraction of the collected filter and foam exposed to the exhaust. A rotary evaporator used was Buchi ROTAVAPOR-R with the water aspirator, EYELA ASPIRATOR A-3S, Tokyo Rikakikai Co., Ltd. High vacuum pump used was GAST model 0523-V103-G21DX. Amount of PAHs was determined by gas chromatograph, HP5890 Series II, Hewlett Packard, USA.

### 3.2 Chemicals and Materials

Crude and refined palm oil were obtained from Olene Co., Ltd. They were used as received without further purification. Methanol and hexane were commercial grade and were distilled at atmospheric pressure before use. Sulfuric acid 95-97% and sodium sulfate, as an anhydrous powder, were purchased from MERCK. Cyclohexane was Scharlau, Multisolvent. Standard polycyclic aromatic hydrocarbons, as a polynuclear aromatic hydrocarbons mixture for EPA 610, was purchased from Supelco Co., Ltd. containing of 16 components at the indicated concentrations ( $\mu\text{g/ml}$ ), namely acenaphthene (1000  $\mu\text{g/ml}$ ), acenaphthylene (2000  $\mu\text{g/ml}$ ), anthracene (100  $\mu\text{g/ml}$ ), benz(a)anthracene (100  $\mu\text{g/ml}$ ), benzo(b)fluoranthene (200  $\mu\text{g/ml}$ ), benzo(k)fluoranthene (100  $\mu\text{g/ml}$ ), benzo(ghi)perylene (200  $\mu\text{g/ml}$ ), benzo(a)pyrene (100  $\mu\text{g/ml}$ ), chrysene (100  $\mu\text{g/ml}$ ), dibenzo(a,h)anthracene (200  $\mu\text{g/ml}$ ), fluoranthene (200  $\mu\text{g/ml}$ ), fluorene (200  $\mu\text{g/ml}$ ), indeno(1,2,3-cd)pyrene (100  $\mu\text{g/ml}$ ), naphthalene (1000  $\mu\text{g/ml}$ ), phenanthrene (100  $\mu\text{g/ml}$ ) and pyrene (100  $\mu\text{g/ml}$ ). Glass-Microfibre filters were Whatman model GF/F (0.7 micron), sized 7 cm of a diameter. Polyurethane foams used have density of 0.22  $\text{g/cm}^3$ .

### 3.3 Test Engine

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

**Table 3.1** Diesel engine specification

Model	ISUZU 4JA 1L, 2500 Di
Numbers of cylinders	4
Displacement volume	2500 cm <sup>3</sup>
Max. horse power	87 PS at 4000 rpm.
Compression ratio	18.4 : 1
Low Idle Speed	800 rpm

### 3.4 Test Fuels

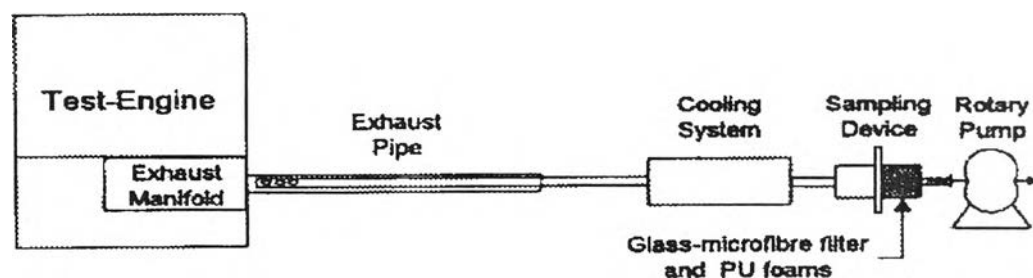
The test diesel fuels used in this study were purchased from the Bangchak Petroleum Public Co., Ltd. The diesel fuel was selected to be the base fuel and then was blended with palm oil methyl ester in ratio of 90:10, 80:20 or 70:30, which represents to bio-diesel fuels referred to, "B10, B20 and B30", respectively. Base diesel fuel was blended with refined palm oil and crude palm oil in ratios of 80:20, known as "RPO20 and CPO20", respectively.

## Preparation of Palm Oil Methyl Ester

An acid-catalyzed transesterification of palm oil was carried out in a 2000-ml round-bottomed two-necked flask equipped with a condenser, thermometer and mechanical stirrer. Firstly, the crude palm oil, which was used directly without further purification, was refluxed with methanol and concentrated sulfuric acid. A solution of concentrated sulfuric acid was dropped gradually to the reaction mixture while stirring. The mixture was heated to 65 °C and stirred for 6 hours. Then, the excess methanol was removed by distillation at atmospheric pressure. After that, the clear less-viscous mixture was allowed to cool to room temperature. Then, the mixture was separated in a separatory funnel by using hexane as an extraction solvent. The dark glycerol layer, which separated and contained most of the impurities, could be removed. The bright yellowish ester layer was purified by washing several times with water (vigorous shaking causes difficult emulsions) and was then dried with anhydrous sodium sulfate and filtered properly. Finally, solvent (hexane) was removed by distillation at atmospheric pressure. The clear yellowish solution was used for the engine tests without further purification.

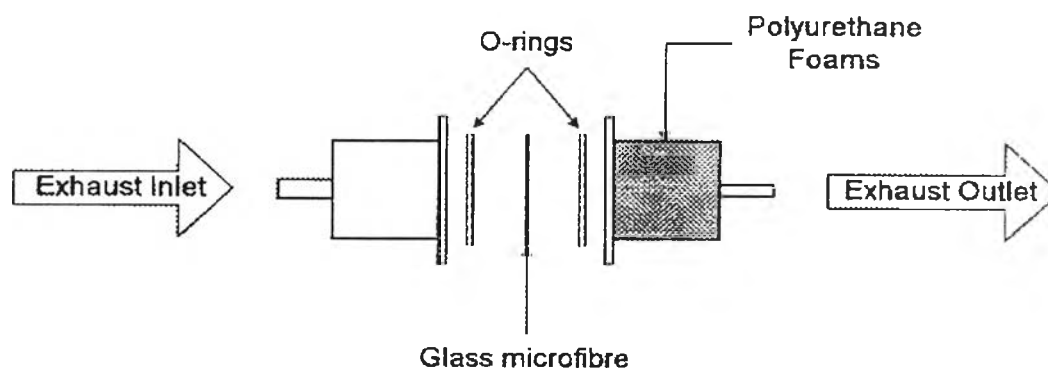
### 3.5 Exhaust Sampling System

Exhaust particulates and semivolatile exhaust samples from the test engine were taken from an exhaust pipe at a 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 a cooling system and then to a sampling device by suction with a high volume vacuum pump. Schematic of the exhaust sampling system is illustrated in Figure 3.1.



**Figure 3.1** Schematic of exhaust sampling system. Reproduced from [4].

In the sampling device, a Whatman glass-microfibre filter and polyurethane foam 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 a constant speed and no load. Samples were collected at the engine speeds of 800, 1600, and 2400 rpm, for each fuel.

The test engine was warmed up for 30 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 for 20 minutes, by the

sampling system as described in Figure 3.1. The pressure of the high vacuum pump was recorded every 5 minutes for determination of an exhaust flow rate. The exhaust was cooled by means of water to ensure that semivolatile compounds were trapped on polyurethane foam. After sampling, the glass-microfibre filter and polyurethane foam were kept dark and refrigerated until the further extraction.

### **3.6.2 Sample Extraction and Concentration**

The glass-microfibre filter and polyurethane foam exposed to the exhaust were Soxhlet extracted with 300 ml cyclohexane for 12 hours and the extract was evaporated using a rotary evaporator until the volume was less than 5 ml. Then, the extract was transferred to a 5-ml volumetric flask. The remaining extract was rinsed with a small amount of cyclohexane and this solution was added to the volumetric flask. Aliquots of cyclohexane extract were refrigerated prior to the chromatographic analysis.

### **3.6.3 PAHs Analysis**

The amounts of PAHs in samples were determined by gas chromatography using a DB-5HT capillary column with conditions shown in Table 3.2. The identification of PAHs in the samples was performed by comparing their retention times with those of a known mixture of polynuclear aromatic hydrocarbons of EPA 610.

Quantitative analysis was carried out by comparison of peak area of the sample to the corresponding standard calibration curve. The results were calculated and reported in micrograms per cubic meter of exhaust sample.

**Table 3.2** GC conditions for PAHs analysis

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GC column	DB-5HT capillary column 30 m x 0.25 mm i.d., film thickness 0.33 $\mu\text{m}$ .
Carrier gas	Helium, 99.999% purity, with flow rate of 1.6 ml/min at 80 °C
Injector temperature	250 °C
Injection mode	Splitless
Injection volume	1 $\mu\text{l}$
GC temperature program	80 °C (1 min) to 200 °C rate 15 °C/min 200 °C to 310 °C rate 3 °C/min
Detector	Flame ionization

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### 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 follow :

1. The standard solutions 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. All standard solutions were kept in a refrigerator at  $-4$  °C prior to the gas chromatographic analysis.

2. The standard solutions were analyzed by GC with the same conditions employed for samples. Retention times and response peak areas of each component were recorded 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.

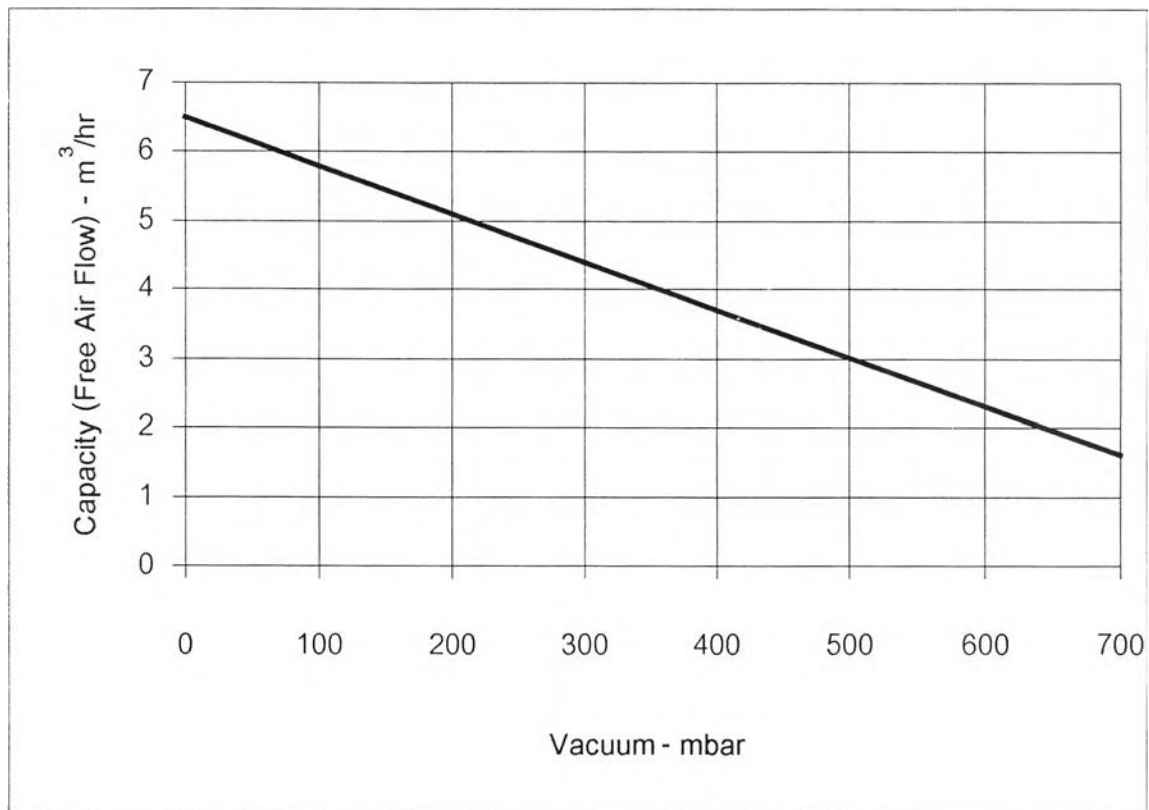
The linear equations of the standard calibrations are listed below :

<i>Standard substances</i>	<i>Linear equations</i>
Naphthalene	$A = (2.93 \times 10^5 \times C) - 3.66 \times 10^5$ (1)
Acenaphthylene	$A = (3.77 \times 10^5 \times C) - 8.93 \times 10^5$ (2)
Acenaphthene	$A = (3.97 \times 10^5 \times C) - 4.67 \times 10^5$ (3)
Fluorene	$A = (4.34 \times 10^5 \times C) - 8.45 \times 10^4$ (4)
Phenanthrene	$A = (6.40 \times 10^5 \times C) - 2.46 \times 10^4$ (5)
Anthracene	$A = (7.15 \times 10^5 \times C) - 1.18 \times 10^4$ (6)
Flouranthene	$A = (1.00 \times 10^6 \times C) - 2.24 \times 10^4$ (7)
Pyrene	$A = (8.99 \times 10^5 \times C) - 6.34 \times 10^2$ (8)
Benz(a)anthracene	$A = (4.43 \times 10^5 \times C) - 1.48 \times 10^4$ (9)
Chrysene	$A = (5.16 \times 10^5 \times C) - 2.19 \times 10^3$ (10)
Benzo(k)fluoranthene	$A = (2.80 \times 10^5 \times C) - 7.61 \times 10^3$ (11)
Benzo(ghi)perylene	$A = (5.03 \times 10^5 \times C) - 4.63 \times 10^4$ (12)

where  $A$  is the response peak area, and  $C$  the concentration of PAH ( $\mu\text{g/ml}$ )

### 3.8 Performance of Vacuum Pump

The vacuum pump used in this research was vacuum rotary vane pump, Gast model 0523-V103-G21DX. The performance curve of this pump, obtained from manufacturer specification, is shown in Figure 3.3.



**Figure 3.3** Performance curve of vacuum pump

The linear equation of this curve is :

$$F = (- 6.97 \times 10^{-3} \times P) + 6.49 \quad (13)$$

where  $F$  is the flow rate of exhaust (m<sup>3</sup>/hr), and  $P$  the pump pressure (mbar)



### 3.9 Calculation of PAHs in Exhaust Samples

The quantity of each PAH found in the exhaust emission were calculated by the following.

#### 3.9.1 Calculation of the Exhaust Volume

The volume of exhaust emission was calculated using the equation :

$$V = F \times T \quad (14)$$

where  $V$  is the volume of exhaust emission ( $\text{m}^3$ ),  $F$  the flow rate ( $\text{m}^3/\text{hr}$ ), and  $T$  the sampling time (hr)

From the average value of pump pressure recorded during the sampling, the flow rate of exhaust emission was calculated by using the equation (13). Thus, the volume of exhaust emission was calculated by substituting the sampling time and exhaust flow rate into Equation (14).

#### 3.9.2 Calculation of PAHs quantity in exhaust samples

The concentration of each PAH in the  $1 \mu\text{l}$  injected sample was calculated by substitute the response peak area in the corresponding calibration curve (equations (1) – (12)). The quantity of PAH per cubic metre of exhaust was calculated using the equation :

$$Q = \frac{(C \times 5)}{V} \quad (16)$$

where  $Q$  is the quantity of PAH per  $1 \text{ m}^3$  exhaust ( $\mu\text{g}/\text{m}^3$ ),  $C$  the concentration of PAH in  $1$  injected sample ( $\mu\text{g}/\text{ml}$ ),  $V$  the volume of exhaust emission ( $\text{m}^3$ ), and  $5$  the final  $5\text{-ml}$  volume of extract sample

For example, the response peak area of acenaphthylene from diesel base fuel at 800 rpm was 4683 and the total exhaust volume (from Equation (14)) was  $0.76 \text{ m}^3$ . Substitute  $A = 4683$  in the linear equation of acenaphthylene calibration curve (Equation (2)).

$$\begin{aligned}
 A &= (3.76 \times 10^5 \times C) - 8.93 \times 10^5 \\
 4683 &= (3.76 \times 10^5 \times C) - 8.93 \times 10^5 \\
 C &= \frac{(4683 + 8.93 \times 10^5)}{3.76 \times 10^5} = 2.36 \text{ } \mu\text{g/ml}
 \end{aligned}$$

Substituting  $C = 2.36$  and  $V = 0.76$  in Equation (16) give

$$\begin{aligned}
 Q &= \frac{(C \times 5)}{V} \\
 Q &= \frac{(2.36 \times 5)}{0.76} = 15.52 \text{ } \mu\text{g/m}^3
 \end{aligned}$$

Consequently, the amount of acenaphthylene in the exhaust emission of the test engine using diesel fuel at 800 rpm is  $15.52 \text{ } \mu\text{g/m}^3$ . The quantitation of the other PAHs in exhaust emission was calculated by the same way.