# Characteristics of Fine Particles and Associated Polycyclic Aromatic Hydrocarbons from Emission of Agricultural Diesel Engine Fueled by Palm Oil Blends

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**ชื่อวิทยานิพนธ์** คุณลักษณะของอนุภาคขนาดละเอียดและพอลิไซคลิกแอโรแมติกไฮโดรคาร์บอนจากไอเสียเครื่องยนต์ทางการเกษตรที่ใช้น้ำมันปาล์มผสมเป็นเชื้อเพลิง
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# บทคัดย่อ

งานวิจัยนี้ศึกษาคุณลักษณะทางกายภาพและทางเคมีของอนุภาคควันที่เกิดจากการเผาไหม้ของเครื่องยนต์ทางการเกษตรที่ใช้น้ำมันปาล์มผสมเป็นเชื้อเพลิง โดยออกแบบการทดลองเพื่อศึกษาความเข้มข้นและการกระจายขนาดของอนุภาค และองค์ประกอบทางเคมีในอนุภาค โดยเฉพาะอย่างยิ่งสารพอลิไซคลิกแอโรแมติกไฮโดรคาร์บอน (PAHs) ที่เป็นกลุ่มสารก่อมะเร็งและสารก่อการกลายพันธุ์ เครื่องยนต์ได้รับการทดสอบบนแท่นทดสอบสมรรถนะเพื่อทำการเก็บตัวอย่างไอเสียที่ผ่านการเจือจางแล้ว ด้วยเครื่องเก็บตัวอย่าง particulate matter air sampler ที่มีขนาดตัดเส้นผ่านศูนย์กลางของอนุภาคเป็น10, 2.5 และ 1 μm โดยทำการเก็บตัวอย่างหลังจากการเดินเครื่องยนต์ระยะยาวช่วงละ 500 ชั่วโมง ในช่วง 2,500-5,000 ชั่วโมง ซึ่งน้ำมันเชื้อเพลิงที่ใช้ศึกษาเป็นน้ำมันดีเซลที่จำหน่ายตามท้องตลาด(PB0) และน้ำมันปาล์มผสมดีเซลที่สัดส่วน 30% (PB30) และ 40% (PB40) โดยปริมาตร หลังจากนั้นใช้เทคนิคลิควิดโครมาโตกราฟีสมรรถนะสูง (HPLC) ร่วมกับตัวตรวจวัดชนิดไดโอดอะเรย์ (HPLC-DAD) เพื่อวิเคราะห์หาปริมาณสารพอลิไซคลิกแอโรแมติกไฮโดรคาร์บอนทั้ง16 ชนิดในตัวอย่างอนุภาค ผลการศึกษาพบว่าอนุภาคควันจากเครื่องยนต์ที่ได้แสดงการกระจายขนาดอนุภาคแบบโหมดเดี่ยว ซึ่งขนาดอนุภาคส่วนใหญ่อยู่ในช่วงของ accumulation mode มีขนาดเล็กกว่า 1 μm โดยที่ขนาดของอนุภาคเฉลี่ยมีค่าลดลงเมื่อเพิ่มสัดส่วนการผสมโดยปริมาตรของน้ำมันปาล์มจาก0-40% แต่เมื่ออายุของเครื่องยนต์เพิ่มมากขึ้นทำให้ความเข้มข้นของอนุภาคและขนาดของอนุภาคเฉลี่ยมีค่าเพิ่มขึ้น จากการศึกษาวิเคราะห์โดยจำแนกตามจำนวนวงแหวนของ PAHs พบว่ารูปแบบการกระจายของสาร PAHs มีการเปลี่ยนแปลงขึ้นอยู่กับขนาดของอนุภาค โดยสาร PAHs ชนิด 2-3 วงแหวนเป็นกลุ่มหลักที่พบจากตัวอย่างอนุภาคที่มีขนาดใหญ่กว่า 10 μm ส่วนอนุภาคที่มีขนาดเล็กกว่า 1 μm จะพบสาร PAHs ชนิด 4-6 วงแหวนเป็นกลุ่มหลัก โดยที่มีไพรีน (pyrene) เป็นสาร PAHs ที่พบมากที่สุด และเมื่อ

เวลาการใช้งานของเครื่องยนต์เพิ่มมากขึ้นพบว่าค่าความเข้มข้นของสาร PAHs เพิ่มขึ้นด้วย อันเป็นผลเนื่องมาจากการสึกหรอของเครื่องยนต์ที่เพิ่มมากขึ้นจากผลการทดลองแสดงให้เห็นได้อย่างชัดเจนว่า เมื่อสัดส่วนการผสมโดยปริมาตรของน้ำมันปาล์มผสมเพิ่มขึ้น ค่าความเข้มข้นของอนุภาคและความเข้มข้นของสาร PAHs จะลดลง ทั้งนี้เนื่องมาจากปริมาณออกซิเจนที่มีมากกว่าทำให้เกิดการเผาไหม้ได้สมบูรณ์มากกว่าในกรณีของน้ำมันดีเซลหรือ PB0

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# ABSTRACT

Physical and chemical characteristics of particulate matters (PM) and associated polycyclic aromatic hydrocarbons (PAHs) from emission of agricultural diesel engines fueled by palm oil blend diesel were investigated. The experimental methods were designed to analyze evolution of concentration, chemical components of particulate matters especially the carcinogenic, mutagenic PAHs and size distribution of PAHs associated with the particulates particularly fine particles smaller than 1 µm (PM1). A 4-stage cascade particulate matter air sampler was used to collect aerosol particles emitted from the engines. The 50% cut-off aerodynamic diameters for the first 3 stages are 10, 2.5 and 1 µm, while the last stage collects all particles smaller than 1 µm. The exhaust from an engine operated on a dynamometer was diluted before it was sampled. In this study, commercial petroleum diesel (PB0), 30% and 40% palm oil blend diesel (PB30 and PB40) were used in the engine running for 2,500-5,000 hours. Sixteen PAH compounds were analyzed using a high performance liquid chromatography (HPLC) with diode array detector (HPLC-DAD). The size distributions of PMs emitted from the engines show a unimodal behavior in the accumulation mode. The dominant PMs were fine particle (<1 µm) and the mass median aerodynamic diameter (MMAD) was reduced when increasing the blending ratio of palm oil from 0% to 40%. It was also found that the PM concentration and MMAD were increased with the running time. The patterns of PAH compounds associated with large particles (>1 µm) indicated a dominance of smaller PAH molecules (2-3 aromatic rings). The most dominant compound was Pyrene. For the fine particles (<1 μm), larger PAH molecules (4-6 aromatic rings) played important role. However, PAH concentration was increased when the running hour of the engine was increased. This could be a result of the engine wear after running for a long period of time. Overall, the results demonstrated significantly reduction of both PMs and total PAH emission as the blending ratio of palm oil was increased because palm oil blend diesel contain higher oxygen content which enables more complete combustion than PB0.

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**Khamphe Phoungthong**

# THE RELEVANCE OF THE RESEARCH WORK TO THAILAND

Outcome of this research will be beneficial to government agencies since biodiesel is an important bio-fuel recently promoted for a diesel substitute in Thailand. Environmental impact results from this study will give them information crucial for the continuing promotion of the fuel.

Organizations that could use the outcome of this thesis work include for examples

- Particulate Control Industries
- Pollution Control Department (PCD)
- Ministry of Energy
- Ministry of Industry
- Ministry of Natural Resources and Environment
- Ministry of Science and Technology

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# LIST OF ABBREVIATION AND SYMBOLS

**Abbreviation**

| | |
|---|---|
| Ace | Acenaphthene |
| Act | Acenaphthylene |
| Ant | Anthracene |
| ASTM | American Society for Testing Materials |
| ATSDR | Agency for Toxic Substances and Disease Registry |
| BaA | Benz(a)anthracene |
| BaP | Benzo(a)pyrene |
| $BaP_{eq}$ | Benzo(a)pyrene equivalency |
| BbF | Benzo(b)fluoranthene |
| BghiPe | Benzo(g,h,i)perylene |
| BkF | Benzo(k)fluoranthene |
| BP | boiling point |
| CFD | Computational Fluid Dynamics |
| Chr | Chrysene |
| CNG | Compressed Natural Gas |
| DAD | Diode array detector |
| DBA | Dibenzo(a,h)anthracene |
| DCM | Dichloromethane |
| DI | Direct injection |
| DME | Dimethyl ether |
| DMSO | Dimethyl sulphoxide |
| DNA | Deoxyribonucleic acid |
| DOM | dissolved organic matter |
| EGR | Exhaust gas recirculation |
| EPA | Environmental protection agency |
| EU | European Union |
| FAs | Fatty acids |
| Fle | Fluorene |

# LIST OF ABBREVIATION AND SYMBOLS (Continued)

| | |
|---|---|
| Flu | Fluoranthene |
| FO | Fuel oil |
| FRMs | Federal Reference Methods |
| HEPA | High efficiency particulate absorbing |
| HFO | Heavy fuel oil |
| HP | Horse power |
| Hph | Horse power per hour |
| HPLC | High performance liquid chromatography |
| HSD | High speed diesel oil |
| IARC | International agency for research on cancer |
| IDI | Indirect injection |
| IDP | Indeno(1,2,3-cd)pyrene |
| LOD | Limit of detection |
| LSD | Low speed diesel oil |
| MMAD | Mass median aerodynamic diameter |
| MOUDI | Micro orifice uniform deposit impactor |
| MP | melting point |
| MW | molecular weight |
| NAAQS | National ambient air quality standard |
| Nap | Naphthalene |
| PACs | Polyaromatic compounds |
| PAHs | Polycyclic Aromatic Hydrocarbons |
| PB | Palm oil blend |
| Phe | Phenanthrene |
| PM | Particulate Matters |
| PTFE | Polytetrafluoroethylene |
| Pyr | Pyrene |
| rpm | round per minute |
| S | water solubility |
| SOF | Soluble organic fraction |

# LIST OF ABBREVIATION AND SYMBOLS (Continued)

| | |
|---|---|
| TDC | Top dead center |
| TEFs | Toxicity equivalency factors |
| TEOM | Tapered element oscillating microbalance |
| THC | Total hydrocarbon |
| TSP | Total suspended particulates |
| *tt*-DDE | trans,trans-2,4-decadienal |
| UE | Ultrasonic extraction |
| UV | Ultraviolet |
| VP | Vapor pressure |
| WVO | Waste vegetable oil |

**Symbols**

| | |
|---|---|
| $d_{ave}$ | average aerodynamic diameter |
| $\mu g$ | microgram |
| $\mu L$ | microliter |
| $\mu m$ | micrometer |
| $mL$ | milliliter |
| $mg$ | milligram |
| $ng$ | nanogram |
| $ppm$ | part per million |
| $C$ | particle concentration (g $m^{-3}$) |
| $cSt$ | centistokes |
| $f$ | mass fraction |
| $M_f$ | mass of filter sample after sampling (g) |
| $M_i$ | mass of blank filter (g) |
| $M_j$ | mass collected in each stage (g) |
| $M_{total}$ | total mass collected (g) |
| $Q$ | flow rate (L $m^{-1}$) |

# LIST OF ABBREVIATION AND SYMBOLS (Continued)

| | |
|---|---|
| $R$ | recovery (%) |
| $S/N$ | signal to noise ratio |
| $V$ | volume ($m^{-3}$) |
| $V_{total}$ | total sampling volume ($m^3$) |
| $\eta(\%)$ | reduction percentage |
| $\lambda$ | wavelength |

# CHAPTER 1
# INTRODUCTION

## 1.1 Background and Rationale

An energy crisis, particularly escalating price of petroleum-based oil, has been a global concern. The use of fossil fuels in the twentieth century was rapidly increased by twenty-fold (Owen et al., 2010). World crude oil demand grew an average of 1.76% per year from 1994 to 2006, with a peak of 3.4% in 2003-2004. World demand for oil is projected to increase 37% from 2006 to 2030 (from 86 million barrels per day in 2006 to 118 million barrels per day in 2030) due to a large increase in demand from the transportation sector (Energy Information Administration, 2007). A study predicted that the oil demand would surpass the potential supply by 2015 (Owen et al., 2010).

Renewable energy has gained enormous attention in the past several years in many countries as an alternative source of energy to substitute the petroleum. In 2004, renewable energy contributed to around 7% of the total global consumption. The renewable energy sector has been growing significantly since the last decade of the twentieth century, and in 2005, total new investment for the renewable energy sector was estimated to be 38 billion US dollars. Alternative fuels such as biodiesel have been popularly discussed in many countries owing to increasing environmental awareness and the rising price of diesel.

Thailand also faces serious energy problem as a major source of energy is imported petroleum. In 2007, Thailand diesel fuel usage topped about 322 thousand million barrels per day so that the government decided to support the introduction of renewable energy in order to decrease the import of petroleum diesel. Biodiesel from agricultural products is the most suitable diesel replacement because of the abundance of raw materials required in the production (Ministry of Energy, 2006).

Biodiesel is an alternative fuel consisting of alkyl esters of fatty acids obtained from vegetable oils or animal fats under transesterification or alcoholysis process using methanol or ethanol as reactants. Recently, biodiesel has become a competitive fuel as the diesel cost keeps increasing due to many reasons including its shortage of supply.

Diesel-powered engines usually generate soot particles resulting in black smoke affecting atmospheric environment especially in urban areas where diesel trucks are a major transportation means in Thailand. Report indicated that nanoparticles were generated during diesel combustion (Moisio et al., 1998). Theses particles subsequently coagulated to form larger submicron-particles.

Study of emission from biodiesel engines is still limited. Moreover, study of particulate matters and their associated polycyclic aromatic hydrocarbons (PAHs) emitted from engines fueled by biodiesel is rare. PAHs are known as carcinogenic potential chemicals generated from biomass burning (Furuuchi et al., 2006). Most PAHs are associated with fine airborne particles, typically 0.5 μm or less (De martinis et al., 2002). Fine particles in this size range efficiently evade the mucocolitis defense system and deposit in the peripheral airways, where they may induce toxic effects. In addition, they can be transported over a long distance. This implies that particles can easily distribute PAHs to the atmosphere and become one of the major sources of air pollution to nearby surroundings. Therefore it is necessary to investigate the emission characteristics of biodiesel engines since this knowledge can be used at policy-level for promoting biodiesel usage subsequently.

Agricultural machinery in Thailand is usually fueled by petroleum diesel. Recently, palm oil blend diesel has been introduced and tested with the machines (Prateepchaikul et al., 2003). Study of PM and PAH emissions from the engine fueled by palm oil blend diesel is then necessary to evaluate the PAH emission potential. In this work, characteristics of fine particulate matters and PAHs associated with the particles emitted from agricultural diesel engines fueled by palm oil blend diesel are investigated.

## 1.2 Review of Literature

One of the major problems from engine exhaust is the emission of gaseous pollutants such as CO, $NO_x$, $SO_x$, and solid particulate matters resulted from an incomplete combustion. Moreover, toxic PAHs are released. They are detected in the gaseous phase (smoke, particulate emission), the solid phase (soot, fly ash, tars, creosote), as well as in the condensable liquids.

PAHs are a large group of organic compounds with two or more fused aromatic rings. They have a relatively low solubility in water while they are highly lipophilic. Most of the PAHs with low vapor pressure in the air are adsorbed on particles. Ultraviolet light from solar radiation and fluorescent lamp bulb can decompose PAHs. PAHs associated with particles in the atmosphere can be related to several air pollutants, e.g. $O_3$, $NO_x$, and $SO_2$ (WHO, 1987).

PAHs are ubiquitous compounds in the environment such as soil, water, sediment, atmosphere, etc. A number of studies have been focused on the anthropogenic sources of PAHs. As products of incomplete combustion, PAHs are commonly found in coal tars and petroleum residues (Harvey et al., 2002). A lot of interest has been drawn in the study of PAHs because of its mutagenic and carcinogenic effects (ASTDR, 1995).

In general, PAHs are a group of over 100 different chemicals. Some of the PAHs are lighter (low molecular weight) and can evaporate into air. They are usually contained in a gas phase. These PAHs decompose by reacting with sunlight and other chemicals in the air. This generally takes days to weeks. The more sunlight, the quicker these PAHs will decompose. Low molecular-weight (2-3 rings) PAHs are less toxic to human and not carcinogenic. On the other hand, heavier PAHs (higher molecular weight, more than 4-6 rings) do not dissolve in water, but stick to solid particles (PAHs in particulate phase) and settle to the sediment in the bottom of lakes, rivers, or streams. These PAHs remain in soil and sediment, and will generally take weeks to months to break down in the environment. Microorganisms in soil and sediment are the main cause of break down. These heavy PAHs are carcinogenic to lab animals and may be carcinogenic to humans (ATSDR, 1995).

Many researchers have studied the health effects of particulate matters on human. Size of particles is directly linked to their potential for causing health problems. Smoke particles smaller than 10 µm in diameter pose the greatest problems, because particles in this size range can travel deep into the lungs. In addition, fine particles, smaller than 2.5 µm, can affect both lung and heart.

Combustion of diesel fuel in engines generally generates PAHs (McCormick et al., 2001). Since biodiesel has recently gained popularity due to its renewable property, study of PAH emission is necessary. In this section, previous investigations of PAHs emitted from combustion of biodiesel or biodiesel-mixed fuel are reviewed.

Up to now there are a few studies devoted to particles smaller than 1 µm (PM1) generated by diesel engines fueled with palm oil blend diesel or biodiesel derived from other vegetables or animals. These studies were focused on emission characteristics of particles, including the particulate-phase PAHs. Some investigations were conducted to analyze the emitted gases. For better understanding of the characteristics of particles emitted from diesel and biodiesel fuel combustion, previous investigations of the size distribution and concentration of particles are reviewed first followed by a review of PAHs generated by combustion of diesel and biodiesel engines.

Sidhu et al. (2001) studied particulate formation from combustion of four different alternative diesel fuels, namely compressed natural gas (CNG), dimethyl ether (DME), biodiesel, and diesel, under fuel-rich conditions in the temperature range of 800-1200°C at a pressure of approximately 24 atm. They found that particles formed from combustion of all fuels were smaller than 0.1 µm in mean diameter. Results of gravimetric analysis showed that under the test conditions, the relative particulate yields from CNG, DME, biodiesel and diesel were 0.30%, 0.026%, 0.52%, and 0.51%, respectively. Chemical analysis showed that particles from DME combustion had the highest soluble organic fraction (SOF) of 71%, followed by biodiesel (66%), CNG (38%) and diesel (20%). This indicated that for both gaseous and liquid fuels, combustion of oxygenated fuels generated a higher SOF than that of non-oxygenated fuels.

Reyes and Sepúlveda (2006) studied PM emissions from diesel engine fueled by blends of diesel-crude biodiesel and diesel-refined biodiesel. Crude biodiesel and refined biodiesel were produced from salmon oil containing high content of free fatty acids, throughout a process of acid esterification followed by alkaline transesterification. Results indicated a maximum power loss of about 3.5% and also near 50% of PM10 reduction with respect to diesel when a 100% of refined biodiesel was used. For blends with less content of either crude biodiesel or refined biodiesel, the power losses were lower and at the same time lower reduction in PM10 emissions was observed.

Shi et al. (2006) investigated emission characteristics of a three compounds oxygenated diesel fuel blend (BE-diesel), on a Cummins-4B diesel engine. The BE-diesel was a new form of oxygenated diesel fuel blend consisting of ethanol, methyl soyate and petroleum diesel. Fuel ratio of ethanol:methyl soy ester:petroleum diesel fuel was 5:20:75. Results indicated significant reduction of PM and 2-14% increasing of $NO_x$ emissions while change of CO emission was not obvious when compared to the emission from the diesel engine. Total hydrocarbon (THC) was lower while acetaldehyde, propionaldehyde and acetone were slightly higher. A small amount of ethanol was also detected in the exhaust gas.

Turrio-Baldassarri et al. (2004) studied emission characteristics of a bus engine fueled with diesel and biodiesel blend. Exhaust gases were generated by a turbocharged EURO 2 heavy-duty diesel engine, operating under steady-state conditions on the European test 13 mode cycle (ECE R49). Regulated and unregulated pollutants, such as PAHs and nitrated derivatives (nitro-PAHs), carbonyl compounds and light aromatic hydrocarbons were quantified. They found insignificant reduction of PAHs and nitro-PAHs when using biodiesel blend, while formaldehyde was increased by 18%. Most of the particulates were in 0.06 to 0.3 μm size range.

Lin et al. (2006a) investigated PAHs in particulate and gas phases and regulated harmful matter emissions from heavy-duty diesel engines fueled by palm biodiesel–diesel blends and paraffinic–palm biodiesel blends. Results showed that the emissions of THC and CO were increased, while the emissions of $NO_x$ and PAHs were decreased with operation time. Using palm biodiesel–diesel blends or paraffinic–palm biodiesel blends instead of pure diesel fuel reduced the emissions of PM (6.11–26.8%), total PAHs (43.0–90.2%), total $BaP_{eq}$ (63.1–89.6%), THC (10.7–44.2%), CO (0.664–15.6%), $CO_2$ (0.763–2.55%), and $NO_x$ (1.25–4.97%).

Lin et al. (2006b) studied emissions of PAHs, carcinogenic potencies ($BaP_{eq}$) and particulate matters (PMs) from a diesel engine operated with several palm biodiesel-diesel blends (P0 to P100). They found that PAH emission decreased with increasing palm biodiesel-diesel blends due to small PAH content in biodiesel. The mean reduction percentages of total PAH emission factor were 13.2% to 98.8% for P10 to P100 compared with P0. The mean reduction percentages of total $BaP_{eq}$ were 15.2% to 97.6% for P10 to P100 compared with P0. PM emission was decreased as the palm biodiesel-diesel blend ratios were increased from 0% to 10%, and it was increased as the palm biodiesel-diesel blend ratios were increased from 10% to 100%.

Yang et al. (2007) investigated characteristics of PAHs and trans,trans-2,4-decadienal (*tt*-DDE) in both particulate and gas phases from a modern 4-cylinder diesel engine operated with diesel and biodiesel blend (B20) fuels. They found that average PAH emission for B20 was lower than that of pure diesel (1403 and 1051 mg $bhp\text{-}h^{-1}$, respectively). They also found that *tt*-DDE was generated in the exhaust of diesel engine using B20. Lower molecular weight PAHs were predominant in gaseous phase for both diesel and B20. Cold-start driving had higher *tt*-DDE and PAH emission factors, as well as a higher percentage of *tt*-DDE in particulate phase, than the warm-start driving.

Agarwal et al. (2006) suggested the drawback of higher $NO_x$ emissions while using biodiesel be overcome by employing exhaust gas recirculation (EGR). EGR can effectively reduce $NO_x$ from diesel engines because it lowered the flame temperature and the oxygen concentration in the combustion chamber. However, EGR resulted in higher particulate matter (PM) emissions. They found that application of EGR with biodiesel blends resulted in reductions in $NO_x$ emissions without significant impact of PM emissions and brake specific fuel consumption.

Chien et al. (2009) tested commercial pure petroleum-based diesel (D100) and three biodiesel blends of 20% (B20), 60% (B60), and 100% (B100) on a dynamometer following the US transient-cycle test procedure. Particle size distributions were measured by a micro-orifice uniform deposit impactor (MOUDI) and Nano-MOUDI of 0.01-10 μm aerodynamic diameter. Results showed that PM emissions were clearly decreased as the blending percentages of biodiesel were increased. For B0, B20, B60 and B100, PAH emission factors were 3704, 2720, 1709 and 1514 μg/Hph (horsepower per hour), respectively. Increasing the biodiesel blending percentage reduced the emission of both PMs and PAHs for all four size ranges. The reductions were significant especially for ultrafine (41.3%) and fine (44.8%) particles. The PAH mass was 32.5%, 32.6%, 34.5%, 30.0% in the ultra-fine size range and 23.8%, 24.3%, 29.2%, 34.5% in the nano size range for B0, B20, B60 and B100, respectively. The $BaP_{eq}$ emission factors for B100 were 27.2, 49.5, 74.2 and 13.0 μg/Hph in nano, ultrafine, fine and coarse size ranges. Results indicated that biodiesel can reduce both PAH emission factors and the PAH corresponding carcinogenic potency in the full size ranges.

## 1.3 Research Objectives

In this work, characteristics of fine particles and associated PAHs from emission of agricultural diesel engines fueled by palm oil blend diesel of several ratios are then investigated. The objectives for this work are:

1. To study concentration and particle size distribution of particulate matters smaller than 1.0 μm (PM1), in particular, and PAHs associated with the particles generated by agricultural diesel engine fueled by palm oil blend diesel.
2. To evaluate the effects of the fuel blending ratios and the engine hours on the emission characteristics.

## 1.4 Scopes of Work

1. Construct a sampling system to connect to the exhaust pipes of the test engine to collect particles from agricultural diesel engines fueled by palm oil blends (PB0, PB30 and PB40).

2. Sample particles using a new intertial-filter cascade particulate matter air sampler.
3. Analyze concentration and size distribution of PAHs associated with the particulates including fine particles using HPLC especially the carcinogenic/mutagenic PAHs.
4. Evaluate the effects of the palm oil blending ratios and the engine hours on the emission characteristics.

# CHAPTER 2

# THEORETICAL BACKGROUND

## 2.1 Particle Collection by Impaction

Impaction is a special case of curvilinear motion that finds extensive application in the collection and measurement of aerosol particles. Impaction is a common method for collecting dust for the evaluation of occupational environments, sampling for size analysis, and many other applications. Otani et al. (2007) devised a new particulate matter air sampler employing inertial filter made from stainless steel fiber mat which can separate particle smaller than 1.0 μm which will be used in this work. It uses the concept of inertial impaction on fibrous filters for the classification of fine particles. Inertial filter developed in the present work has a low pressure drop (<20-30 kPa) compared to a low pressure impactor and therefore the volatilization of volatile organic compounds is suppressed during the atmospheric aerosol sampling, as well as a sufficiently high sampling flow rate that permits the rapid collection of particles.

### 2.1.1 Impaction mechanism

Inertial impaction is commonly used in an impactor as a precleaner to remove particles or an aerosol sampler. The most common type of impactor consists of a single jet of particle-laden gas (aerosol) impinging on a flat plate, as shown in Fig. 2.1. Particles larger than the cut size of the impactor will slip across the streamlines and impact on the plate, while smaller particles will follow the streamlines and will not be collected. The most important impactor characteristic is the collection efficiency curve. The collection efficiency is defined as the fraction of particles passing through the nozzle that are collected on the impaction plate. The ideal impactor has a perfectly sharp efficiency curve, which means that, all particles larger than the cut size of the impactor are collected on the plate, while all smaller particles follow the gas flow out of the impaction region.

The particles deposited on the impaction plate can be evaluated by a variety of methods. A few of the more common methods are: (1) the particles are collected on a glass plate, a membrane filter, or a foil and are inspected or counted under a microscope; (2) the particles are collected on a foil and weighed to determine the mass of particles; (3) the particles are collected on a quartz crystal, and the mass of particles is determined by the change in the natural frequency of the crystals; (4) the particles are charged before passing through the impactor, and the current is measured to determine the number of particles being collected. The first two methods provide size distribution data integrated over time, while the latter two methods provide size distribution data in near real time.

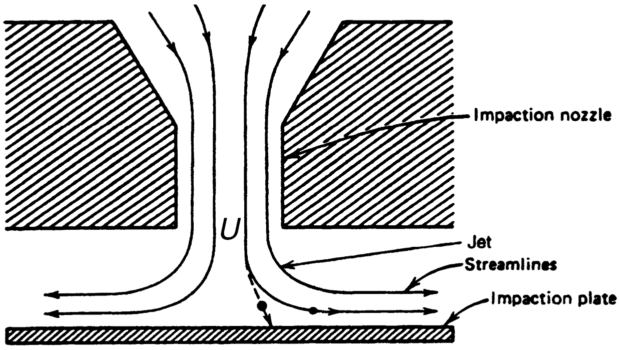


**Figure 2.1** Schematic diagram of a conventional impactor (Baron, 2005).

Impactor theory seeks to explain the shape of the curve of collection efficiency *E* versus particle size as shown in Fig. 2.2.

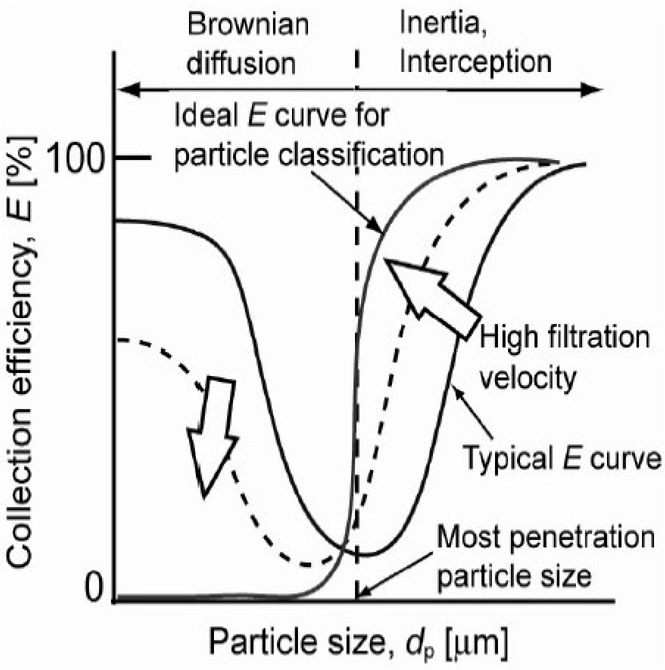


**Figure 2.2** Principle of inertial impaction.

The parameter that governs collection efficiency is the Stokes number, or impaction parameter, which is defined for an impactor as the ratio of the particle stopping distance:

$$Stk = \frac{C_C \rho_p d_p^2 u}{9\mu \ d_f} \tag{2.1}$$

Where $C_c$ is the Cunningham slip correction factor, $\rho_p$ the particle density, $d_p$ the particle diameter, $u$ the filtration velocity, µ the viscosity, $d_f$ the fiber diameter, and $D$ the Brownian diffusivity of particles.

### 2.1.2 Inertial impaction

In the inertial filter, large particles are collected by inertial impaction at a high filtration velocity while small particles are removed from air by Brownian diffusion. The measurement of the degree of inertial impaction and Brownian diffusion are Stokes number ( $Stk$ ) and Peclet number ( $Pe$ ), respectively. The Peclet nuber is defined as:

$$Pe = \frac{u \ d_f}{D} \tag{2.2}$$

The collection efficiency of a filter increases with increasing *Stk* and decreasing *Pe*. Therefore, by using an extremely high filtration velocity, high collection efficiency for larger particles and low collection efficiency for smaller particles are achieved. Changes in fractional collection efficiency with the filtration velocity are shown in Fig. 2.3. At a low filtration velocity of 0.05 m $s^{-1}$, the collection efficiency monotonically decreases with particle size. By increasing the filtration velocity to 5 m $s^{-1}$, the collection efficiency of particles smaller than 1.0 µm decreases because of less Brownian diffusion collection but that of particles larger than 1.0 µm remains rather small. At the filtration velocity of 50 m $s^{-1}$, the collection efficiency curve becomes an ideal separation curve. By using the stainless steel fiber mat, it is possible to achieve 50% cutoff diameter of particles as small as 50 nm at the filtration velocity of 50 m $s^{-1}$. This sampler will be used in this project in order to analyze PAHs associated with the particles generated by agricultural diesel engine fueled by palm oil blends.

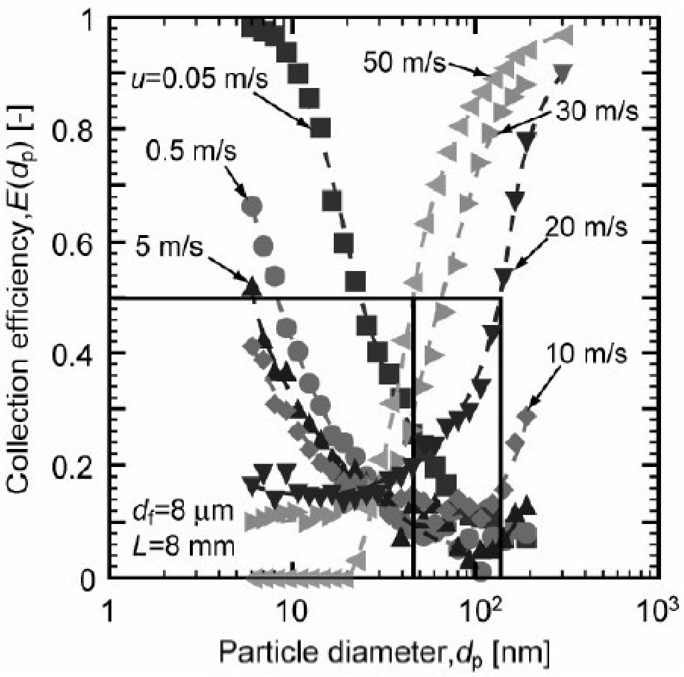


**Figure 2.3** Fractional collection efficiency of inertial filter at various filtration velocities.

### 2.1.3 Cascade impactor

By adding a series of impactor stages and a downstream filter yields an important aerosol sampling instrument called a cascade impactor, as shown in Fig. 2.4. Sampling an aerosol with such an impactor can provide information about its particle size distribution. The mass of the particles collected on the impactor plates and of those collected on the filter are determined by weighing them before and after sampling.

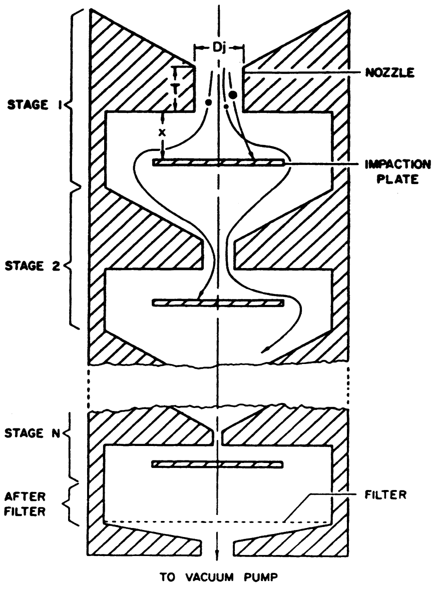


**Figure 2.4** Schematic diagram of a cascade impactor (Baron, 2005).

An impactor separates the sampled particulate mass into two particle size ranges: that contributed by particles larger than the cutoff size (collected on the impaction plate) and that contributed by particles smaller than the cutoff size (escaped from the impactor). By operating the impactor at several velocities, each corresponding to a different cutoff diameter, several points on the cumulative mass distribution curve can be obtained. There are practical limitations on the range of velocity that can be used, and the aerosol size distribution must remain constant for all the samples (Hinds, 1999).

An example of a commercial cascade impactor is an eight-stage Andersen sampler (Dylec, AN200) as shown in Fig. 2.5. The impactor has 50% cut-off aerodynamic diameters of 11.0, 7.0, 4.7, 3.3, 2.1, 1.1, 0.65 μm for stage 1-8, respectively, and collects all particles smaller than 0.43 micron on a backup filter when operated at or 28.3 L min$^{-1}$. Particles were collected on 80-mm filters placed on the plate of each stage in the sampler.

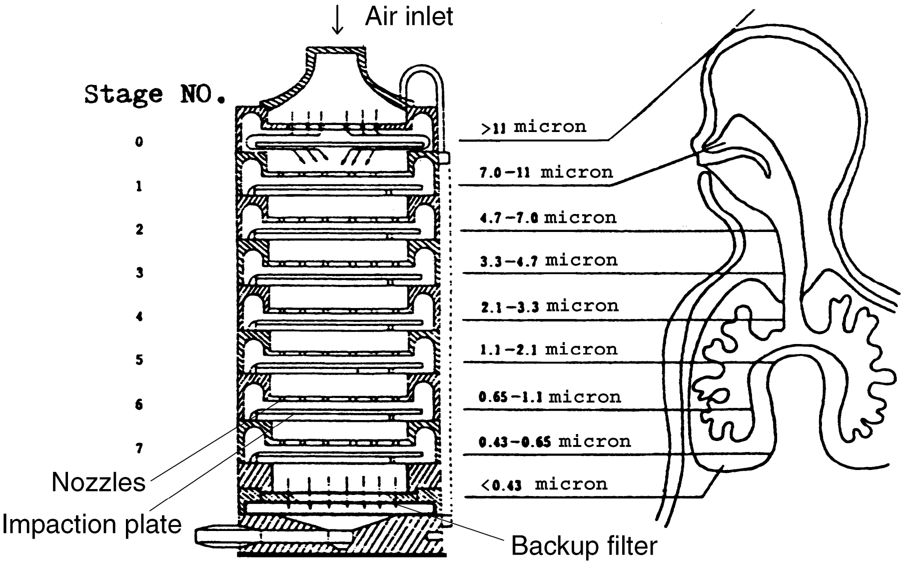


**Figure 2.5** An eight-stage Andersen impactor.

The recently developed particulate matter air sampler consists of four stages (PM10/PM2.5/PM1), an inertial filter and a backup filter, as shown in Fig. 2.6. The sampler was designed to operate at a flow rate of 40 L min$^{-1}$, which allows both the sufficiently fast sampling of atmospheric PMs and portability as a field sampling device. The particles were collected on quartz fiber filters. Donut-shape filters with 65x30 mm diameter were used in the first 3 impaction stages, and a 47 mm diameter circular filter was used in the backup stage. The stage above the backup filter contained 8 mm thick stainless steel fiber mat with fiber diameter of 8 μm and packing density of 0.0065. The inertial filter was designed so that the webbed stainless steel fibers were packed on a support of stainless steel wires in a plastic holder (polyoxymethylene, POM), and the holder was placed in the throat of the nozzle. The adoption of a filter holder facilitates the handling of samples and it can be easily replaced with a new holder on site without directly touching the fibers. The filter holder can be reused after cleaning and are also disposable.

Because the cut-off for the inertial filter was not sharp enough and bounce-off from the filter took place, particle collected on this stage were combined with those collected on the backup filter to give the amount of particles smaller than 1.0 μm.

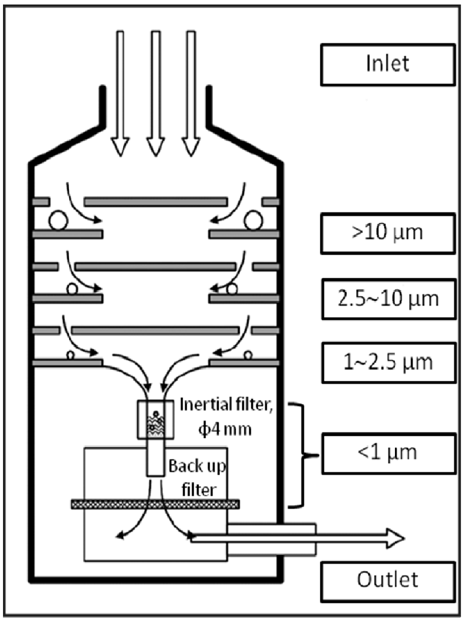


**Figure 2.6** A schematic diagram of the particulate matter air sampler (Kanomax, Japan) indicating the cut-off diameters.

### 2.1.4 Mass median aerodynamic diameter (MMAD)

The mass and number distributions for the same sample of particles have different means, medians, geometric means, graphical representations, and probability density functions. The median of the distribution of mass is called the mass median aerodynamic diameter (MMAD). An equivalent diameter that finds wide application in aerosol technology is the aerodynamic diameter. This is defined, for a particular particle, as the diameter of the spherical particle with a density of 1000 kg $m^{-3}$ [1 g $cm^{-3}$] (the density of a water droplet) that has the same settling velocity as the particle. The aerodynamic diameter can be thought of as the diameter of a water droplet having the same aerodynamic properties as the particle. If a particle has an aerodynamic diameter of 1 µm, it behaves in an aerodynamic sense like a 1-µm water droplet regardless of its shape, density, or physical size. Furthermore, it is aerodynamically indistinguishable from other particles of different size, shape, and density having aerodynamic diameters of 1 µm. MMAD is defined as the diameter for which half the mass is contributed by particles larger and half by particles smaller. It is the diameter that divides the graphical representation of the distribution of mass into two segments of equal area. Fifty per cent of the particles by weight will be smaller that the MMAD, and another 50% will be larger.

## 2.2 Palm Oil

Palm oil is an edible plant oil derived from the fruit and kernels (seeds) of the oil palm Elaeis guineensis. Palm oil is one of the few vegetable oils relatively high in saturated fats (like coconut oil). Both palm oil and palm kernel oil are high in saturated fatty acids, about 50% and 80%, respectively (Knother et al., 2005)

Fatty acids are saturated and unsaturated aliphatic carboxylic acids with carbon chain in the range of C3 up to C28. An example of a fatty acid is palmitic acid, $CH_3–(CH_2)_{14}–COOH$. Palm oil products are made using milling and refining processes. By melting and degumming, impurities can be removed and then the oil is filtered and bleached to remove smells and colors. The refined bleached deodorized palm oil, and free fatty acids can be used as an important raw material in the manufacture of soaps, washing powder and other hygiene and personal care products.

Palm oil is also used in biodiesel production, as either simply-mixing with petroleum diesel, or processing through transesterification to obtain a palm oil methyl or ethyl ester blend, with glycerin as a byproduct.

## 2.3 Petroleum Diesel Fuel

Diesel fuel or petroleum diesel or fossil diesel is fuel used in diesel engines. Diesel fuel is produced from petroleum distillate fractional of crude oil between 200°C to 350°C at atmospheric pressure, resulting in a mixture of hydrocarbon chains that typically contain between 8 and 21 carbon atoms per molecule. The density of petroleum diesel is about 0.85 kg $L^{-1}$. When burnt, diesel typically releases about 38.6 MJ $L^{-1}$. The characteristics of diesel fuel include: heat value, specific gravity, flash point, pour point, viscosity, cetane index and so on. The choice of fuel depends on engine design and usage.

1. Automotive diesel oil or gas oil is for high speed diesel engine such as vehicle diesel engine, locomotive engine, ship engine, industrial diesel engine with speed more than 1,000 rpm. This fuel is called high speed diesel oil (HSD) or solar oil.

2. Industrial diesel oil used with engine speed less than 1,000 rpm such as stationary lower speed engine, so called low speed diesel oil (LSD). Sometimes, it happenes between distillate and fuel oil (FO) or heavy fuel oil (HFO).

## 2.4 Biodiesel

Biodiesel is a clean alternative fuel from vegetable oil or animal fat based fuel consisting of long-chain alkyl esters. Biodiesel can be blended at any level with petroleum diesel to create a biodiesel blend such as B5 (petroleum diesel 95% + biodiesel 5%). It can be used in diesel engines. Biodiesel is biodegradable, nontoxic, and essentially free of sulfur and aromatics.

### Types of biodiesel

1) virgin oils or waste oils from vegetable oil such as coconut oil, palm oil, soy bean oil, rapeseed oil and animal fats without adding any chemical. This type can be used directly with diesel engine, especially the engine with low speed such as agricultural diesel engine.

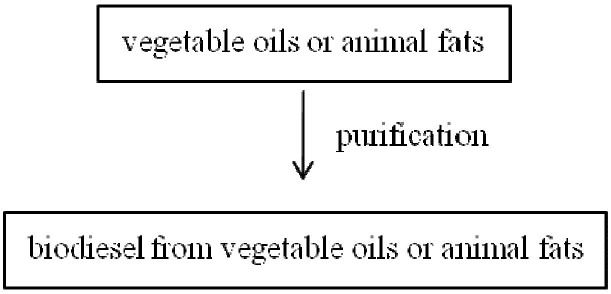


**Figure 2.7** The process of biodiesel from vegetable oils or animal fats.

2) biodiesel blends with petroleum diesel. This type is derived from petroleum diesel and biodiesel from type one in different ratios to obtain properties nearly to petroleum diesel such as coco-diesel, the blends of coconut oil and petroleum diesel; palm-diesel, the blend of palm oil and petroleum diesel.

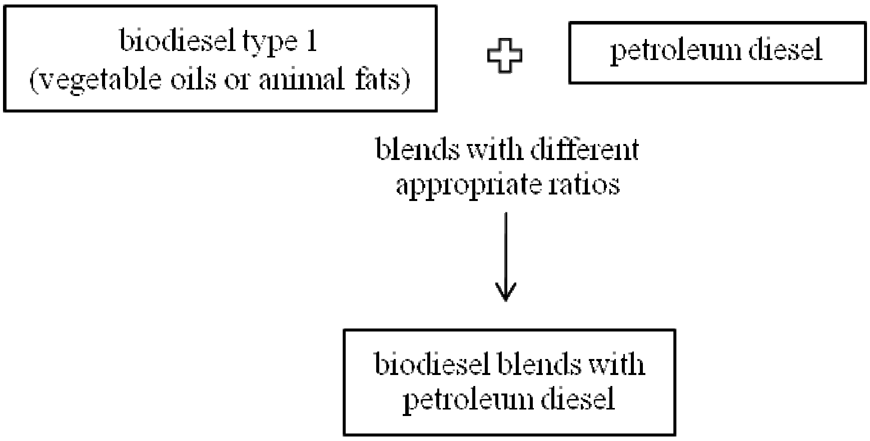


**Figure 2.8** The process of biodiesel from biodiesel blend with petroleum diesel.

3) methyl or ethyl ester biodiesel. This type of biodiesel is produced through either transesterification or alcoholysis. The process involves reacting vegetable oils or animal fats catalytically with a short-chain aliphatic alcohols (typically methanol or ethanol).

**Steps in the process:**

- pretreatment, if waste vegetable oil (WVO) is used, it is filtered to remove dirt, charred food, and other non-oil material often found. Water is removed because its presence causes the triglycerides to hydrolyze, giving salts of the fatty acids (soaps) instead of undergoing transesterification to give biodiesel.
- treatment of free fatty acids, a sample of the cleaned feedstock oil is titrated with a standardized base solution in order to determine the concentration of free fatty acids.
- reactions, while adding the base, the calculated quantity of base is added slowly to the alcohol and it is stirred until in reactor it dissolves.

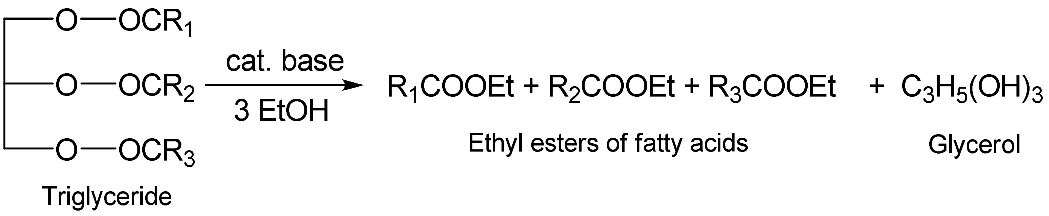


**Figure 2.9** The reaction for transesterification of producing biodiesel.

- purification, products of the reaction include not only biodiesel, but also byproducts, soap, glycerin, excess alcohol, and trace amounts of water. All of these byproducts must be removed, though the order of removal is process-dependent.
- product quality, prior to use as a commercial fuel, the finished biodiesel must be analyzed using sophisticated analytical equipment to ensure it meets any required specifications operations in diesel engine (http://en.wikipedia.org/wiki/Biodiesel).

### 2.5 Exhaust of Diesel Engine

Exhaust gas is emitted as a result of the incomplete combustion of fuels such as natural gas, gasoline, diesel, fuel oil or coal. It is discharged into the atmosphere through an exhaust pipe, flue gas stack or propelling nozzle. Although the largest part of most combustion gases is relatively harmless nitrogen ($N_2$), water vapor ($H_2O$) and carbon dioxide ($CO_2$), a relatively small part of it is undesirable noxious or toxic substances, such as carbon monoxide (CO), polynuclear hydrocarbons, nitrogen oxides ($NO_x$), partly unburnt fuel, and particulate matters. In diesel engines, different form in a spark-ignition engine (gasoline engine), power is controlled by controlling the fuel supply directly, not by controlling the air supply. As a result, when the engine is running at low power, there is enough oxygen present to burn the fuel, and diesel engines only make significant amounts of carbon monoxide when running under load. The following list contains the identified chemicals emitted from diesel engine.

**Table 2.1** The identified chemical compounds emitted from diesel engine. (http://en.wikipedia.org/wiki/Diesel_exhaust_air_contaminants).

| Contaminant | Note |
|---|---|
| acetaldehyde | IARC Group 2B carcinogens |
| acrolein | IARC Group 3 carcinogens |
| aniline | IARC Group 3 carcinogens |
| antimony compounds | Toxicity similar to arsenic poisoning |
| arsenic | IARC Group 1 Carcinogens, endocrine disruptor |
| benzene | IARC Group 1 Carcinogens |
| beryllium compounds | IARC Group 1 Carcinogens |
| biphenyl | It has mild toxicity. |
| bis(2-ethylhexyl)phthalate | Endocrine disruptor |
| 1,3-butadiene | IARC Group 2A carcinogens |
| cadmium | IARC Group 1 Carcinogens, endocrine disruptor |
| chlorine | Chlorine is a toxic gas that irritates the respiratory system. |
| chlorobenzene | It has "low to moderate" toxicity. |
| chromium compounds | IARC Group 3 carcinogens |
| cobalt compounds | higher levels of exposure similar to nickel |
| cresol isomers | - |
| cyanide compounds | Cyanide is an inhibitor of the enzyme cytochrome oxidase |
| dibutyl phthalate | Endocrine disruptor |
| 1,8-dinitropyrene | Carcinogen |
| dioxins and dibenzofurans | Dioxin causes a wide variety of toxic effects |
| ethyl benzene | Exposure to high levels can cause eye and throat irritation |
| formaldehyde | IARC Group 1 Carcinogens |
| inorganic lead | Endocrine disruptor |
| manganese compounds | - |
| mercury compounds | IARC Group 3 carcinogens |
| methanol | It may cause blindness. |
| methyl ethyl ketone | It may cause birth defect. |
| naphthalene | IARC Group 2B carcinogens |
| nickel | IARC Group 2B carcinogens |
| 3-nitrobenzanthrone | One of the strongest carcinogens known |
| 4-nitrobiphenyl | The substance is toxic to aquatic organisms. |
| phenol | Endocrine disruptor |
| phosphorus | Phosphate can cause health problems such as kidney damage and osteoporosis |

| | |
|---|---|
| polycyclic organic matter, including polycyclic aromatic hydrocarbons (PAHs) | PAHs is a very carcinogenic, mutagenic and teratogenic |
| propionaldehyde | Harmful if swallowed or inhaled and in contact with skin. |
| selenium compounds | IARC Group 3 carcinogens |
| styrene | IARC Group 2B carcinogens |
| toluene | IARC Group 3 carcinogens |
| xylene isomers and mixtures, o-xylenes, m-xylenes, p-xylenes | IARC Group 3 carcinogens |

## 2.6 Pollutions of Biodiesel

Biodiesel is the alternative fuel. It is necessary to have a complete evaluation of emission results and potential health effects from the biodiesel combustion. Biodiesel can reduce the emission of particulates by as much as 20 percent compared with low-sulfur (<50 ppm) diesel (Knother et al., 2005). Particulate emissions as the result of production are reduced by around 50 percent compared with fossil-sourced diesel. Biodiesel has a higher cetane rating than petroleum diesel, which can improve performance and clean up emissions compared to crude petro-diesel (with cetane lower than 40). Biodiesel is estimated to produce about 10% more nitrogen oxide $NO_x$ tailpipe-emissions than petroleum diesel. However, modern diesel engines already use exhaust aftertreatment and EGR (exhaust gas recirculation) to reduce $NO_x$ emissions.

**Biodiesel emissions:** (http://www.hempcar.org/petvshemp.shtml)

Biodiesel emissions have been found to contain very low amounts of unburnt hydrocarbons and particulate material than mineral oil emissions. The presence of unburnt hydrocarbons usually shows how much of the fuel has actually been utilized. Reduction of the same means that, with the use of biodiesel the fuel utilisation quotient is higher and very minimum amount of fuel is being wasted in the form of unburnt hydrocarbon. Thus in terms of fuel utilisation too biodiesel is one step ahead. Further, particulate matter that is ejected with emissions and is extremely harmful to humans is also drastically reduced in biodiesel emissions.

- the ozone (smog) forming potential of biodiesel hydrocarbons is less than diesel fuel.
- sulfur emissions (components of acid rain) are essentially eliminated with pure biodiesel (B100).
- criteria pollutants are reduced with biodiesel use. Tests show the use of biodiesel in diesel engines results in substantial reductions of unburned hydrocarbons, carbon monoxide, and particulate matter. Emissions of nitrogen oxides stay the same or are slightly increased.
- carbon monoxide. The exhaust emissions of carbon monoxide from biodiesel are lower than carbon monoxide emissions from diesel.
- particulate matter. Breathing particulate has been shown to be a human health hazard. The exhaust emissions of particulate matter from biodiesel are lower than overall particulate matter emissions from diesel.
- hydrocarbons. The exhaust emissions of total hydrocarbons (a contributing factor in the localized formation of smog and ozone) are lower for biodiesel than diesel fuel.
- nitrogen oxides. $NO_x$ emissions from biodiesel increase or decrease depending on the engine family and testing procedures. However, biodiesel’s lack of sulfur allows the use of $NO_x$ control technologies such as catalytic converters that cannot be used with conventional diesel.
- biodiesel reduces the health risks associated with petroleum diesel. Biodiesel emissions show decreased levels of polycyclic aromatic hydrocarbons (PAHs) and nitrated polycyclic aromatic hydrocarbons (nPAHs), which have been identified as potential cancer causing compounds.

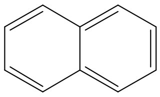
## 2.7 Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are a group of hydrocarbon compounds containing fused aromatic rings with synonyms polynuclear aromatic hydrocarbons, arenes, or polyarenes. PAH can be formed mainly as a result of incomplete combustion (pyrolysis) or high temperature pyrolytic process during combustion of fossil fuels/organic materials, as well as in natural processes such as carbonization (pyrosynthesis). Thus, PAHs are the constituents of the products of incomplete combustion (PIC). PAHs on reaction with other atmospheric pollutants viz., $NO_x$, $SO_2$, $O_2$, etc. may form hetro-PAHs. The carcinogenecity and mutagencity of many of these hetero-PAHs compounds is greater than their parent compounds.

Submicron aerosol has a half life of about 5-30 days in the atmosphere thus particulate-laden PAHs may be transported and deposited at other surface in very remote region at highly reduced concentration as a result of the effects of atmospheric dispersion and chemical reaction. They can be transported from air to soil and water via physical processes involving impaction surfaces, gravitational settling and scavenging by rain and snow. Transfer rates are also highly sensitive to particle size. The physical removal or transport of airborne particles is a function of the particles size and meteorological conditions. The occurrence of some PAH in remote areas such as arctic and marine atmospheres was mainly by aerial transport from distant anthropogenic sources. A number of research workers have demonstrated that many PAHs are susceptible to photo chemical and or chemical oxidation under simulated atmospheric conditions.

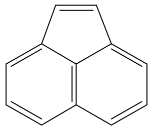
There are 1896 possible structures for PAHs containing two to eight aromatic rings. Chemical transformation of PAHs in the environment results in the formation of homocyclic and heterocyclic derivatives of PAHs containing nitrogen, oxygen, or sulfur atoms. When combined with PAHs, this larger group of aromatic compounds are referred to polyaromatic compounds (PACs). Fig. 2.10 shows the molecular structures of the sixteen PAHs or EPA16, which have been designated by the United States Environmental Protection Agency (USEPA) as priority pollutants.

Anthropogenic input of PACs to the environment stems from incomplete combustion of fossil fuels, waste incineration, and industrial operations, such as coke oven and aluminum smelter operations. PAHs are also produced when foods, especially meats, are cooked at high temperatures by smoking, roasting, or grilling. Leachate from oil and coal products, including asphalt and creosote, used as a wood preservative, can contain high level of PAHs. Except for spills and leaching, anthropogenic PAHs enter the environment as air pollutants and are transported over time in to water, soil, sediments, and biota. Forest fires, volcanic eruptions, and soil diagenesis (primarily perylene) are the greatest natural source of PACs.



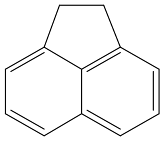
Naphthalene

(Nap)



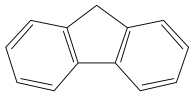
Acenaphthylene

(Act)



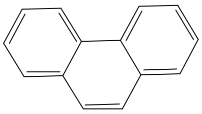
Acenaphthene

(Ace)



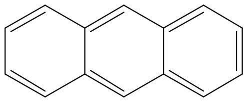
Fluorene

(Fle)



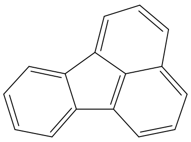
Phenanthrene

(Phe)



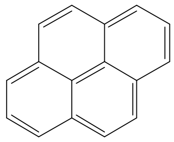
Anthracene

(Ant)



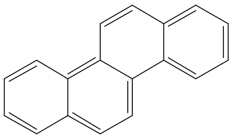
Fluoranthene

(Flu)



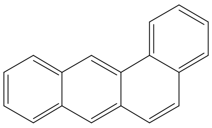
Pyrene

(Pyr)



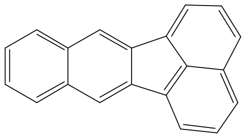
Chrysene

(Chr)



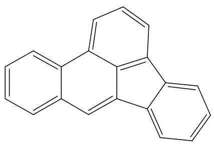
Benz(a)anthracene

(BaA)



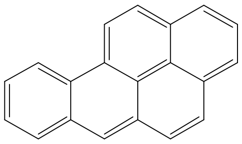
Benzo(k)fluoranthene

(BkF)



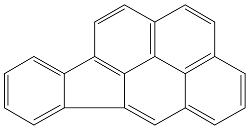
Benzo(b)fluoranthene

(BbF)



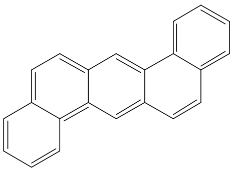
Benzo(a)pyrene

(BaP)



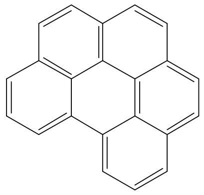
Indeno(1,2,3cd)pyrene

(IDP)



Dibenzo(a,h)anthracene

(DBA)



Benzo(g,h,i)perylene

(BghiPe)

**Figure 2.10** Structures of sixteen PAH compounds ($EPA_{16}$).

The physical properties of selected PAHs is shown in Table 2.2. The vapor pressure of PAHs decreases over 11 orders of magnitude as the number of fused rings increases from two to seven order. Because of naphthalene's high vapor pressure, it tends to partition to a greater degree into the vapor phase in the environment. Larger PAHs (3- and 4-rings) will partition between the gaseous and solid phases in the environment. PAHs with five or more aromatic rings are found almost exclusively associated with particulate or solid phases. Water solubility of PAHs with two to six-rings decreases over five orders of magnitude with increasing molecular weight. Therefore, 2- and 3-ring PAHs are more likely to be found in aquatic environments, in dissolved organic matter (DOM), and in solid phases such as soot. The tendency of PAHs to accumulate in soil, sediments, and biota also increases with the size of the molecule. Since chromatographic separations are primarily based on differences in physical properties, the considerable variability described above for PAHs makes sampling, sample preparation, and especially analysis challenging. When several PAHs are measured as a group, a single sample collection, extraction or analysis method may not be adequate. This is further complicated when the more polar derivatives of PAHs are added to the list of compound to be analyzed.

PAH concentrations in various envious environmental compartments depend on the proximity of emission source, meteorological conditions, seasons, and the physical properties of the compounds themselves.

**Table 2.2** Physical Properties of selected PAHs.

| Compound | Abbreviation | MW (g mol$^{-1}$) | MP (°C) | BP (°C) | VP (Pa) | S (g m$^{-3}$) |
|---|---|---|---|---|---|---|
| Naphthalene | Nap | 128 | 81 | 218 | 10.4 | 31 |
| Acenaphthene | Ace | 152 | 96 | 278 | 3x10$^{-1}$ | 38 |
| Acenaphthylene | Act | 154 | 92 | 265 | 9x10$^{-2}$ | 16 |
| Fluorene | Fle | 166 | 116 | 295 | 9x10$^{-2}$ | 1.9 |
| Anthracene | Ant | 178 | 216 | 340 | 1x10$^{-3}$ | 0.045 |
| Phenanthrene | Phe | 178 | 101 | 339 | 2x10$^{-2}$ | 1.1 |
| Fluoranthene | Flu | 202 | 111 | 375 | 1.2x10$^{-3}$ | 0.26 |
| Pyrene | Pyr | 202 | 156 | 360 | 6x10$^{-4}$ | 0.13 |
| Benz[a]anthracene | BaA | 228 | 160 | 435 | 2.8x10$^{-5}$ | 0.011 |
| Chrysene | Chr | 228 | 255 | 448 | 5.7x10$^{-7}$ | - |
| Benzo[b]fluoranthene | BbF | 252 | 168 | 481 |  | 0.0015 |
| Benzo[k]fluoranthene | BkF | 252 | 217 | 481 | 5.2x10$^{-8}$ | 0.0008 |
| Benzo[a]pyrence | BaP | 252 | 175 | 495 | 7x10$^{-7}$ | 0.0038 |
| Indeno[1,2,3-cd]pyrene | IDP | 276 | 164 | 536 | - | 0.00019 |
| Benzo[ghi]Perylene | BghiPe | 276 | 277 | - | - | 0.00026 |
| Dibenz[a,h]anthracene | DBA | 278 | 267 | 524 | 3.7x10$^{-10}$ | 0.0006 |

Note: MW = molecular weight, MP = melting point, BP = boling point, VP = vapor pressure of the solid, S = water solubility (Leo, 2006).

PAHs are generally unreactive and have low acute toxicities, but degraded and biotransformed products of PAHs can be very potent mutagens and carcinogens. PAHs may induce cancer of the lungs, bladder, and skin. Several PAHs have been classified by the International Agency for Research on Cancer (IARC) as probable human carcinogens. Exposure to high levels of PAHs has been shown to produce immunosuppressive effects.

PAHs require metabolic activation to produce their mutagenic or carcinogenic effects. The primary mechanism of PAH biotransformation in higher organisms is by cytochrome P450-based monooxygenases leading to detoxification and excretion. However, an attack by cytochrome P4501A1 can activate certain PAHs, such as BaP to form a mutagenic diol epoxide capable of forming DNA adducts. The carcinogenesis of nitro-PAHs involves ring oxidation and nitro-reduction to form N-hydroxyamino-PAH intermediates that can bind with DNA. The formation of hydroxyl-PAH metabolites allows PAHs to be excreted by higher organisms. PAHs can be bioconcentrated or bioaccumulated in aquatic invertebrates such as mollusks that do not posses the ability for their biotransformation, while fish can effectively biotransform PAHs, preventing biomagnification up the food chain.

### Regulations

There are no specific regulations limiting PAH levels or emissions in the atmosphere, although USEPA and the EU have set limits on the amount of particulate matter (PM) in ambient air. This provides indirect regulations for PAHs, since most are so strongly associated with atmospheric particles. The EU Working Group on Polycyclic Aromatic Hydrocarbon is currently assessing the need for a PAH atmospheric monitoring program. The U.K. Expert Panel on Air Quality Standards (EPAQS) has recommended an annual of 0.25 ng $m^{-3}$ using BaP as a marker (Lerde et al., 2009). The Occupational Safety and Health Administration (OSHA) set a limit of 0.2 milligrams of PAHs per cubic meter of air (0.2 mg $m^{-3}$) (http://www.osha.gov/). The OSHA Permissible Exposure Limit (PEL) for mineral oil mist that contains PAHs is 5 mg $m^{-3}$ averaged over an 8-hour exposure period (http://www.osha.gov/). The National Institute for Occupational Safety and Health (NIOSH) recommends that the average workplace air levels for coal tar products not exceed 0.1 mg $m^{-3}$ for a 10-hour workday, within a 40-hour workweek.

Risk assessment for PAHs is complicated by a lack of understanding of the cancer potency of PAH mixtures. Toxicity equivalency factors (TEFs) have been determined for many PAHs relative to BaP. The concentration of PAH x TEF for each individual PAH gives a concentration known as the BaP equivalent. Since the background level of PAH is generally below 1 mg $kg^{-1}$ for most rural sites, USEPA remediation goals are usually set at that level for BaP equivalents, and 10 mg $kg^{-1}$ for industrial sites or well-vegetated areas, where human contact with soil is less likely (Leo, 2006). The NIOSH has set exposure limits for Nap, Phe, Ant, Pyr, Chr, BbF and

BaP of 50, 0.1, 0.2, 0.1, 0.2, 0.1 and 0.1 mg $m^{-3}$, respectively, in ambient air (Buratti et al., 2007). For in sewage sludge to be spread on agricultural land, the EU has set limits for Flu, BbF, and BaP of 5, 2.5, and 2 mg $kg^{-1}$, respectively (Leo, 2006).

# CHAPTER 3
# EXPERIMENT

The main objective of the present work is to study the characteristics of particulate matters (PMs) and associated polycyclic aromatic hydrocarbons (PAHs) from emission of the agricultural diesel engine fueled by palm oil blends, in comparison to commercial petroleum diesel. The experimental method was designed to analyze the evolution of concentration, size distribution and chemical components especially the carcinogenic and mutagenic PAHs associated with the particulate matters, especially PM1.

## 3.1 Chemicals

### 3.1.1 Standard chemical

The standard PAHs used in the analyses are EPA 610 Polycyclic Aromatic Hydrocarbons Mix (certified solution with purity 95.9% - 99.9%, Supelco, USA):

Acenaphthene : 1000 µg $mL^{-1}$
Acenaphthylene : 2000 µg $mL^{-1}$
Anthracene : 100.2 µg $mL^{-1}$
Benz (a) anthracene : 99.9 µg $mL^{-1}$
Benzo (a) pyrene : 100.1 µg $mL^{-1}$
Benzo (b) fluoranthene : 200.0 µg $mL^{-1}$
Benzo ( g, h, i) perylene : 199.9 µg $mL^{-1}$
Benzo (k) fluoranthene : 99.9 µg $mL^{-1}$
Chrysene : 100.2 µg $mL^{-1}$
Dibenz (a,h) anthracene : 199.9 µg $mL^{-1}$
Fluoranthene : 200.0 µg $mL^{-1}$
Fluorene : 200.1 µg $mL^{-1}$
Indeno (1, 2, 3-cd) pyrene : 100.1 µg $mL^{-1}$

Naphthalene : 1000 $\mu g\ mL^{-1}$
Phenanthrene : 100.1 $\mu g\ mL^{-1}$
Pyrene : 99.9 $\mu g\ mL^{-1}$

### 3.1.2 Chemicals for PAH extraction

In an extraction of PAHs, the following chemicals including grade and manufacture are used:

Acetonitrile (HPLC grade, Lab-scan, Thailand)
Dichloromethane (HPLC grade, Lab-scan, Thailand)
Dimethylsulphoxide (HPLC grade, Lab-scan, Thailand)

### 3.1.3 Chemicals for HPLC assay

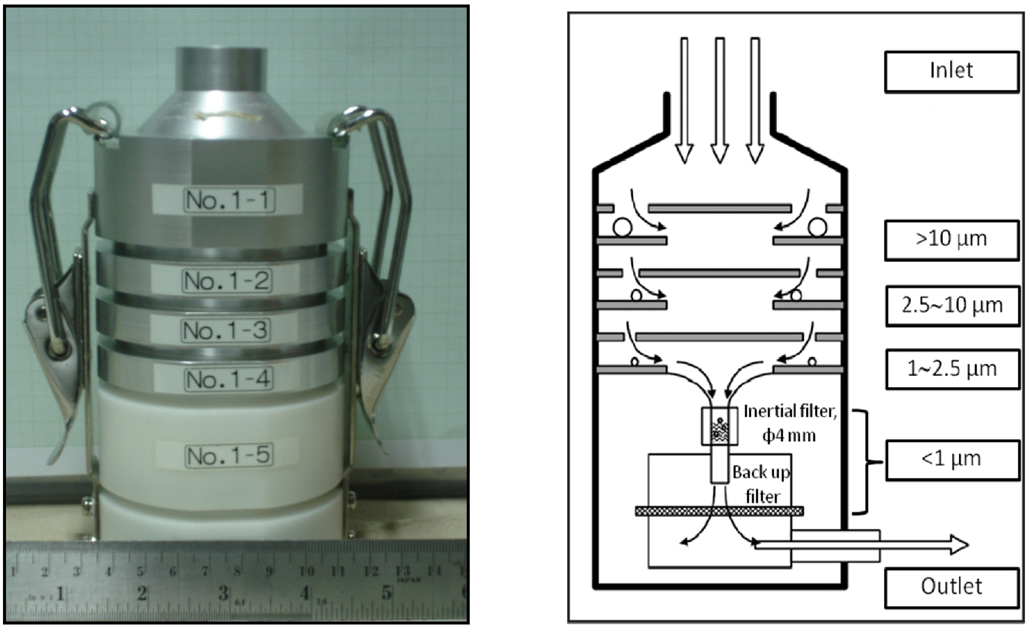
Chemicals used in HPLC analyses including grade and manufacture are as follows:

Ultra pure water (de-ionized with reverse osmosis system and purified with a Maxima ultrapure water instrument to obtain the resistivity of 18.2 MΩ, ELGA, England)
Acetonitrile (HPLC grade, Lab-scan, Thailand)

## 3.2 Instrumentation

### 3.2.1 Sampler

In order to assess the health effect of these particles, the primary work is to determine the chemical compositions of particles with respect to particle size because inhaled particles are deposited in different regions of the lung depending on the particle size. To determine the size distribution of PM from emission of an agricultural diesel engine using different blend ratio fuels, the particles were collected and size-fractionated by the particulate matter air sampler, as shown in Fig. 3.1. The sampler employs impaction in particle collection in the first three-stage impactors, inertial filtration in the fourth stage using an inertial filter (Otani et al., 2007) combined with a back-up filter. The 50% cut-off aerodynamic diameters of for the first 3 stages are 10, 2.5 and 1.0 µm, while the last stage collects all particles smaller than 1.0 µm. The sampler was designed to operate at a flow rate of 40 L $min^{-1}$, which allows both the sufficiently fast sampling of atmospheric PMs and portability as a field sampling device. The advantage of the sampler is that the sampling flow rate can be readily changed, depending on the needs in the field. This will, of course, result in a change in the cut-off diameters in all stages. The particles were collected on quartz fiber filters. Donut-shape filters with 65x30 mm diameter were used in the first three impaction stages, and a 47 mm diameter filter was used in the backup stage. For the stage above the backup filter, 8 mm thick stainless steel fiber mat with fiber diameter of 8 µm and packing density of 0.0065. The inertial filter was designed so that the webbed stainless steel fibers were packed on a support of stainless steel wires in a plastic holder (polyoxymethylene, POM), and the holder was placed in the throat of the nozzle. The adoption of a filter holder facilitates the handling of samples and it can be easily replaced with a new holder on site without directly touching the fibers. The filter holder can be reused after cleaning and are also disposable (Otani et al., 2007). The reason to combine the particles collected on the last two stages, inertial filter and back-up filter, is that the cut-off diameter for the inertial filter was not sharp enogh during the experiment.



(a) (b)

**Figure 3.1** The particulate matter air sampler (Kanomax, Japan): (a) a photograph, and (b) a schematic diagram indicating the cut-off diameters.

### 3.2.2 Apparatus used for dilution air system

A purpose of a dilution system is to lower the concentration of a given aerosol while leaving the particle size distribution unchanged. This is necessary because original concentration of the exhaust aerosol from engine combustion is very high. In addition, the exhaust gas contains a high degree of moisture which can largely affect the sampled aerosol characteristics. In this work a commercial aerosol dilutor (Palas, VKL-10) with a dilution ratio of 10 was used to homogeneously mix a definite amount of clean air with a definite amount of aerosol. The external clean air flows through an ejector-nozzle system. This causes an under-pressure which sucks in the aerosol. Consequently, the dilution stage is a self-sucking system.

Figure 3.2 shows a cross-section of the dilution stage. Particle-free air with a volume flow rate $V_r$ determined by the pre-pressure $p$, flows through an annular slit around the inlet nozzle. The resulting under-pressure $dp_0$ causes the aerosol which is to be diluted, to be pulled in and to be mixed with clean air in the mixing chamber. If the clean air flow rate is increased, the flow speed within the annular nozzle increases correspondingly. This causes, according to Bernoulli equation, the under-pressure $dp_0$ at the inlet nozzle to increase, and the flow rate increases, too. Both flow rates are connected through the under-pressure, and equally depend on it. Consequently, the ratio of the flow rates remains constant for different pre-pressure.

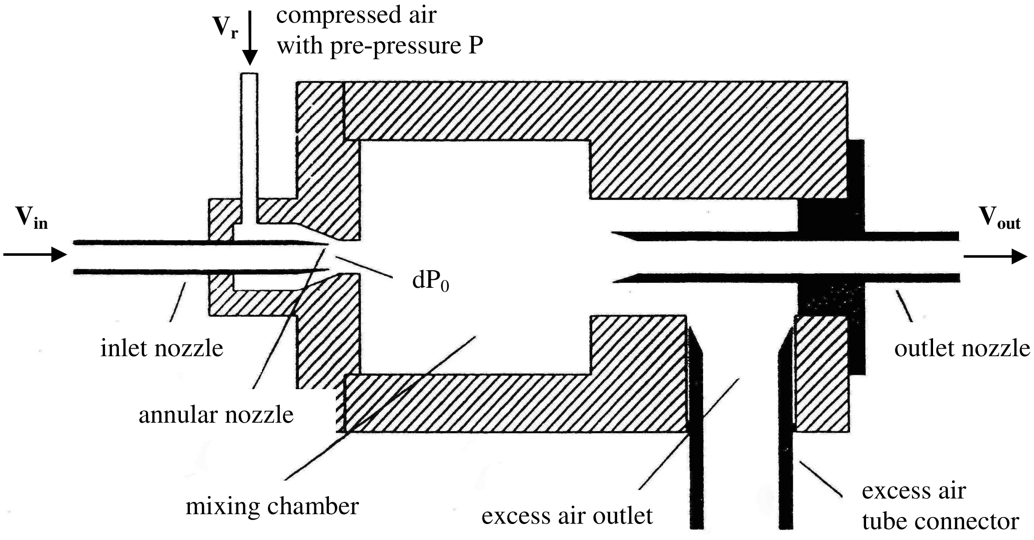


**Figure 3.2** Cross section of dilution stage.

### 3.2.3 Engine dynamometer

Ltd., ETB 1244 (Engineers Workingham Berks, England)

#### General description

A 12-horsepower hydraulic dynamometer (Plint&Partners, ETB 1244) was used for measuring force, moment of force (torque), or power. The power produced by an engine, motor or other rotating prime mover can be calculated by simultaneously measuring torque and rotational speed (rpm). The dynamometer bed has supports which can be adjusted to take up different sizes of engine.

### 3.2.4 Apparatus used for measure the rotation speed of the motor

The rotation speed of a motor shaft was measured by a tachometer (Digicon, DT-240P).

### 3.2.5 Fuels

Fuels used in this study are commercial petroleum diesel (PB0) and two different blending mixtures of PB0 with palm oil (PB100) of volumetric percentages 30% and 40%, namely PB30 and PB40 respectively. Before blending with PB0, PB100 was degummed by phosphoric acid and deacidified by neutralizing with sodium hydroxide to reduced free fatty acid to less than 1%. The petroleum diesel and palm oil blends are supplied by department of mechanical engineering, faculty of engineering, Prince of Songkla University, Hat Yai, Songkhla, Thailand. The fuel properties of PB0 and PB100, listed in Table 3.1, are determined according to related ASTM standard methods.

**Table 3.1** Fuel properties of PB0 and PB100 (Prateepchaikul et al., 2003).

| Fuel properties | PB0 | PB100 | Method |
|---|---|---|---|
| Flash point ($^{o}$C) | 102 | 135 | ASTM-D93 |
| Viscosity at 40 $^{o}$C (cSt) | 3.013 | 50.35 | ASTM-D445 |
| Density (g mL$^{-1}$ at 15 $^{o}$C) | 0.833 | 0.880 | ASTM-D1298 |
| Cloud point ($^{o}$C) | 3 | 8 | ASTM-D2500 |
| Pour point ($^{o}$C) | 4 | 11 | ASTM-D97 |
| Water (%wt) | 0.078 | 0.218 | ASTM-D721 |
| Copper Strip Corrosion | 1b | 1b | ASTM-D130 |
| Cetane Number | NA | 50 | ASTM D-613 |
| Carbon residue (wt%) | <0.001 | 0.217 | ASTM D-4530 |
| Ash (wt%) | NA | 0.001 | ASTM D-482 |
| Distillation temp ($^{o}$C) | NA | 319 | ASTM D-86 |
| High heating value (MJ kg$^{-1}$) | 44.3 | 41.7 | ASTM D-240 |

NA: Not Available, 1b: satisfaction

### 3.2.6 Engines

Agricultural diesel engines (Kubota, RT 80) shown in Fig. 3.3 with specifications shown in Table 3.2 are used in this work.

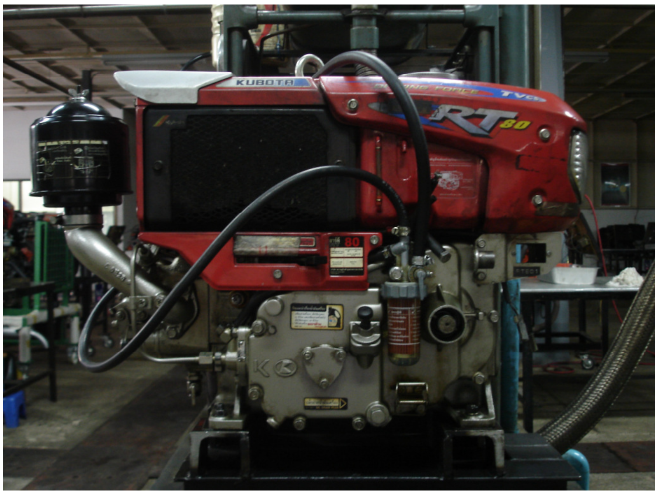


**Figure 3.3** The agricultural diesel engine used in this experiment.

**Table 3.2** Agricultural diesel engine specifications.

| Parameters | Specifications |
|---|---|
| Engine type | 4 cycle strokes, water cooled |
| Cylinder | 1 horizontal |
| Injection | Indirect injection (IDI) |
| Displacement | 465 c.c. |
| Bore x stroke | 84 x 84 mm |
| Volumetric compression ratio | 23 : 1 |
| Maximum power | 5.9 kW @ 2,400 rpm (8 HP @ 2,400 rpm) |
| Maximum torque | 2.8 kg-m @ 1,600 rpm |
| Ignition system | Compression, Spherical combustion system (swirl chamber) |
| Weight of engine | 88 kg |

### 3.2.7 Apparatus used for filter extraction

Ultrasonic bath (Tru-sweep, 2800 HT) for filter extraction.

Rotary evaporator (Buchi, R-210)

PTFE Syringe filters with pore size of 0.45 μm, diameter of 25 mm and 4 mm (Vertical, Thailand)

Filter paper No. 42 with diameter of 125 mm (Whatman, USA)

PTFE membrane disc filter with pore size of 0.45 μm and diameter of 47 mm (Vertical, Thailand)

Nylon membrane disc filter with pore size of 0.45 μm and diameter of 47 mm (Vertical, Thailand)

Disposable syringe, 3 mL (Vertical, Thailand)

Amber vial, 2 mL with polypropylene screw cap, blue and white silicone/red PTFE septa (Vertical, Thailand)

Microliter pipette : model NPX-200, 50-200 μL (Nichiryo, Japan)

General glasswares, such as round bottom flask, volumetric flask, etc.

### 3.2.8 Apparatus used for HPLC assay

High-performance liquid chromatography (Agilent, 1100) with diode array detector (HPLC-DAD) consists of a pump model 1311A (Agilent, USA), autosampler model G1313A (Agilent, USA), degasser model G1322A (Agilent, USA), photodiode array detector model G1315A (Agilent, USA), Chemstation software (Agilent, USA), and computer system (Hewlette Packard, USA). Reverse phase HPLC was performed using Vertisep C18 column (250 x 4.6 mm I.D., particle size 5 μm) with a Vertisep C18 guard column (7.5 x 4.6 mm I.D., particle size 5 μm).

## 3.3 Methods

### 3.3.1 Engine, dynamometer and operating conditions

The experiments were carried out using three identical agricultural diesel engines (Kubota, RT 80) with single cylinder and indirect injection. This type of engine has been extensively used by farmers in Thailand and also in developing countries for rice-field tillage by operating with tractor or wheel plough. In addition, it has been modified to use for adding oxygen to water in giant tiger prawn farms. The engine was operated with a 12-horsepower dynamometer (Plint&Partners, ETB 1244). A tachometer (Digicon, DT-240P) was used to measure the engine speed within the range of 5-100,000 rpm and the resolution of 1 rpm.

Before each PM sampling, the engine was mounted on a stand and coupled with a 7.5 kW, 230 Volts, 32.6 Amps and 50 Hertz electric generator (Mindong Yanan Electric Machine) for 500 hours which was equivalent to two years for distance. The generated electricity was supplied to a series of light bulbs for adjusting engine loads. Fig. 3.4 shows the engine and the generator used for a long-term testing.

After every 500 hours of running, in which the driving cycle of the testing was in accordance with the small-size water-cooled diesel engines in land use the engine was operated on the dynamometer for 20 minutes after 10 minutes warm-up to avoid effects from residue of other fuel in the previous run (JIS B8018, 1989). The engine warm-up included an idle state of about 5 minutes until the speed of 2000 rpm was achieved. The transient cycle comprise a 75% of full load with constant speed at 2200 rpm according to a previously reported procedure (Prateepchaikul et al., 2003).

**Figure 3.4** The engine and the generator used in this work.

A dilutor (Palas, VKL 10) was used to dilute the exhaust gas at the dilution ratio of 10 prior to each sampling. The samples were collected isokinetically. Dilution air obtained from an air compressor was passed through a regulator, a laboratory gas drying unit (Drierite, USA) and a high efficiency particulate absorbing (HEPA) filter for moisture, oil and particle removal from the air stream.

### 3.3.2 Treatment of filters

Before sampling, the filters were treated in a dark desiccator at constant temperature (~25°C) and constant humidity (~50% relative humidity) for at least 72 hours. The filters were then weighed using a five-digit readability analytical balance (Sartorius, CP225D). After sampling, the filters were folded in half and separately put in a polyethylene bag and then were treated under the same conditions as before. The weight of the collected particles on each filter sample was measured using the identical analytical balance. The set of filter samples was kept together, wrapped with an aluminum foil, and then put in a polyethylene bag. All samples were stored in a refrigerator at -20°C in order to avoid evaporation and degradation of PAHs by UV until extraction before analysis.

### 3.3.3 Measurement of size distribution of particulate matters

To determine the size distribution of PM from emission of an agricultural diesel engine using different blend ratio fuels, particles were collected and size-fractionated by the particulate matter air sampler version 3.5 (Kanomax, Japan). It has 50% cut-off aerodynamic diameters of 10, 2.5 and 1.0 μm. A constant air flow rate of 40 L min$^{-1}$ was drawn by a vacuum pump, and controlled by a needle valve and a rotameter as shown in Fig. 3.5. The particles were collected on quartz fiber filtes (Pallflex, 2500QAT-UP). Donut-shape filters with 65x30 mm diameter were used in the first three impaction stages, and a 47 mm diameter circular filter was used in the backup stage. For the stage above the backup filter, 8-mm-thick stainless steel fiber mat with fiber diameter of 8 μm and packing density of 0.0065 (Otani et al., 2007) was used. Figure 3.6 shows the filters used in all stages of the particulate matter air sampler.

To determine the size distribution of particulate matters, the normalized mass fraction $(f/\Delta d)$ is plotted as a function of the average aerodynamic diameter, $d_{ave}$. Here, $f$ is the mass fraction and $\Delta d$ is the particle size interval of each stage of the particulate matter air sampler. Mass fraction ($f$) can then be determined from:

$$f = \frac{M_j}{M_{total}}$$

where $M_{total}$ is the total mass collected, calculated from:

$$M_{total} = \sum_{n=1}^{n} M_j$$

Here $M_j$ is the mass collected in each stage, which is:

$$M_j = (m_f - m_i)$$

where $m_f$ is the mass of the filter after sampling and $m_i$ is the mass of the filter before sampling.

The total mass concentration can then be calculated from:

$$Total \quad mass \quad concentration \quad = \quad \frac{M_{total}}{V_{total}}$$

Where $V_{total}$ is the total sampling volume, determined from:

$$V_{total} \quad = \quad Qt$$

Here $Q$ is the flow rate and $t$ is the sampling time.

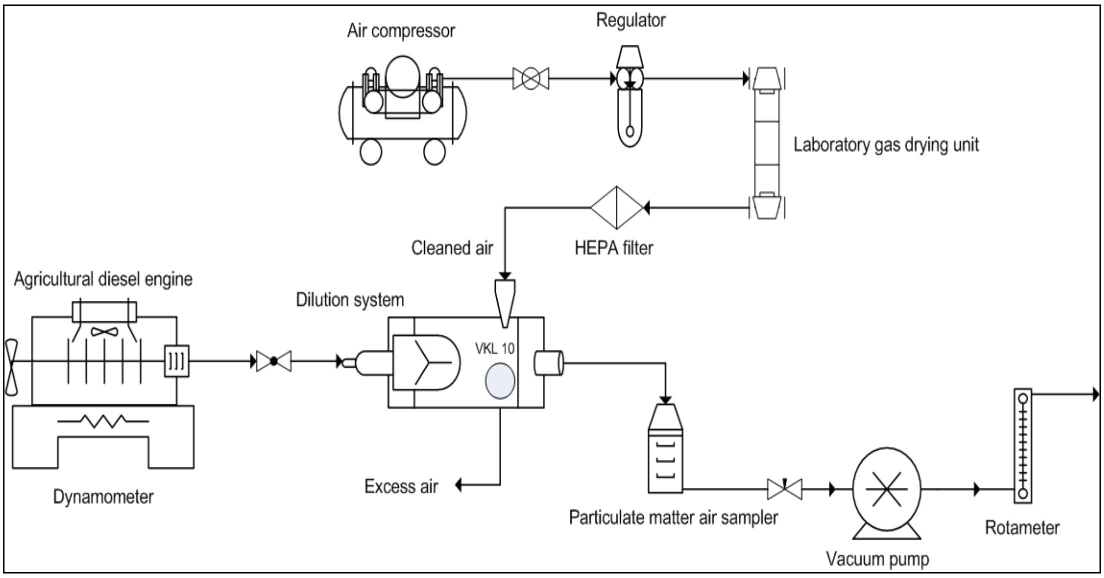


**Figure 3.5** The schematic diagram of the experimental set up for measuring the size distribution of particulate matters.

**(a)**

(b)

**Figure 3.6** Photographs of filters used in all stages of particulate matter air sampler: (a) before sampling and (b) after sampling.

### 3.3.4 Analysis of polycyclic aromatic hydrocarbons

The 16 PAH compounds were monitored including Naphthalene (Nap), Acenaphthylene (Act), Acenaphthene (Ace), Phenanthrene (Phe), Anthracene (Ant), Fluorene (Fle), Fluoranthene (Flu), Pyrene (Pyr), Benzo[a]anthracene (BaA), Chrysene (Chr), Benzo[a]pyrene (BaP), Benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene (BkF), Dibenz[a,h]anthracene (DBA), Indeno[1,2,3-cd]pyrene (IDP), and Benzo[g,h,i]perylene (BghiPe). The filters were extracted using the method modified from those of Ohura et al. (2004) and Furuuchi et al. (2006).

The filters were twice extracted ultrasonically with 40 mL of dichloromethane for 30 min each while the water in the ultrasonic bath was replaced frequently in order to prevent overheating. The extracts were combined and filtered through filter paper and PTFE syringe filter (0.45 µm) for removal of insoluble particles. After 50 µL of dimethylsulphoxide (DMSO) was added for preservation of PAHs, the elution was concentrated using a rotary evaporator (bath temperature ≤30°C) to remove the solvent. The residues were then re-dissolved with 450 µL of acetonitrile. Interfering compounds once again were removed with a 0.45 µm PTFE syringe filter. The filtrate was kept in a 1.5 mL amber glass vial and stored at 4°C in a refrigerator prior to analysis. Summary of extraction procedure is shown in Fig. 3.7. The 16 PAHs were analyzed using a high performance liquid chromatography (HPLC) with diode array detector (DAD), as shown in Fig. 3.8.

The HPLC (Agilent, 1100) with a Chemstation program was performed following methods previously used by Chomanee et al. (2009). This HPLC was used with a VertiSep UPS C 18 reversed phase column (4.6x250 mm, 5 μm) and a guard column with an injection volume of 25 μL. The system of HPLC performed using a solvent gradient elution of acetonitrile and ultra pure water within 40 min at a flow rate of 1.0-1.2 ml $min^{-1}$. The detector (DAD) was operated at a wavelength of 254 nm. The gradient and the HPLC conditions are summarized in Tables 3.3 and 3.4. The HPLC system was calibrated using external standards. The standard solutions were prepared from EPA 610 polycyclic aromatic hydrocarbons mix (Supelco, catalog No.4-8743).

The resulting chromatograms present all 16 PAH compounds, which are then identified by matching retention times with the chromatogram of the reference standards. The concentration of each PAH is quantified from the peak area. A good linear correlation between the concentration and peak areas was found with $R^2$ values in the range of 0.999-1 for all PAH compounds. Fig. 3.9 presents the HPLC chromatogram of the mixture of 16 PAH standard.

Field blank filters as well as solvent blanks were also analyzed using the same procedure to ensure that there were no significant background interferences.

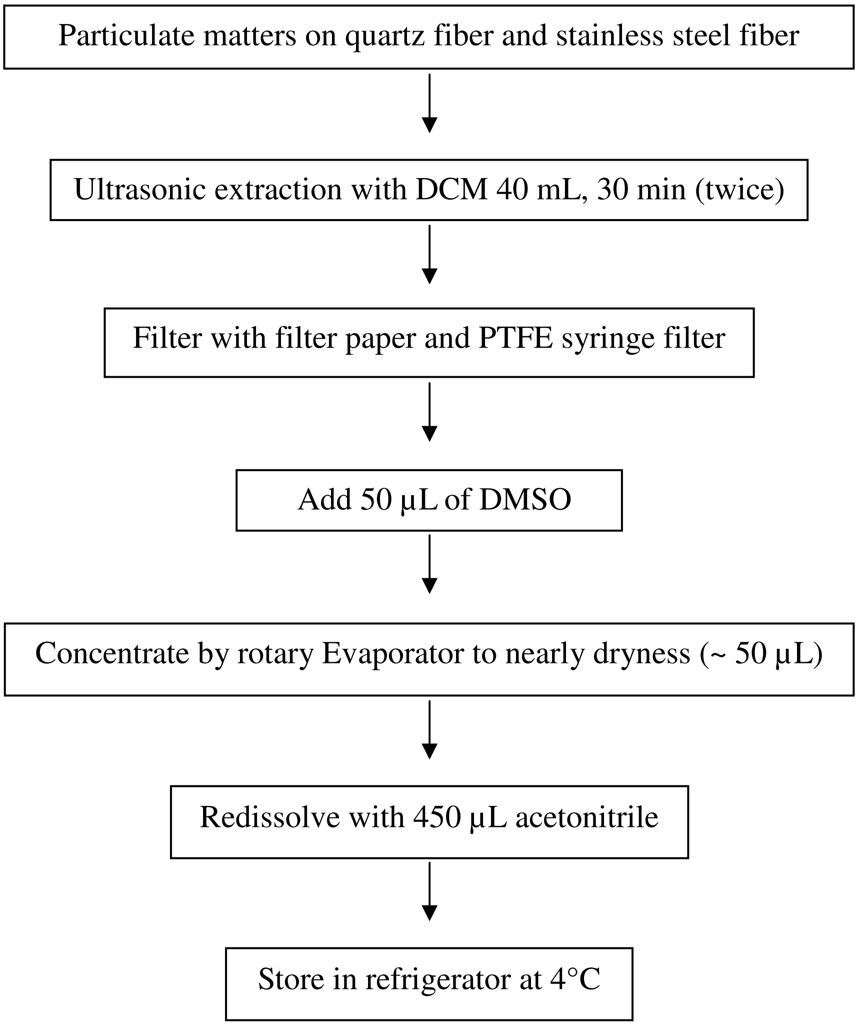


**Figure 3.7** Procedure of the sample extraction.

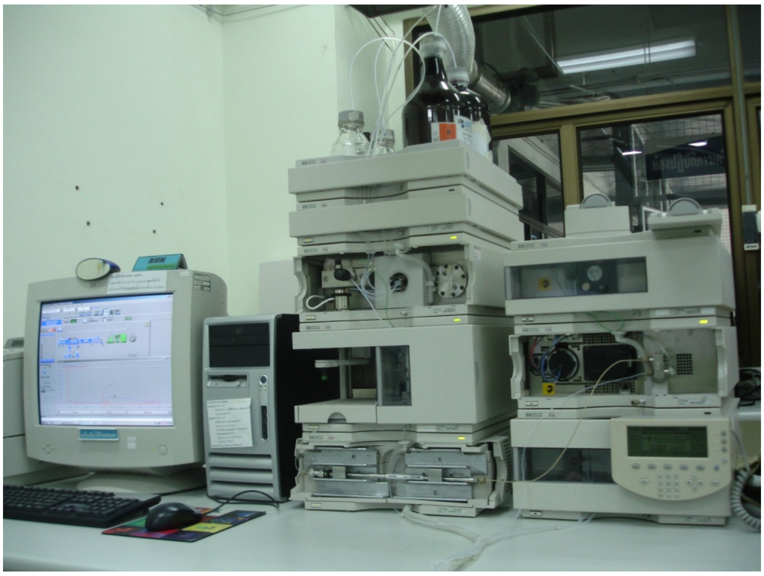


**Figure 3.8** Photograph of the HPLC/DAD system (Agilent, 1100) used for PAH analysis.

**Table 3.3** Gradient conditions used for HPLC analysis in this work.

| Time (min) | Acetonitrile (%) | Ultra pure water (%) | Flow rate (mL min$^{-1}$) |
|---|---|---|---|
| 0 | 35 | 65 | 1.0 |
| 5 | 35 | 65 | 1.0 |
| 20 | 80 | 20 | 1.0 |
| 35 | 100 | 0 | 1.2 |
| 37 | 100 | 0 | 1.2 |
| 40 | 100 | 0 | 1.0 |

**Table 3.4** HPLC conditions used in this work (Chomanee et al., 2009).

| | |
|---|---|
| Column | VertiSep UPS C18 column 4.6x250 mm, 5 µm |
| Guard | VertiSep 5 µm |
| Temperature | 25 °C |
| Mobile Phase | A : Acetonitrile<br>B : Ultra pure water |
| Inject Volume | 25 µL |
| λ for detection | 254 nm |

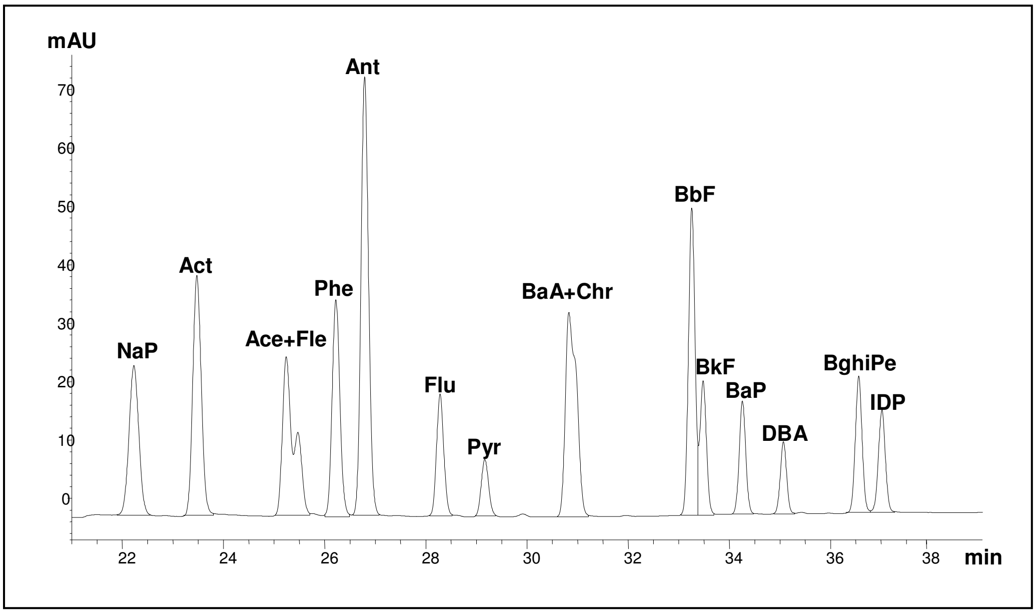


**Figure 3.9** The HPLC/DAD Chromatogram of 16 PAH standards used in this work.

### Standard solution preparation

The standard solutions for HPLC calibration were prepared from the stock solution, which was the ten-times dilution of the 16 PAHs mix standard (Supelco catalog number 4-8743). The solvent used for dilution was acetonitrile. The concentrations of each PAH in the stock solution are given in Table 3.5. Then the PAH standard solutions in the range of 0.51-10.14 µg mL$^{-1}$ Nap were prepared by diluting the stock solution with acetonitrile. Each concentration was injected into the HPLC system operated at conditions shown in Tables 3.3 and 3.4.

**Table 3.5** Concentrations of each PAH compound in the stock solution.

| **PAHs** | **Abbreviation** | **Concentration (µg mL$^{-1}$)** |
|---|---|---|
| Naphthalene | Nap | 101.4 |
| Acenaphthylene | Act | 200.6 |
| Fluorene | Fle | 20.12 |
| Acenaphthene | Ace | 101.2 |
| Phenanthrene | Phe | 10.09 |
| Anthracene | Ant | 10.10 |
| Fluoranthene | Flu | 20.20 |
| Pyrene | Pyr | 10.44 |
| Benz(a)anthracene | BaA | 9.97 |
| Chrysene | Chr | 10.18 |
| Benzo(b)fluoranthene | BbF | 20.10 |
| Benzo(k)fluoranthene | BkF | 10.32 |
| Benzo(a)pyrene | BaP | 9.76 |
| Dibenzo(a,h)anthracene | DBA | 21.46 |
| Benzo(g,h,i)perylene | BghiPe | 20.75 |
| Indeno(1,2,3-cd)pyrene | IDP | 10.56 |

### Limit of detection (LOD)

Limit of detection is considered as the lowest concentration that the diode array detector can detect and provide a signal to noise ratio (S/N) greater than or equal to 3. To determine the limit of detection, the PAH standard solutions were prepared for concentrations in the range of 0.0101-10.1400 μg $mL^{-1}$ of Nap. The detection limits of individual PAHs were below 3.9-80.2 ng $mL^{-1}$. The limit of detection for all PAHs or the concentrations of PAHs which gives a S/N of more than 3.0 are summarized in Table 3.6.

**Table 3.6** The limit of detection for individual PAHs by HPLC analysis in this study.

| **PAHs** | **Limit of detection (ng $mL^{-1}$)** |
|---|---|
| NaP | <40.56 |
| Act | <80.24 |
| Ace+Fle | <48.53 |
| Phe | <4.04 |
| Ant | <4.04 |
| Flu | <8.08 |
| Pyr | <4.18 |
| BaA+Chr | <8.06 |
| BbF | <8.04 |
| BkF | <4.13 |
| BaP | <3.90 |
| DBA | <8.58 |
| BghiPe | <8.30 |
| IDP | <4.22 |

### Recovery

The term recovery (*R*) is used to indicate the yield of an analyte in the pre-concentration or extraction stage in an analytical method. Actually, the recovery value is presented as a percent recovery (%R) and it can be calculated from equation given by (Robinson, 1987):

$$\%R = \frac{Measured\,value}{Real\,value} \times 100$$

To determine PAH recovery, the PAH standard solutions of three concentrations were prepared and spiked on blank filters using micropipette then the filters were allowed to dry in the dark desiccator for 72 hours. The spiked filters were extracted and analyzed by HPLC/DAD with the same conditions used for the samples. The results show that the recovery efficiency of PAHs varied in the range between 41-117% for each compound. The percent recovery of 16 PAHs are shown in Table 3.7.

**Table 3.7** The percent recovery for individual PAH.

| **PAHs** | **Recovery (%)** |
|---|---|
| Nap | 61.86 |
| Act | 42.50 |
| Ace+Fle | 101.77 |
| Phe | 62.38 |
| Ant | 41.03 |
| Flu | 59.29 |
| Pyr | 117.95 |
| BaA+Chr | 84.62 |
| BbF | 88.28 |
| BkF | 94.18 |
| BaP | 99.03 |
| DBA | 74.42 |
| BghiPe | 92.20 |
| IDP | 88.38 |

# CHAPTER 4

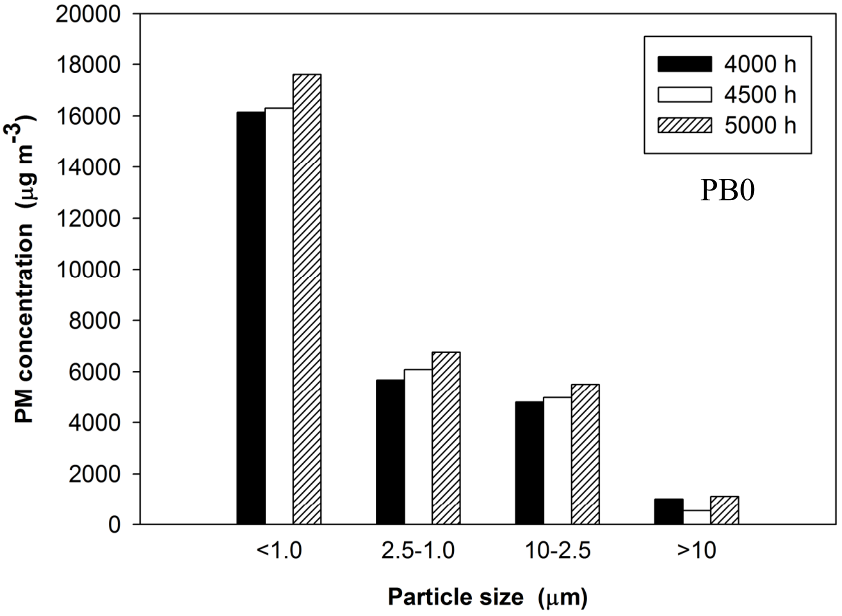
# RESULTS AND DISCUSSION

In the present work, emissions from the agricultural diesel engine using palm oil blends (PB30 and PB40) as an alternative fuel were studied in comparison to commercial petroleum diesel (PB0). Particulate Matters and the associated PAHs in diluted exhaust gas were collected by a particulate matter air sampler. Influence of the blending ratios of palm oil blends and the engine hours on the emission characteristics of PM and PAHs were investigated. Though a focus of this work is on PM 1, larger size ranges will also be included in the study.

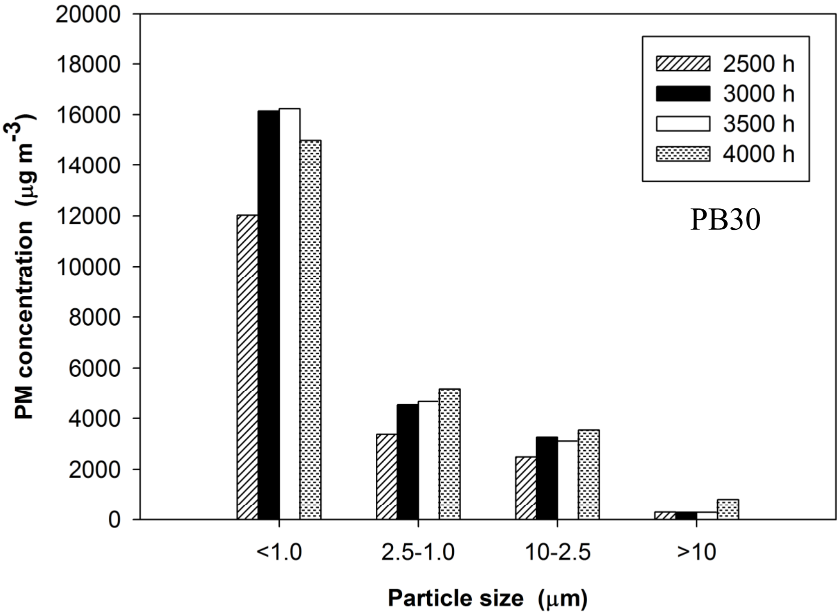
## 4.1 Characteristics of Particulate Matters from Smoke Emission

### 4.1.1 Size distribution and concentration of PMs

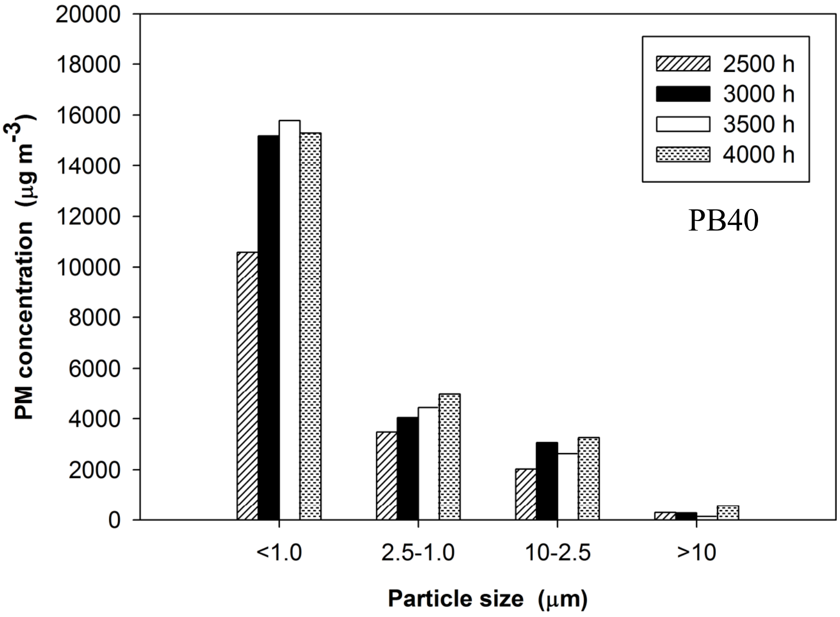
Particulate matters in exhaust gas resulted from combustion of PB0 by an agricultural diesel engine at operating times of 4000, 4500 and 5000 h. The combustion of palm oil blends (PB30 and PB40) was performed at operating times of 2500, 3000, 3500 and 4000 h. This work began when the engine was run for almost 4000 h for PB0 combustion and 2500 h for PB30 and PB40 combustion. The size distributions of PM emitted from the engine fueled by PB0, PB30 and PB40 were investigated and the results are shown in Figs. 4.1 and 4.2. Apparently for all cases, the size distributions of the PM show a unimodal behavior in the accumulation mode (<1.0 μm). In this study, it was found that most particulates amass in the <1.0 μm diameter range. These particles are carbonaceous agglomerates loaded with adsorbed matters. The particles in this mode are formed during exhaust dilution and cooling, and may also include solid carbon (Kittelsen, 1998). For every blend ratio, the PM amount of every particles size was increased when increasing the engine hours due to the erosion of the engine used (Fig. 4.1). This can generate more PM from the incomplete combustion and the mass median aerodynamic diameters (MMAD) of PM are summarized in Table 4.1. Results show that MMAD was reduced when the blending percentage of palm oil was increased from 0% to 40% while the running time was the same as shown in Fig. 4.2, similar to earlier results (Haas et al., 2001; Lapuerta et al., 2008 and Chien et al., 2009). When the engine hours were increased, MMAD was also increased because the engines using palm oil blend diesel generate the smaller fine particle PM than that of the diesel-fueled engines. Consequently, the smaller MMAD of particles from palm oil blend was achieved. The particulates smaller than 2.5 μm traverse easily through the upper respiratory tract into the bronchioles and alveoli of the lungs, and pose a direct health effect. This gives important information related to health hazards of engine exhaust.



(a)



(b)



(c)

**Figure 4.1** Size distribution of PMs from agricultural diesel engine at different running time for (a) PB0, (b) PB30, and (c) PB40.

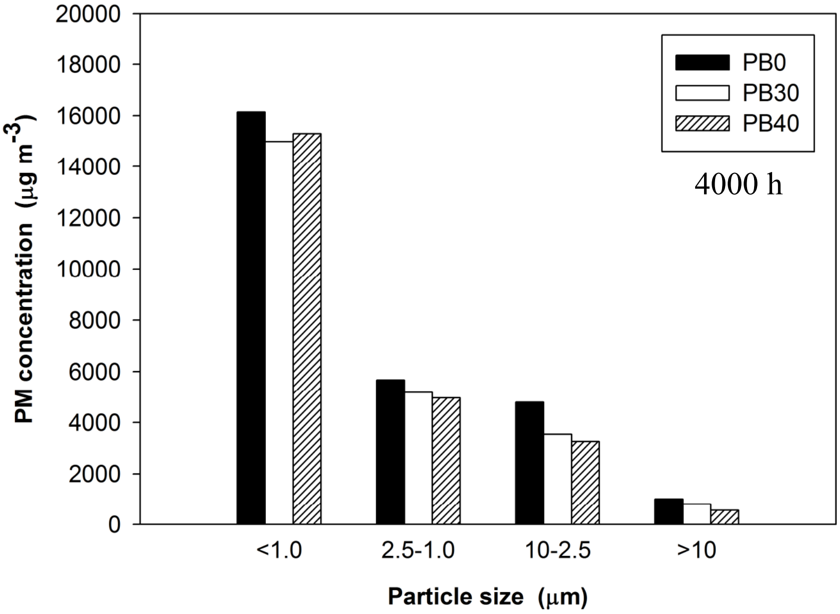


**Figure 4.2** Size distribution of PMs from agricultural diesel engine for different palm oil blend ratios at a running time of 4000 h.

**Table 4.1** MMAD determined from agricultural diesel engine at different conditions.

| Engine hour (h) | MMAD (µm) | | |
|---|---|---|---|
| | PB0 | PB30 | PB40 |
| 2500 | - | 0.606 | 0.606 |
| 3000 | - | 0.621 | 0.611 |
| 3500 | - | 0.616 | 0.621 |
| 4000 | 0.758 | 0.653 | 0.626 |
| 4500 | 0.810 | - | - |
| 5000 | 0.817 | - | - |

The total PM concentrations from agricultural diesel engines fueled by PB0, PB30 and PB40 are shown in Fig. 4.3 against operation time. The variation of concentrations of PM for PB0 was from 27616 to 31012 µg m$^{-3}$ after running for 4000 to 5000 h. The total PM concentrations were reduced when the fraction of blended palm oil is increased because palm oil blend can be more completely combusted. The total PM concentrations for PB30 were found to increase from 18181 to 24523 µg m$^{-3}$ after running for 2500 to 4000 h. PM concentrations for PB40 are lower than that for PB30 and were found to be from 16376 to 24079 µg m$^{-3}$ after running for 2500 to

4000 h. Reduction of PM emission for palm oil blend diesel can be attributed to the fact that palm oil contains no aromatic constituent in comparison to diesel (Wang et al., 2000).

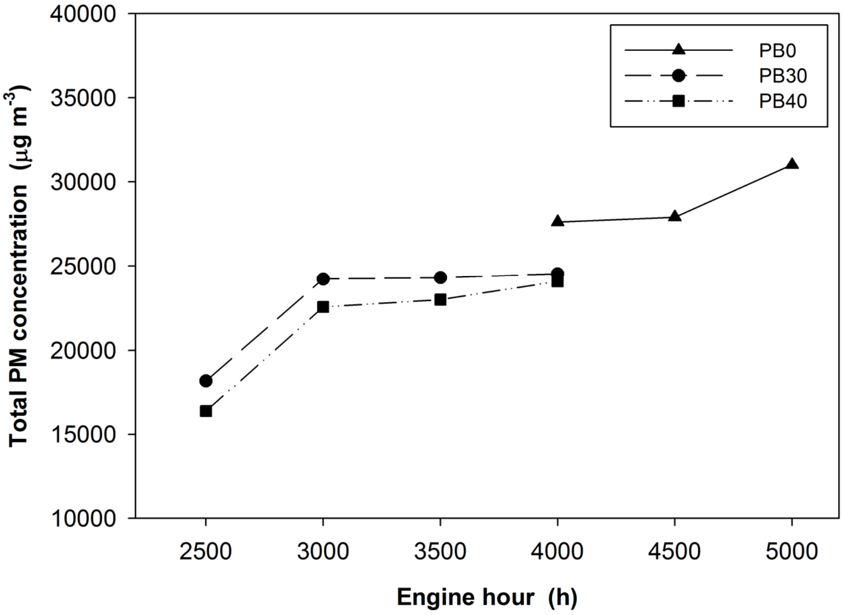


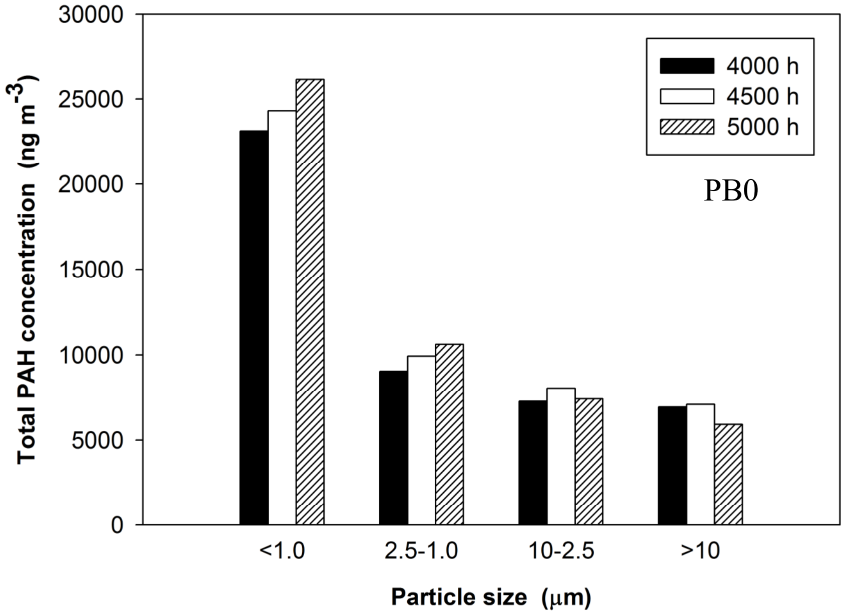
**Figure 4.3** Concentration of PMs from agricultural diesel engine using PB0, PB30 and PB40 during engine hour of 2500-5000 h.

This is a desirable result and it agrees with many previous investigations. Bagley et al. (1998) found that 65% of submicron (0.01-0.1 μm) PM concentration was reduced when using soybean-oil biodiesel in an indirect injection diesel engine. Jung et al. (2006) used pure rapeseed-oil biodiesel as fuel and found a 38% PM reduction. Turrio-Baldassrri et al. (2004) blended 20% rapeseed-oil with diesel and used it as fuel for buses. Their results indicated that most of the emitted PM was in the size range of 0.06-0.3 μm. The PM concentrations were, however, increased when the operating time of the engine was increased. This could be a result of the engine wear after running for a long period of time. This is because a large portion of PM is generated from the engine wear which can also cause the greater degree of the incomplete combustion compared to the new engine. In addition, the higher blend ratio will provide the more complete combustion according to the mentioned reason.

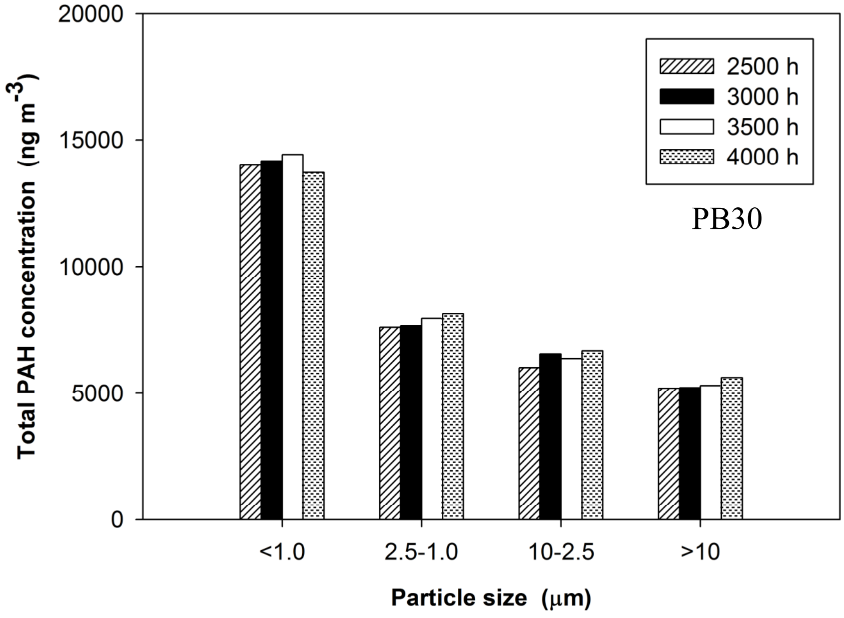
### 4.1.2 Size distribution and concentration of PAHs

The 16 PAH compounds monitored in this study consist of: Naphthalene (Nap), Acenaphthylene (Act), Acenaphthene (Ace), Phenanthrene (Phe), Anthracene (Ant), Fluorene (Fle), Fluoranthene (Flu), pyrene (Pyr), Benz[a]anthracene (BaA), Chrysene (Chr), Benzo[a]pyrene (BaP), Benzo[b]fluranthene (BkF), Benzo[k]fluoranthene (BkF), Dibenz[a,h]anthracene (DBA), Indeno[1,2,3-cd]pyrene (IDP), and Benzo[ghi]perylene (BghiPe). The total PAH concentration refers to the summation of all 16 PAH concentrations.

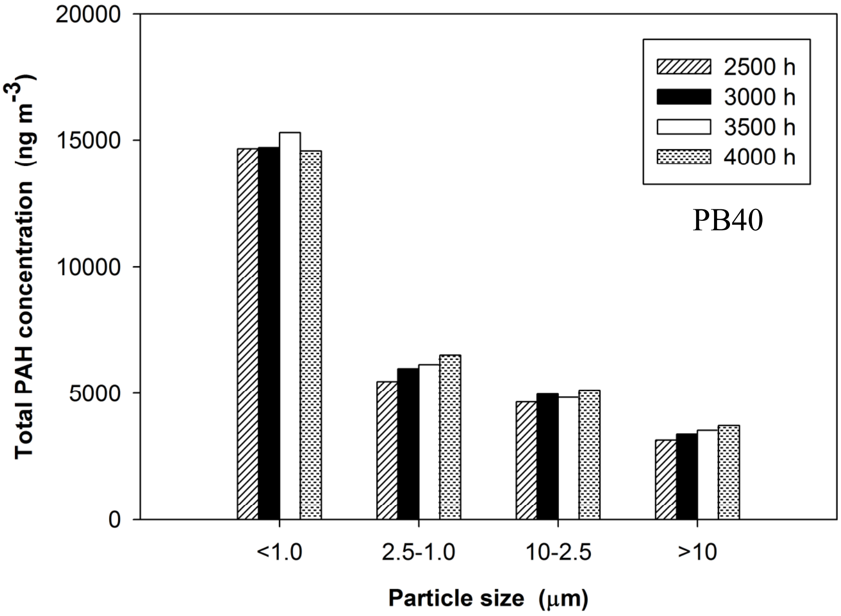
Variations of concentration and size distribution of total sixteen PAH compounds emitted from engine fueled with PB0, PB30 and PB40 are shown in Fig. 4.4. The size distributions of total PAHs behave in a similar fashion to PM. The reduction rate of total PAH concentration with the increasing particle size is similar to that of the PM concentration. In addition, total PAH concentration is increased when increasing engine operating hour for all blend ratios and almost all of particle sizes. It was found that, for each blend ratio, the total PAH concentration was maximized when the particle sizes are less than 1.0 μm. These results are in agreement with the PM concentration. This is expected since the analyzed PAHs are bound with PM. Particle-bound PAH emissions are closely related to PM emissions.


30000
25000
20000
15000
10000
5000
0
Total PAH concentration (ng m$^{-3}$)
4000 h
4500 h
5000 h
PB0
<1.0
2.5-1.0
10-2.5
>10
Particle size (μm)

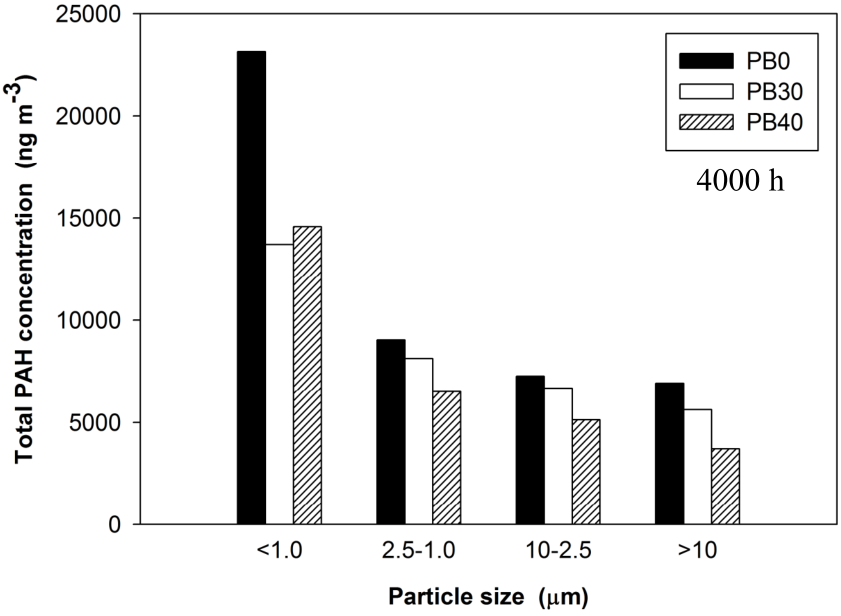
(a)


20000
15000
10000
5000
0
Total PAH concentration (ng m$^{-3}$)
2500 h
3000 h
3500 h
4000 h
PB30
<1.0
2.5-1.0
10-2.5
>10
Particle size (μm)

(b)



(c)



(d)

**Figure 4.4** Size distribution of particle-bound PAHs from agricultural diesel engine using (a) PB0, (b) PB30, (c) PB40 and (d) after the same operating time of the engines at 4000 h.

As shown in Fig. 4.5, the total PAH concentration from emission of engine using PB0 was increased from 46361 to 50098 ng m$^{-3}$ for engine hours of 4000 to 5000 h. In the case of PB30, the total PAH concentrations was increased from 32801 to 34145 ng m$^{-3}$ after running for 2500 to 4000 h. For PB40, the total PAH concentration was lower than that for PB30 and was found to be 27918 to 29937 ng m$^{-3}$ after running for 2500 to 4000 h. The emission from the engine fueled by PB30 and PB40 contains less total PAH than that fueled by PB0. Reduced PAH emission is caused by the fact that PAHs are derived from unburned fuel and from lubricating oil of physical and/or chemical condensation.

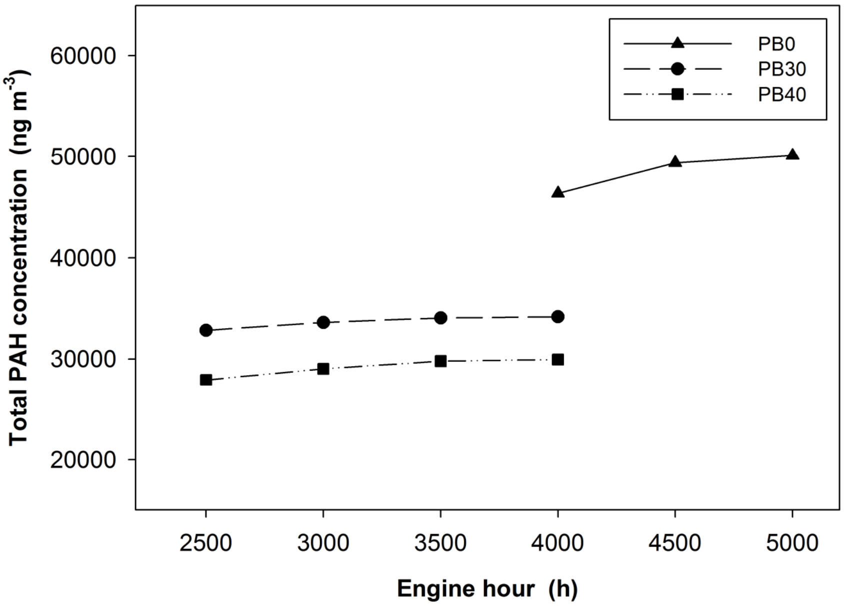


**Figure 4.5** Concentration of particle-bound PAHs from agricultural diesel engine using PB0, PB30 and PB40 during engine hour of 2500-5000 h.

The small aromatic content of palm oil blend fuel could contribute to reduction of particulate-phase PAHs. More importantly biodiesel's oxygen content most likely enables more complete combustion than diesel fuel, causing a decrease in PAH emissions. This phenomenon is especially true in this study because only particulate-phase PAHs were analyzed. Since PM emissions are reduced for the biodiesel blending mixtures, the particulate-associated PAHs would be reduced as well.

In addition, the concentration of total PAHs was increased with the operating time of the engine. This could be a result of the engine wear after running for a long period of time.

The 4-6 ring particle-bound PAH concentrations for many periods of engine hour are shown in Fig. 4.6. These types of PAH were selected to study according to the high toxicity and carcinogenicity. For PB0, the 4-6 ring PAH concentration was increased from 26999 to 31488 ng m$^{-3}$ for engine hours of 4000 to 5000 h. When using PB30, the value was increased from 16482 to 17032 ng m$^{-3}$ after running for 2500 to 4000 h, and from 14724 to 15329 ng m$^{-3}$ after running for 2500 to 4000 h for PB40. The behavior of 4-6 ring PAH concentration for PB30 and PB40 are similar to those of total PAH concentration but the difference between PB30 and PB40 is rather small. This indicates that the difference of PAHs concentration between PB30 and PB40 is a contribution of 2-3 ring PAHs.

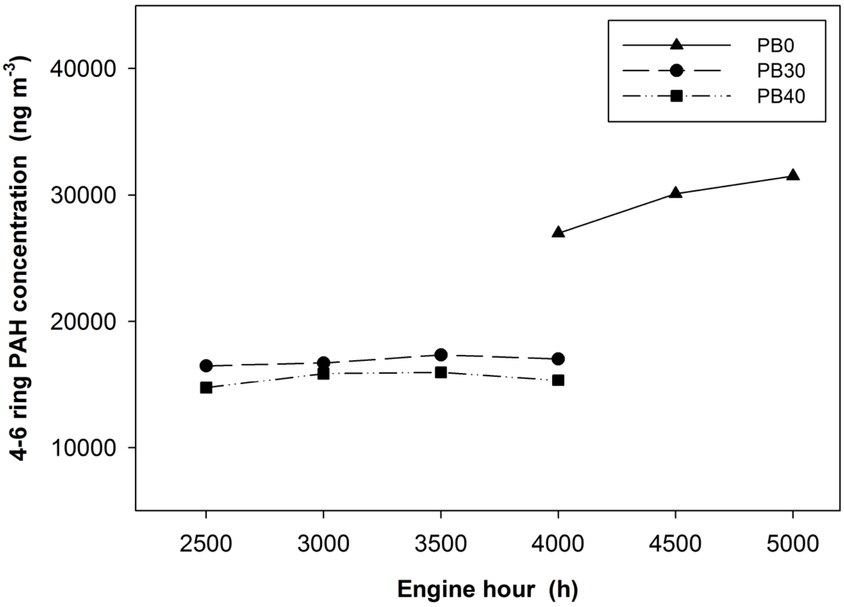
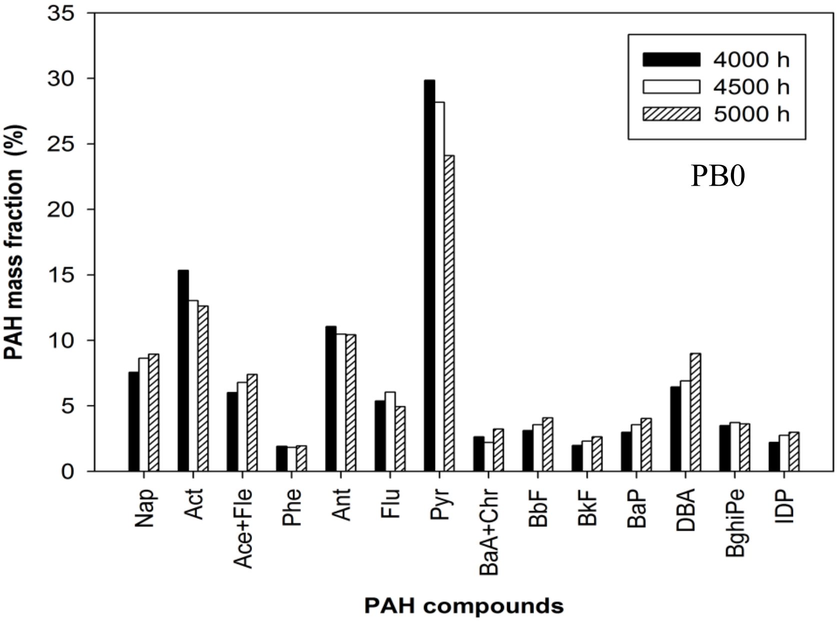


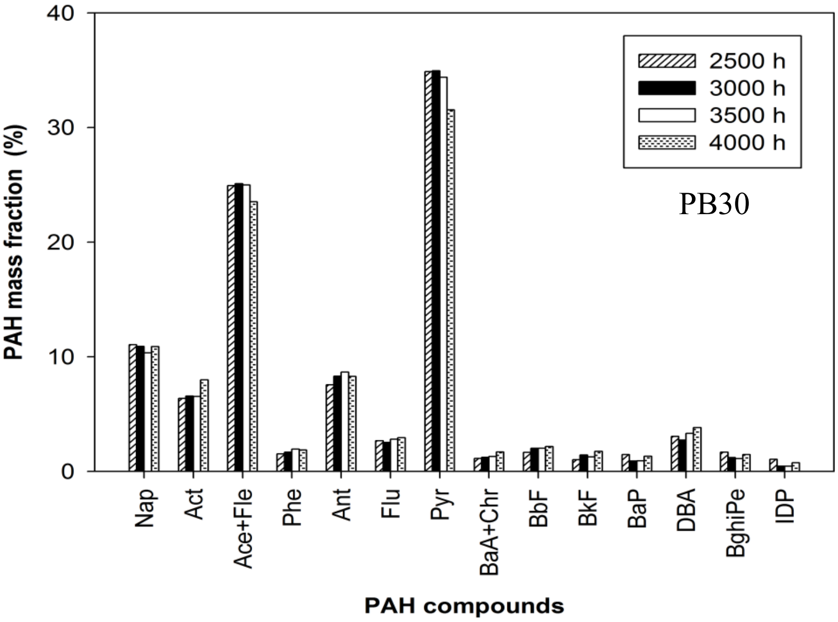
**Figure 4.6** Concentration of 4-6 ring particle-bound PAHs from agricultural diesel engine using PB0, PB30 and PB40 during engine hour of 2500-5000 h.

### 4.1.3 Profile of PAHs

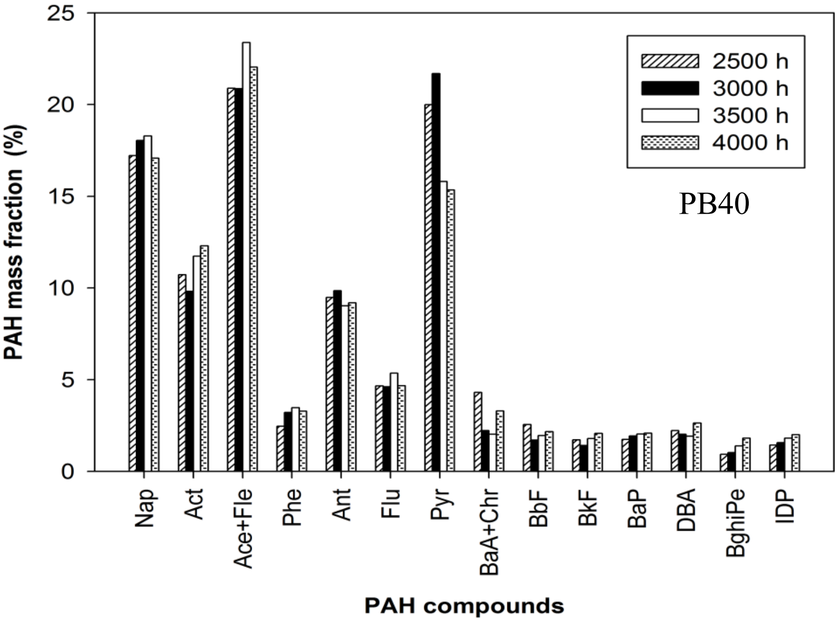
The mass fraction of individual PAH compounds in PM generated from combustion of PB0, PB30 and PB40 by agricultural diesel engines with different engine hour are presented in Fig. 4.7. It can be seen that the contribution of Pyr compound is dominant, which is in average accounted for 27% of the total PAHs. The fractions of 2-3 ring PAH compounds (Nap, Act, Ace+Fle, Phe and Ant) contribute to more than 41% of the total PAHs for all particle size ranges for PB0, and 52% and 63% of the total PAHs for PB30 and PB40, respectively. It was obviously found that the amount of 2-3 ring PAH from mass fraction of PB30 and PB40 was more than that of PB0 due to the different characteristic between diesel oil and palm oil. These results indicated that the PAHs in the palm oil blend diesel fuel were primarily dominant by the low molecular weight compounds (Lin et al., 2006b).



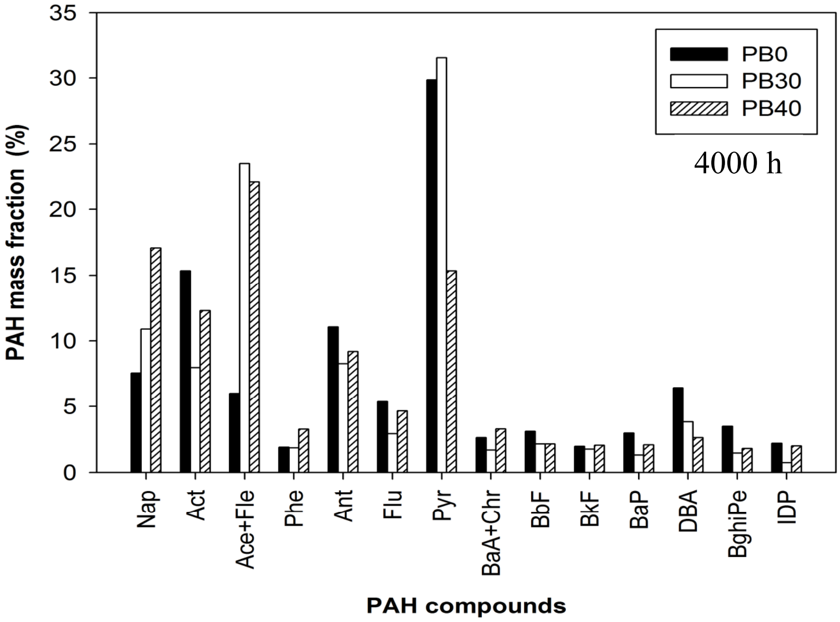
(a)


40
30
20
10
0
PAH mass fraction (%)
2500 h
3000 h
3500 h
4000 h
PB30
Nap
Act
Ace+Fle
Phe
Ant
Flu
Pyr
BaA+Chr
BbF
BkF
BaP
DBA
BghiPe
IDP
PAH compounds

(b)


25
20
15
10
5
0
PAH mass fraction (%)
2500 h
3000 h
3500 h
4000 h
PB40
Nap
Act
Ace+Fle
Phe
Ant
Flu
Pyr
BaA+Chr
BbF
BkF
BaP
DBA
BghiPe
IDP
PAH compounds

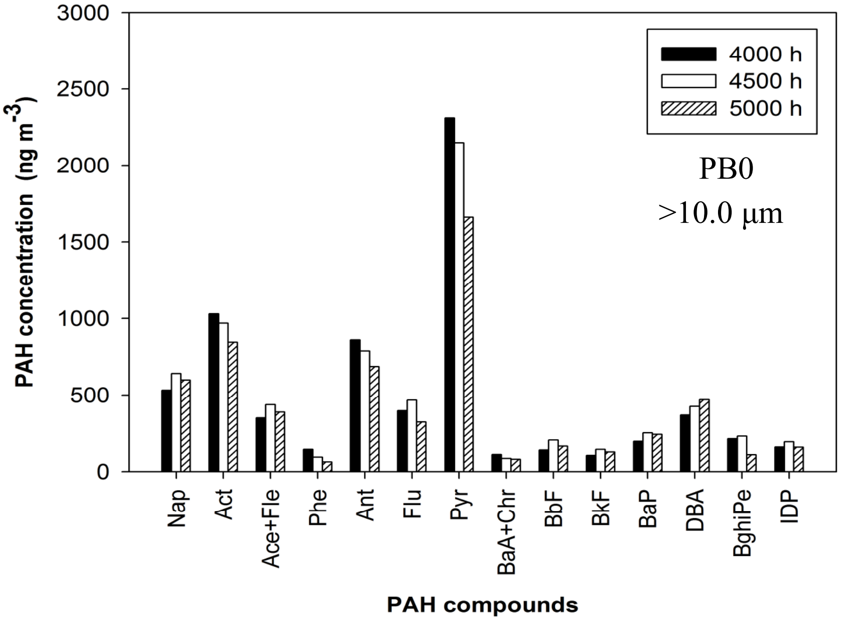
(c)



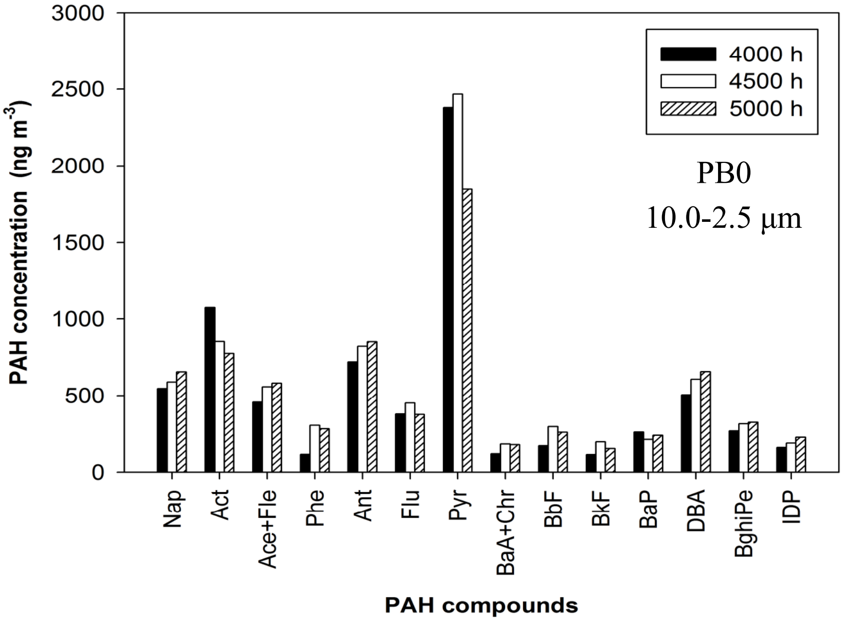
(d)

**Figure 4.7** Mass fraction of PAHs from agricultural diesel engine using (a) PB0, (b) PB30, (c) PB40 and (d) after the same operating time of the engines at 4000 h.

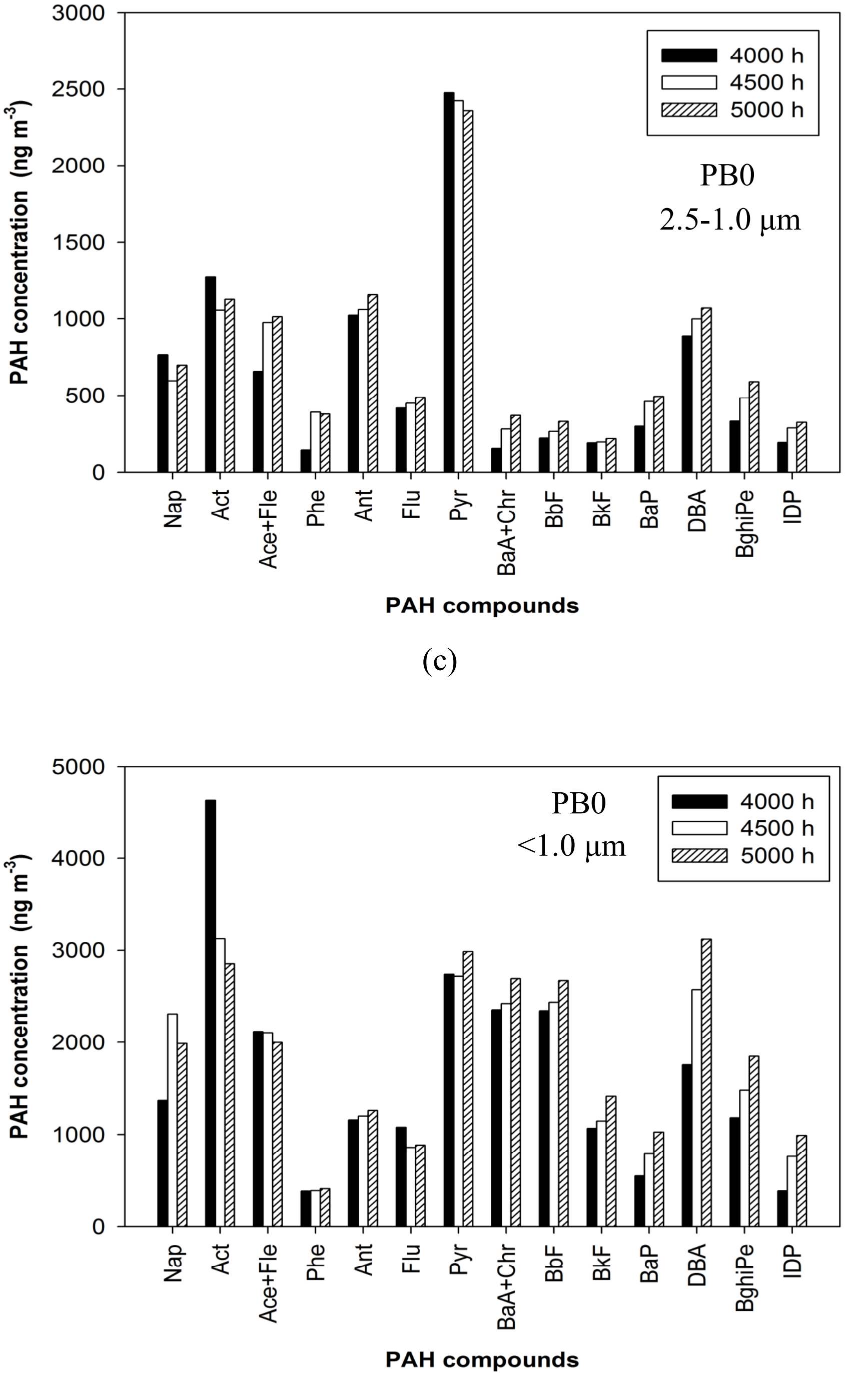
Fig. 4.8 show the concentration of individual PAH composition in each particle size range of particles sampled from agricultural diesel engines fueled by PB0. The patterns of PAH compounds associated with large particles (>10.0 µm) indicate a dominance of smaller molecule PAHs (2-3 aromatic rings). The most dominant compound is Pyr. For the small particle (<1.0 µm), larger molecule PAHs (4-6 aromatic rings) play an important role. The comparison in each blend ratio revealed that PB0 generated the more 2-3 ring PAH when the particle size was smaller than 1.0 µm, with the largest amount of Pyr found. The greater engine operation hours resulted in the higher generated PAH amount due to the engine wear. For the particle smaller than 1.0 µm, it was found that 4-6 ring PAHs were dominant over the 2-3 ring PAHs, and Act was the most emitted PAH observed.


PAH concentration (ng m$^{-3}$)
3000
2500
2000
1500
1000
500
0
4000 h
4500 h
5000 h
PB0
>10.0 µm
Nap
Act
Ace+Fle
Phe
Ant
Flu
Pyr
BaA+Chr
BbF
BkF
BaP
DBA
BghiPe
IDP
PAH compounds

(a)


PAH concentration (ng m$^{-3}$)
3000
2500
2000
1500
1000
500
0
4000 h
4500 h
5000 h
PB0
10.0-2.5 µm
Nap
Act
Ace+Fle
Phe
Ant
Flu
Pyr
BaA+Chr
BbF
BkF
BaP
DBA
BghiPe
IDP
PAH compounds

(b)

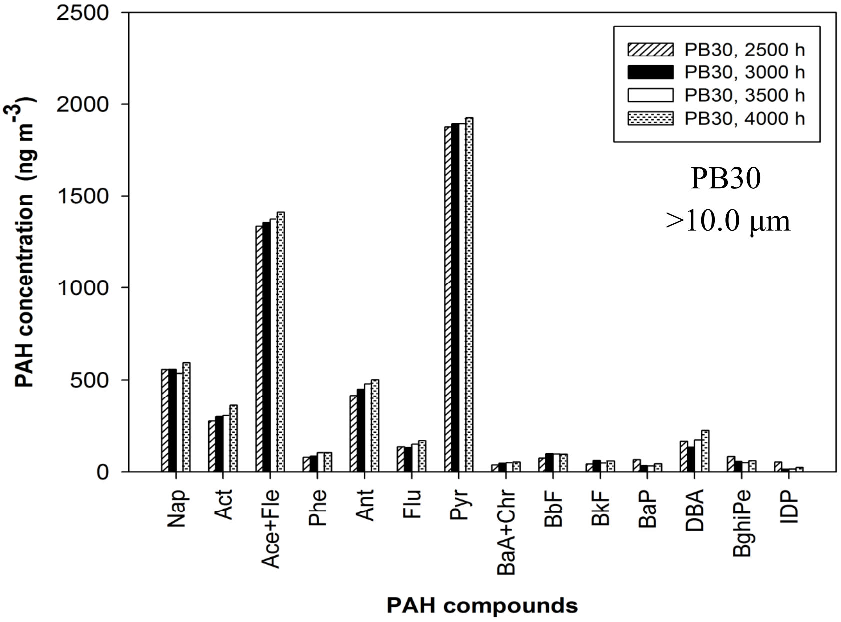


(c)

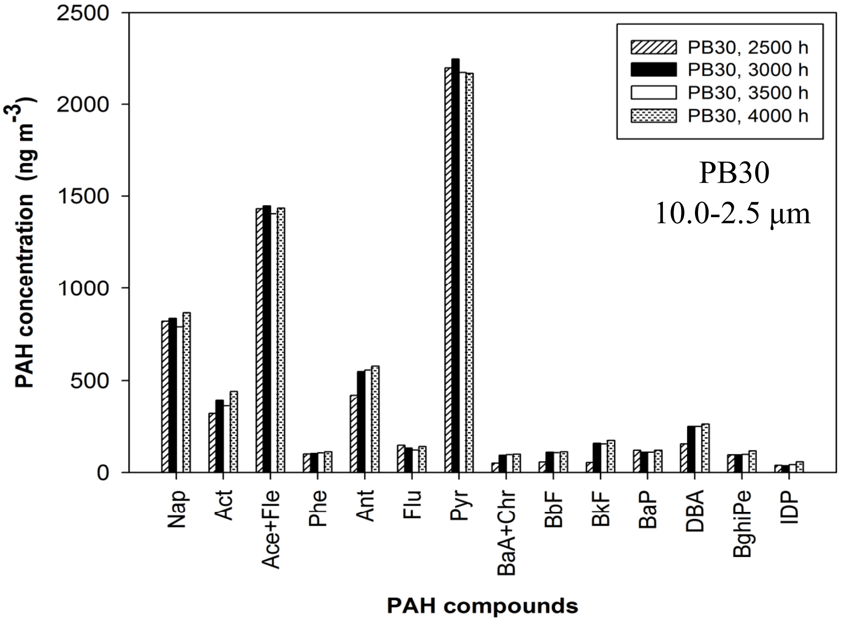
(d)

**Figure 4.8** Concentration of individual PAH compound of particles sampled from agricultural diesel engine fueled by PB0 for particle size ranges of (a) >10.0 μm, (b) 10.0-2.5 μm, (c) 2.5-1.0 μm and (d) <1.0 μm.

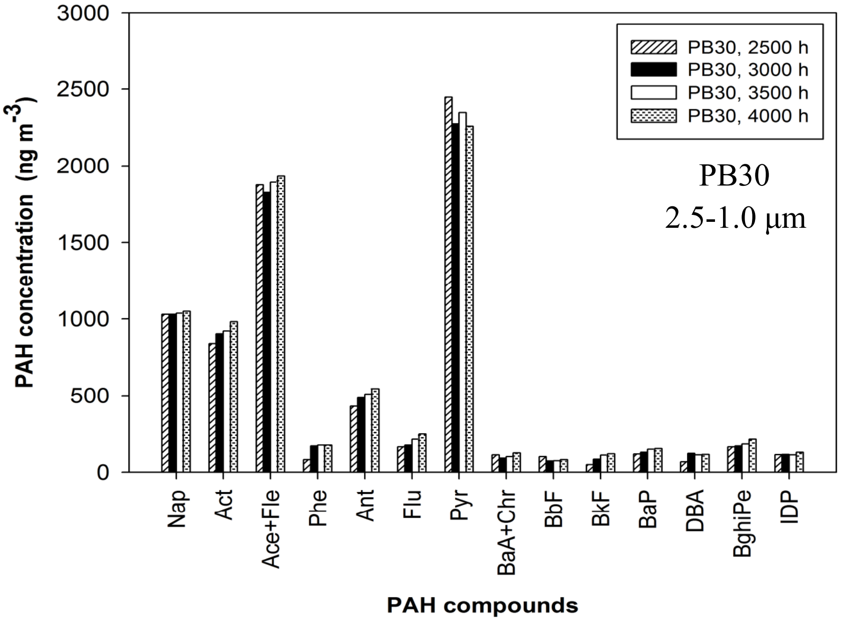
PAH patterns for PB30 and PB40 are shown in Figs. 4.9 and 4.10. Fig. 4.11, shows the pattern after the same engine operating time of 4000 h. The concentrations of individual PAHs from emission of the engines fueled by PB30 and PB40 were lower than those fueled by PB0. For PB30 and PB40, the patterns of particles larger than 1.0 µm were similar to PB0 with less amount of each PAH. Pyr and Ace+Fle were the most PAHs found. The amount of Ace+Fle was increased when the particle size was decreased. For particle smaller than 1.0 µm, 2-3 ring compounds play a greater role than the emission of the engine fueled by PB0.



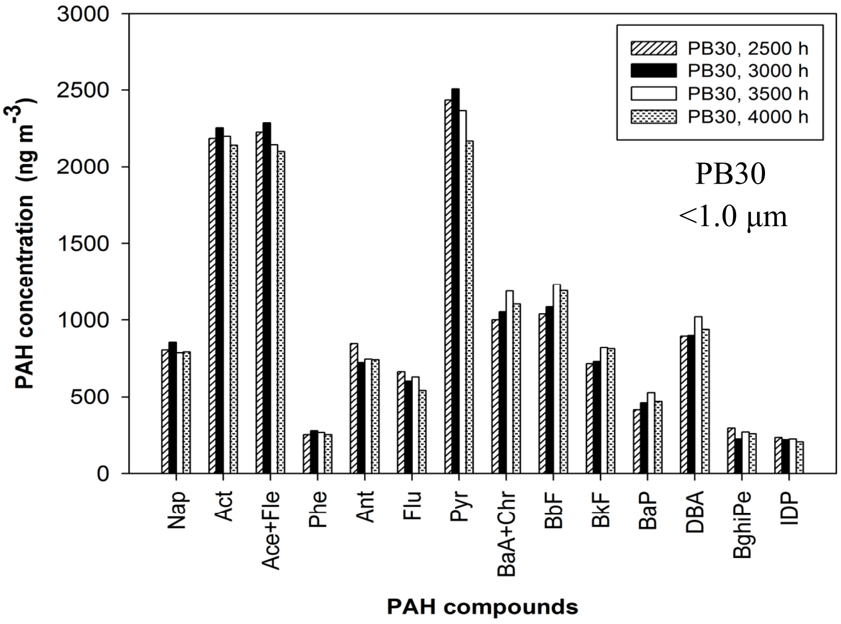
(a)


PB30, 2500 h
PB30, 3000 h
PB30, 3500 h
PB30, 4000 h
PB30
10.0-2.5 μm
PAH concentration (ng m$^{-3}$)
0
500
1000
1500
2000
2500
Nap
Act
Ace+Fle
Phe
Ant
Flu
Pyr
BaA+Chr
BbF
BkF
BaP
DBA
BghiPe
IDP
PAH compounds

(b)

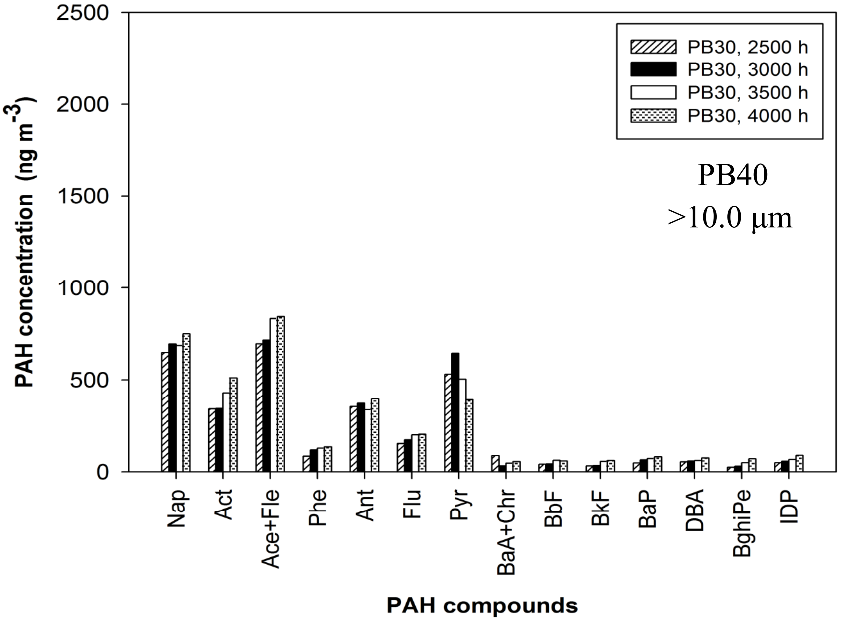

PB30, 2500 h
PB30, 3000 h
PB30, 3500 h
PB30, 4000 h
PB30
2.5-1.0 μm
PAH concentration (ng m$^{-3}$)
0
500
1000
1500
2000
2500
3000
Nap
Act
Ace+Fle
Phe
Ant
Flu
Pyr
BaA+Chr
BbF
BkF
BaP
DBA
BghiPe
IDP
PAH compounds

(c)

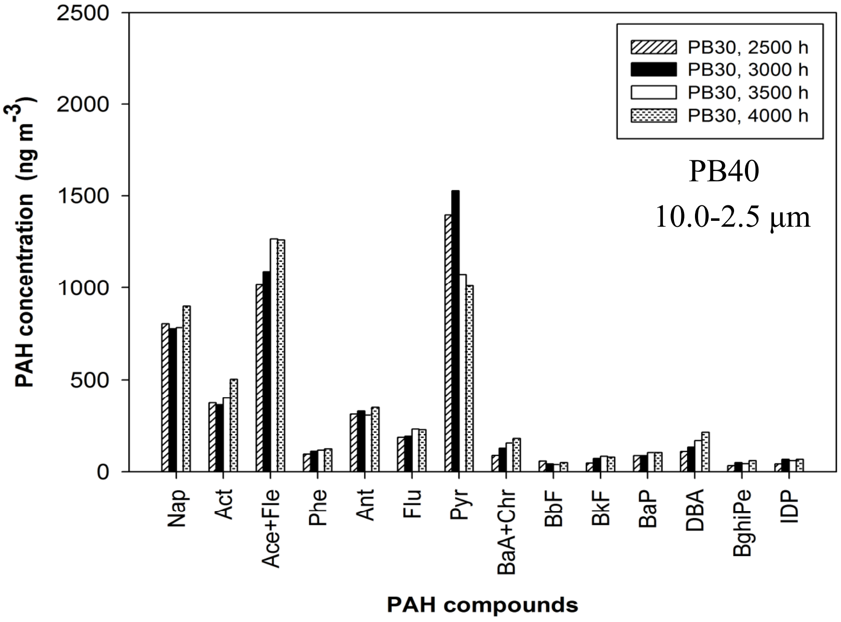


(d)

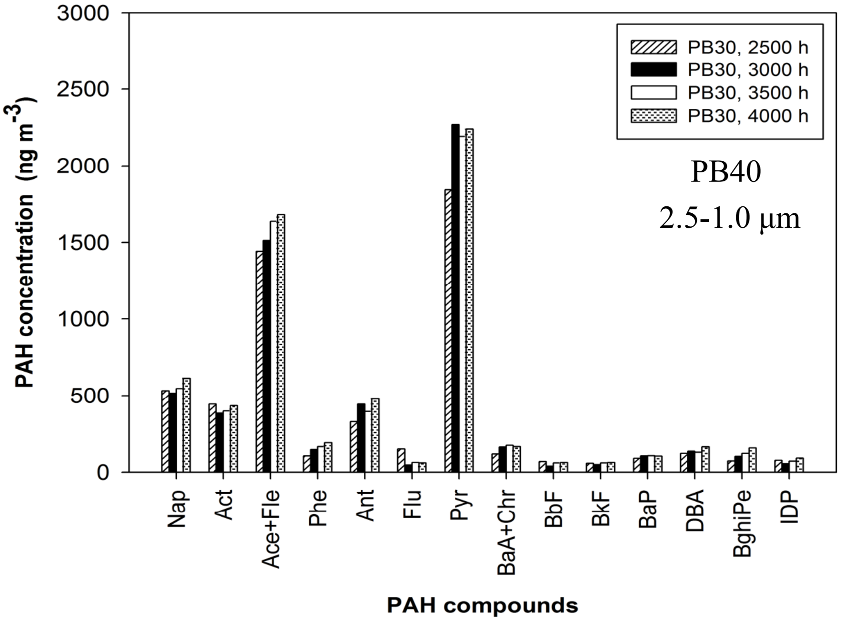
**Figure 4.9** Concentration of individual PAH compound of particles sampled from agricultural diesel engine fueled by PB30 for particle size ranges of (a) >10.0 µm, (b) 10.0-2.5 µm, (c) 2.5-1.0 µm and (d) <1.0 µm.



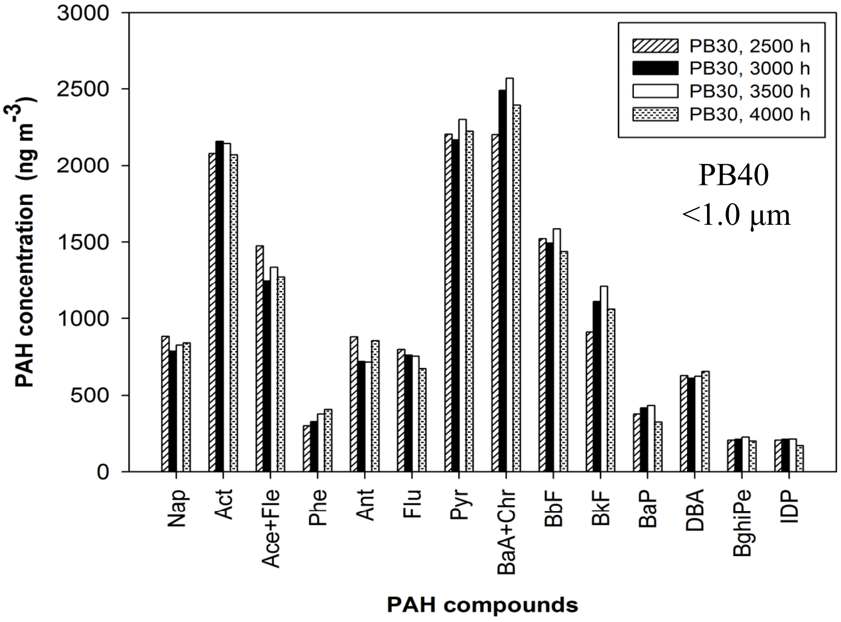
(a)


PAH concentration (ng m-3)
2500
2000
1500
1000
500
0
PB30, 2500 h
PB30, 3000 h
PB30, 3500 h
PB30, 4000 h
PB40
10.0-2.5 μm
Nap
Act
Ace+Fle
Phe
Ant
Flu
Pyr
BaA+Chr
BbF
BkF
BaP
DBA
BghiPe
IDP
PAH compounds

(b)

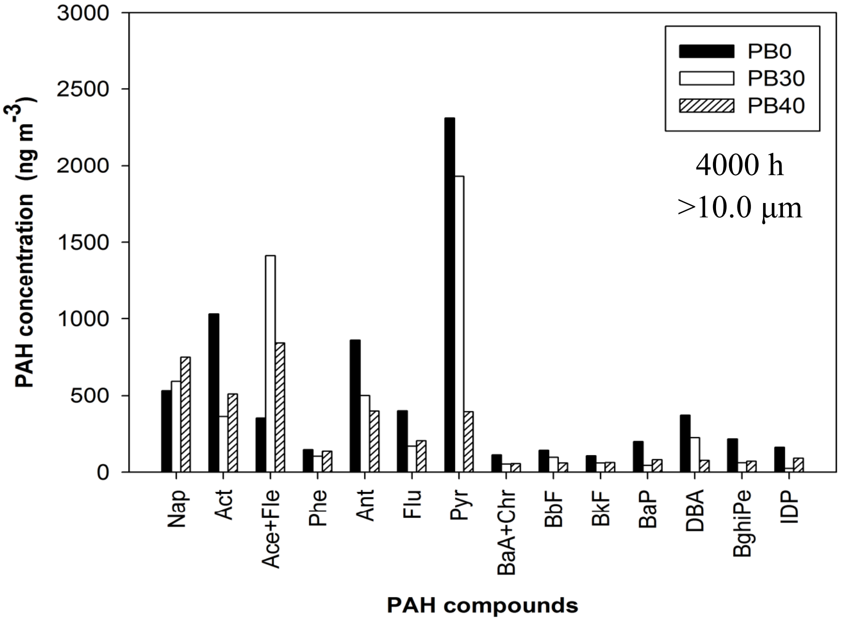

PAH concentration (ng m-3)
3000
2500
2000
1500
1000
500
0
PB30, 2500 h
PB30, 3000 h
PB30, 3500 h
PB30, 4000 h
PB40
2.5-1.0 μm
Nap
Act
Ace+Fle
Phe
Ant
Flu
Pyr
BaA+Chr
BbF
BkF
BaP
DBA
BghiPe
IDP
PAH compounds

(c)

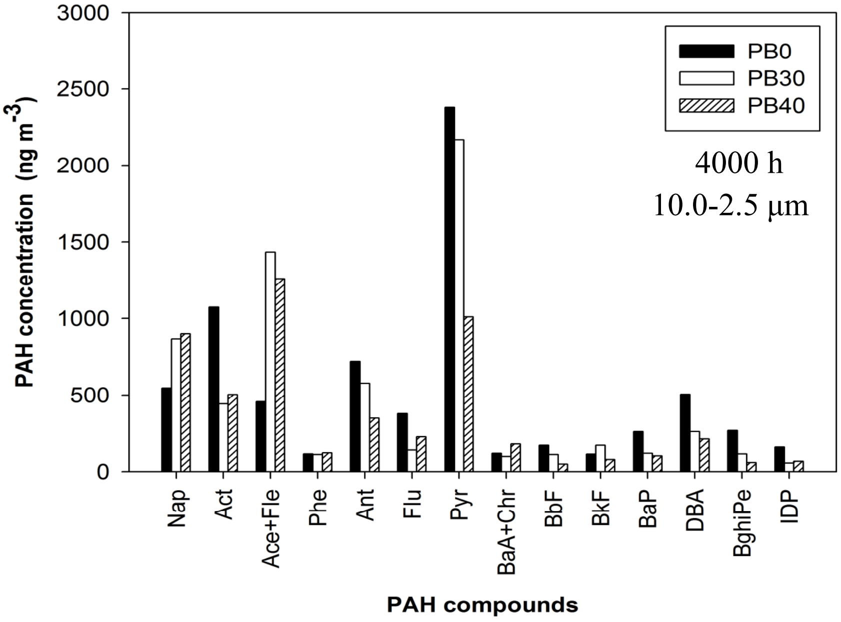


(d)

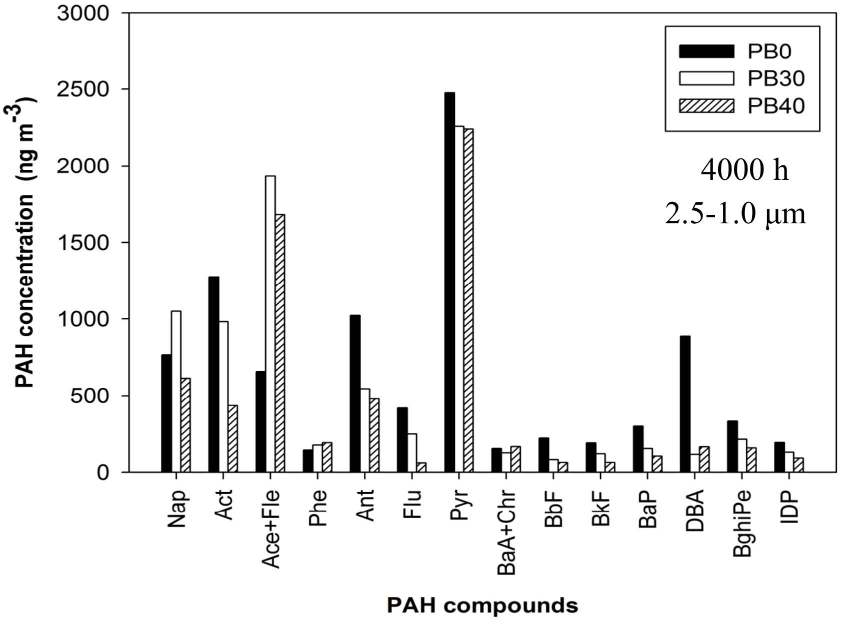
**Figure 4.10** Concentration of individual PAH compound of particles sampled from agricultural diesel engine fueled by PB40 for particle size ranges of (a) >10.0 µm, (b) 10.0-2.5 µm, (c) 2.5-1.0 µm and (d) <1.0 µm.



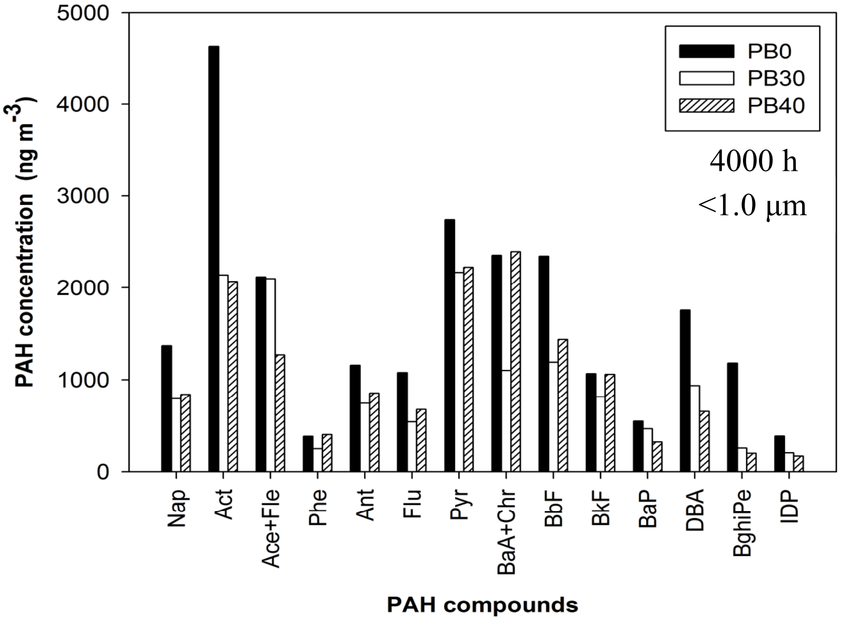
(a)


PAH concentration (ng m$^{-3}$)
3000
2500
2000
1500
1000
500
0
PB0
PB30
PB40
4000 h
10.0-2.5 μm
Nap
Act
Ace+Fle
Phe
Ant
Flu
Pyr
BaA+Chr
BbF
BkF
BaP
DBA
BghiPe
IDP
PAH compounds

(b)


PAH concentration (ng m$^{-3}$)
3000
2500
2000
1500
1000
500
0
PB0
PB30
PB40
4000 h
2.5-1.0 μm
Nap
Act
Ace+Fle
Phe
Ant
Flu
Pyr
BaA+Chr
BbF
BkF
BaP
DBA
BghiPe
IDP
PAH compounds

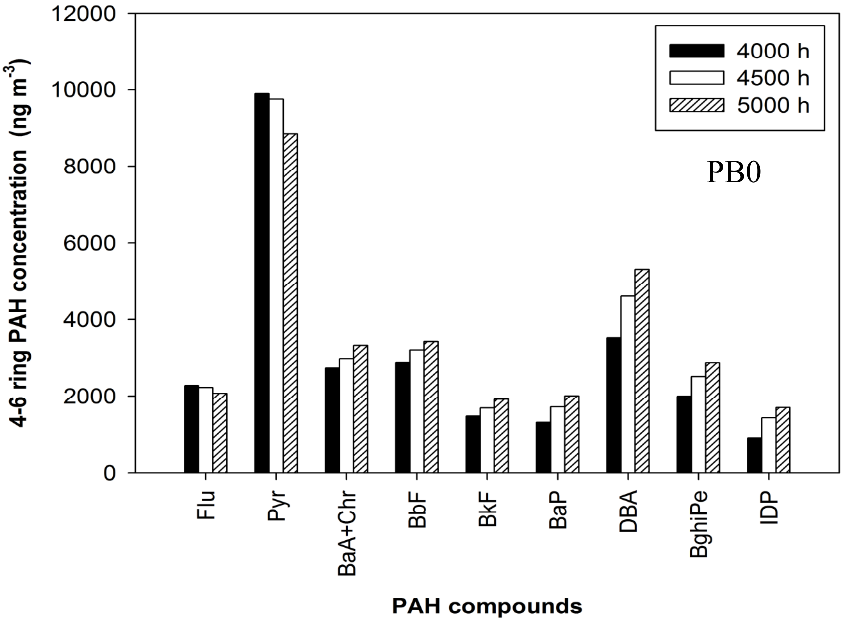
(c)



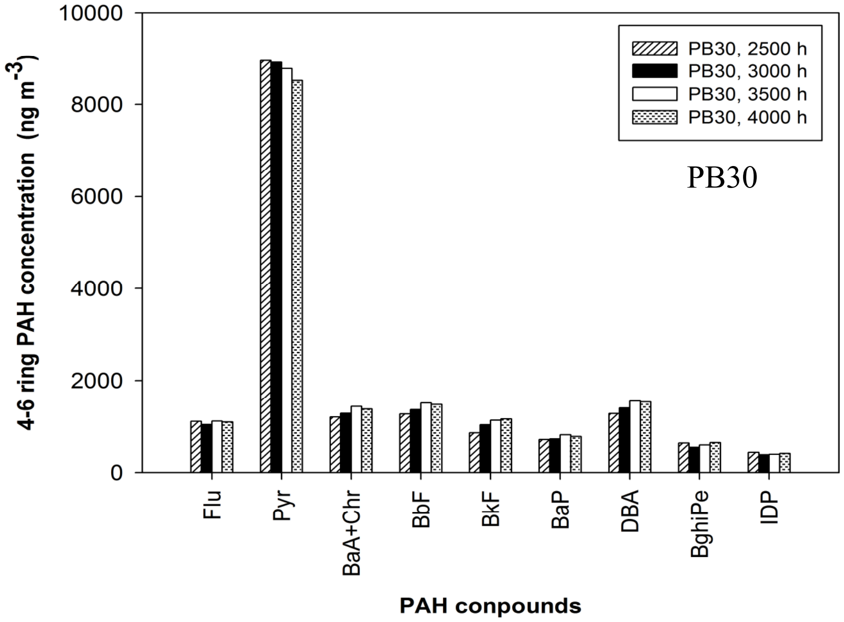
(d)

**Figure 4.11** Concentration of individual PAH compound of particles sampled from agricultural diesel engine for engine hours of 4000 for particle size ranges of (a) >10.0 µm, (b) 10.0-2.5 µm, (c) 2.5-1.0 µm and (d) <1.0 µm.

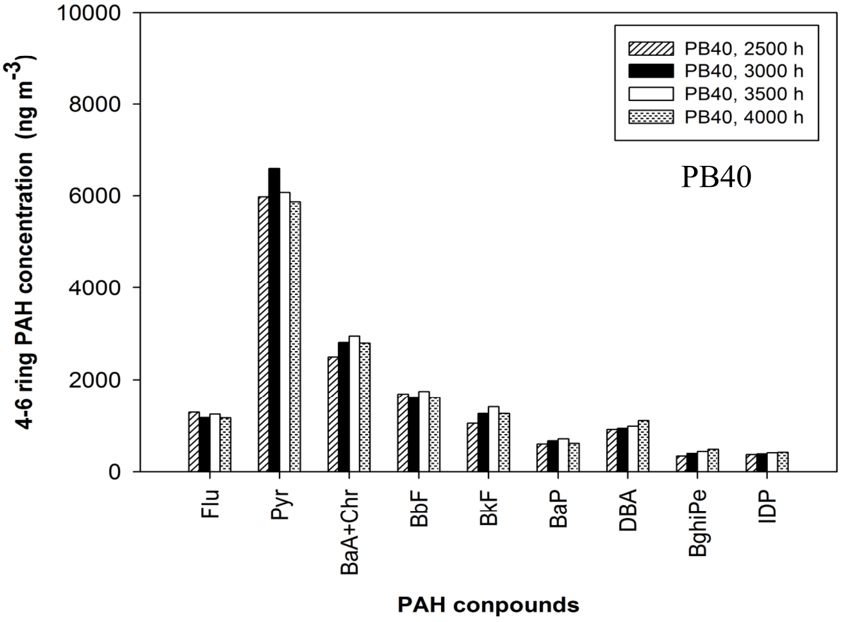
The fractions of total PAHs with larger molecular sizes (4-6 rings) for all size ranges are shown in Fig. 4.12. Overall, the results demonstrate that the concentration of 4-6 ring PAH was increased when the running time of the engine was increased with a few exceptions for Flu and Pyr. For PB0, more of the 4-6 ring PAHs were generated compared with PB30 and PB40, with the largest amount of Pyr. The more engine hours resulted in a higher generated 4-6 ring PAH amount due to the wear of engine for every blend ratio. However, Pyr was decreased when the engine hour was increased.


12000
10000
8000
6000
4000
2000
0
4-6 ring PAH concentration (ng m$^{-3}$)
4000 h
4500 h
5000 h
PB0
Flu
Pyr
BaA+Chr
BbF
BkF
BaP
DBA
BghiPe
IDP
PAH compounds

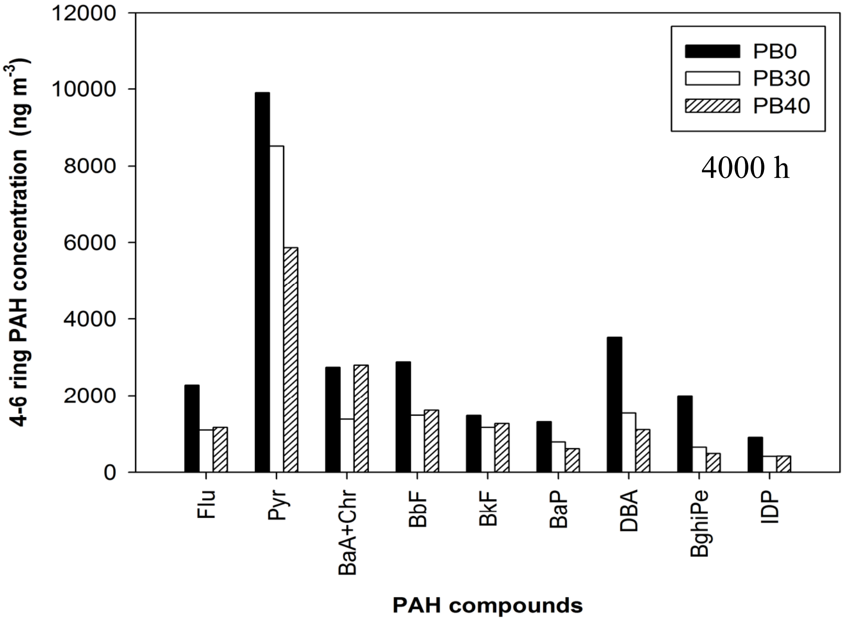
(a)


10000
8000
6000
4000
2000
0
4-6 ring PAH concentration (ng m$^{-3}$)
PB30, 2500 h
PB30, 3000 h
PB30, 3500 h
PB30, 4000 h
PB30
Flu
Pyr
BaA+Chr
BbF
BkF
BaP
DBA
BghiPe
IDP
PAH conpounds

(b)



(c)



(d)

**Figure 4.12** Concentration of 4-6 ring individual PAH compound of particles sampled from agricultural diesel engine fueled by (a) PB0, (b) PB30, (c) PB40 and (d) after the same operating time of the engines at 4000 h.

## 4.2 Influences of Palm Oil Blends on PM and PAH Emissions

The influences of biodiesel blending on PM and PAH emissions were investigated by comparing the effects of the different ratios of palm oil blend fuels (PB30 and PB40) with the pure commercial petroleum diesel (PB0). The PAH reduction percentage (η) can be calculated by the following equation (Chien et al., 2009);

$$\eta(\%) = \left[\frac{(Emission\ with\ PB0 - Emission\ with\ palm\ oil\ blend)}{Emission\ with\ PB0}\right] \times 100 \qquad (4.1)$$

This means that the emissions are reduced by palm oil blend if the reduction percentage is positive. The reduction percentage of total PM and total PAH emissions at the same time for 4000 engine hour is shown in Fig. 4.13, which the total PAH reduction percentage in particles of different size ranges is shown in Fig. 4.14. These results show that the PM and the associated PAH emissions from engines using palm oil blend diesel for all the four size ranges were reduced compared with PB0. For PB30 and PB40 in comparison with PB0, the reduction percentages for total PM emissions were 11% and 12%, respectively, and for total PAH emissions were 26% and 35%, respectively. As the blending ratio of palm oil was increased, the PM and PAH emissions were reduced. Influences of palm oil blend on PAH emissions are similar to PM; i.e., the reduction percentage for PAH emission was increased as the palm oil blending ratio was increased. The percentage of PAH emission reduction was actually higher than that of PM emission for most palm oil blend mixtures for all four size ranges. Thus emission of palm oil blends (PB30 and PB40) contains much lower PAH contents. Palm oil blend has oxygen content which enables more complete combustion than commercial petroleum diesel fuel, causing a decrease in PAH emissions (Agarwal et al., 2007).

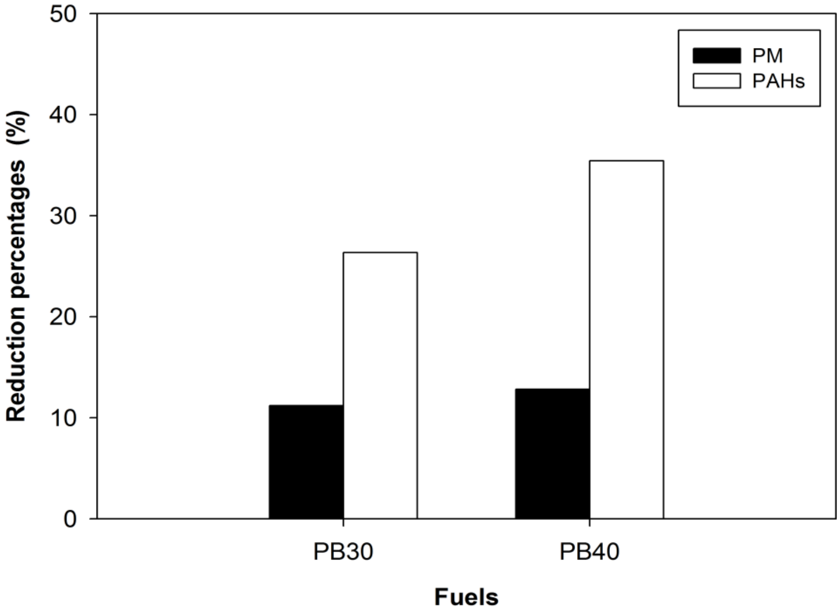


**Figure 4.13** Total PM and PAHs reduction percentages from emissions by palm oil blending mixtures compared with PB0 with engine hour of 4000 h.

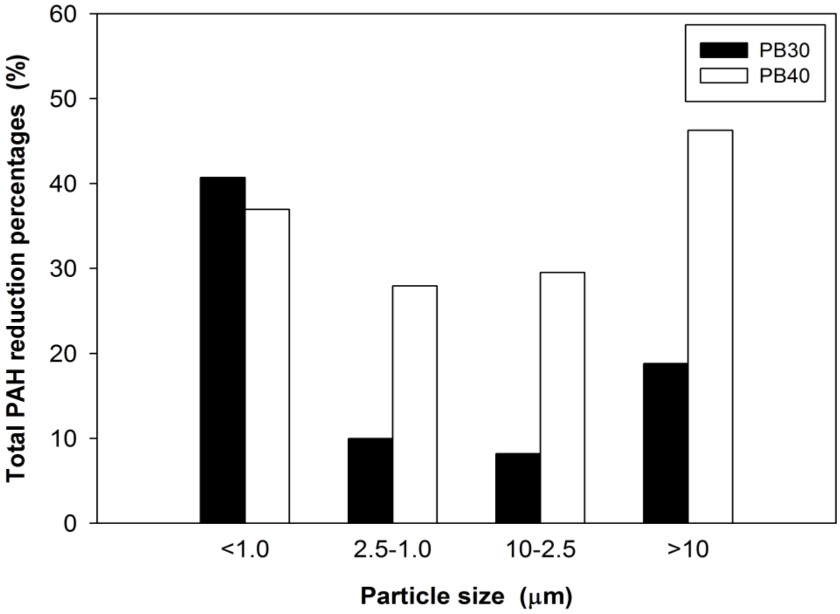


**Figure 4.14** Total PAH reduction percentages from emissions by palm oil blending mixtures compared with PB0 in each size of particles range with engine hour of 4000 h.

### 4.3 Evaluation of PAH Corresponding Carcinogenicity

Polycyclic aromatic hydrocarbons (PAHs) are toxic pollutants released by various combustion sources. Benzo[a]pyrene (BaP) is a representative member of the class of PAHs for toxicity evaluation. Health risk assessment associated with inhalatory PAH uptake is often estimated on the basis of the BaP concentration equivalent in air. For mixtures of PAHs, BaP is chosen as the reference chemical because its toxicity is well characterized. The toxicity equivalency factor for each PAH is an estimated relative toxicity compared to BaP.

In this study, toxic equivalency factors (TEFs) are applied for the 16 analyzed PAHs to assess the carcinogenic potencies of emissions from agricultural diesel engine fueled by PB0, PB30 and PB40 with different engine hours. The TEFs have been devised as a way of comparing the carcinogenic potency of the individual PAH with the carcinogenity of BaP (Nisbet and LaGoy, 1992). The BaP equivalent concentration is a calculation that sums together carcinogenic PAH compound based on the individual PAH compound toxic equivalency factors (TEFs), using BaP as a reference value of 1. The Benzo[a]pyrene equivalent ($BaP_{eq}$) concentration can be calculated from

$$BaP_{eq} = \sum_{i=1}^{n} TEF_i \times [PAH_i] \tag{4.2}$$

Where $TEF_i$ is the toxic equivalent factor for PAH congener i and $PAH_i$ is the concentration of PAH congener i summing together each species concentration multiplies by its respective TEFs.

Table 4.2 shows the emission concentration of each PAH and $BaP_{eq}$ measured from agricultural diesel engine under different experimental conditions. After the same operating time of the engines at 4000 h, PB0 emitted higher $BaP_{eq}$ amount than PB30 and PB40. The results also show that PB0 has the highest $BaP_{eq}$ emissions in all size ranges compared with the two palm oil blend diesel mixtures. The $BaP_{eq}$ emission for PB0 are 5770, 7430 and 8559 ng $m^{-3}$ after engine hour for 4000, 4500 and 5000 h, respectively. As the palm oil blending ratio was increased, the

$BaP_{eq}$ emissions was decreased gradually. The $BaP_{eq}$ emission for PB30 was found to increase from 2433 to 2817 ng $m^{-3}$ after running for 2500 to 4000 h. $BaP_{eq}$ emission for PB40 were lower than that for PB0 and PB30 and were found to be from 2036 to 2293 ng $m^{-3}$ after running for 2500 to 4000 h.

Results from the previous study of Leevijit et al. (2010) indicated that the erosion of the some engines used in this study was increased when the running time increased. Besides, the most eroded part was compression ring. Among the three engines fueled by PB0, PB30 and PB40, the PB0 fueled engine showed the most eroded compression ring. Therefore the increasing of PAH emission with the running hour of engines may be caused by the increasing of compressing ring erosion.

Leevijit et al. (2010) also found that the commercial diesel fueled engine generated another exhaust such as $NO_x$, $CO_2$ and CO in larger amount than the palm oil blends fueled engine. The emissions patterns of $NO_x$, $CO_2$ and CO were similar to the PM and PAHs emission pattern found in this study.

In conclusion, the important reason which causes the diesel fueled engine generates more PAHs is the erosion of engine parts, especially the compression ring. The other reason is the more oxygen content in palm oil which can enhance more complete combustion.

Thus reduction of PAHs related carcinogenic potencies emitted from agricultural diesel engine fueled by PB30 and PB40 can be attributed to the fact that palm oil contains no aromatic constituent in comparison to diesel and palm oil blend contains more oxygen amount than diesel oil most likely enables more complete combustion than diesel fuel.

However, for each type of fuel, when running time of engine increases, the amount of PAHs is also increased. This may be the consequent from the eroded engine parts can not fully operate. So, the efficiency of fuel combustion is decreased and more PAHs are generated.

**Table 4.2** Concentration of each PAH and $BaP_{eq}$ measured from agricultural diesel engine different conditions. Unit is in ng $m^{-3}$.

| PAHs | PB0 | | | PB30 | | | | PB40 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 4000 h | 4500 h | 5000 h | 2500 h | 3000 h | 3500 h | 4000 h | 2500 h | 3000 h | 3500 h | 4000 h |
| Nap | 3213 | 4135 | 3937 | 3212 | 3277 | 3149 | 3302 | 2867 | 2774 | 2841 | 3103 |
| Act | 8013 | 5999 | 5598 | 3619 | 3843 | 3785 | 3924 | 3238 | 3248 | 3374 | 3519 |
| Ace+Fle | 3581 | 4075 | 3982 | 6866 | 6912 | 6813 | 6877 | 4628 | 4565 | 5071 | 5056 |
| Phe | 791 | 1179 | 1136 | 512 | 636 | 651 | 643 | 585 | 704 | 785 | 854 |
| Ant | 3763 | 3870 | 3958 | 2109 | 2211 | 2292 | 2367 | 1877 | 1863 | 1754 | 2077 |
| Flu | 2273 | 2225 | 2073 | 1114 | 1043 | 1117 | 1101 | 1289 | 1172 | 1248 | 1167 |
| Pyr | 9902 | 9757 | 8851 | 8956 | 8919 | 8778 | 8520 | 5973 | 6607 | 6070 | 5865 |
| BaA+Chr | 2740 | 2974 | 3322 | 1203 | 1284 | 1435 | 1380 | 2497 | 2812 | 2946 | 2795 |
| BbF | 2881 | 3203 | 3427 | 1271 | 1366 | 1511 | 1480 | 1689 | 1618 | 1747 | 1609 |
| BkF | 1477 | 1687 | 1917 | 863 | 1036 | 1135 | 1165 | 1048 | 1263 | 1409 | 1264 |
| BaP | 1311 | 1715 | 2006 | 718 | 729 | 821 | 784 | 600 | 671 | 711 | 612 |
| DBA | 3517 | 4602 | 5313 | 1282 | 1404 | 1553 | 1538 | 916 | 939 | 984 | 1109 |
| BghiPe | 1996 | 2511 | 2876 | 639 | 546 | 598 | 649 | 338 | 395 | 440 | 488 |
| IDP | 902 | 1433 | 1702 | 438 | 387 | 394 | 415 | 375 | 388 | 411 | 420 |
| *Total* | 46360 | 49365 | 50098 | 32802 | 33593 | 34032 | 34145 | 27920 | 29019 | 29791 | 29938 |
| 2-3 ring | 19361 | 19258 | 18611 | 16318 | 16879 | 16690 | 17113 | 13195 | 13154 | 13825 | 14609 |
| 4-6 ring | 26999 | 30107 | 31487 | 16484 | 16714 | 17342 | 17032 | 14725 | 15865 | 15966 | 15329 |
| Σ $BaP_{eq}$ | 5770 | 7430 | 8559 | 2433 | 2584 | 2864 | 2817 | 2036 | 2169 | 2295 | 2293 |

# CHAPTER 5

# CONCLUSION AND RECOMMENDATION FOR FUTURE WORK

## Conclusion

Physical and chemical characteristics of emission from agricultural diesel engine fueled by palm oil blend diesel with different operating time of engine were studied. Moreover the experimental method was designed to analyze evolution of concentration, chemical components of particulate samples especially the carcinogenic, mutagenic PAHs and size distribution of PAHs associated with the particulates including PM1. As a result of the present study, the following conclusions can be reached:

(1) The PM size distributions of emission from agricultural diesel engine fueled by PB0, PB30 and PB40 sampling measured using a 5-stage particulate matter air sampler show a unimodal behavior in the accumulation mode and the MMAD was dependent on both the blending ratio and engine hour. Increasing the blending ratio caused a reduction of MMAD while it was increased when the operation time was increased. This is because the engines using PB30 and PB40 generate the smaller fine particle PM than that of the PB0 engines. The higher blend ratio will provide the more complete combustion because the palm oil blend contained more oxygen amount than diesel oil.

(2) The variation of concentrations of PM emitted from engines with different operating times are shown in Table 5.1.

**Table 5.1** Total PM concentration of emission from agricultural diesel engines under different conditions.

| Engine hour (h) | Total PM concentration ($\mu g\ m^{-3}$) | | |
|---|---|---|---|
| | PB0 | PB30 | PB40 |
| 2500 | - | 18181 | 16376 |
| 3000 | - | 24220 | 22562 |
| 3500 | - | 24293 | 22991 |
| 4000 | 27616 | 24523 | 24079 |
| 4500 | 27900 | - | - |
| 5000 | 31012 | - | - |

(3) The size distributions of PAHs behave in a similar fashion as PM. Concentrations of PAHs also display the same behaviors as PM. The patterns of PAH compounds associated with large particles (>1.0 μm) indicate a dominance of smaller molecule PAHs (2-3 aromatic rings). The most dominant compound is pyrene (Pyr). For the small particle (<1.0 μm), larger molecule PAHs (4-6 aromatic rings) play important role. Due to the low vapor pressure, the high molecular weight PAHs are predominantly adsorbed on soot and particulate matter.

(4) PAH emissions for the four size ranges were all reduced when increasing the palm oil blending ratio. Reduced PAH emission is caused by the fact that PAHs are derived from unburned fuel and from lubricating oil of physical and/or chemical condensation. In addition, biodiesel, has higher oxygen content, causes more complete combustion than diesel fuel, resulting in a decrease in PAH emissions in all size ranges.

(5) The influences of palm oil blend on PAH emissions were similar to PM; i.e., the reduction percentages for PAH emissions were increased when increasing the palm oil blending ratio. PAHs emitted from agricultural diesel engine fueled by PB0 had the strongest PAH related carcinogenic potencies. The results also show that PB0 had the highest $BaP_{eq}$ emissions in all size ranges compared with the two palm oil blend mixtures. As the palm oil blending ratio was increased, the

$BaP_{eq}$ was decreased gradually. The results indicate that palm oil blends could reduce both PAH emission factors and the PAH corresponding carcinogenicity potency in the full size ranges.

(6) Overall, the results demonstrate clear reduction of both PM and total PAH emissions as the blending ratio of palm oil was increased. Hence palm oil blend diesel (PB30 and PB40) contains much lower PAH content. Palm oil blend diesel (PB30 and PB40) has oxygen content which enables more complete combustion than commercial petroleum diesel (PB0) fuel, causing a decrease in PAH emissions.

## Recommendation for Future Work

In this work the experimental parameter especially flow rate could not be controlled exactly at 40 L $min^{-1}$ because the designed flow rate is the limit of the pump. In the future, it is probably necessary to use a larger pump for particle sampling so that high accuracy in term of cutoff size can be attained.

Furthermore, PAH in gaseous phase should be studied. This will give full information of PAH emission from the engines fueled by either diesel or palm oil blend diesel. This is very important because agricultural machines are used extensively in Thailand and palm oil diesel has recently received interest as a source of the renewable energy.

Because smoke and vapors emitted into the air by incomplete combustion can cause health problems, such as mouth, throat, bladder and lung cancer (Andrikopoulos et al., 2004; Wu and Yen, 2004) it is necessary to study full effect of the PAH emission from the engine fueled by palm oil diesel on the health of population.

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# APPENDIX A

**Table A-1** Concentration of 16 PAHs standard mix solutions at each level.

| **No.** | **Polycyclic aromatic hydrocarbon** | **Concentration (μg $ml^{-1}$)** | | | | | |
|---|---|---|---|---|---|---|---|
| | | **1st** | **2nd** | **3rd** | **4th** | **5th** | **6th** |
| 1 | Naphthalene | 10.14 | 5.07 | 2.03 | 1.27 | 1.01 | 0.63 |
| 2 | Acenaphthylene | 20.06 | 10.03 | 4.01 | 2.51 | 2.01 | 1.25 |
| 3 | Fluorene | 2.01 | 1.01 | 0.40 | 0.25 | 0.20 | 0.13 |
| 4 | Acenaphthene | 10.12 | 5.06 | 2.02 | 1.27 | 1.01 | 0.63 |
| 5 | Phenanthrene | 1.01 | 0.50 | 0.20 | 0.13 | 0.10 | 0.06 |
| 6 | Anthracene | 1.01 | 0.51 | 0.20 | 0.13 | 0.10 | 0.06 |
| 7 | Fluoranthene | 2.02 | 1.01 | 0.40 | 0.25 | 0.20 | 0.13 |
| 8 | Pyrene | 1.04 | 0.52 | 0.21 | 0.13 | 0.10 | 0.06 |
| 9 | Benz(a)anthracene | 1.00 | 0.50 | 0.20 | 0.12 | 0.10 | 0.06 |
| 10 | Chrysene | 1.02 | 0.51 | 0.20 | 0.13 | 0.10 | 0.06 |
| 11 | Benzo(b)fluoranthene | 2.01 | 1.00 | 0.40 | 0.25 | 0.20 | 0.13 |
| 12 | Benzo(k)fluoranthene | 1.03 | 0.52 | 0.21 | 0.13 | 0.10 | 0.06 |
| 13 | Benzo(a)pyrene | 0.98 | 0.49 | 0.19 | 0.12 | 0.10 | 0.06 |
| 14 | Dibenzo(a,h)anthracene | 2.15 | 1.07 | 0.43 | 0.27 | 0.21 | 0.13 |
| 15 | Benzo(g,h,i)perylene | 2.07 | 1.04 | 0.41 | 0.26 | 0.21 | 0.13 |
| 16 | Indeno(1,2,3-cd)pyrene | 1.06 | 0.53 | 0.21 | 0.13 | 0.10 | 0.07 |

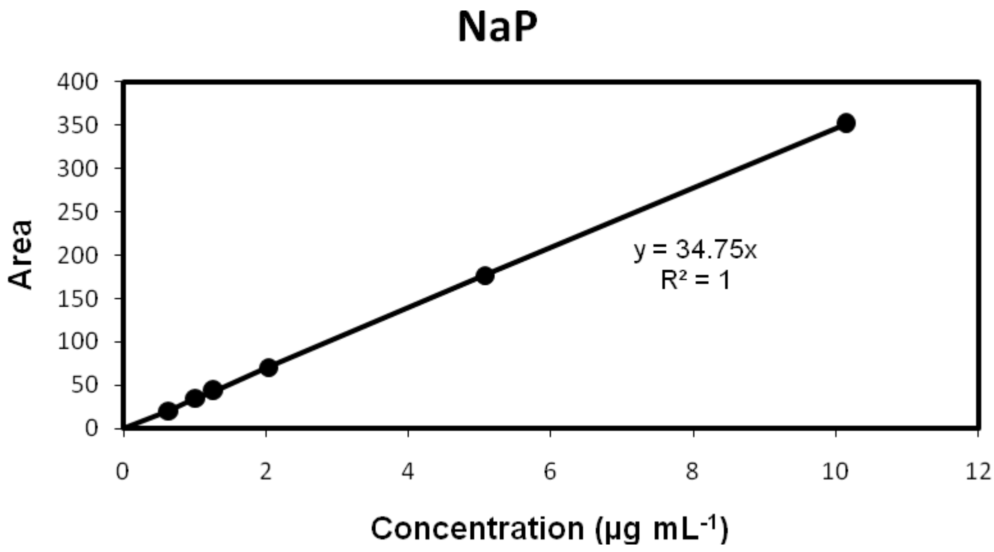

**Figure A-1** Standard calibration curve of Naphthalene.

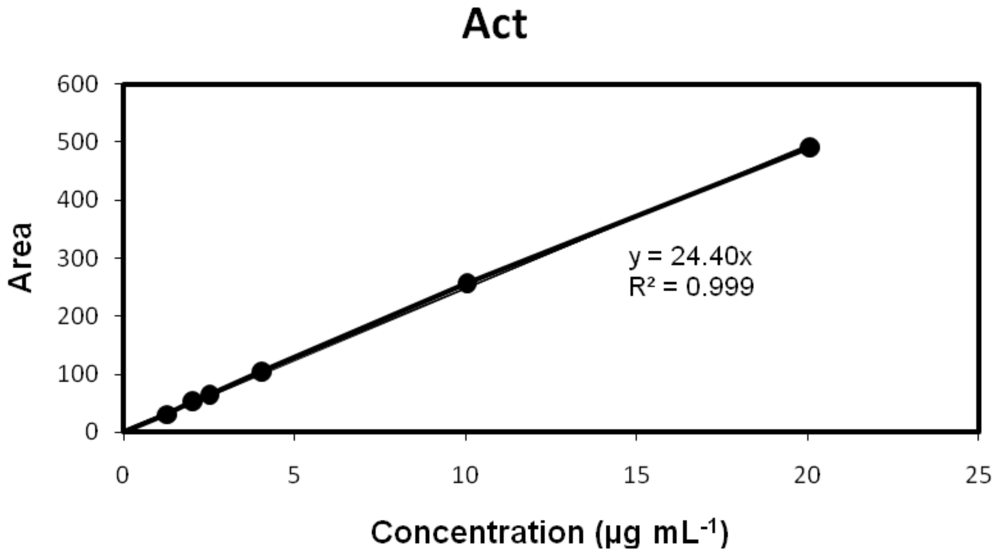

**Figure A-2** Standard calibration curve of Acenaphthylene.

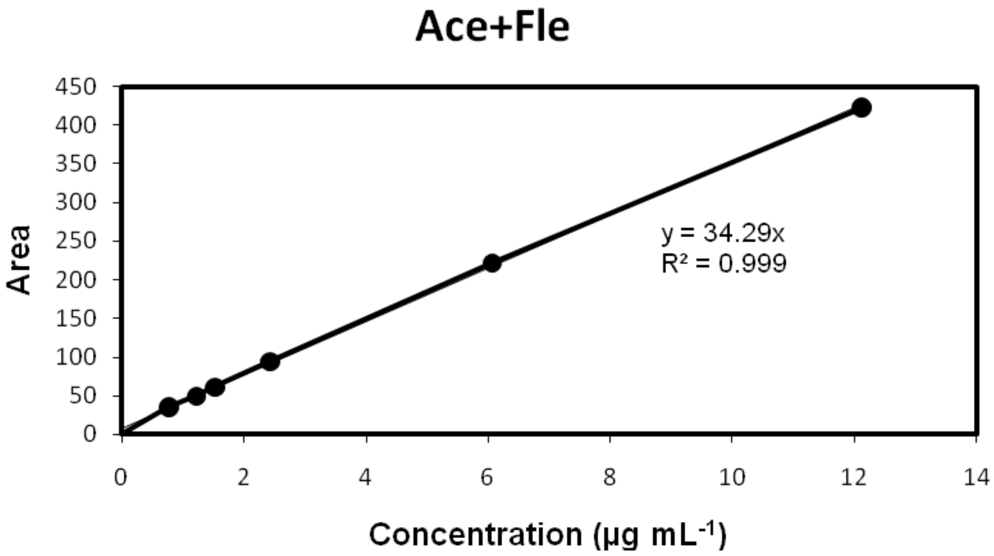

**Figure A-3** Standard calibration curve of Fluorene + Acenaphthene.

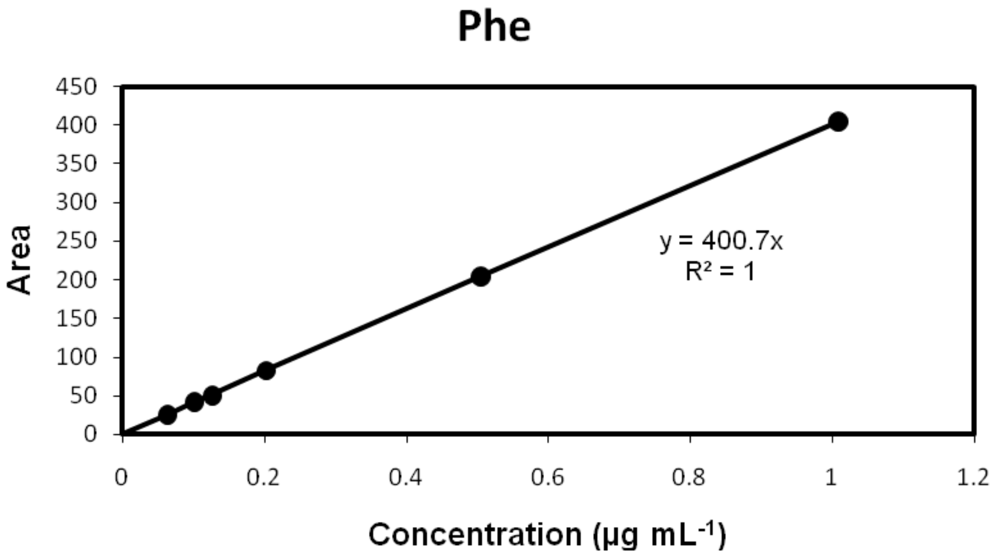

**Figure A-4** Standard calibration curve of Phenanthrene.

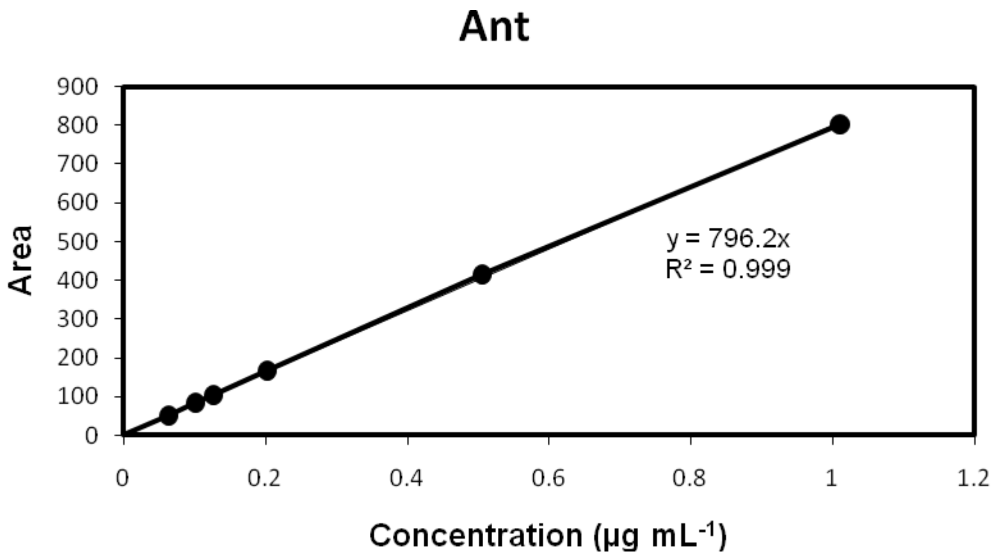

**Figure A-5** Standard calibration curve of Anthracene.

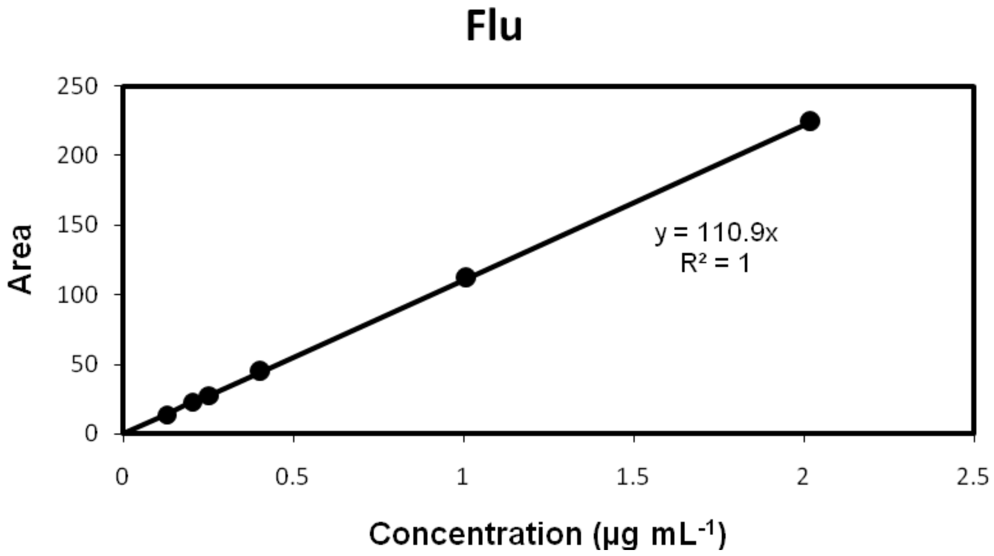

**Figure A-6** Standard calibration curve of Fluoranthene.

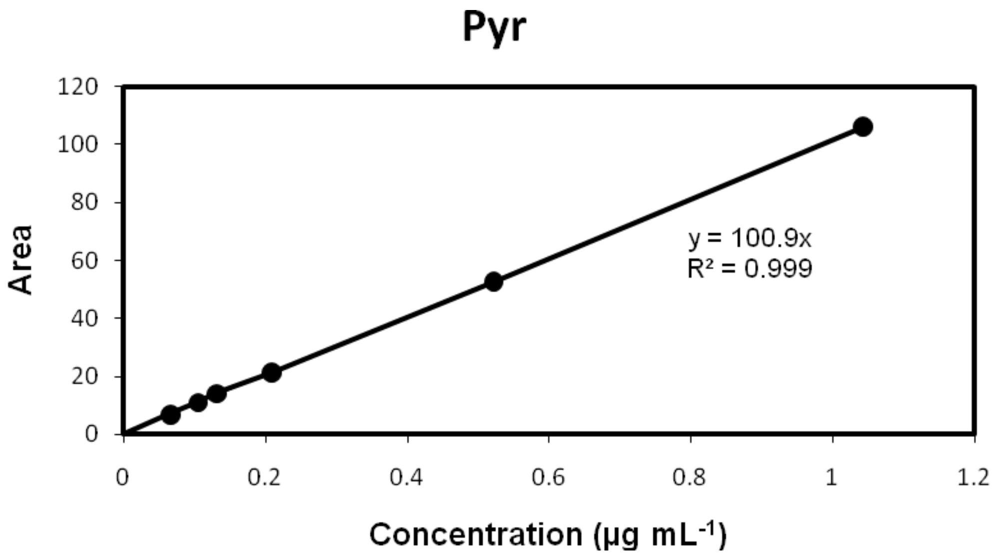

**Figure A-7** Standard calibration curve of Pyrene.

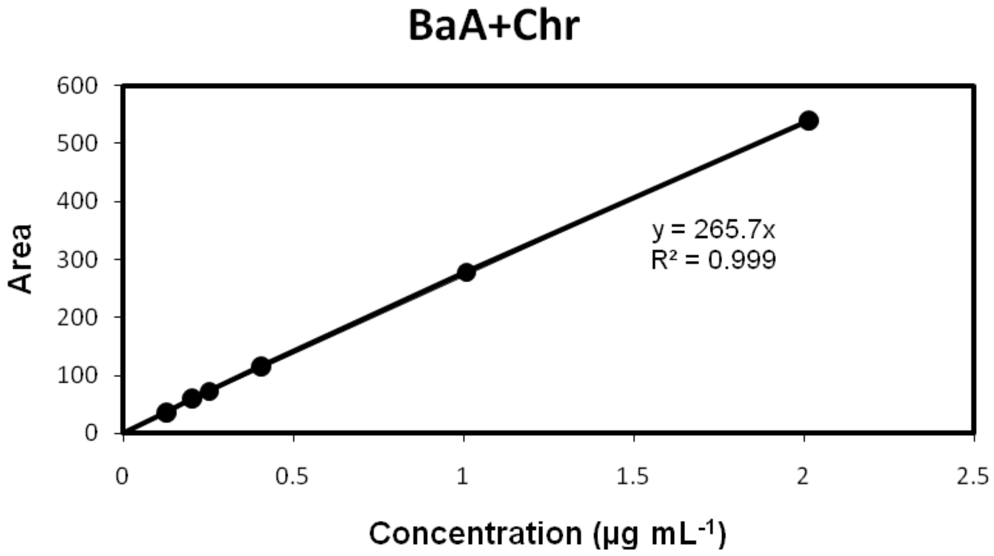

**Figure A-8** Standard calibration curve of Benz(a)anthracene +Chrysene.

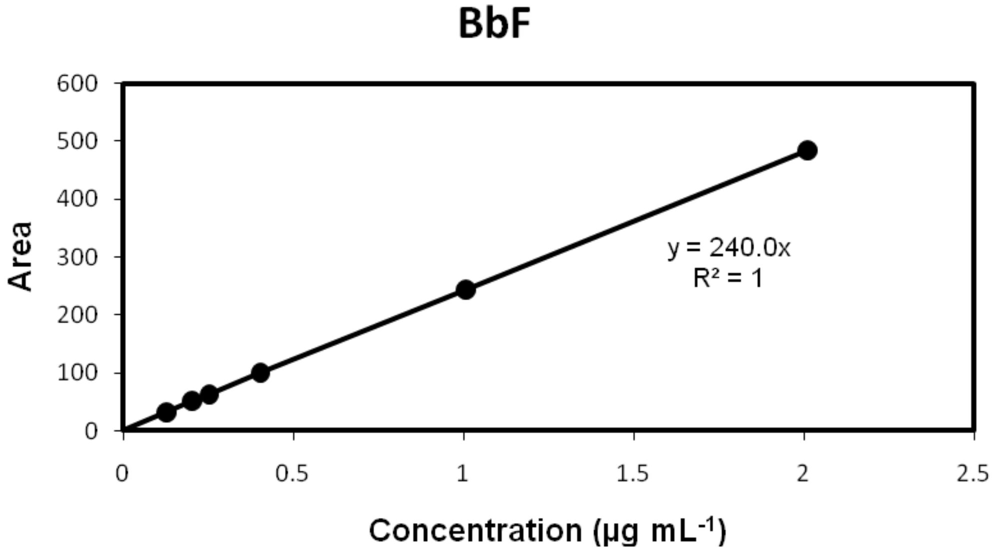

**Figure A-9** Standard calibration curve of Benzo(b)fluoranthene.

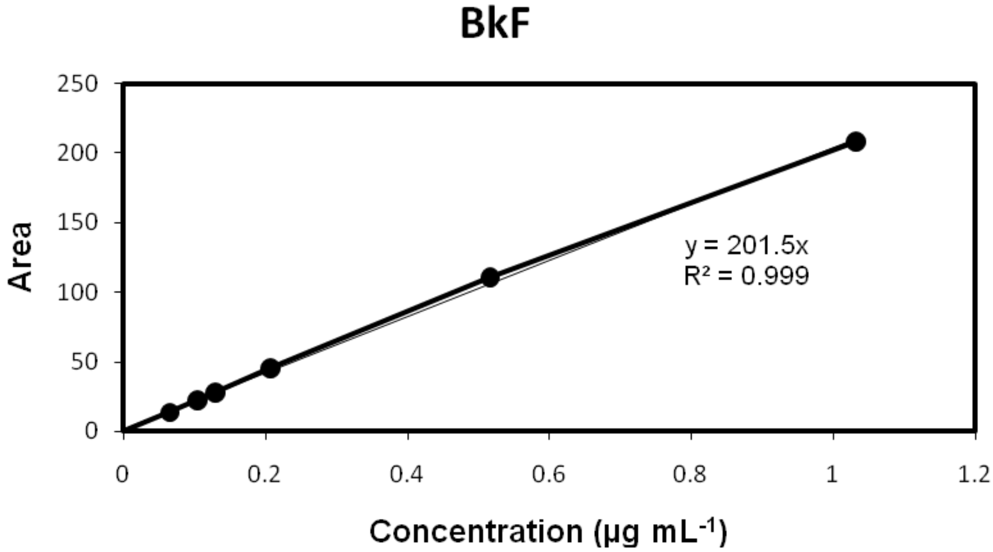

**Figure A-10** Standard calibration curve of Benzo(k)fluoranthene.

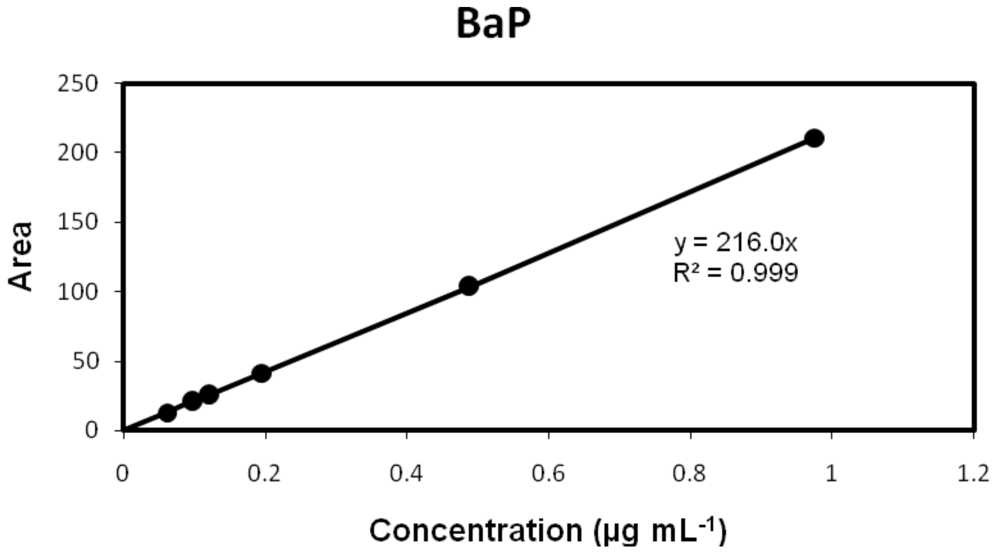

**Figure A-11** Standard calibration curve of Benzo(a)pyrene.

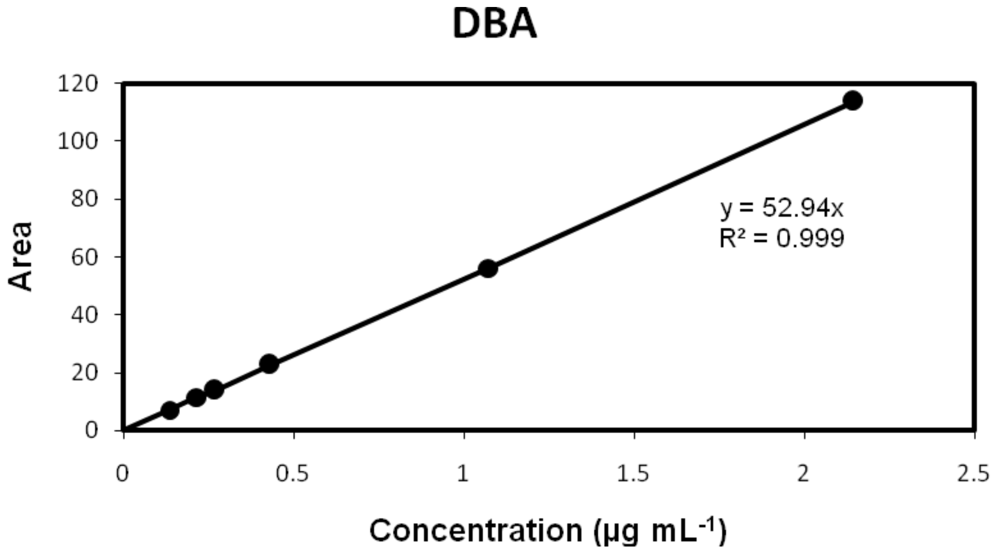

**Figure A-12** Standard calibration curve of Dibenzo(a,h)anthracene.

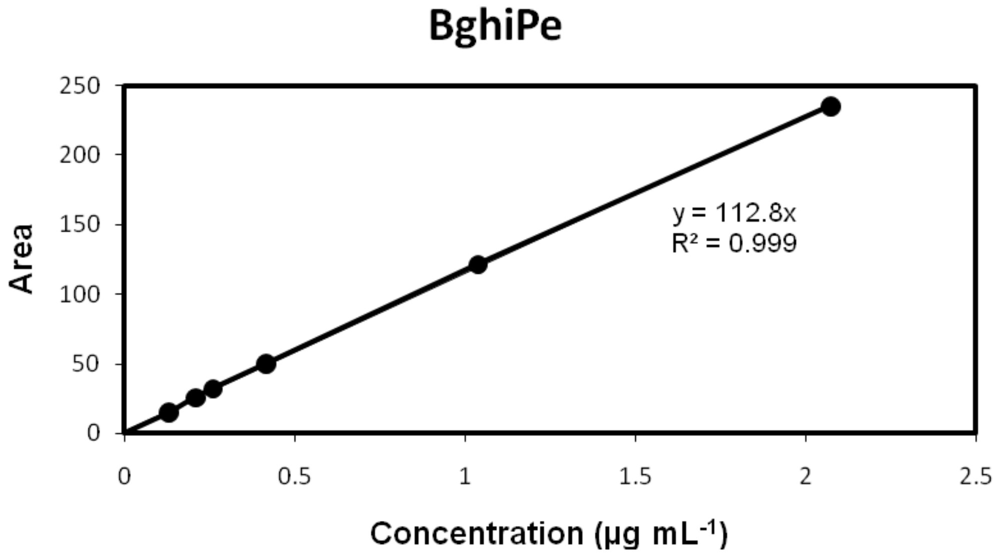

**Figure A-13** Standard calibration curve of Benzo(g,h,i)perylene.

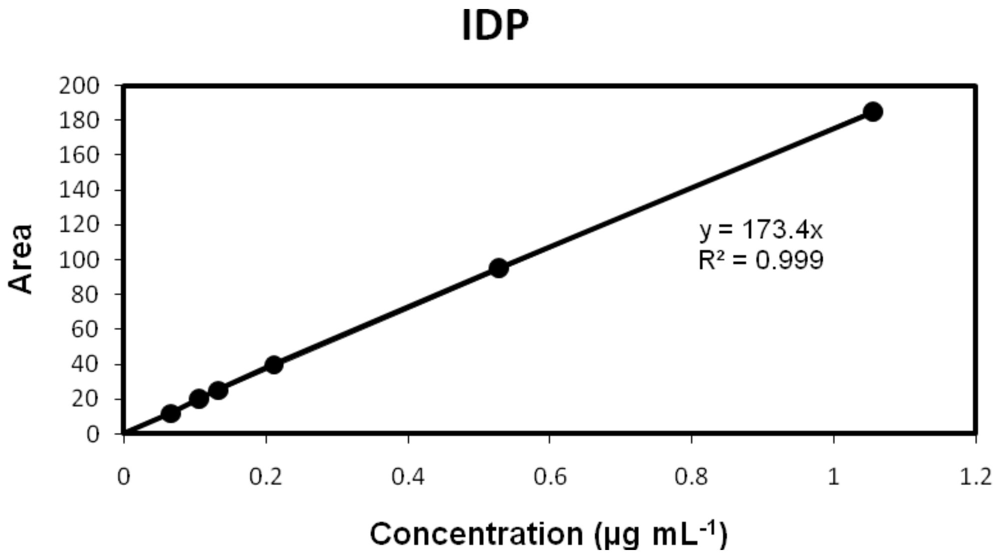

**Figure A-14** Standard calibration curve of Indeno(1,2,3-cd)pyrene.

# APPENDIX B

**Table B-1** For example particle size distribution and concentration of PMs from agricultural diesel engine fueled by PB0 with engine hour of 4500 h data.

| Size range (μm) | $d_{ave}$ (μm) | Before (g) | After (g) | Diluted mass of dust (mg) | Original mass of dust (mg) | Cumulative oversize (%) |
|---|---|---|---|---|---|---|
| <1.0 | 0.5 | 1.57159 | 1.57277 | 1.18 | 11.80 | 58.416 |
| 1.0-2.5 | 1.75 | 0.18981 | 0.19025 | 0.44 | 4.40 | 80.198 |
| 2.5-10.0 | 6.25 | 0.16545 | 0.16581 | 0.36 | 3.60 | 98.020 |
| >10.0 | - | 0.18787 | 0.18791 | 0.04 | 0.40 | 100.000 |
|  |  |  | Total | 2.02 | 20.20 |  |

Smoke particle concentration = 27.90 mg $m^{-3}$

## Calculate the MMAD for a Particle Distribution

There are numerous methods to calculate the MMAD for an aerodynamic particle size distribution generated via cascade impactor. One can plot the cumulative distribution and effective cutoff diameters on log probability graph paper which is to use the two values, one above and one below the 50% cumulative collection efficiency value, to plot the line representing the size distribution. The intersection of this line with the 50% cumulative efficiency value is taken as the MMAD. The ISO standard (International Organization for Standardization) suggests that plotting more points could result in the value being determined with less accuracy. It is argued that points further from the 50% cumulative value have less accuracy because they represent a smaller fraction of the collected mass.

- Plot the distribution data cumulative oversize (%) from Table B-1 on log-probability paper. The straight line indicates that the particle size data set is lognormal.
- Using the graph, determine the approximate particle size at 50 percent probability.
- Determine the mass median aerodynamic particle diameter (MMAD).

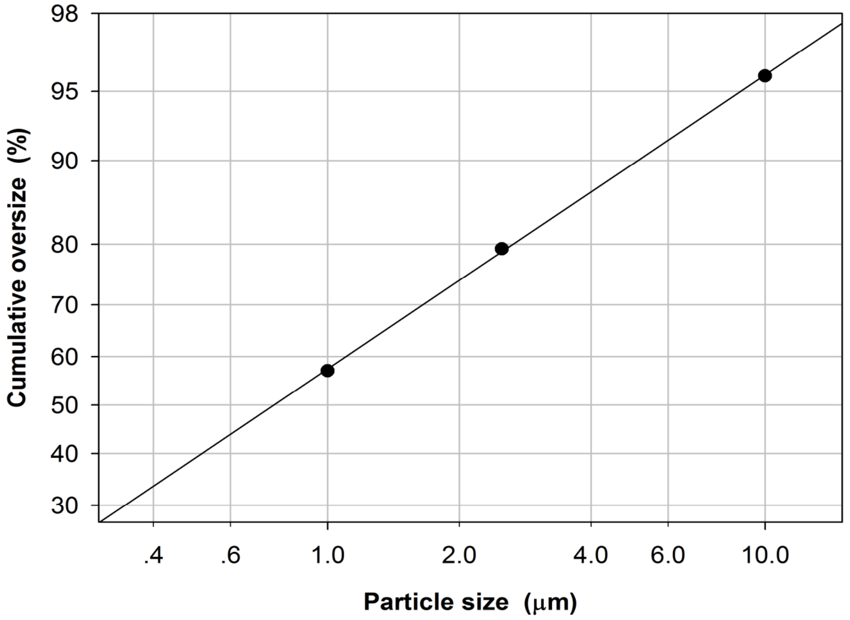

**Figure B-1** Size distribution (log-probability plot) from agricultural diesel engine fueled by PB0 with engine hour of 4500 h.

**Table B-2** For example concentration of PAHs from agricultural diesel engine fueled by PB0 with engine hour of 4500 h for particle size range of >10.0 µm data.

| PAHs | AREA of chromatogram for the standard | Concentration of standard (µg mL$^{-1}$) | AREA | M (ng) | C (ng m$^{-3}$) | C' (ng µg$^{-1}$) |
|---|---|---|---|---|---|---|
| Nap | 186.5948 | 5.07 | 3.8954 | 46.3543 | 640.253 | 0.1158 |
| Act | 254.2699 | 10.03 | 3.5547 | 70.1114 | 968.389 | 0.1752 |
| Ace+Fle | 247.0651 | 6.07 | 2.5723 | 31.5781 | 436.161 | 0.0789 |
| Phe | 213.6568 | 0.50 | 5.7854 | 6.8304 | 94.343 | 0.0170 |
| Ant | 430.3992 | 0.51 | 97.304 | 57.0849 | 788.464 | 0.1427 |
| Flu | 114.1045 | 1.01 | 7.6248 | 33.7457 | 466.1 | 0.0843 |
| Pyr | 55.2159 | 0.52 | 32.9049 | 155.5380 | 2148.314 | 0.3888 |
| BaA+Chr | 278.3765 | 1.01 | 3.4774 | 6.2928 | 86.917 | 0.0157 |
| BbF | 250.5885 | 1.01 | 7.4304 | 14.9000 | 205.801 | 0.0372 |
| BkF | 107.3893 | 0.52 | 4.4137 | 10.6039 | 146.462 | 0.0265 |
| BaP | 110.5542 | 0.49 | 8.3299 | 18.3847 | 253.932 | 0.0459 |
| DBA | 57.7279 | 1.07 | 3.3082 | 30.7457 | 424.664 | 0.0768 |
| BghiPe | 111.0500 | 1.04 | 3.5977 | 16.8063 | 232.131 | 0.0420 |
| IDP | 87.2245 | 0.53 | 4.6620 | 14.1104 | 194.895 | 0.0352 |
|  |  |  | Total | 513.0866 | 708.6826 | 1.2820 |

Total filter mass = 1879.10 µg

Filter mass used for analysis = 1879.10 µg

Sampling volume = 0.72 m$^3$

TSP concentration = 552.49 µg m$^{-3}$

The M (ng) is calculated as follows:

$$M = \frac{concentration\ of\ std. \times area\ of\ chromatogram\ for\ sample}{area\ of\ chromatogram\ for\ std.} \times \frac{total\ filter\ mass}{filter\ mass\ used\ for\ analysis} \times 0.5 \times 1000$$

The C (ng m$^{-3}$) is calculated as follows:

$$C = \frac{M}{sampling\ volume} \times 10$$

The C′ (ng μg$^{-1}$) is calculated as follows:

$$C' = \frac{C}{TSP\ concentration}$$

# VITAE

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**Scholarship Awards during Enrolment**

Scholarship was awarded by

- The scholarship from Higher Education Development Project: Center of Excellence for Innovation in Chemistry (PERCH-CIC), funded by The Royal Thai Government.
- The annual research grant from Prince of Songkla University for fiscal years 2008-2009.
- Graduate school, Prince of Songkla University.

Awards and Honors

- Outstanding poster presentation in The International Congress for Innovation in Chemistry (PERCH-CIC Congress VI), May 3-6 , 2009, Thailand.
- JSPS Exchange Program for East Asian Young Researchers, "Building of Young Researchers' Network for Environmental Preservation", September 14, 2009, Kanazawa University, Japan.

**List of Proceedings**

1. Phoungthong, K.; Tekasakul, S. and Tekasakul, P. Characteristics of Particulate Matters from Emission of Engine Fueled by Biodiesel Blends.: The International Congress for Innovation in Chemistry (PERCH-CIC Congress VI), Jomtien Palm Beach Hotel & Resort Pattaya, Chonburi, Thailand, May 3-6, 2009. (Poster)

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