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โครงการคุณลักษณะของอนุภาคและโพลีไซคลิกอะโรแมติกไฮโดรคาร์บอน
จากเครื่องยนต์ที่ใช้น้ำมันปาล์มผสมเป็นเชื้อเพลิง

Characteristics of particulate matters and associated
polycyclic aromatic hydrocarbon from emission of engines
fueled by palm oil blends

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บทคัดย่อ

งานวิจัยนี้ศึกษาคุณลักษณะทางกายภาพและทางเคมีของอนุภาคควันที่เกิดจากการเผาไหม้ของเครื่องยนต์ทางการเกษตรและเครื่องยนต์ที่ใช้ในยานพาหนะรุ่นเก่าที่ใช้น้ำมันปาล์มผสมเป็นเชื้อเพลิง โดยออกแบบการทดลองเพื่อศึกษาความเข้มข้นและการกระจายขนาดของอนุภาค และองค์ประกอบทางเคมีในอนุภาค โดยเฉพาะอย่างยิ่งสารพอลิไซคลิกแอโรแมติกไฮโดรคาร์บอน (PAHs) ที่เป็นกลุ่มสารก่อมะเร็งและสารก่อการกลายพันธุ์ เครื่องยนต์ได้รับการทดสอบบนแท่นทดสอบสมรรถนะเพื่อทำการเก็บตัวอย่างไอเสียที่ผ่านการเจือจางแล้ว ด้วยเครื่องเก็บตัวอย่าง particulate matter air sampler ที่มีขนาดตัดเส้นผ่านศูนย์กลางของอนุภาคเป็น 10, 2.5 และ 1 μm ซึ่งน้ำมันเชื้อเพลิงที่ใช้ศึกษาเป็นน้ำมันดีเซลที่จำหน่ายตามท้องตลาด (PBO) และน้ำมันปาล์มผสมดีเซล หลังจากนั้นใช้เทคนิคลิควิดโครมาโตกราฟีสมรรถนะสูง (HPLC) ร่วมกับตัวตรวจวัดชนิดไดโอดอะเรย์ (HPLC-DAD) เพื่อวิเคราะห์หาปริมาณสารพอลิไซคลิกแอโรแมติกไฮโดรคาร์บอนทั้ง 16 ชนิดในตัวอย่างอนุภาค ผลการศึกษาพบว่าอนุภาคควันจากเครื่องยนต์ที่ได้แสดงการกระจายขนาดอนุภาคแบบโหมดเดียว ซึ่งขนาดอนุภาคส่วนใหญ่อยู่ในช่วงของ accumulation mode มีขนาดเล็กกว่า 1 μm โดยที่ขนาดของอนุภาคเฉลี่ยมีค่าลดลงเมื่อเพิ่มสัดส่วนการผสมโดยปริมาตรของน้ำมันปาล์มจาก 0-40% สำหรับเครื่องยนต์ทางการเกษตรแต่แนวโน้มไม่ชัดเจนสำหรับเครื่องยนต์ที่ใช้ในยานพาหนะรุ่นเก่า เมื่ออายุของเครื่องยนต์เพิ่มมากขึ้นพบว่าความเข้มข้นของอนุภาคและขนาดของอนุภาคเฉลี่ยมีค่าเพิ่มขึ้น 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 และเมื่อเวลาการใช้งานของเครื่องยนต์เพิ่มมากขึ้น พบว่าค่าความเข้มข้นของสาร PAHs เพิ่มขึ้นด้วยอันเป็นผลเนื่องมาจากการสึกหรอของเครื่องยนต์ที่เพิ่มมากขึ้น จากผลการทดลองแสดงให้เห็นได้อย่างชัดเจนว่า เมื่อสัดส่วนการผสมโดยปริมาตรของน้ำมันปาล์มผสมเพิ่มขึ้น ค่าความเข้มข้นของอนุภาคและความเข้มข้นของสาร PAHs จะลดลง ทั้งนี้เนื่องมาจากปริมาณออกซิเจนที่มีมากกว่าทำให้เกิดการเผาไหม้ได้สมบูรณ์มากกว่าในกรณีของน้ำมันดีเซลหรือ PBO

ABSTRACT

Physical and chemical characteristics of particulate matters (PM) and associated polycyclic aromatic hydrocarbons (PAHs) from emission of agricultural diesel and conventional 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, and palm oil blend diesel were used in the engines. 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% for the agricultural machine engines but the trend was not clear for the conventional engines. 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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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 subsidize 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). These 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, one type of the biodiesel, 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 Objectives

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.

1.3 Scope 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) and conventional diesel engines fueled by palm oil blends (PB0, PB20 and PB40).

2. Sample particles using a new inertial-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.

1.4 Expected Outcome

Outcome of this research will be beneficial to government agencies overseeing energy and environment policies as biodiesel is an important biofuel 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. Necessary measures may be needed if adverse effects are to be found.

2. LITERATURE REVIEW AND THEORY

2.1 Literature Review

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. O₃, NO_x, and SO₂ (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 light (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 5 μm in diameter pose the greatest problems, because particles in this size range can travel into the respiratory system. 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. Insignificant reduction of PAHs and nitro-PAHs was found 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 running 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%), CO₂ (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-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.

2.2 Theory

2.2.1 Particle collection by impaction

Impaction is a special case of curvilinear motion that finds extensive applications in the collection and measurement of aerosol particles. Impaction is a common method for collecting dust for evaluation of occupational environment, 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 . This instrument 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 (LPI) 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.

2.2.2 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 escape. 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.

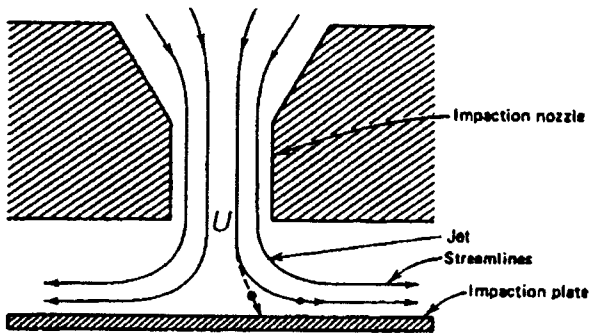


Fig. 2.1 Schematic diagram of a conventional impactor (Baron, 2005).

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

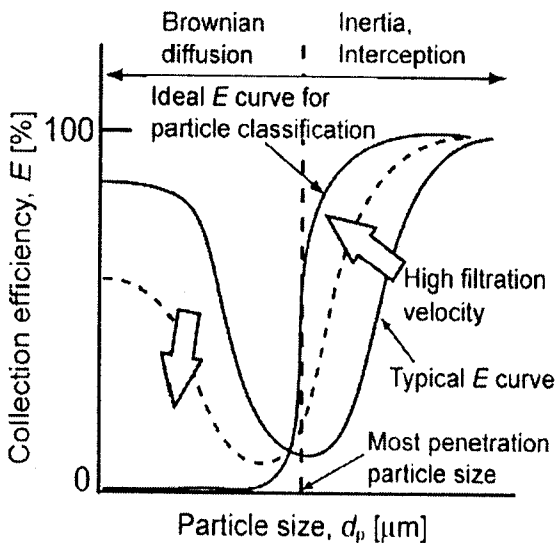


Fig. 2.2 Principle of inertial impaction.

The parameter that governs collection efficiency is the Stokes number, or impaction parameter, which is defined for an impactor as

$$Stk = \frac{C_c \rho_p d_p^2 u}{9\mu d_f} \quad (2.1)$$

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

2.2.3 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 number is defined as:

$$Pe = \frac{u d_f}{D} \quad (2.2)$$

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 $1.0 \text{ }\mu\text{m}$ decreases because of less Brownian diffusion collection but that of particles larger than $1.0 \text{ }\mu\text{m}$ 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 filter will be used in a sampler in this project in order to analyze PAHs associated with the particles generated by agricultural diesel engine fueled by palm oil blends.

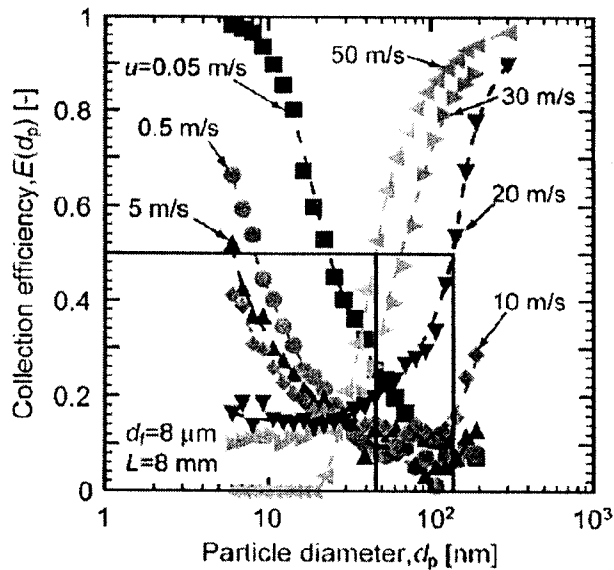


Fig. 2.3 Fractional collection efficiency of inertial filter at various filtration velocities.

2.2.4 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.

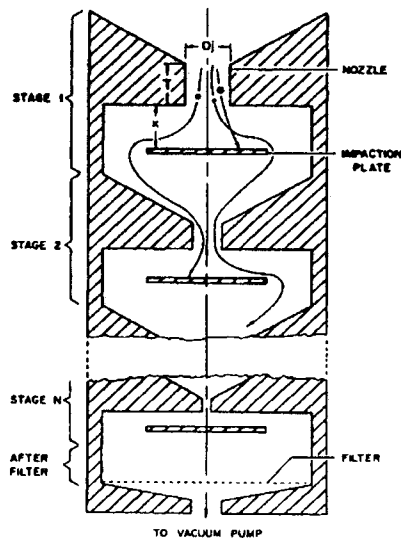


Fig. 2.4 Schematic diagram of a cascade impactor (Baron, 2005).

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 separation 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.

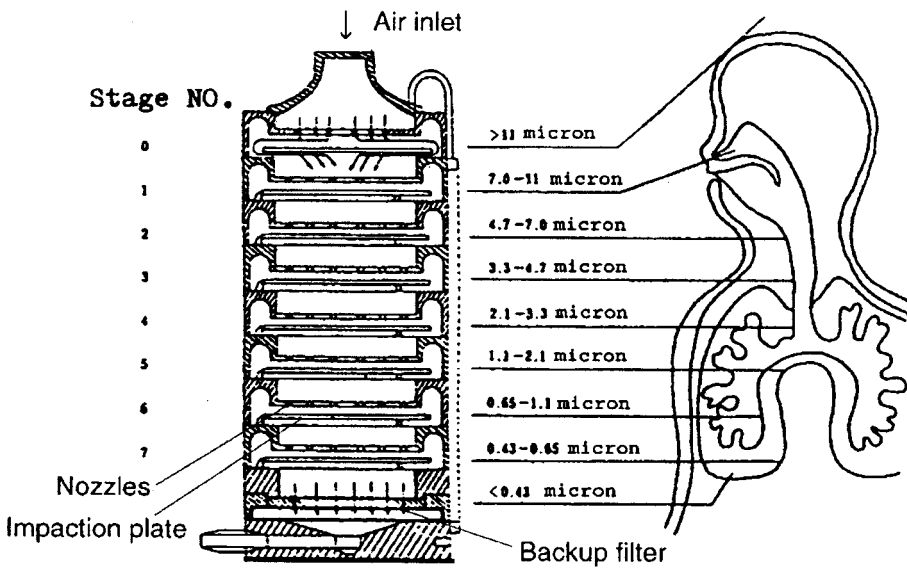


Fig. 2.5 An eight-stage Andersen impactor.

The recently developed particulate matter air sampler consists of four stages (PM₁₀/PM_{2.5}/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 .

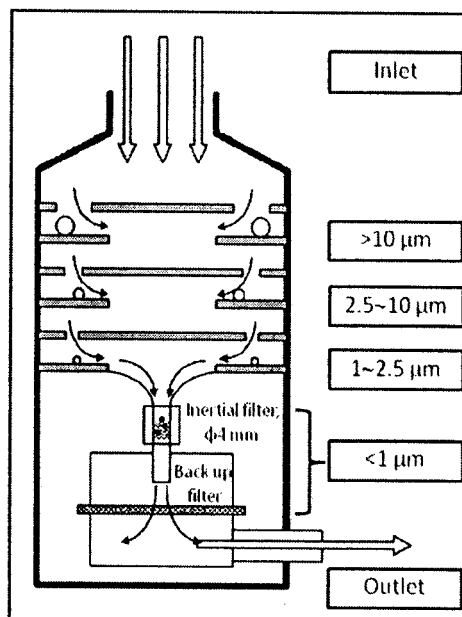


Fig. 2.6 A schematic diagram of the particulate matter air sampler (Kanomax, Japan) indicating the cut-off diameters.

2.2.5 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 than the MMAD, and another 50% will be larger.

2.2.6 Palm oil

Palm oil is 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, $\text{CH}_3-(\text{CH}_2)_{14}-\text{COOH}$. 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.

2.2.7 Petroleum diesel fuel

Diesel fuel or petroleum diesel or fossil diesel is fuel used in diesel engines. Diesel fuel is produced from petroleum distillate fraction 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 happens between distillate and fuel oil (FO) or heavy fuel oil (HFO).

2.2.8 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 (Fig. 2.7). This type can be used directly with diesel engine, especially the engine with low speed such as agricultural diesel engine.

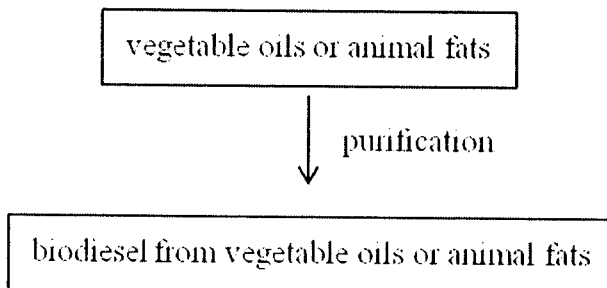


Fig. 2.7 Process of biodiesel from vegetable oils or animal fats.

2. Biodiesel blends with petroleum diesel. This type is derived from petroleum diesel and biodiesel from type one in different ratios (Fig. 2.8) 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.

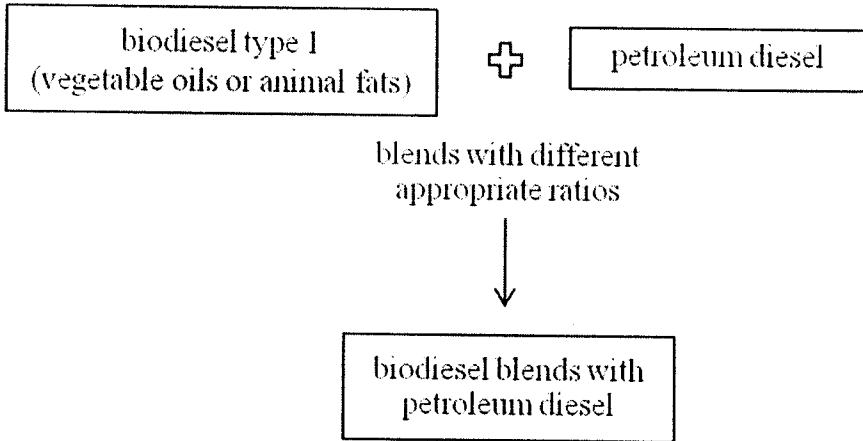


Fig. 2.8 The process of biodiesel from biodiesel blend with petroleum diesel.

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 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 (Fig. 2.9).

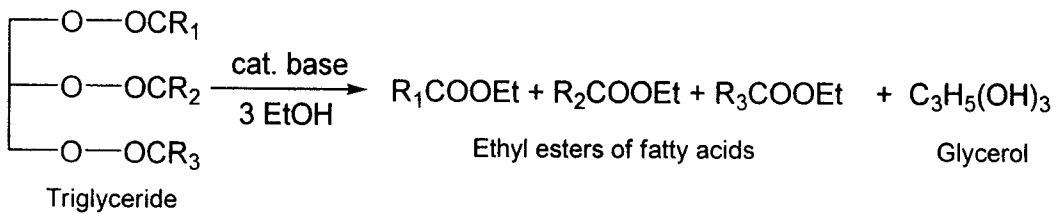


Fig. 2.9 Reaction for transesterification in producing biodiesel.

- 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.

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 (N₂), water vapor (H₂O) and carbon dioxide (CO₂), 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 from 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).

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	PAHs is a very carcinogenic, mutagenic and

matter, including polycyclic aromatic hydrocarbons (PAHs)	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

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

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 (<http://www.hempcar.org/petvshemp.shtml>).

- 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.

2.2.9 Polycyclic aromatic hydrocarbons (PAHS)

Polycyclic aromatic hydrocarbons (PAHs) are a group of hydrocarbon compounds containing fused aromatic rings with synonyms of 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

e.g., NO_x, SO₂, O₂, etc. may form hetro-PAHs. The carcinogenicity and mutagenicity of many of these hetero-PAHs compounds are greater than their parent compounds.

Submicron aerosol particles have 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, 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 is 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 sources of PACs.

The physical properties of selected PAHs are 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 orders. 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.

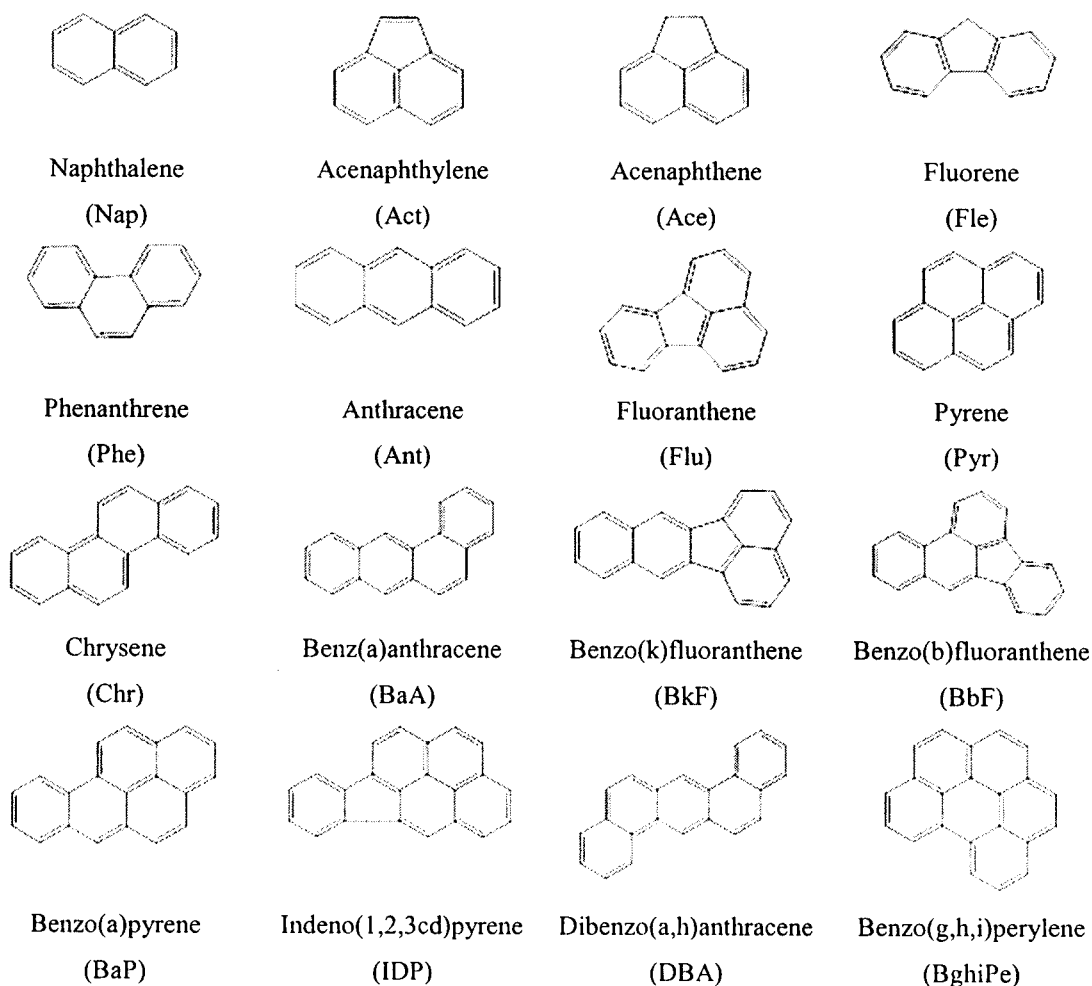


Fig. 2.10 Structures of sixteen PAH compounds (EPA₁₆).

PAH concentrations in various 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]pyrene	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 = boiling point, VP = vapor pressure of the solid, S = water solubility (Leo, 2006).

PAHs are generally non-reactive 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 possess 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).

3. METHODOLOGY

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 and conventional diesel engines 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 chemicals

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

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

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 M Ω , 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 suitable for field sampling. 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, cause a change in the cut-off diameters in all stages. The particles were collected on quartz fiber filters. Donut-shape filters with 65x30 mm diameters 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 was used as an inertial filter. 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 enough during the experiment. The improvement of the cut-off is under study.

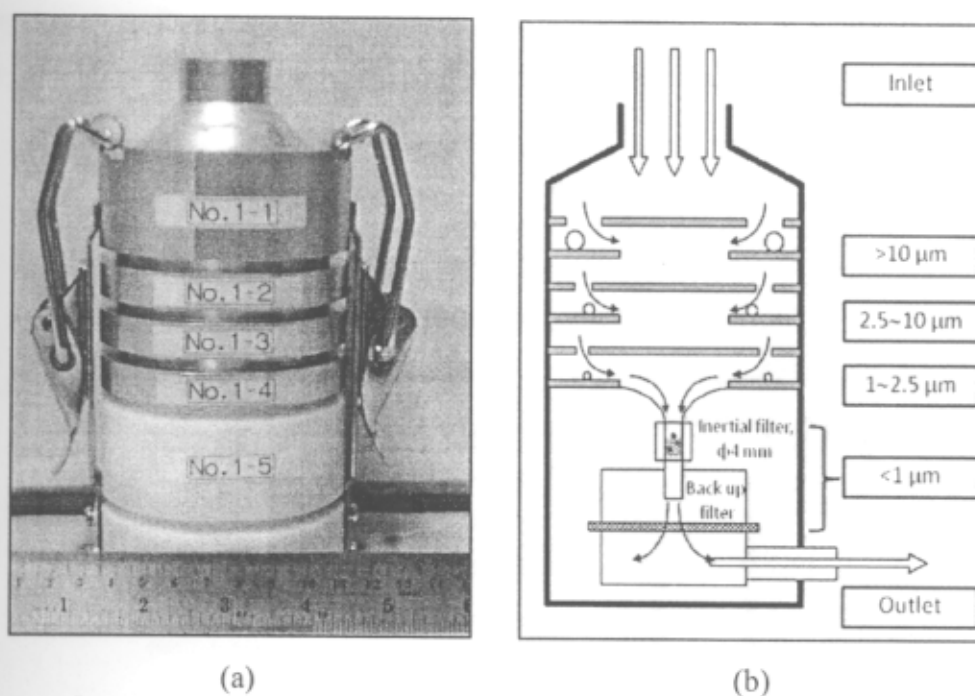


Fig. 3.1 The particulate matter air sampler: (a) a photograph, and (b) a schematic diagram indicating the cut-off diameters.

3.2.2 Dilution system

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 pulls in the aerosol. Consequently, the dilution stage is a self-introduction system.

Figure 3.2 shows a cross-section of the dilution stage. Particle-free air with a volume flow rate V_e , 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.

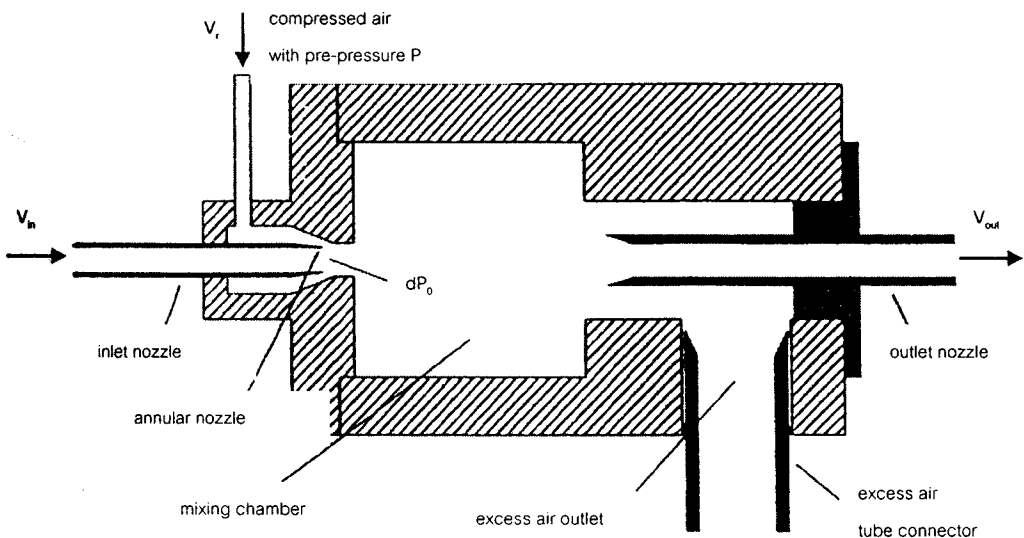


Fig. 3.2 Cross section of the dilution stage.

3.2.3 Engine dynamometers

A 12-horsepower hydraulic dynamometer (Plint&Partners, ETB 1244) was used for measuring force, moment of force (torque), or power in the experiment for agricultural diesel engines. 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. For conventional diesel engine test, another dynamometer (ESSOM, MT504) was used.

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

3.2.4 Fuels

Fuels used in this study are commercial petroleum diesel (PB0) and two different blending mixtures of PB0 with palm oil (PB100). The mixtures containing 30% and 40% palm oil by volume, namely PB30 and PB40 respectively, were used for agricultural diesel engines, while PB20 and PB40 were used in conventional diesel engines. Before blending with diesel, Palm oil 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 (°C)	102	135	ASTM-D93
Viscosity at 40 °C (cSt)	3.013	50.35	ASTM-D445
Density (g mL ⁻¹ at 15 °C)	0.833	0.880	ASTM-D1298
Cloud point (°C)	3	8	ASTM-D2500
Pour point (°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 (°C)	NA	319	ASTM D-86
High heating value (MJ kg ⁻¹)	44.3	41.7	ASTM D-240

NA: Not Available, 1b: satisfaction

3.2.5 Engines

Agricultural diesel engines

Agricultural diesel engines (Kubota, RT 80) used in the present study is shown in Fig. 3.3 with specifications described in Table 3.2.

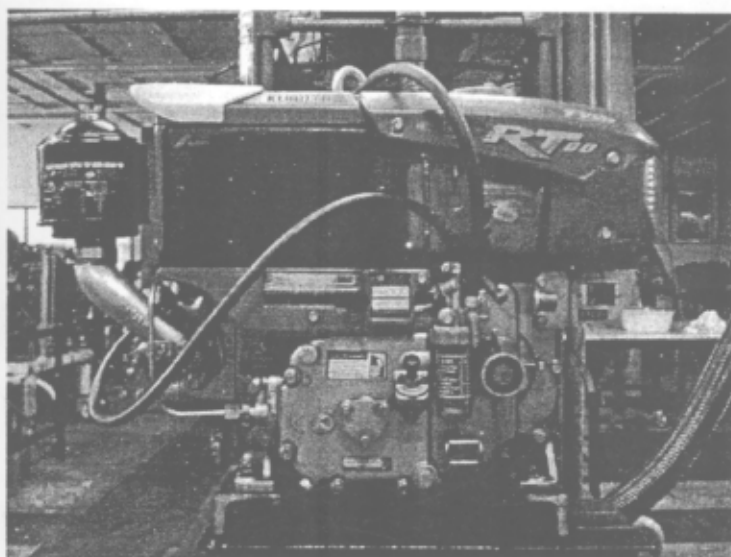


Fig. 3.3 The agricultural diesel engine used in this experiment.

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

Conventional diesel engines

Conventional indirect injection turbocharged diesel engines (Toyota, Type 2LT) shown in Fig. 3.4 was used in this experiment. Its specifications are described in Table 3.3.

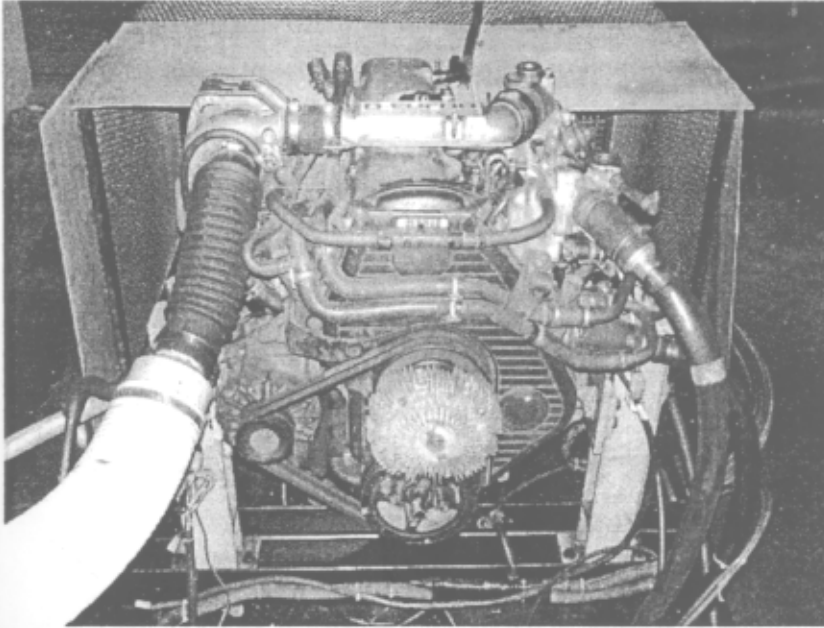


Fig. 3.4 The conventional diesel engine used in this experiment.

Table 3.3 Conventional indirect injection turbocharged diesel engine specifications.

Parameters	Specifications
Brand	Toyota
Model	2LT
Engine type	Water cooling serial 4 cylinder SOHC turbo diesel engine
Injection	Indirect injection (IDI)
Displacement	2446 c.c.
Bore x stroke	92 x 92 mm
Volumetric compression ratio	20.0 : 1
Maximum power	69.14 kW @ 4,000 rpm (94 HP @ 4,000 rpm)
Maximum torque	22.0 kg-m @ 2,400 rpm (215.75 N-m @ 2,400 rpm)
Fuel system	Bosch type distribution type (jet pump)

3.2.6 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 μ m, 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 μ m and diameter of 47 mm (Vertical, Thailand)
- Nylon membrane disc filter with pore size of 0.45 μ m 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 μ L (Nichiryo, Japan)
- General glasswares, such as round bottom flask, volumetric flask, etc.

3.2.7 Apparatus used for HPLC assay

High-performance liquid chromatography (Agilent, 1100) with diode array detector (HPLC-DAD) used in the present study 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 μ m) with a Vertisep C18 guard column (7.5 x 4.6 mm I.D., particle size 5 μ m).

3.3 Experimental Methods

3.3.1 Engine, dynamometer and operating conditions

Agricultural diesel engines

The experiments were conducted 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. 3.5 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 comprises a 75% of full load with constant speed at 2200 rpm according to a previously reported procedure (Prateepchaikul et al., 2003).

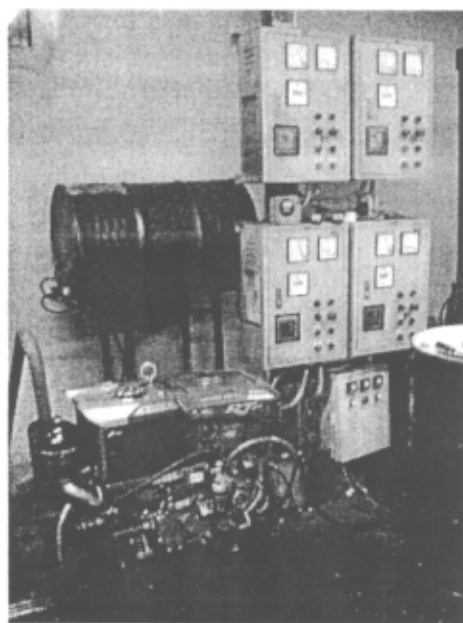


Fig. 3.5 The engine and the generator used in this work.

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.

Conventional diesel engines

Long-term test was conducted to examine effects of palm oil blends on engine durability comparing to diesel fuel. The engine was operated with ESSOM dynamometer (model MT504), in which the driving cycle of the testing was in accordance with a constant speed test at 2400 rpm under loads in the range of 5-37.5 kW. It was also tested with a full-loaded variable speed test for speeds in the range of 2000-2800 rpm. The engine was tested on an ambient temperature, relative humidity, air and fuel flow rates, brake torque, engine speed, and exhaust gas temperature (EGT) were recorded using the a data acquisition system of the dynamometer according to the previously investigation (Leevijit and Prateepchaikul, 2011). Then the engine was disassembled to be visually checked for wear and weight loss of piston rings, cylinder head, piston pump and inlet and exhaust valves. Lubricating oil was changed at every 100 hours.

Before PM sampling, the engine was mounted on a stand and was coupled with an electric generator for 200 hours which was equivalent to 200 km of a driving distance. The generated electricity was supplied to a series of light bulbs for adjusting engine loads. After every 200 hour of running, in which the driving cycle of the testing was in accordance with the small-size water-cooled diesel engines in land use (JIS B8018, 1989), it was operated with a dynamometer for a period of 20 minutes after 10 minutes warm-up to avoid effects from residue of other fuel in the previous run. The engine warm-up included an idle state of about 5 minutes until accelerated speed to 2200 rpm was achieved. The transient cycle comprised a 70% of full load with constant speed of brake horsepower at 2400 rpm.

3.3.2 Filter treatment

Before sampling, the filters were treated in a dark desiccator at constant temperature ($\sim 25^{\circ}\text{C}$) and constant humidity ($\sim 50\%$ 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 placed 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. 3.6. 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. Fig. 3.7 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 Δd is the particle size interval of each stage of the particulate matter air sampler. Mass fraction can then be determined from:

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

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

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

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:

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

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

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

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

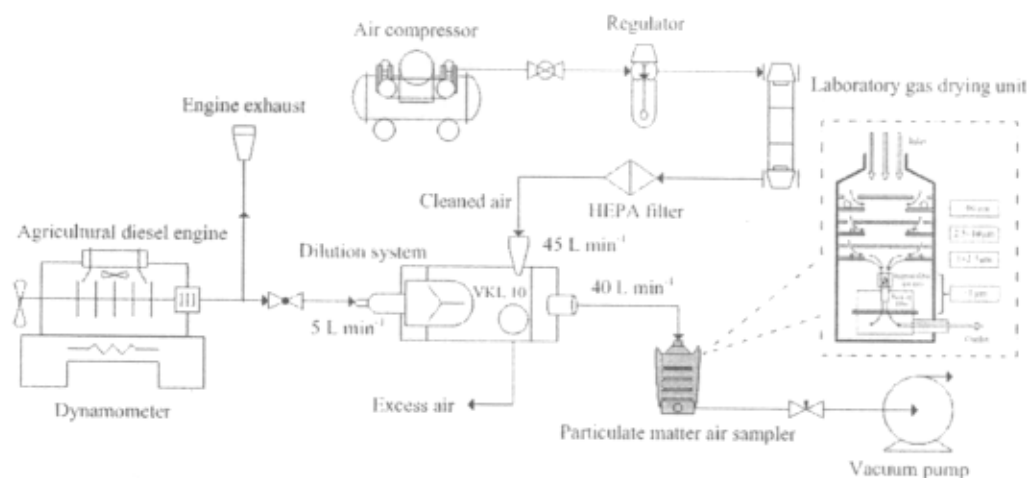


Fig. 3.6 The schematic diagram of the experimental set up for measuring the size distribution of particulate matters.

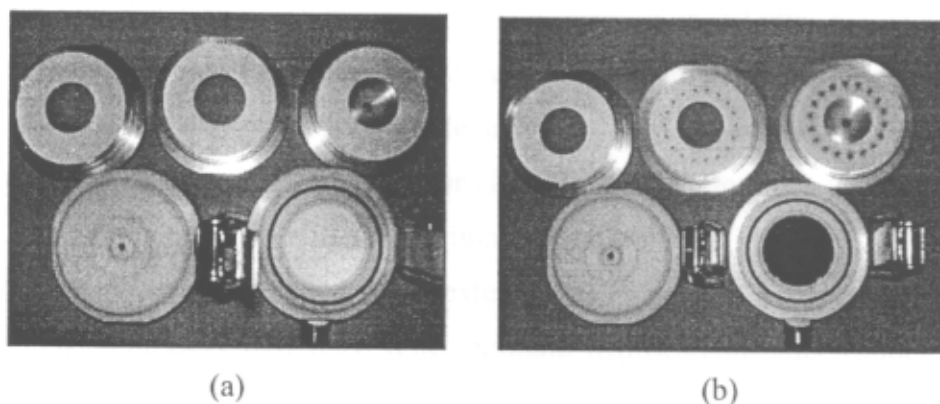


Fig. 3.7 Photographs of filters used in all stages of particulate matter air sampler: (a) before sampling and (b) after sampling.

3.3.4 Analysis of polycyclic aromatic hydrocarbons

Sixteen 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 by 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 $\leq 30^\circ\text{C}$) 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. 3.8. The 16 PAHs were analyzed using a high performance liquid chromatography (HPLC) with diode array detector (DAD), as shown in Fig. 3.9.

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 3.4 and 3.5. 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. 3.10 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.

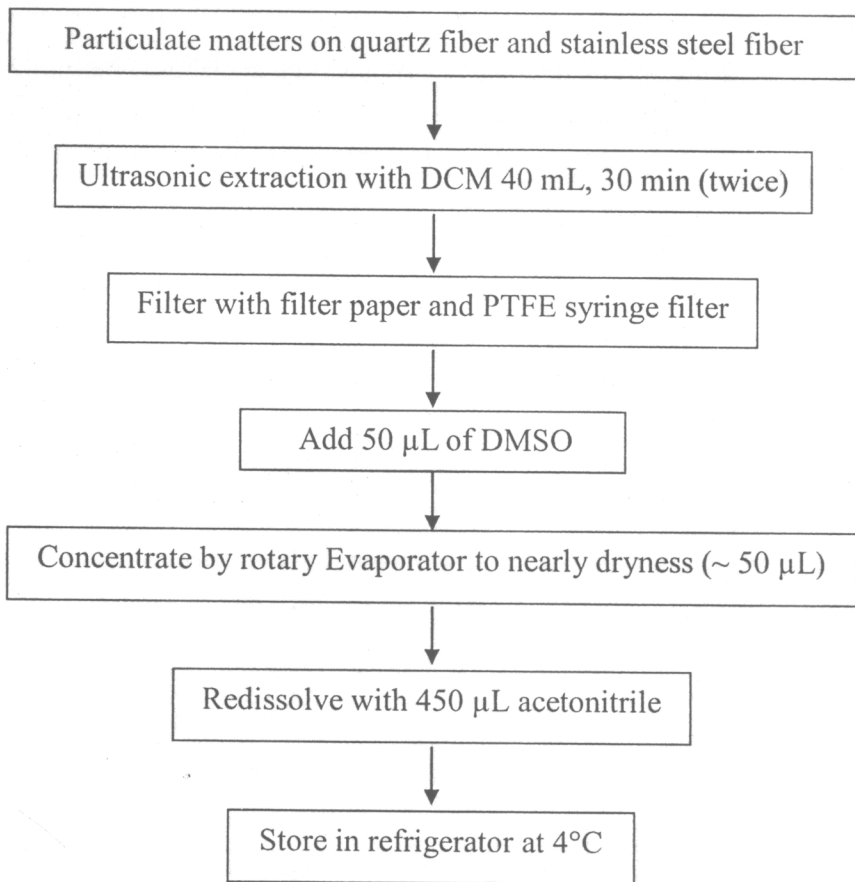


Fig. 3.8 Procedure of the sample extraction.

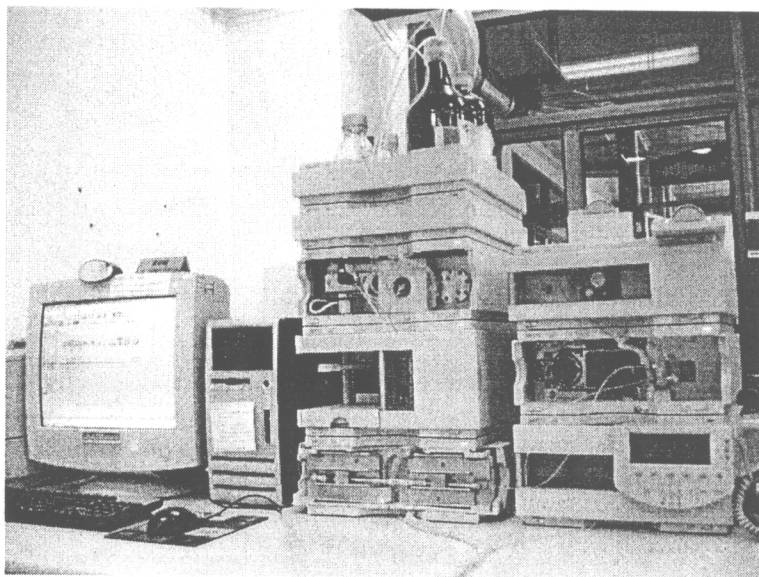


Fig. 3.9 Photograph of the HPLC/DAD system (Agilent, 1100) used for PAH analysis.

Table 3.4 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 3.5 HPLC conditions used in this work (Chomanee et al., 2009).

Column	VertiSep UPS C18 column 4.6x250 mm, 5 μ m
Guard	VertiSep 5 μ m
Temperature	25 °C
Mobile Phase	A : Acetonitrile B : Ultra pure water
Inject Volume	25 μ L
λ for detection	254 nm

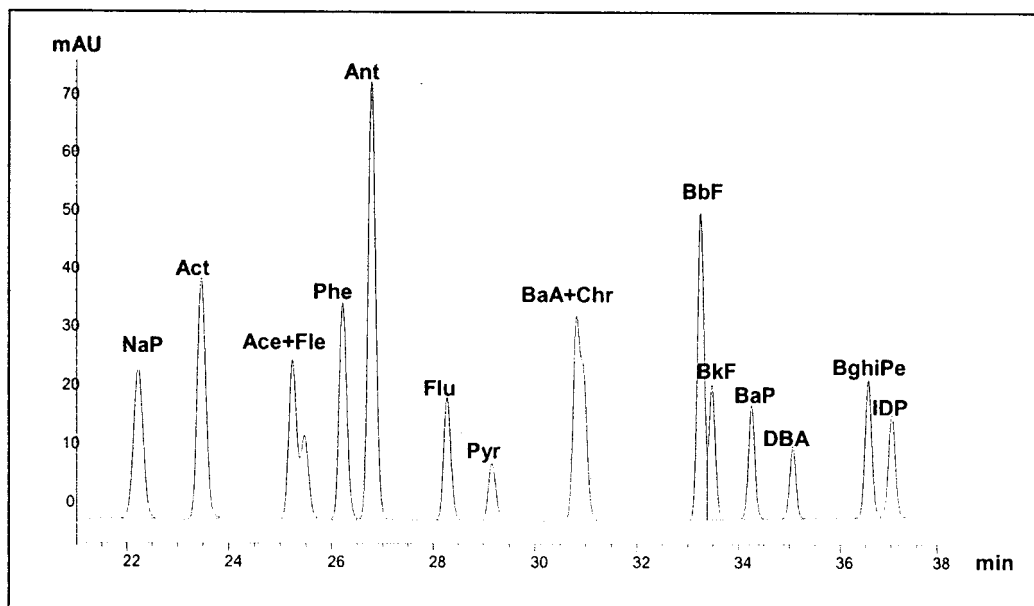


Fig. 3.10 HPLC/DAD chromatogram of 16 PAH standards used in the present study.

Standard solution preparation

The standard solutions for HPLC calibration were prepared from the stock solution, which was the ten-time 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 3.6. Then the PAH standard solutions in the range of 0.51-10.14 $\mu\text{g mL}^{-1}$ Nap were prepared by diluting the stock solution with acetonitrile. Each concentration was injected into the HPLC system operated at conditions shown in Tables 3.4 and 3.5.

Table 3.6 Concentrations of each PAH compound in the stock solution.

PAHs	Abbreviation	Concentration ($\mu\text{g mL}^{-1}$)
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

Limit of detection (LOD) 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 $\mu\text{g mL}^{-1}$ of Nap. The detection limits of individual PAHs of the present analysis 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 3.7.

Table 3.7 The limit of detection for individual PAHs by HPLC analysis in the present 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 (Robinson, 1987):

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

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 (Table 3.8). The recovery percentage exceeding 100% can be attributed to impurities that may be present on the filters.

Table 3.8 The percent of 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

3.4 Experimental Conditions

The conditions for experiment in the present study for two types of the diesel engines are given in Table 3.9. Degummed de-acid palm oil blended with commercial diesel fuel (PB) for different palm oil to diesel fuel ratios were used. The number accompanying PB represents the percentage of palm oil in the blend.

Table 3.9 Conditions for experiment.

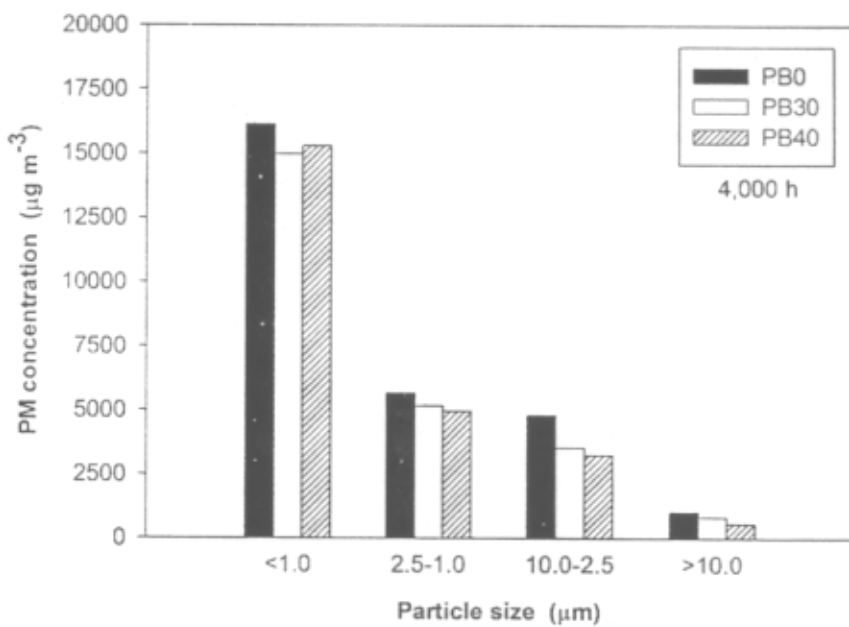
Engine	Fuel	Blend ratio
Agricultural machine engine	Degummed de-acid palm oil : Diesel	PB0, PB30, PB40
Conventional diesel engine	Degummed de-acid palm oil : Diesel	PB0, PB20, PB40

4. RESULTS AND DISCUSSION

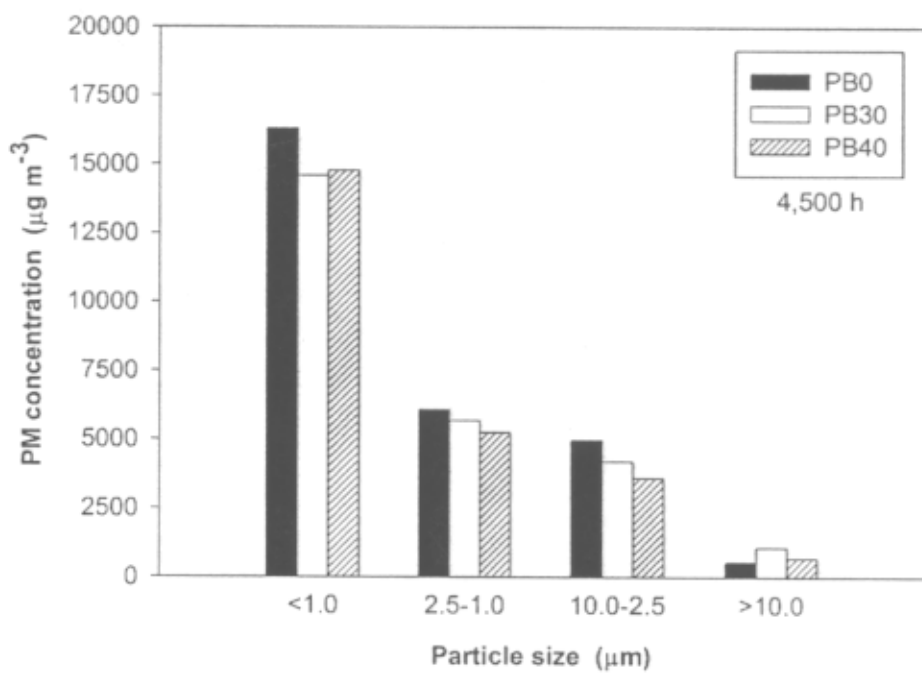
4.1 Agricultural Diesel Engines

4.1.1 Size distribution and concentration of PMs

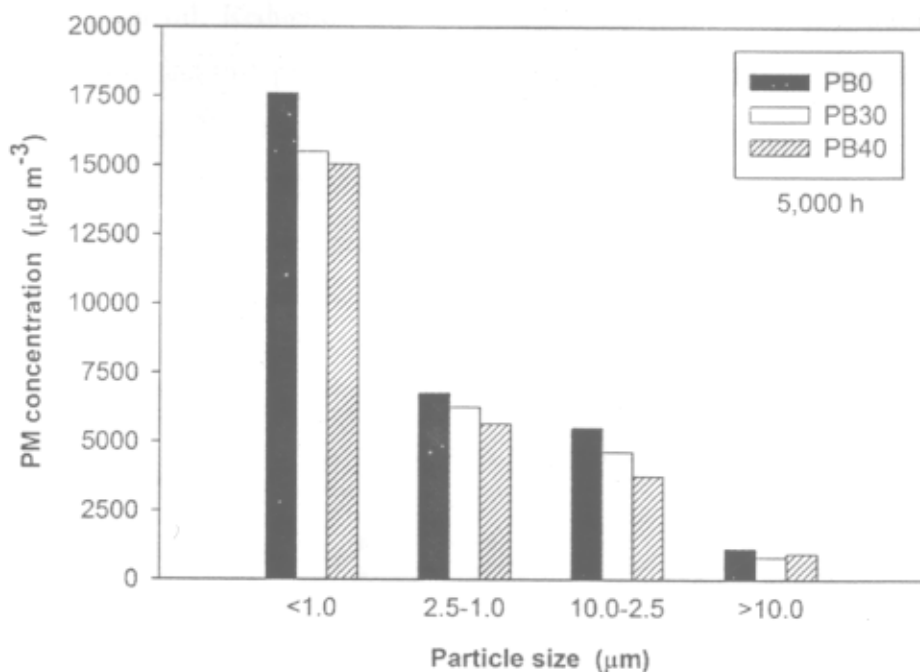
This work began when the engines were run for almost 4000 h for PB0 combustion and 2500 h for PB30 and PB40 combustion following engine test of the preceding project. Final running hour was 5,000 h for all engines. The size distributions of PM emitted from the engine fueled by PB0, PB30 and PB40 were investigated and the results are shown in Fig. 4.1. Size distributions of the PMs show a unimodal behavior in the accumulation mode ($<1.0 \mu\text{m}$). In the present study, it was found that most particulates amass in the $<1.0 \mu\text{m}$ 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 hour due to the erosion of the engine used. 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 blend ratio of palm oil was increased from 0% to 40%, similar to earlier results (Chien et al., 2009). When the engine hours were increased, MMAD was also increased.



(a)



(b)



(c)

Fig. 4.1 Size distribution of PMs from agricultural diesel engine using PB0, PB30 and PB40 at the engine hours of (a) 4000 h, (b) 4500 h and (c) 5000 h.

Table 4.1 MMAD from exhaust aerosol in agricultural diesel engine combustion at different conditions.

Engine hour (h)	MMAD (µm)		
	PB0	PB30	PB40
2,500	-	0.606	0.606
3,000	-	0.621	0.611
3,500	-	0.616	0.621
4,000	0.758	0.653	0.626
4,500	0.810	0.764	0.686
5,000	0.817	0.796	0.698

The total PM concentrations from agricultural diesel engines fueled by PB0, PB30 and PB40 are shown in Fig. 4.2 against running time. The total PM concentrations were increased when engine hour was increased as previously described. This is because of the engine wear that causes more incomplete combustion. The reduction of PM concentration when increasing the palm oil fraction

is because palm oil blend can be more completely combusted due to more oxygen content in palm oil. 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).

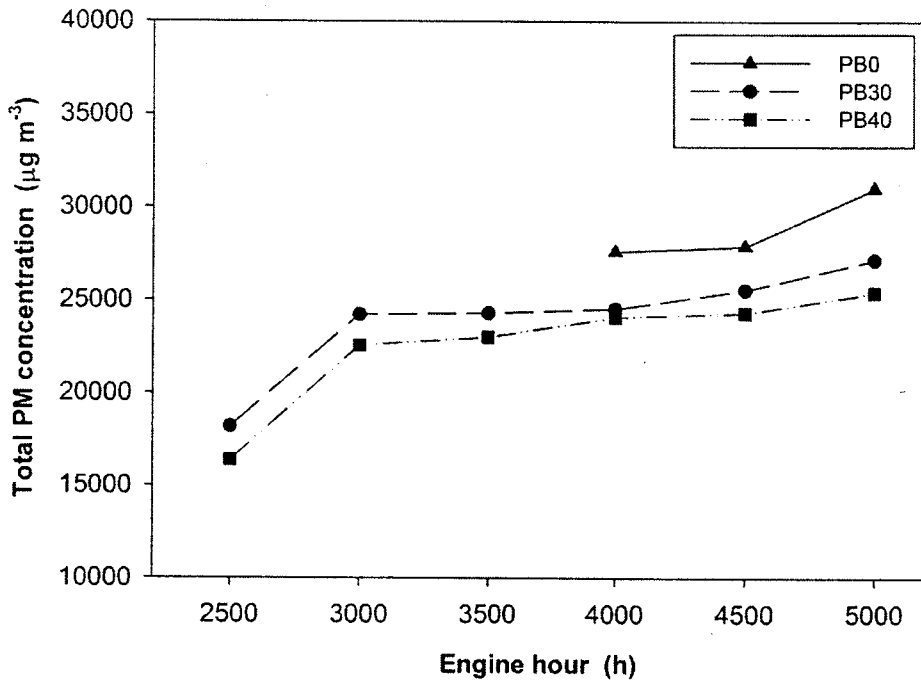
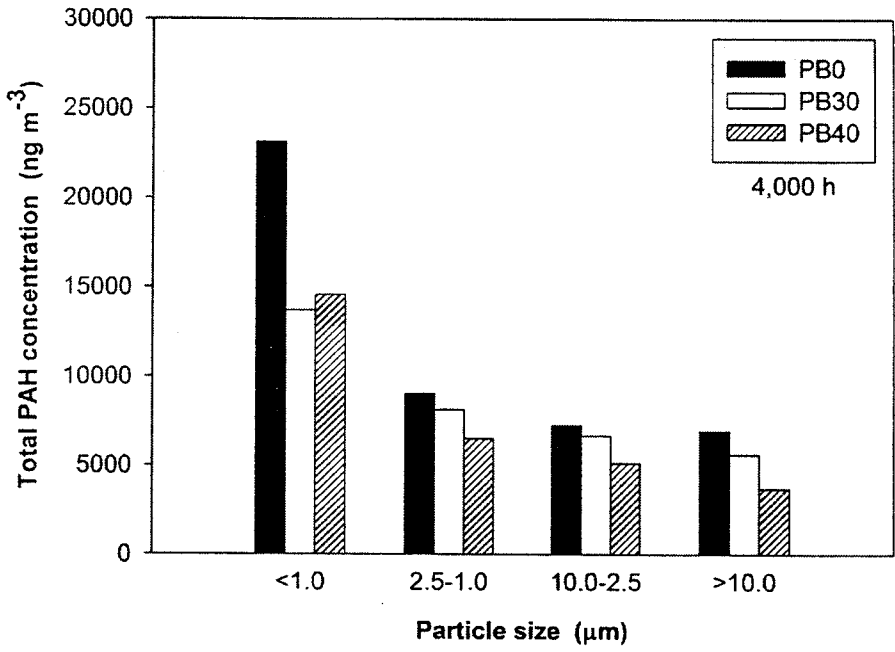


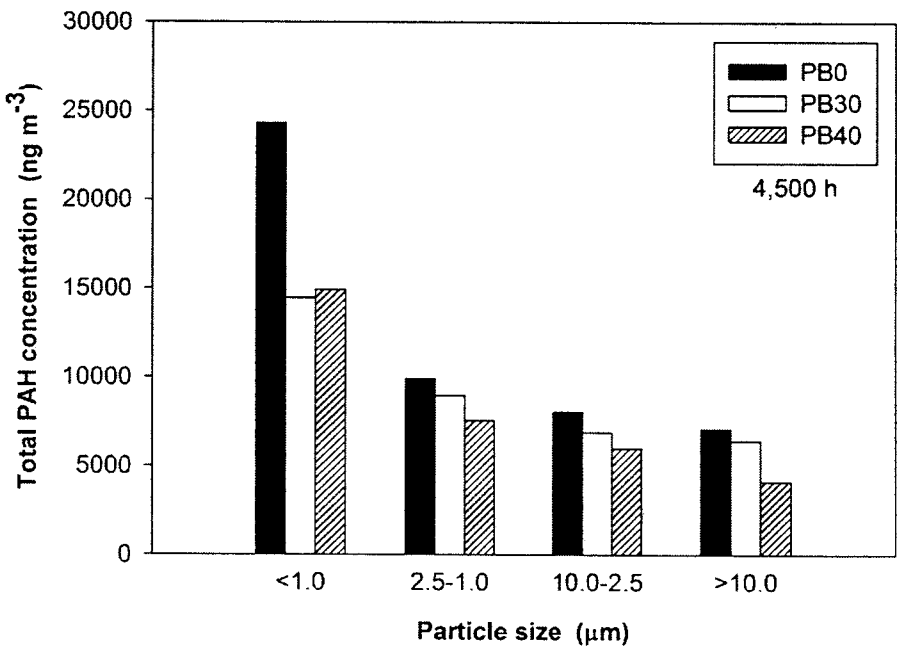
Fig. 4.2 Concentration of PMs from agricultural diesel engine using PB0, PB30 and PB40 during engine hours of 2500-5000 h.

4.1.2 Size distribution and concentration of PAHs

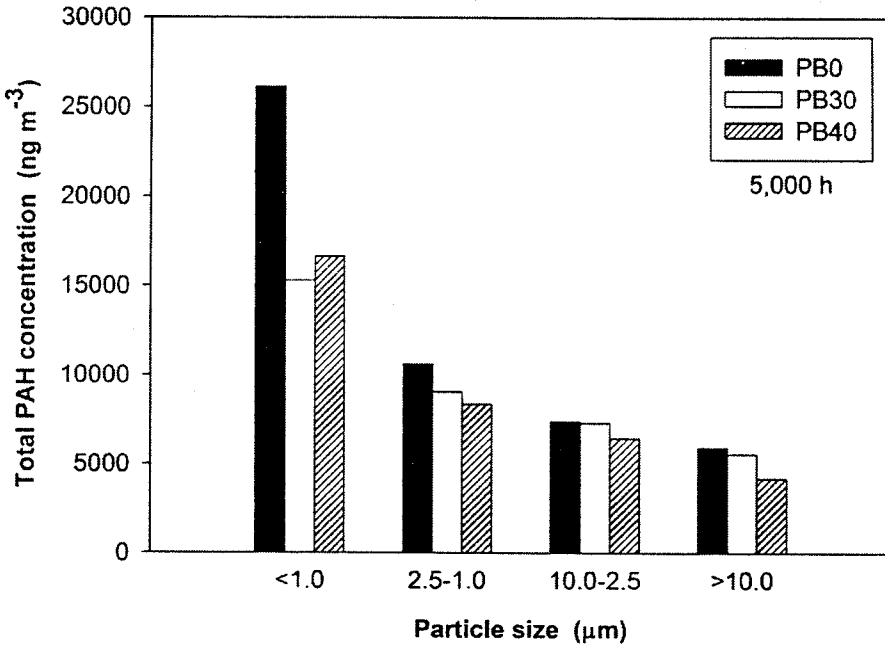
Variations of concentration and size distribution of total sixteen PAH compounds emitted from agricultural diesel engines fueled with PB0, PB30 and PB40 are shown in Fig. 4.3. The size distributions of total PAHs behave in a similar fashion to PM. The reduction rate of total PAH concentration with the 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 finer than 1.0 µm. This could be because of the larger surface area of the particles. 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.



(a)



(b)



(c)

Fig. 4.3 Size distribution of particle-bound PAHs from agricultural diesel engine using PB0, PB30 and PB40 at the engine hours of (a) 4000 h, (b) 4500 h and (c) 5000 h.

The total PAHs concentrations of particle-bound from agricultural diesel engines fueled by PB0, PB30 and PB40 against running time are shown in Fig. 4.4. The tendency of the increase of PAH concentration along the running hour is similar to PM concentration. This is reasonable as the PAHs are associated to the particulate emitted. Moreover, the emission from the engine fueled by PB30 and PB40 contains less total PAHs than that fueled by PB0 as expected. 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. The small aromatic content of palm oil blend fuel could contribute to reduction of particulate-phase PAHs. More importantly oxygen content in palm oil blend diesel 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 palm oil blending mixtures, the particulate-associated PAHs would be reduced as well.

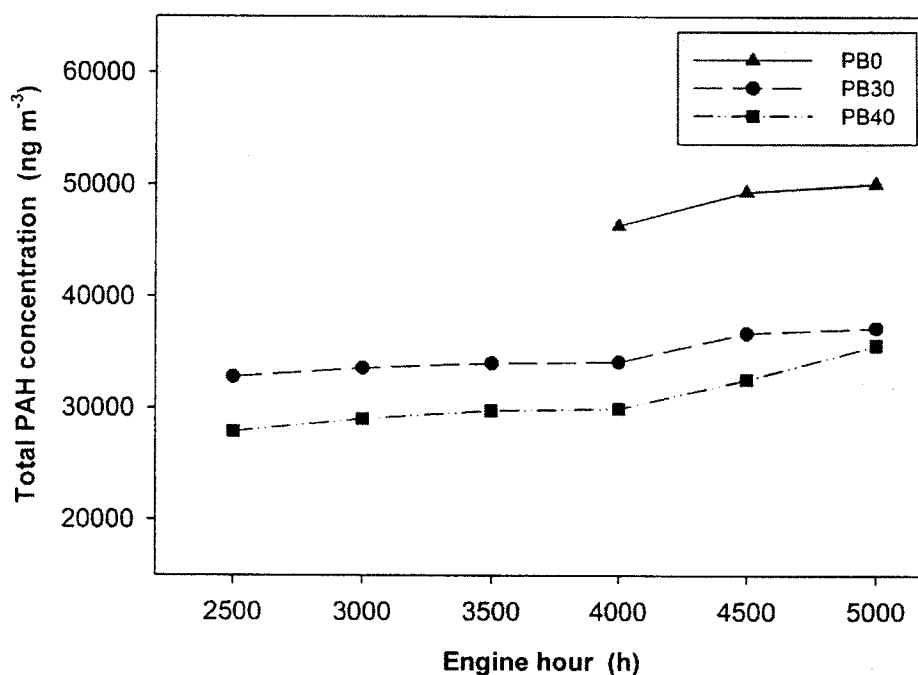


Fig. 4.4 Concentration of particle-bound PAHs from agricultural diesel engine using PB0, PB30 and PB40 during engine hours of 2500-5000 h.

4.1.3 Profile of PAHs

The average mass fraction of individual PAH compounds in PM generated from combustion of PB0, PB30 and PB40 by agricultural diesel engines is presented in Fig. 4.5. It can be seen that the contribution of Pyr compound is dominant. It was obviously found that the amount of 2-3 ring PAH compounds, especially Nap and Ace+Fle, from average mass fraction of PB30 and PB40 was more than that of PB0 due to the different characteristic between diesel oil and palm oil. The results indicated that the PAHs in the palm oil blend diesel fuel were primarily dominant by the low molecular weight PAH compounds. These findings might be caused by an increase in the soluble organic fraction (SOF). The SOF value did increase gradually with increasing fraction of palm oil blends (Lin et al., 2006b).

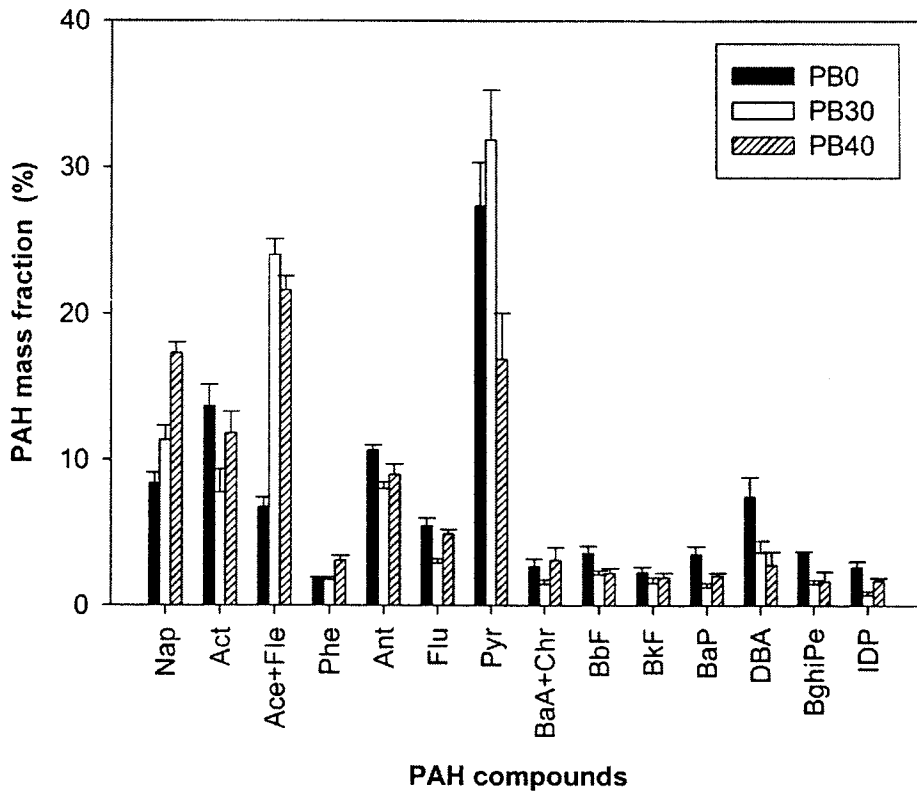


Fig. 4.5 Average mass fraction of PAHs from agricultural diesel engine using PB0, PB30 and PB40.

4.1.4 Influences of palm oil blends on PM and PAH emissions

Influences of palm oil diesel 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);

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

This means that the emissions are reduced by palm oil blend if the reduction percentage is positive. The reduction percentages of total PM and PAH emissions at 4000, 4500 and 5000 engine hour are shown in Figs. 4.6 and 4.7. These results show that the PM and the associated PAH emissions from engines using palm oil blend diesel were reduced compared with PB0. As the blend ratio of palm oil was increased,

the PM and PAH emissions were reduced (~10-20% and ~25-35%, respectively). 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 blend ratio was increased. The percentage of PAH emission reduction was actually higher than that of PM emission for most palm oil blend mixtures. 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).

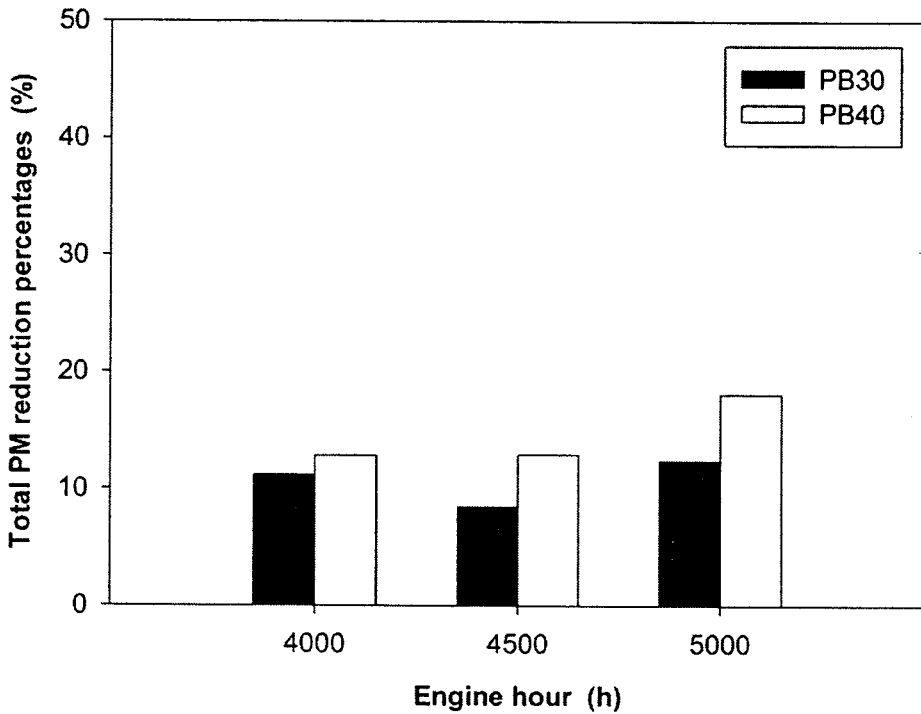


Fig. 4.6 Total PM reduction percentages from emissions by palm oil blending mixtures compared with PB0 at the engine hours of 4000, 4500 and 5000 h.

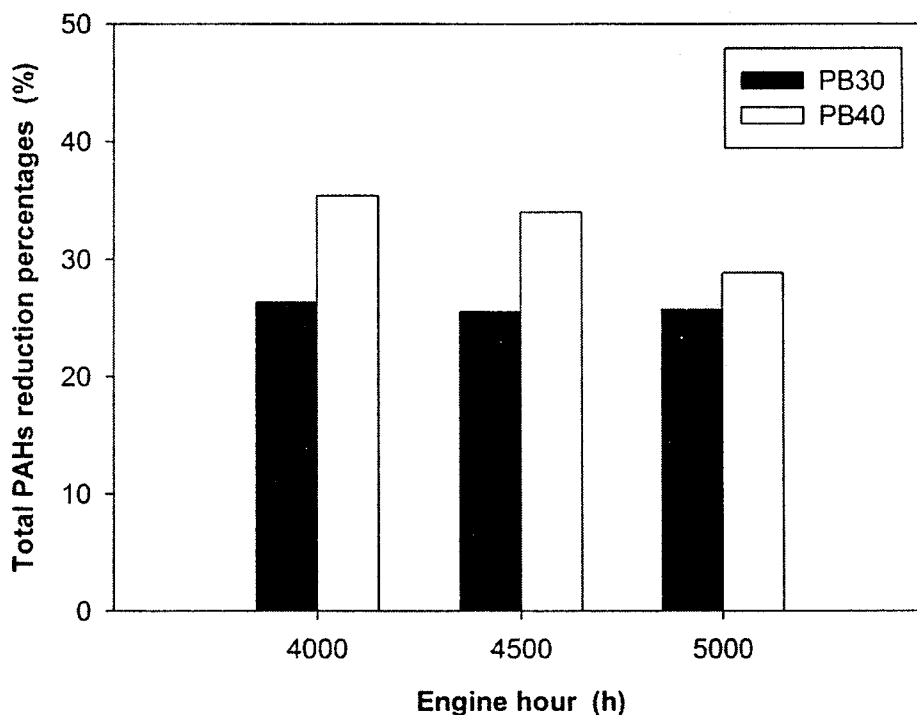


Fig. 4.7 Total PAHs reduction percentages from emission by palm oil blending mixtures compared with PB0 at the engine hours of 4000, 4500 and 5000 h.

4.1.5 Evaluation of PAH corresponding carcinogenicity

In the present 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 at different engine hours. The TEFs have been devised as a way to compare the carcinogenic potency of the individual PAH with the carcinogenicity 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 TEFs, using BaP as a reference value of 1. The Benzo[a]pyrene equivalent (BaP_{eq}) concentration can be calculated from

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

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 BaP_{eq} measured from agricultural diesel engine under different experimental conditions. The results also

show that PB0 has the highest BaP_{eq} emissions compared with the two palm oil blend diesel mixtures. As the palm oil blend ratio was increased, the BaP_{eq} emissions were decreased. BaP_{eq} was found to increase with engine running hours.

In conclusion, the important reason which causes the diesel fueled engine generating more PAHs along the running course is the erosion of engine parts, especially the compression ring. The reason for reduction of PAHs in palm oil blend diesel is because of high 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 which contains higher oxygen amount than diesel oil. They most likely enables more complete combustion than diesel fuel.

Table 4.2 BaP_{eq} for different conditions of agricultural diesel engines.

Engine hour (h)	ΣBaP_{eq} (ng m ⁻³)		
	PB0	PB30	PB40
2,500	-	2433	2036
3,000	-	2584	2169
3,500	-	2864	2295
4,000	5770	2817	2293
4,500	7430	3234	2837
5,000	8559	3344	3215

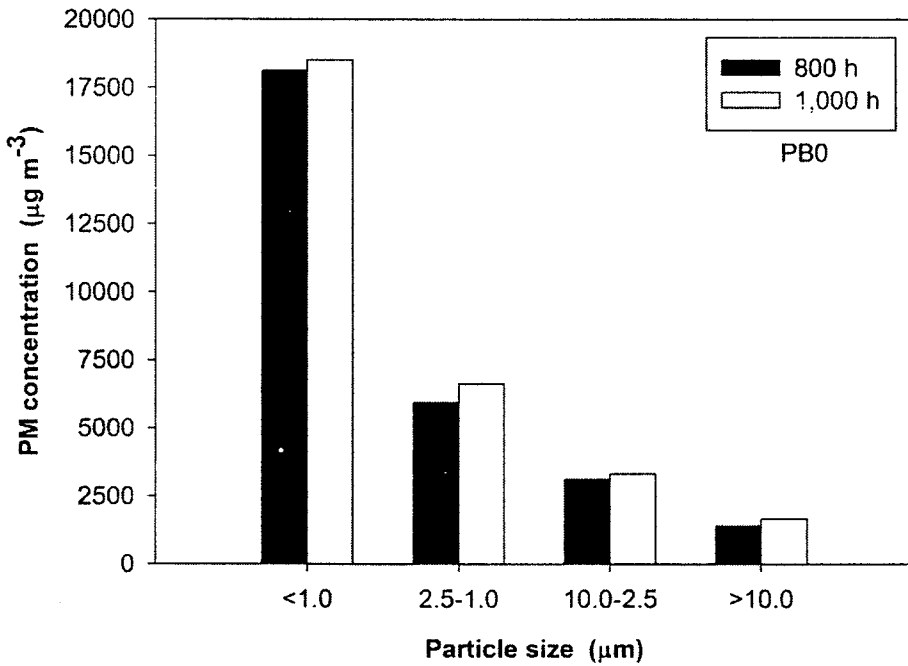
4.2 Conventional Diesel Engines

4.2.1 Size distribution and concentration of PMs

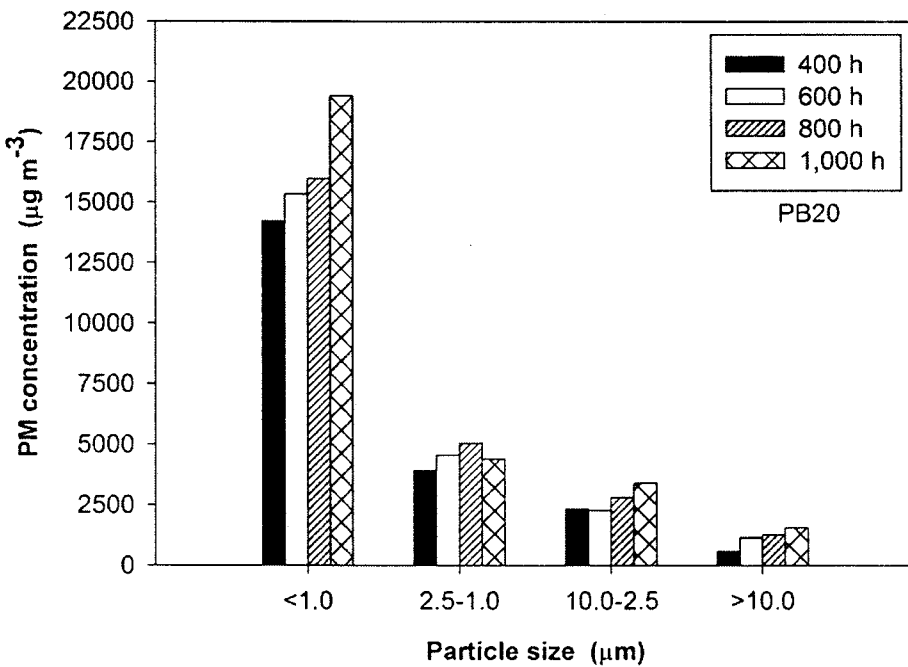
Two identical engines used in the present study were re-built used engines. Experiment began when the engines were run for almost 800 h for PB0 combustion, 400 h for PB20 combustion following another project. After the PB0 experiment was accomplished, the same engine was re-tuned and run with PB40. Final running hour is 1,000 h for every engine.

The size distributions of PM emitted from the engine fueled by PB0, PB20 and PB40 were investigated. The size distributions of particulate matters from engines using PB0 and palm oil blends for many periods are shown in Fig. 4.8. For every

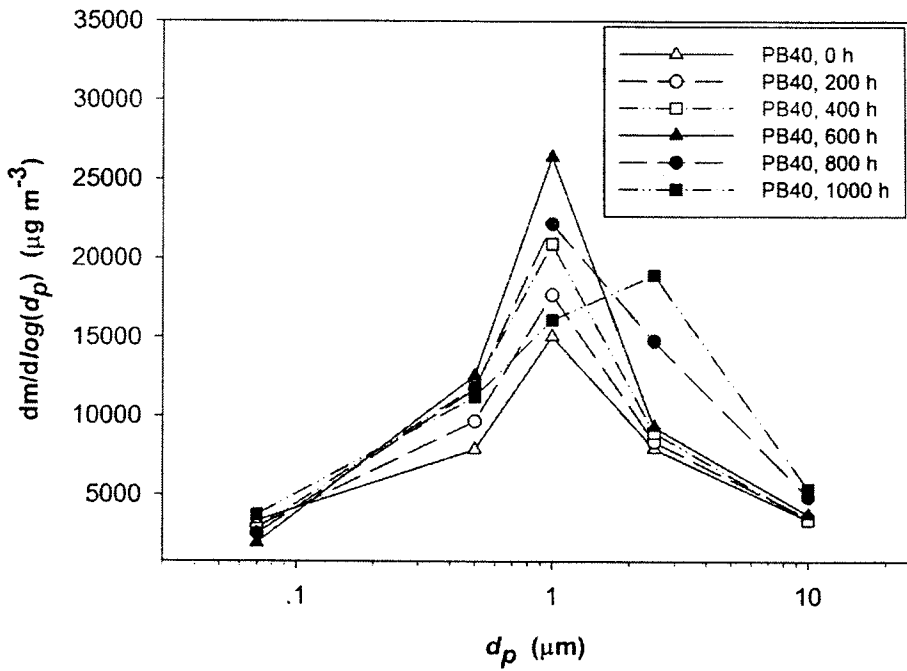
blend ratio, the PM amount of every particles size was increased when increasing the engine hour due to the wear of the engine used as in the case of the agricultural diesel engines. MMAD of PM are summarized in Table 4.3.



(a)



(b)



(c)

Fig. 4.8 Size distribution of PMs from conventional diesel engine using (a) PB0, (b) PB20 and (c) PB40.

Table 4.3 MMAD determined from conventional diesel engine at different conditions.

Engine hour (h)	MMAD (μm)		
	PB0	PB20	PB40
0	-	-	0.261
200	-	-	0.305
400	-	0.469	0.349
600	-	0.425	0.439
800	0.485	0.483	0.467
1,000	0.518	0.499	0.491

The total PM concentrations from conventional diesel engines fueled by PB0, PB20 and PB40 against running time are shown in Fig. 4.9. PM emission was decreased as the blend ratio of palm oil increases. Since the palm oil blends contain more oxygen than diesel, oxygenated diesel fuel blends are known to reduce total PM emissions as described in the previous case for agricultural engines. The higher palm oil blend ratio provides more complete combustion which is similar to the earlier

studies by Chien et al. (2009), Haas et al. (2001) and Wang et al. (2000). The concentrations of PM were increased when the operating time of the engine was increased. This could be a result of the engine wear after running for a long time usage of which can cause a greater degree of incomplete combustion and a larger portion of PM is generated when compares to new engines. Weighing the parts of the engine at the beginning of the test and after each 1,000 h of running was a way to evaluate engine wear. It was found that the weight loss of compression rings of the engine increased with engine hour.

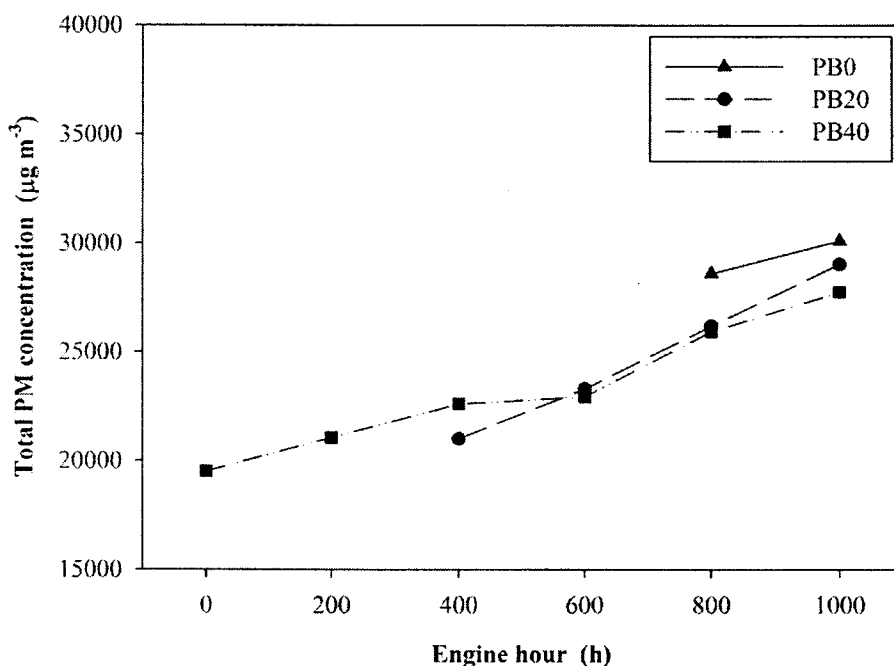
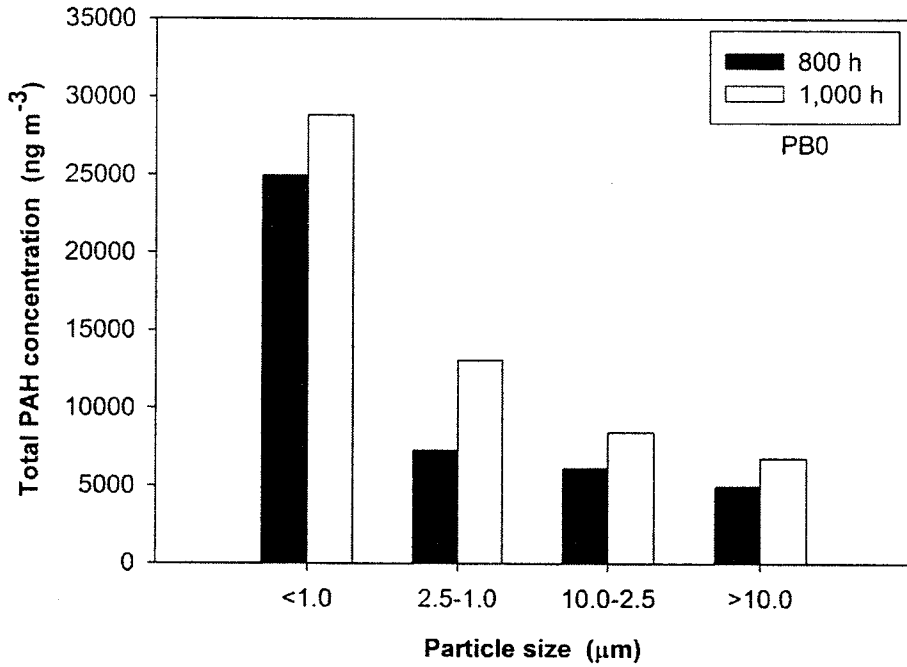


Fig. 4.9 Concentration of PMs from conventional diesel engine using PB0, PB20 and PB40 during engine hours of 0-1000 h.

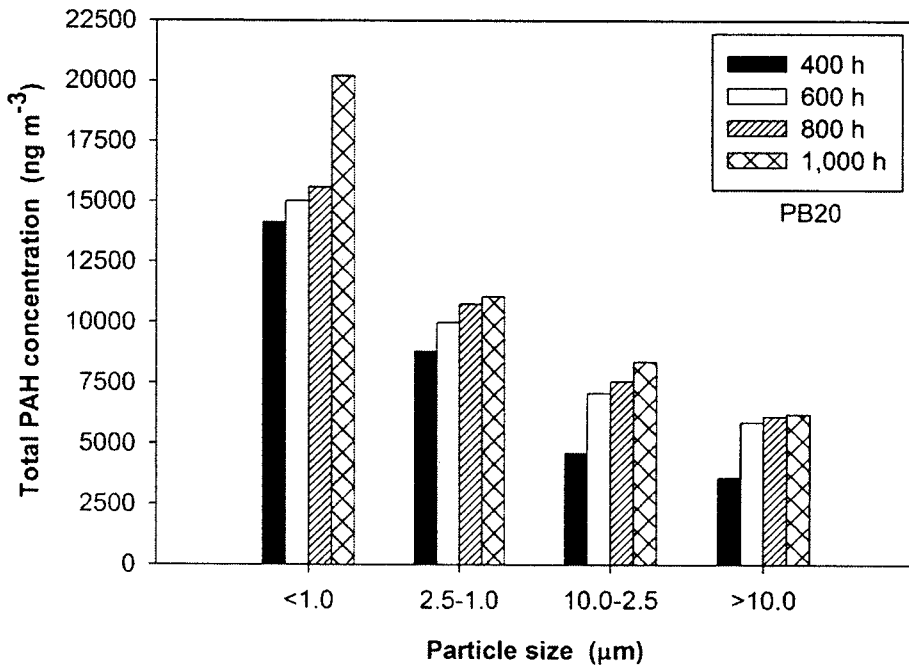
4.2.2 Size distribution and concentration of PAHs

The total particulate-bound PAH concentrations for many periods of engine run are shown in Fig. 4.10. The size distributions of particulate matters (PM) for PB0, PB20 and PB40 indicate the dominance of small particles (<1 µm). The size distributions of PAHs behave in a similar fashion. Concentrations of particulate matters and PAHs display the same behaviors. They are reduced when the fraction of palm oil blend is increased. This is a desirable result and it agrees with many previous investigations. The concentrations are, however, increased when the running time of the engine is increased. This could be a result of the engine wear after running for a

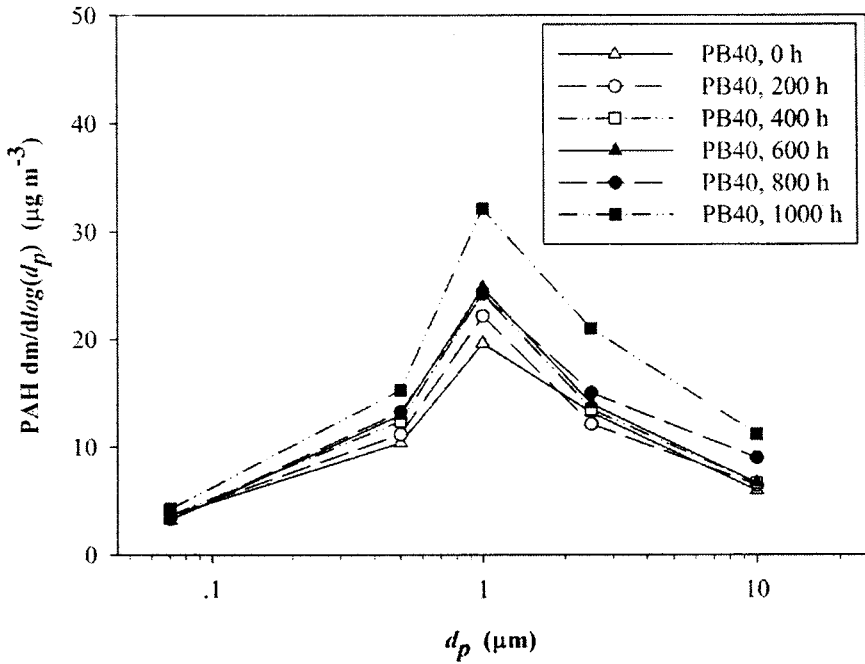
long period of time. Concentration of individual PAH compound of particles sampled from conventional diesel engine fueled by PB0, PB20 and PB40 for all particle size ranges is shown in Figs. 4.10.



(a)



(b)



(c)

Fig. 4.10 Size distribution of particle-bound PAHs from conventional diesel engine using (a) PB0, (b) PB20 and (c) PB40.

Total PAHs concentrations of particle-bound from conventional diesel engine fueled by PB0, PB20 and PB40 against running time are shown in Fig. 4.11. The tendency of the increase of PAH concentration along the running hour was similar to PM concentration but for PB20 and PB40 there were no significant difference for the PAH concentration. In addition, total PAH concentration was increased when increasing engine operating hour for all blend ratios and almost all of particle sizes. Reduction of PAH emission for palm oil can be attributed to the fact that palm oil contains no aromatic constituent in comparison to diesel (Wang et al., 2000).

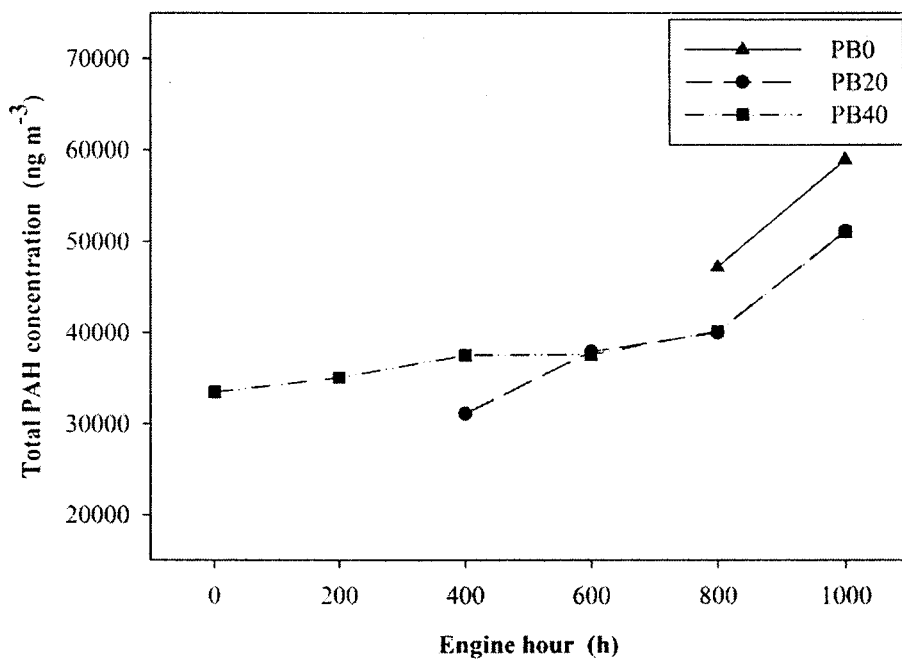


Fig. 4.11 Concentration of particle-bound PAHs from conventional diesel engine using PB0, PB20 and PB40 during engine hours of 0-1000 h.

4.2.3 Profile of PAHs

The average mass fraction of individual PAH compounds from conventional diesel engines using PB0, PB20 and PB40, are presented in Fig. 4.12. It can be seen that the difference between diesel and palm oil blends were the patterns of PAH compounds associated with 2-3 and 4-6 aromatic rings. It was obviously found that the amount of 2-3 rings PAH from mass fraction of palm oil blends were more than that of PB0 due to the different characteristics 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). The results demonstrate that the concentration of 4-6 rings PAH was increased when the running time of the engine was increased. For PB0, more of the 4-6 ring PAHs were generated compared with PB20 and PB40. The greater engine hours resulted in a higher generated 4-6 ring PAH amount due to wear of the engine for every blend ratio.

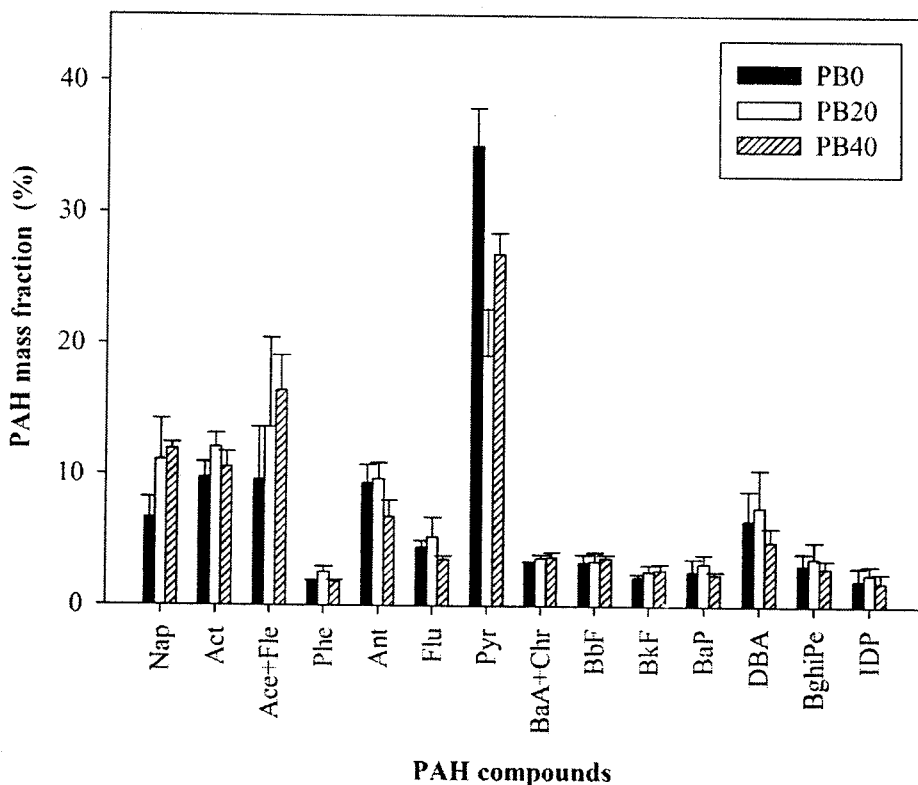


Fig. 4.12 Average mass fraction of PAHs from conventional diesel engine using PB0, PB20 and PB40.

4.2.4 Influences of palm oil blends on PM and PAH emissions

Reduction of PM and total PAH emissions by palm oil blending were investigated by comparing the effects of the different ratios of PB20 and PB40 with the PB0. The reduction percentages of PM and total PAH emissions at the same engine hours of 800 h and 1,000 h, are shown in Fig. 4.13 and Fig. 4.14.

Comparison, the PM was reduced by ~3-9% and PAHs was reduced by ~13-15% when using PB20 and PB40, respectively. These results show that the PM and total PAH emissions from conventional diesel engines using palm oil blends for all size ranges of particles are reduced compared to PB0, though not as high as in the case of agricultural diesel engines. As the blend ratio of palm oil was increased, the reduction percentages of PM and PAH emissions were bincreased. This is because PAH in palm oil is lower than commercial diesel, so a high fraction of biodiesel blends resulted in a lower PAH emission, which is the main reason for the reduction in PAH emissions. Palm oil can reduce not only PAH emission but also the PAH corresponding carcinogenic potency.

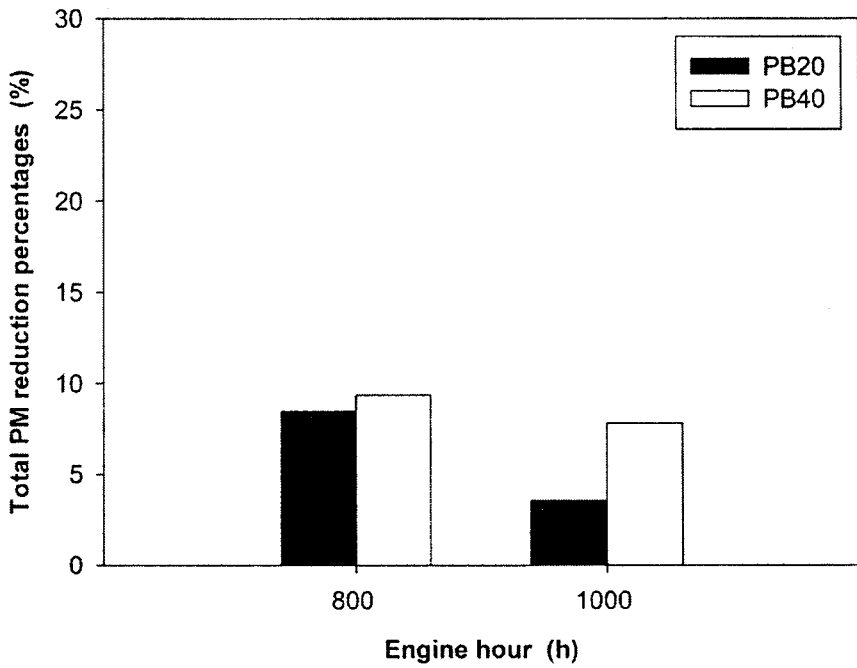


Fig. 4.13 Total PM reduction percentages from emissions by palm oil blending mixtures compared with PB0 at the engine hours of 800 and 1000 h.

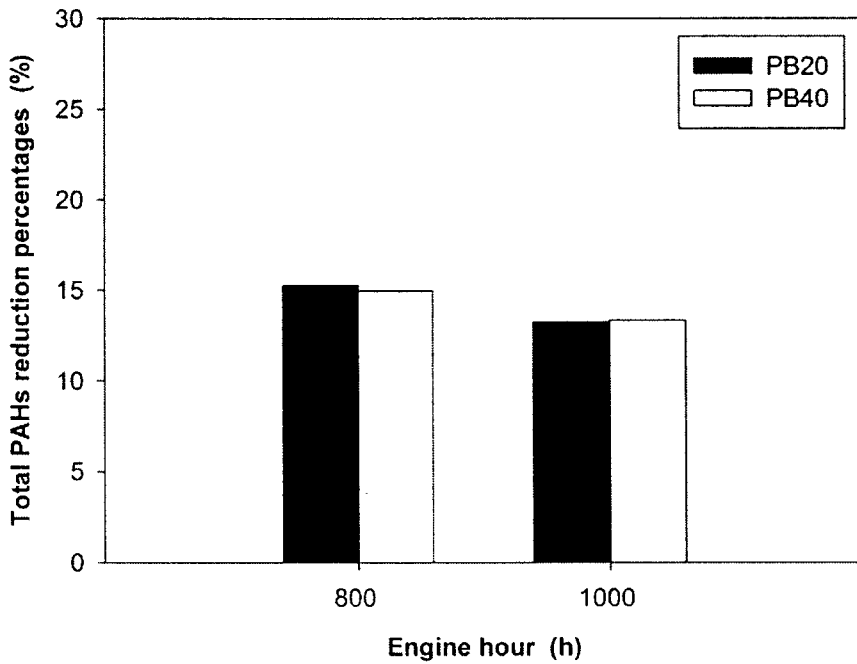


Fig. 4.14 Total PAHs reduction percentages from emissions by palm oil blending mixtures compared with PB0 at the engine hours of 800 and 1000 h.

4.2.5 Evaluation of PAH corresponding carcinogenicity

Table 4.4 shows the BaP_{eq} measured from conventional diesel engine under different experimental conditions. In this study, BaP_{eq} was applied for the 16 analyzed PAHs to assess the carcinogenic potencies of emissions from the engine fueled by PB0, PB20 and PB40 with long-term usage. The BaP_{eq} has been devised as a way of comparing the carcinogenic potency of individual PAH with the carcinogenicity of BaP. The results also show that PB0 has the highest BaP_{eq} emissions compared with the two palm oil blend diesel mixtures. As the palm oil blend ratio was increased, the BaP_{eq} emission was decreased. BaP_{eq} was found to increase with engine running hours. The largest BaP_{eq} was observed from PB0 at 1,000 h with 9319 ng m^{-3} , and 7609 and 5153 ng m^{-3} for PB20 and PB40 at 1,000 h. As the palm oil blend ratio was increased, the BaP_{eq} emission decreased gradually. The BaP_{eq} emission was also found to increase with the engine hours. These results indicate that the higher molecular weight PAHs are more carcinogenic than the lower molecular weight PAHs.

Table 4.4 BaP_{eq} for different test conditions of conventional diesel engines.

Engine hour (h)	$\Sigma BaP_{eq} \text{ (ng m}^{-3}\text{)}$		
	PB0	PB20	PB40
0	-	-	2642
200	-	-	3071
400	-	3059	3495
600	-	5573	3611
800	6228	5965	4536
1,000	9319	7609	5153

4.3 Output of the Project

4.3.1 Publications

1. Phoungthong, K., Tekasakul, S., Tekasakul, P., Prateepchaikul, G., Jindapetch, N., Furuuchi, M. and Hata, M. "Effects of Mixed Crude Palm Oil

Blending on Particulate Matter and Associated Polycyclic Aromatic Hydrocarbons Emitted from Agricultural Diesel Engine”. *Biomass&Bioenergy*, Submitted, 2012.

2. Phoungthong, K., Tekasakul, S., Tekasakul, P., Prateepchaikul, G., Furuuchi, M. and Hata, M. “Characteristics of Particles Emissions and Polycyclic Aromatic Hydrocarbons from IDI-Turbo Diesel Engine Fueled with Palm Oil Blend Diesel”. Proceedings of the Seventh Asian Aerosol Conference, August 17-20, 2011, Xi'an, China.

3. Phoungthong, K., Tekasakul, S., Tekasakul, P., Prateepchaikul, G., Furuuchi, M., Otani, Y. and Hata, M. “Characteristics of Particulate Matters and Associated Polycyclic Aromatic Hydrocarbons from Emission of Agricultural Diesel Engines Fueled by Palm Oil Blends”. Proceedings of the Sixth Asian Aerosol Conference, November 24-27, 2009. Bangkok, Thailand.

4. 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), May 3-6, 2009. Chonburi, Thailand.

3.7.2 Graduate Student

1. Mr. Khamphe Phoungthong

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

Degree: Master of Science in Physical Chemistry

Year of Graduation: 2010.

5. CONCLUSION AND RECOMMENDATION FOR FUTURE WORK

5.1 Conclusion

Physical and chemical characteristics of emission from agricultural diesel and conventional diesel engines fueled by palm oil blend diesel with different running time and palm oil blend ratio 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 engines fueled by PB0, PB30 and PB40, and conventional diesel engines fueled by PB0, PB20 and PB40 were measured using a 4-stage particulate matter air sampler. Results show a unimodal behavior in the accumulation mode and the MMAD is dependent on both the blending ratio and engine hour. Increasing the blending ratio causes a clear reduction of MMAD for the agricultural machine engines but not as clear for the conventional engines. MMAD is increased when the running time is increased. This is because the engines using palm oil blend generate finer particles than that of the PB0 engines. The higher blend ratio provides the more complete combustion because the palm oil blend contained more oxygen amount than diesel oil and no aromatic constituents.

2. 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 ($>1.0 \mu\text{m}$) indicate a dominance of smaller molecule PAHs (2-3 aromatic rings). The most dominant compound is pyrene (Pyr). For the small particle ($<1.0 \mu\text{m}$), larger molecule PAHs (4-6 aromatic rings) play an important role. Due to the low vapor pressure, the high molecular-weight PAHs are predominantly adsorbed on soot and particulate matters.

3. 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, palm oil diesel has higher oxygen content. This causes more complete combustion than pure diesel fuel and it results in a decrease in PAH emissions in all size ranges.

4. The influences of palm oil blend on PAH emissions are similar to PM; i.e., the reduction percentages for PAH emissions were increased when increasing the palm oil blending ratio. PAHs emitted from the engines fueled by FBD had the strongest PAH related carcinogenic potencies. The results also show that PB0 has the highest BaP_{eq} emissions in all size ranges compared with the two palm oil blend mixtures. As the palm oil blending ratio is increased, the BaP_{eq} is decreased gradually. Results indicate that palm oil blends could reduce both PAH emission factors and the PAH corresponding carcinogenicity potency in the full size ranges.

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

5.2 Recommendation for Future Work

In the future, PAHs 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. The investigation of gaseous PAHs is underway.

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

Manuscript for Journal Publication

1 **Emissions of particulate matter and associated polycyclic aromatic**
2 **hydrocarbons from agricultural diesel engine fueled with degummed,**
3 **deacidified mixed crude palm oil blends**

4
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17
18
19 **ABSTRACT**

20
21 Mixed crude palm oil (MCPO), the mixture of palm fiber oil and palm kernel oil, has become of
22 interest as a renewable energy source due to it can be easily produced from whole dried palm
23 fruits. In the present work, the degummed, deacidified MCPO was blended in petroleum diesel
24 (PB0) at portions of 30 and 40 % by volume (called PB30 and PB40, respectively) and then
25 tested in the agricultural diesel engines for long term usage. The particulates from the exhaust of
26 the engines were collected every 500 h using a four-stage cascade air sampler. The 50% cut-off
27 aerodynamic diameters for the first 3 stages were 10, 2.5 and 1 μm , while the last stage collected
28 all particles smaller than 1 μm . The particle bound polycyclic aromatic hydrocarbons (PAHs)
29 were analyzed for the 16 PAHs using a high performance liquid chromatography (HPLC). The
30 results indicated that the size distribution of particulate matter (PM) was in the accumulation
31 mode and the pattern of total PAHs associated with fine-particles (<1 μm) showed a dominance
32 of larger molecular weight PAHs (4-6 aromatic rings), especially pyrene (Pyr). The mass median
33 diameter (MMAD), PM and total PAH concentrations decreased apparently when increasing the
34 palm oil content, but increased when the running hours of the engine were increased. In addition,
35 PB0 gave the highest value of carcinogenic potency equivalent (BaP_{eq}) for all particle size ranges.

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36 As the palm oil was increased, the BaP_{eq} decreased gradually. Therefore the degummed-
37 deacidified MCPO blends are recommended for diesel substitute.

38

39 **Keywords:** Mixed crude palm oil; Palm oil blend; Agricultural diesel engine; Polycyclic aromatic
40 hydrocarbon; Particulate matter

41

42 **1. Introduction**

43 The world energy crisis due to escalation of fuel prices and diminishing of petroleum-
44 based oil and the deterioration of environmental pollution related to fossil fuel usage have been a
45 global concern. Vegetable oils and biodiesels derived from vegetable oils which can be renewable
46 have gained enormous attention in many countries as an alternative source of energy [1-3]. In
47 addition, the physicochemical properties of biodiesels meet the requirements of diesel engine
48 combustion. In Thailand, palm oil is currently shown to be the highest potential feedstock for
49 biodiesel production because of the abundance of raw material and the price of palm oil which is
50 cheaper than other vegetable oils such as soybean oil, coconut oil, olive oil and rapeseed oil.
51 Some diesel engines can also be operated using preheated crude palm oil [4,5], refined palm oil
52 [6] and degummed-deacidified mixed crude palm oil [7,8]. Both palm oil and biodiesel are highly
53 oxygenated fuels and can reduce pollutant emissions such as total hydrocarbons (THC), carbon
54 monoxide (CO), sulfur oxides (SO_x) and polycyclic aromatic hydrocarbons (PAHs), but nitrogen
55 oxides (NO_x) slightly increase as compare to commercial petroleum diesel [4,9-12].

56 Diesel engine generates fine smoke particles which contain many chemical compounds
57 affecting atmospheric environment especially in urban areas where diesel trucks are a major
58 transportation means. The emissions depend on vehicle and fuel type, engine technology and its
59 tuning, maintenance, and way of driving [13]. It was reported that nano-particles are generated
60 during diesel combustion and these particles subsequently coagulate to form larger particles in

61 submicron range [14]. The particulate matter (PM) emissions from diesel-powered engines are
62 typically 10-100 times higher than those from gasoline-powered engines. The diesel emissions
63 contain hundreds of organic and inorganic compounds, partitioned in the gaseous and particulate
64 phases [13]. Due to their toxicity, carcinogenicity and mutagenicity, PAHs are known to be the
65 principal pollutants from incomplete combustion of motor vehicles, home cooking, fossil fuel
66 combustion, industrial process, or biomass burning [15]. Most PAHs are associated with fine-
67 particles, typically 0.5 μm or less [16]. The size of PM is an important factor affecting human
68 health. The fine particles can evade the mucociliary defense system and deposit in the peripheral
69 airways, where they may induce toxic effects. In addition, they can be transported over a long
70 distance. This implies that particles can easily distribute PAHs to the atmosphere and become one
71 of the major sources of air pollution to nearby surroundings.

72 Studies of PM and associated PAHs emitted from agricultural diesel engines fueled with
73 palm oil blends is limited. Most of the studies have been focused on emission of biodiesel
74 (methyl-ester or ethyl-ester) combustion. Nevertheless, PAHs and regulated harmful emissions
75 from palm oil blended diesel and the effect of the engine operating times on emission have
76 seldom been addressed. This study focused on examining emissions of the agricultural diesel
77 engine using blends of degummed-deacidified mixed crude palm oil and comparing with
78 commercial diesel. The effects of blending ratios on emissions of PM, PAHs and carcinogenic

79 potencies while the engine was in operation for long-term tests with constant load and a speed of
80 2200 rpm were investigated. The mixed crude palm oil (MCPO) which is a mixture of palm fiber
81 oil and palm kernel oil has become of interest as a feedstock for diesel substitute especially for
82 farmers living in or near sufficient economic communities in Thailand [7]. MCPO can be easily
83 produced with a screw-press of whole dried palm fruits. Therefore the knowledge from this work
84 will lead to the most economical use of MCPO as an alternative fuel and can be used at policy-
85 level for promoting alternative fuel usage subsequently.

86

87 **2. Materials and methods**

88 *2.1 Reagents*

89 All chemicals for PAH extraction and HPLC assay such as acetonitrile, dichloromethane
90 and dimethylsulfoxide (DMSO) were of HPLC grade and purchased from Lab-scan (Thailand).
91 Ultra pure water, de-ionized with reverse osmosis system and purified with a Maxima ultrapure
92 water instrument (ELGA, England) to obtain the resistivity of 18.2 M Ω -cm, was used throughout
93 the study. A certified standard solution containing 16 compounds of EPA 610 polycyclic
94 aromatic hydrocarbons was purchased from Supelco (USA).

95 *2.2 Fuels*

96 Commercial petroleum diesel (PB0) and two different blending mixtures of diesel with
97 crude palm oil: PB30 and PB40 which are 30% and 40% by volume of crude palm oil,

98 respectively, were tested in this study. Crude palm oil used was mixed crude palm oil (MCPO)
99 obtained from local palm oil mill. It is a viscous liquid containing gum and high free fatty acid
100 (FFA). Before blending with diesel, MCPO was degummed using phosphoric acid and
101 deacidified using sodium hydroxide to reduce free fatty acid to less than 1%. The preparation
102 method of tested blends is given in the previously study [7]. The properties of PB0, PB30, PB40
103 and PB100 (degummed-deacidified MCPO), determined according to related ASTM standard
104 methods, are listed in Table 1.

105 *2.3 Engine and operating conditions*

106 The experiments were carried out using three identical agricultural diesel engines (Kubota,
107 Type RT80) which are 4-cycle stroke, water cooled, single horizontal cylinder and indirect
108 injection (IDI) diesel engines. The bore to stroke ratio is 84:84 mm and the compression ratio is
109 23:1. The maximum power is 5.9 kW at 2,400 rpm and maximum torque is 27.5 Nm at 1,600 rpm.
110 This type of engine has been used by farmers in Thailand for rice-field tillage by operating with
111 tractor or wheel plough. In addition, the modified engines have been used to add oxygen to water
112 in giant tiger prawn farms. In this study, the engine was performed according to the previously
113 studied procedure [8] and operated at 75% of full load with constant speed of 2200 rpm. After
114 every 500 h of running, the engine performance was tested according to JIS B8018 (1989) and
115 then the particulate matters were collected from the engine exhaust. Since the emission

116 concentration was high, a dilutor (Palas, VKL 10) was used to dilute the exhaust emission at the
117 dilution ratio of 10 prior to each sampling. The clean air for the dilution system was obtained
118 from an air compressor and passed through a regulator, a gas drying unit and a high efficiency
119 particulate air (HEPA) filter for removal of moisture, oil and particles. The temperature in the
120 dilutor was less than 40 °C.

121 *2.4 Measurement of size distribution of PM*

122 The four-stage cascade particulate matter air sampler (Kanomax, Japan) which has 50%
123 cut-off aerodynamic diameters of 10, 2.5 and 1 μm was used to determine the size distribution of
124 particles emitted from the engine. A constant flow rate (40 L min^{-1}) of diluted exhaust gas was
125 drawn by a vacuum pump, and controlled by a needle valve and a rotameter. The particles were
126 collected on a quartz fiber filter (Pallflex, Type 2500QAT-UP). Donut-shape filters with 65x30
127 mm diameter were used in impaction stages, a 47 mm diameter filter was used in the backup
128 stage, and 8 mm thick stainless steel fiber mat with fiber diameter of 8 μm and packing density of
129 0.0065 [17] was used at the inertial filter stage above the backup filter. The schematic diagrams
130 of the particulate matter air sampler and the experimental set up are shown in Fig. 1. Before
131 sampling, the filters were treated in the dark desiccator at constant temperature (25 °C) and
132 constant humidity (50% relative humidity) for at least 72 h then weighed using an analytical
133 balance with precision of 0.01 mg (Sartorius, CP225D). After sampling, the filters were treated

134 under the same conditions as before sampling and weighted using the identical analytical balance.
135 The weights of the collected particles on each filter were then calculated. The set of filter samples
136 was kept together, wrapped with aluminum foil, put in a polyethylene bag and then stored at -
137 20°C in order to avoid evaporation and degradation of PAHs until extraction.

138 *2.5 Analysis of PAHs*

139 The 16 PAH compounds including Naphthalene (Nap), Acenaphthylene (Act),
140 Acenaphthene (Ace), Phenanthrene (Phe), Anthracene (Ant), Fluorene (Fle), Fluoranthene (Flu),
141 Pyrene (Pyr), Benzo[a]anthracene (BaA), Chrysene (Chr), Benzo[a]pyrene (BaP),
142 Benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene (BkF), Dibenz[a,h]anthracene (DBA),
143 Indeno[1,2,3-cd]pyrene (IDP), and Benzo[g,h,i]perylene (BghiPe) were monitored. The filters
144 were extracted ultrasonically twice with 40 mL of dichloromethane for 30 min each while the
145 water in the ultrasonic bath was controlled to be 4-10 °C in order to prevent overheating. This
146 technique was modified from the methods used in previous studies [18,19]. The extracts were
147 combined, filtered using a syringe filter unit (0.45 µm PTFE) for removal of insoluble particles,
148 and 50 µL of DMSO was added for PAH preservation. Then the solvent was removed using a
149 rotary evaporator, and the residues were redissolved in 450 µL of acetonitrile. The solution was
150 filtered again by a 0.45 µm PTFE syringe filter, kept in a 1.5 mL amber glass vial, and stored at
151 4°C prior to analysis.

152 The PAH analysis was performed using HPLC (Agilent, 1100) with a Chemstation
153 program and following the previous method [20] with appropriate modifications. The HPLC
154 system consisted of a VertiSep UPS C 18 reversed phase column (4.6x250 mm, 5 μm) with a
155 guard column, an injection volume of 25 μL and a diode array detector (DAD). The solvent
156 gradient elution of acetonitrile and ultrapure water was used for 40 min at the flow rates of 1.0-
157 1.2 mL min^{-1} . The resulting chromatograms of all 16 PAHs were identified by matching retention
158 times with reference standards and confirmed by spiking method. The concentration of each PAH
159 was quantified from the peak area. A good linear correlation between the concentrations and peak
160 areas was found with R^2 values in the range of 0.999-1 for all PAH compounds. Field blank
161 filters as well as solvent blanks were analysed by the same procedure and found that integrated
162 areas were less than detection limit to ensure that there were no significant background
163 interference. The detection limit of individual PAH was defined as the lowest concentration that
164 the detector could provide a signal-to-noise ratio of 3, and found between 3.9-80.2 ng mL^{-1} . The
165 recovery efficiency was confirmed to be 0.79 ± 0.23 ($n=3$) by spiking known amounts of external
166 PAH standards onto the pre-treated filters and then processing by the same analytical procedure
167 used for the samples.

168

169 3. Results and discussion

170 3.1 Size distribution of PM and associated PAHs

171 This work began when the engine using PB0 was run for almost 4000 h and the engines
172 using PB30 and PB40 were run for 2500 h. Therefore the combustion of PB0 was tested at
173 operating times of 4000, 4500 and 5000 h, while the combustions of PB30 and PB40 were
174 performed at operating times of 2500, 3000, 3500, 4000, 4500 and 5000 h. The size distributions
175 of PM emitted from the engines fueled with PB0, PB30 and PB40 are shown in Fig. 2(a).
176 Apparently for all cases, the PM size distributions show a behavior in the accumulation mode
177 ($<1.0 \mu\text{m}$). Most particulate mass was found in the $<1.0 \mu\text{m}$ diameter range. These particles are
178 carbonaceous agglomerates loaded with adsorbed matters. The particles in this mode are formed
179 during exhaust dilution and cooling, and may also include solid carbon [14]. The mass median
180 aerodynamic diameters (MMAD) of PM are summarized in Table 2. The results showed that
181 MMAD decreased when the blending percentages of palm oil were increased from PB0 to PB40
182 which implied that the combustion of PB30 and PB40 generated particles with smaller size than
183 that of PB0. The reason for this is the higher palm oil blend ratio provides more complete
184 combustion since palm oil blends contain more oxygen content and no or less aromatic
185 hydrocarbons than commercial petroleum diesel [21].

186 The reduction of total particle-bound PAHs with increasing particle size was similar to
187 that of the PM concentrations which can be also seen in Fig. 2(b). For each blend ratio, the total

188 PAH concentration was maximized when the particle sizes were less than 1 μm . These results
189 were in agreement with the PM concentration since the particle-bound PAH emissions are closely
190 related to PM emissions.

191 *3.2 Effect of long-term engine operation on PM and PAH emissions*

192 The total PM and associated PAH concentrations for the engine fueled with PB0, PB30
193 and PB40 were found to increase with the engine operation time as shown in Fig. 3. As
194 comparison in the same period of engine operation time from 4000 to 5000 h, the total PM
195 concentration increased by 12.30%, 10.81% and 5.50% while the total PAH concentration
196 increased by 8.06%, 8.97%, and 19.07% for PB0, PB30 and PB40, respectively.

197 The MMAD and concentrations of PM and associated PAHs, however, increased when
198 the operating time of the engine was increased. This could be a result of the engine wear after
199 running for a long period of time (500 h of the endurance test was equivalent to two years for
200 distance) which can cause a greater degree of incomplete combustion and a larger portion of PM
201 is generated when compares to the new engine. Weighing the parts of the engine at the beginning
202 of the test and after each 500 h of running was a way to evaluate engine wear. It was found that
203 the occurrence lated weight loss of compression rings of the engine increased with engine hour.

204 *3.3 Effect of palm oil blends on PM and PAH emissions*

205 As can be seen in Fig. 3, the total PM and PAH concentrations reduced when the fraction
206 of blended palm oil was increased. Comparison at the end of 5000 h, the total PM was reduced by
207 12.38% and 18.09% when using PB30 and PB40, respectively and contained less PAHs than
208 when using PB0 by 25.73-28.85%. This indicates that palm oil blends can be more completely
209 combusted in comparison to commercial petroleum diesel which is a desirable result and it agrees
210 with many previous investigations [22,23]. The more oxygen content of palm oil blends most
211 likely enables more complete combustion than diesel fuel, causing a reduction in PM emission
212 and the particulate-associated PAHs should be reduced as well [4,7]. In addition, the less aromatic
213 content of palm oil blends could contribute to the reduction of particulate-phase PAHs.

214 The reduction percentage (η) of PM and PAH emissions can be calculated by the
215 following equation [10];

$$216 \quad \eta(\%) = \left[\frac{(\text{Emission with PB0} - \text{Emission with palm oil blend})}{\text{Emission with PB0}} \right] \times 100$$

217 Fig. 4 clearly shows that as the blending ratio of palm oil was increased, the reduction
218 percentages of PM and PAH emissions increased. The reduction of PAH emission was actually
219 higher than that of PM emission; i.e., the emissions of palm oil blends (PB30 and PB40)
220 contained much lower PAH contents.

221 *3.4 Concentration of 16-PAH compounds*

222 The average mass fraction of individual PAH in PM generated from combustion of PB0,
223 PB30 and PB40 are presented in Fig. 5. It can be seen that the contribution of Pyr compound was
224 dominant. The fractions of 2-3 ring PAH compounds (Nap, Act, Ace+Fle, Phe and Ant)
225 contributed to more than 41% of the total PAHs for PB0, and 53% and 63% of the total PAHs for
226 PB30 and PB40, respectively. These results indicated that the PAH emission from the palm oil
227 blend combustion was primarily dominant by the low molecular weight compounds [24].
228 However, when the fine-particles (<1 μm) were taken into account, the mass fraction of
229 associated PAHs, shown in Fig. 6, indicated that the larger molecule PAHs (4-6 aromatic rings)
230 which are high toxicity and carcinogenicity were predominant.

231 *3.5 Evaluation of PAH corresponding carcinogenicity*

232 The toxic equivalent factors (TEFs) have been devised as a way of comparing the
233 carcinogenic potency of the individual PAH, using BaP as a reference value of 1 [25]. The
234 Benzo[a]pyrene equivalent (BaP_{eq}) can be calculated from

$$235 \quad BaP_{eq} = \sum_{i=1}^n (TEF_i \times [PAH_i])$$

236 Where TEF_i is the toxic equivalent factor for PAH congener i [25] and [PAH_i] is the
237 concentration of PAH congener i. Table 3 shows the total BaP_{eq} calculated for different
238 experimental conditions. When compared at the same engine operating time, PB0 emitted much
239 higher BaP_{eq} than PB30 and PB40. As the palm oil blending ratio was increased, the BaP_{eq}

240 emission decreased gradually. The BaP_{eq} emission was also found to increase with the engine
241 hours.

242

243 **4. Conclusions**

244 The size distribution of particulate matters emitted from the agricultural diesel engine
245 fueled with commercial petroleum diesel (PB0) and degummed-deacidified mixed crude palm oil
246 blends of 30% (PB30) and 40% (PB40) showed in the accumulation mode and the MMAD was
247 dependent on both the blending ratio and engine hour. Increasing the blending ratio caused a
248 reduction of MMAD while increasing the operation time caused an increase of MMAD. The size
249 distribution and concentration of PAHs also displayed the same behaviors as PM. The results
250 indicate that lower molecular weight PAHs predominate in agricultural diesel engine exhaust. For
251 PAH compounds associated with fine-particles (<1 μm) indicated a dominance of larger
252 molecular PAHs (4-6 aromatic rings). The most dominant compound was pyrene (Pyr). Overall,
253 the results demonstrated clear reduction of PM, total PAHs and PAH corresponding carcinogenic
254 potency emissions as the blending ratio of palm oil was increased. Because, palm oil contains less
255 aromatic constituent and contains more oxygen amount thus most likely enables more complete
256 combustion than commercial petroleum diesel fuel.

257 In addition, blends of degummed-deacidified mixed crude palm oil in commercial
258 petroleum diesel up to 40 % by volume have shown to be satisfactory for long-term usage with
259 agricultural diesel engines. This will be useful both to save energy and take better care of the
260 environment. Also, it will benefit the livelihood of agriculturists when a long-term plan for large-
261 scale commercialization is implemented.

262

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268

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Table 1**Fuel properties.**

Property	PB0	PB100	Test method
Cetane Number	45-52	~42	ASTM D613
Viscosity at 40 °C (cSt)	3.54	46.70	ASTM D445
Flash point (°C)	73	>240	ASTM D93
Specific gravity (at 15.6 °C)	0.840	0.930	ASTM D4052
Lower heating value (MJ kg ⁻¹)	41.6	39.3	ASTM D240
Acid value (mgKOH g ⁻¹)	0.006	5.2	ASTM D664
Water (%)	0.009	0.218	ASTM D721
Copper Strip Corrosion	1b	1b	ASTM D130
Carbon residue (%)	0.10	0.217	ASTM D4530
Distillation temp (°C)	<357	319	ASTM D86

• 1b: satisfaction

Table 2

MMAD of PM from agricultural diesel engines.

Engine hour (h)	MMAD (μm)		
	PB0	PB30	PB40
2,500	-	0.61	0.61
3,000	-	0.62	0.61
3,500	-	0.62	0.62
4,000	0.76	0.65	0.63
4,500	0.81	0.76	0.69
5,000	0.82	0.80	0.70

Table 3Concentration of each BaP_{eq} measured from emissions of agricultural diesel engines.

Engine hour (h)	$\Sigma \text{BaP}_{\text{eq}} (\mu\text{g m}^{-3})$		
	PB0	PB30	PB40
2,500	-	2.43	2.04
3,000	-	2.58	2.17
3,500	-	2.86	2.30
4,000	5.77	2.82	2.29
4,500	7.43	3.23	2.84
5,000	8.56	3.34	3.21

1 **List of figure captions**

2 **Fig. 1.** Schematics of emission sampling.

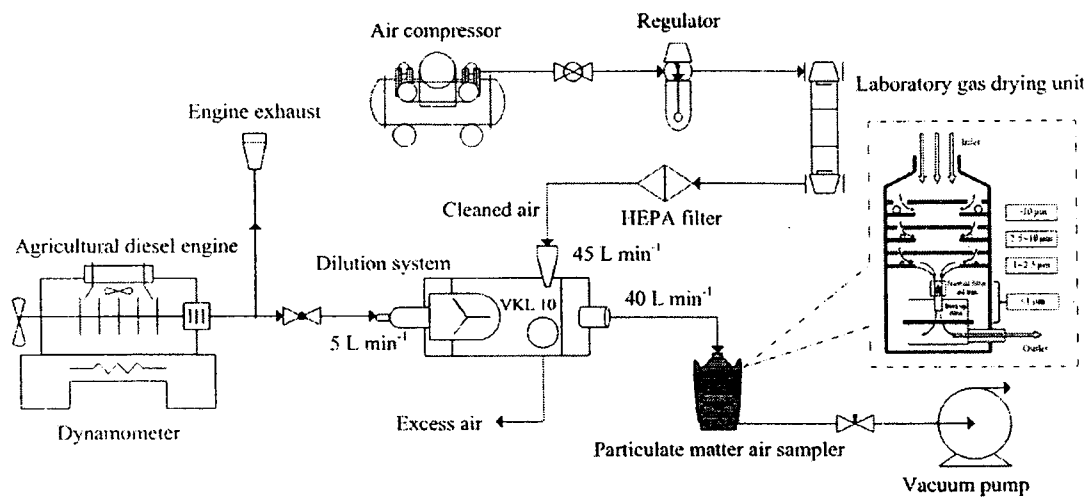
3 **Fig. 2.** Size distribution of (a) PM and (b) particle-bound PAHs from agricultural diesel engines
4 using PB0, PB30 and PB40.

5 **Fig. 3.** Concentration of (a) PM and (b) particle-bound PAHs from agricultural diesel engines
6 using PB0, PB30 and PB40 during engine hours of 2500-5000 h.

7 **Fig. 4.** Reduction percentages of total PM and total PAH emissions by palm oil blends compared
8 with PB0 at engine hours of 4000, 4500 and 5000 h.

9 **Fig. 5.** Mass fraction of each PAH bound on (a) all size range particles and (b) fine particles (<1
10 μm) emitted from agricultural diesel engines using PB0, PB30 and PB40.

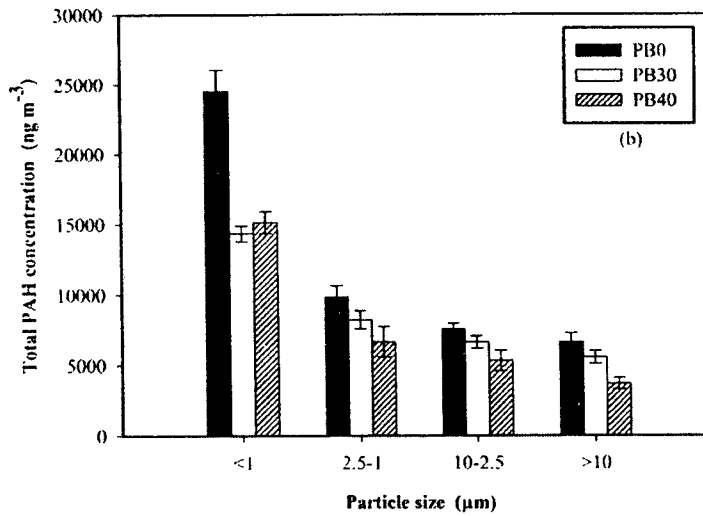
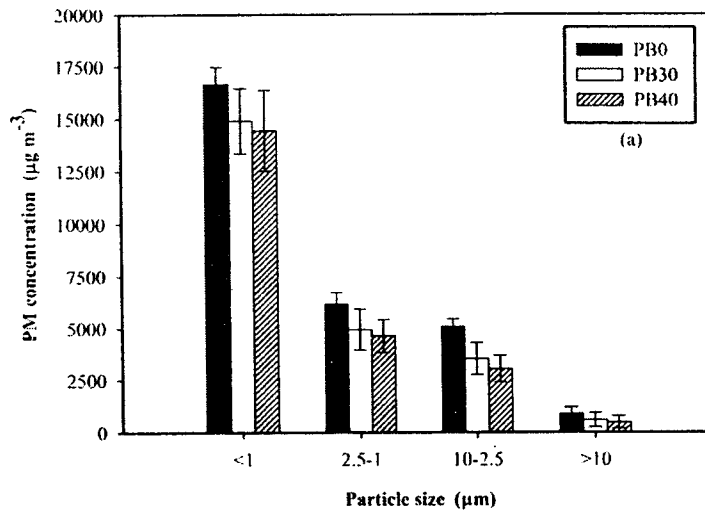
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12

13 **Fig. 1.** Schematics of emission sampling.

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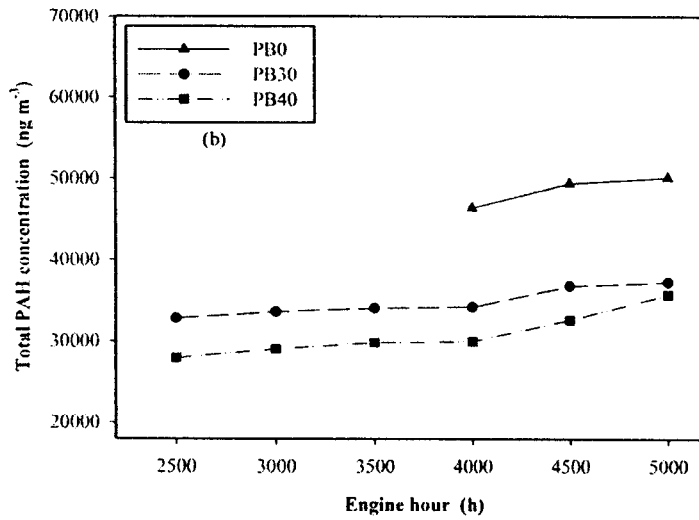
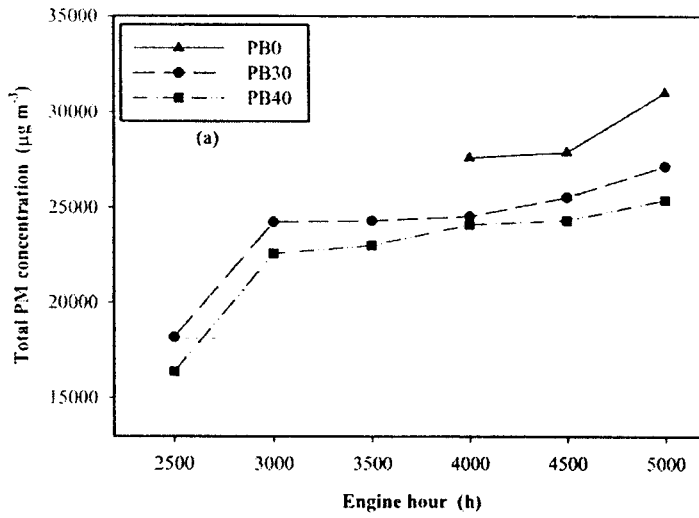
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18 using PB0, PB30 and PB40.

19



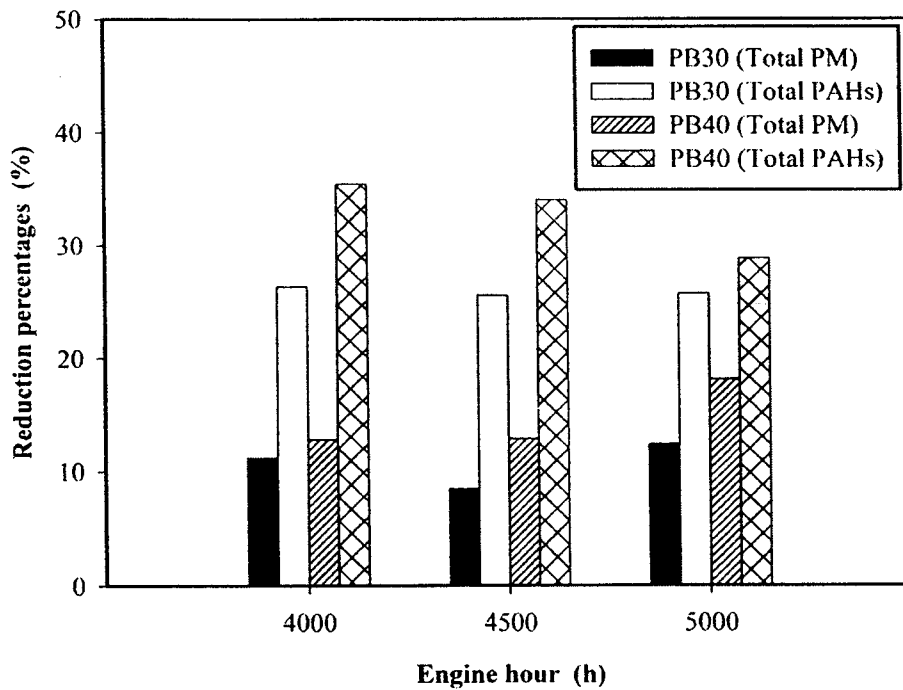
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21

22 **Fig. 3.** Concentration of (a) PM and (b) particle-bound PAHs from agricultural diesel engines

23 using PB0, PB30 and PB40 during engine hours of 2500-5000 h.

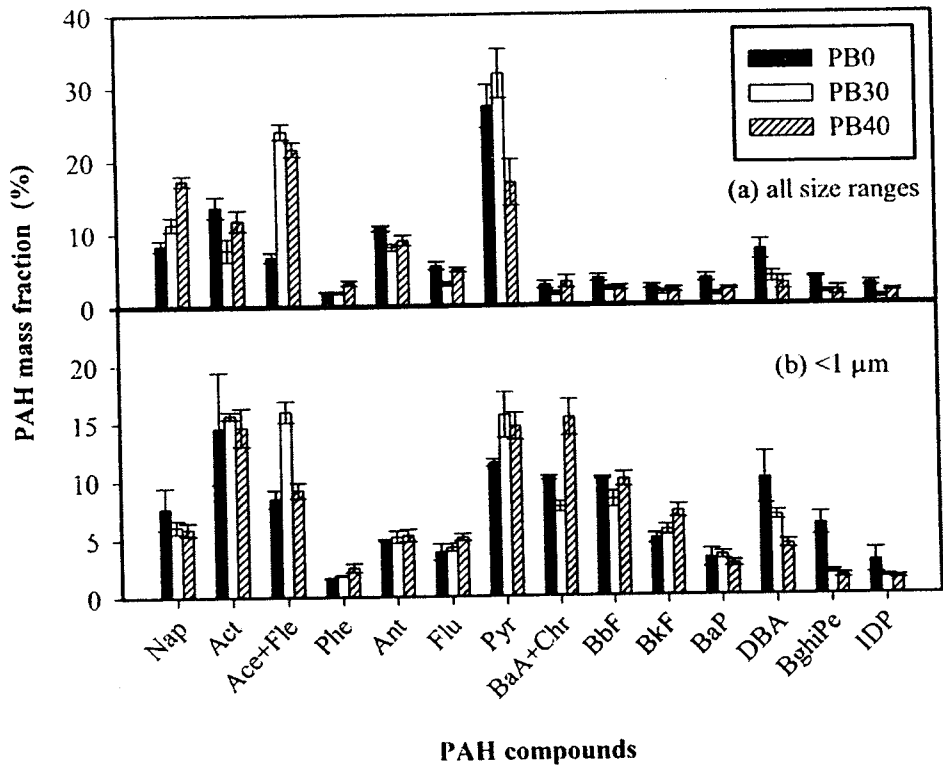
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26 **Fig. 4.** Reduction percentages of total PM and total PAH emissions by palm oil blends compared
 27 with PB0 at engine hours of 4000, 4500 and 5000 h.

28



29

30 Fig. 5. Mass fraction of each PAH bound on (a) all size range particles and (b) fine particles (<1

31 μm) emitted from agricultural diesel engines using PB0, PB30 and PB40.

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