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

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### Abstract

Mixed crude palm oil (MCPO), the mixture of palm fiber oil and palm kernel oil, has become of great interest as a renewable energy source. It can be easily extracted from whole dried palm fruits. In the present work, the degummed, deacidified MCPO was blended in petroleum diesel at portions of 30% and 40% by volume and then tested in agricultural diesel engines for long term usage. The particulates from the exhaust of the engines were collected every 500 hr using a four-stage cascade air sampler. The 50% cut-off aerodynamic diameters for the first three stages were 10, 2.5 and 1  $\mu\text{m}$ , while the last stage collected all particles smaller than 1  $\mu\text{m}$ . Sixteen particle bounded polycyclic aromatic hydrocarbons (PAHs) were analyzed using a high performance liquid chromatography. The results indicated that the size distribution of particulate matter was in the accumulation mode and the pattern of total PAHs associated with fine-particles ( $< 1 \mu\text{m}$ ) showed a dominance of larger molecular weight PAHs (4–6 aromatic rings), especially pyrene. The mass median diameter, PM and total PAH concentrations decreased when increasing the palm oil content, but increased when the running hours of the engine were increased. In addition, Commercial petroleum diesel (PB0) gave the highest value of carcinogenic potency equivalent ( $\text{BaP}_{\text{eq}}$ ) for all particle size ranges. As the palm oil was increased, the  $\text{BaP}_{\text{eq}}$  decreased gradually. Therefore the degummed-deacidified MCPO blends are recommended for diesel substitute.

**Key words:** mixed crude palm oil; palm oil blend; agricultural diesel engine; polycyclic aromatic hydrocarbon; particulate matter

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### Introduction

The world energy crisis due to escalation of fuel prices and diminishing of petroleum-based oil and the deterioration of environmental pollution related to fossil fuel usage have been a global concern. Vegetable oils and biodiesels derived from vegetable oils which are renewable have gained enormous attention in many countries as an alternative source of energy (Murugesan et al., 2009; Shahid and Jamal, 2008; Balat and Balat, 2008). In addition, the physicochemical properties of biodiesels meet the requirements of diesel engine combustion. In Thailand, palm oil is currently shown to have the highest potential feedstock for

biodiesel production because of the abundance of raw material and the price of palm oil which is cheaper than other vegetable oils such as soybean oil, coconut oil, olive oil and rapeseed oil. Some diesel engines can also be operated using preheated crude palm oil (Kalam and Masjuki, 2004; Bari et al., 2002), refined palm oil (Raadnuj and Meenak, 2003) and degummed-deacidified mixed crude palm oil (Leevijit and Prateepchaikul, 2011; Prateepchaikul and Apichato, 2003). Palm oil is a highly oxygenated fuel, and its combustion can reduce pollutant emissions such as total hydrocarbons, carbon monoxide (CO), sulfur oxides and polycyclic aromatic hydrocarbons (PAHs), though slightly increases nitrogen oxides as compared to commercial petroleum diesel (Kalam and Masjuki, 2004; Wang et al.,

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2000; Chien et al., 2009; Lin et al., 2006; Hess et al., 2007).

Diesel engine generates fine smoke particles which contain many chemical compounds affecting atmospheric environment especially in urban areas where diesel trucks are a major transportation means. It was reported that nano-particles are generated during diesel combustion and these particles subsequently coagulate to form larger particles in submicron range (Kittelson, 1998). The particulate matter (PM) emissions from diesel-powered engines are typically 10–100 times higher than those from gasoline-powered engines. The diesel emissions contain hundreds of organic and inorganic compounds, partitioned in the gaseous and particulate phases. The emission profile of these chemical compounds depends on fuel type, engine technology, its tuning and maintenance (Corrêa and Arbilla, 2006). Due to their toxicity, carcinogenicity and mutagenicity, PAHs are known to be the principal pollutants from incomplete combustion of motor vehicles, home cooking, fossil fuel combustion, industrial process, or biomass burning (Phoungthong et al., 2009). Most PAHs are associated with fine-particles, typically 0.5  $\mu\text{m}$  or less (De Martinis et al., 2002). The size of PM is an important factor affecting human health. The fine particles can 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.

Studies of PM and associated PAHs emitted from agricultural diesel engines fueled with palm oil blends have been limited. Most of the studies focused on the emission of biodiesel (methyl-ester or ethyl-ester) combustion. Nevertheless, PAHs and regulated harmful emissions from palm oil blended diesel and the effect of the engine operating times on emission have seldom been addressed. This study focused on examining emissions of the agricultural diesel engine using blends of degummed-deacidified mixed crude palm oil and comparing with commercial diesel. The effects of blending ratios on emissions of PM, PAHs and carcinogenic potencies while the engine was in operation for long-term tests with constant load and a speed of 2200 r/min were investigated. The MCPO which is a mixture of palm fiber oil and palm kernel oil is of keen interest as a feedstock for diesel substitute especially for farmers living in or near sufficient economic communities in Thailand (Leevijit and Prateepchaikul, 2011). MCPO can be easily produced with a screw-press of whole dried palm fruits. Therefore the knowledge from this work will lead to the most economical use of MCPO as an alternative fuel and can be used at policy-level for promoting alternative fuel usage.

## 1 Materials and methods

### 1.1 Reagents

All chemicals PAHs extraction and high performance liquid chromatography (HPLC) assay such as acetonitrile, dichloromethane and dimethylsulfoxide (DMSO) were of HPLC grade (Lab-scan, Thailand). Ultra pure water, de-ionized with reverse osmosis system and purified with a Maxima ultrapure water instrument (ELGA, England) to obtain the resistivity of 18.2  $\text{M}\Omega\text{-cm}$ , was used throughout the study. A certified standard solution containing 16 compounds of EPA 610 polycyclic aromatic hydrocarbons was purchased from Supelco (USA).

### 1.2 Fuels

Commercial petroleum diesel (PB0) and two different blending mixtures of diesel with crude palm oil: PB30 and PB40, 30% and 40% by volume of crude palm oil, were tested. The MCPO was obtained from a local palm oil mill. It is a viscous liquid containing gum and high free fatty acid. Before blending with diesel, MCPO was degummed using phosphoric acid and deacidified using sodium hydroxide to reduce free fatty acid to less than 1%. The preparation method of tested blends was given in the previous study (Leevijit and Prateepchaikul, 2011). The properties of PB0 and PB100 (degummed-deacidified MCPO), determined according to related ASTM standard methods, are listed in **Table 1**.

### 1.3 Engine and operating conditions

The experiments were carried out using three identical agricultural diesel engines (Type RT80, Kubota, Thailand) which are 4-cycle stroke, water cooled, single horizontal cylinder and indirect injection diesel engines. The bore to stroke ratio is 84 mm: 84 mm and the compression ratio is 23: 1. The maximum power is 5.9 kW at 2400 r/min and maximum torque is 27.5 Nm at 1600 r/min. This type of engine has been used by farmers in Thailand for rice-field tillage by operating with tractor or wheel plough. Also the modified engines are used to add oxygen to water in giant tiger prawn farms. In this study, the engine was performed according to the previously study procedure

**Table 1** Fuel properties

Property	PB0	PB100	Test method
Cetane number	45–52	ca. 42	ASTM D613
Viscosity at 40°C (mm <sup>2</sup> /sec)	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)	41.6	39.3	ASTM D240
Acid value (mg KOH/g)	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.

PB0: commercial petroleum diesel; PB100: degummed-deacidified mixed crude palm oil.

(Prateepchaikul and Apichato, 2003) and operated at 75% of full load with constant speed of 2200 r/min. After every 500 hr of running, the engine performance was tested according to JIS B8018 (1989) and then the particulate matters were collected from the engine exhaust. Since the emission concentration was high, a dilutor (VKL 10, Palas, Germany) was used to dilute the exhaust emission at the dilution ratio of 10 prior to each sampling. The clean air for the dilution system was obtained from an air compressor and passed through a regulator, a gas drying unit and a high efficiency particulate air filter for removal of moisture, oil and particles. The temperature in the dilutor was less than 40°C.

#### 1.4 Measurement of size distribution of PM

The four-stage cascade particulate matter air sampler (Kanomax, Japan) which has 50% cut-off aerodynamic diameters of 10, 2.5 and 1  $\mu\text{m}$  was used to determine the size distribution of particles emitted from the engine. A constant flow rate (40 L/min) of diluted exhaust gas was drawn by a vacuum pump, and controlled by a needle valve and a rotameter. The particles were collected on a quartz fiber filter (Type 2500QAT-UP, Pallflex, USA). Donut-shape filters with 65  $\times$  30 mm diameter were used in impaction stages, a 47-mm diameter filter was used in the backup stage, and 8 mm thick stainless steel fiber mat with fiber diameter of 8  $\mu\text{m}$  and packing density of 0.0065 (Otani et al., 2007) was used at the inertial filter stage above the backup filter. The schematic diagrams of the particulate matter air sampler and the experimental set up are shown in Fig. 1. Before sampling, the filters were treated in a dark desiccator at constant temperature (25°C) and constant humidity (50% relative humidity) for at least 72 hr then weighed using an analytical balance with precision of 0.01 mg (CP225D, Sartorius, Germany). After sampling, the filters were treated under the same conditions as before sampling and weighed using the

identical analytical balance. The weights of the collected particles on each filter were then calculated. The set of filter samples was kept together, wrapped with aluminum foil, put in a polyethylene bag and stored at  $-20^\circ\text{C}$  in order to avoid evaporation and degradation of PAHs until extraction.

#### 1.5 Analysis of PAHs

The 16 PAH compounds 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) were monitored. The filters were extracted ultrasonically twice with 40 mL of dichloromethane for 30 min each while the water in the ultrasonic bath was controlled to be 4–10°C in order to prevent overheating. This technique was modified from the methods used in previous studies (Ohura et al., 2004; Furuuchi et al., 2006). The extracts were combined, filtered using a syringe filter unit (0.45  $\mu\text{m}$  PTFE) for removal of insoluble particles, and 50  $\mu\text{L}$  of DMSO was added for PAH preservation. Then the solvent was removed using a rotary evaporator, and the residues were redissolved in 450  $\mu\text{L}$  of acetonitrile. The solution was filtered again by a 0.45  $\mu\text{m}$  PTFE syringe filter, kept in a 1.5 mL amber glass vial, and stored at 4°C prior to analysis.

The PAH analysis was performed using HPLC (1100, Agilent, USA) with a Chemstation program and following the previous method (Chomanee et al., 2009) with appropriate modifications. The HPLC system consisted of a C18 reversed phase column, 4.6  $\times$  250 mm, 5  $\mu\text{m}$  (VertiSep UPS, Vertical Chromatography, Thailand) with a guard column, an injection volume of 25  $\mu\text{L}$  and a diode array

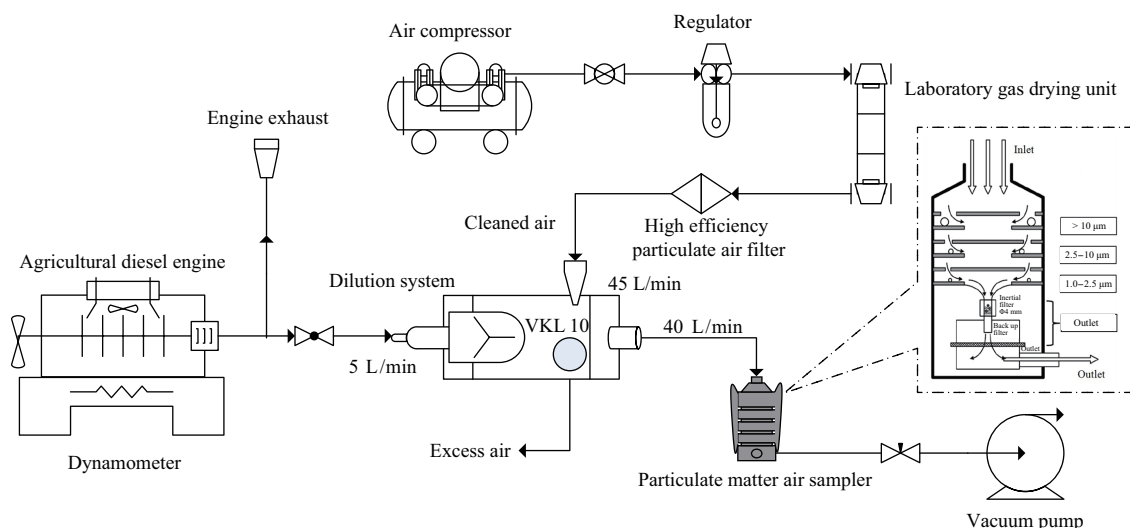


Fig. 1 Schematics of emission sampling.

detector. The solvent gradient elution of acetonitrile and ultrapure water was used for 40 min at the flow rates of 1.0–1.2 mL/min. The resulting chromatograms of all 16 PAHs were identified by matching retention times with reference standards and confirmed by spiking method. The concentration of each PAH was quantified from the peak area. A good linear correlation between the concentrations and peak areas was found with  $R^2$  values in the range of 0.999–1 for all PAH compounds. Field blank filters as well as solvent blanks were analysed by the same procedure and found that integrated areas were less than detection limit to ensure that there were no significant background interference. The detection limit of individual PAH was defined as the lowest concentration that the detector could provide a signal-to-noise ratio of 3, and found between 3.9–80.2 ng/mL. The recovery efficiency was confirmed to be  $0.79 \pm 0.23$  ( $n = 3$ ) by spiking known amounts of external PAH standards onto the pre-treated filters and then processing by the same analytical procedure used for the samples.

## 2 Results and discussion

### 2.1 Size distribution of PM and associated PAHs

This work began when the engine using PB0 was run for almost 4000 hr and the engines using PB30 and PB40 were run for 2500 hr. Therefore the combustion of PB0 was tested at operating times of 4000, 4500 and 5000 hr, while the combustions of PB30 and PB40 were performed at operating times of 2500, 3000, 3500, 4000, 4500 and 5000 hr. The size distributions of PM emitted from the engines fueled with PB0, PB30 and PB40 are shown in **Fig. 2a**. For all cases, the PM size distributions show a behavior in the accumulation mode ( $< 1 \mu\text{m}$ ). Most particulate mass was found in the  $< 1 \mu\text{m}$  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 (Kittelson, 1998). The mass median aerodynamic diameters (MMAD) of PM are summarized in **Table 2**. The

results showed that MMAD decreased when the blending percentages of palm oil were increased from PB0 to PB40 which implied that the combustion of PB30 and PB40 generated particles with smaller size than that of PB0. The reason for this is the higher palm oil blend ratio provides more complete combustion since palm oil blends contain more oxygen content and less aromatic hydrocarbons than commercial petroleum diesel (De Almeida et al., 2002).

As shown in **Fig. 2b**, the reduction of total particle-bound PAHs with increasing particle size was similar to that of the PM concentrations. For each blend ratio, the total PAH concentration was maximized when the particle sizes were less than  $1 \mu\text{m}$ . These results were in agreement with the PM concentration since the particle-bound PAH emissions are closely related to PM emissions (Chien et al., 2009).

### 2.2 Effect of long-term engine operation on PM and PAH emissions

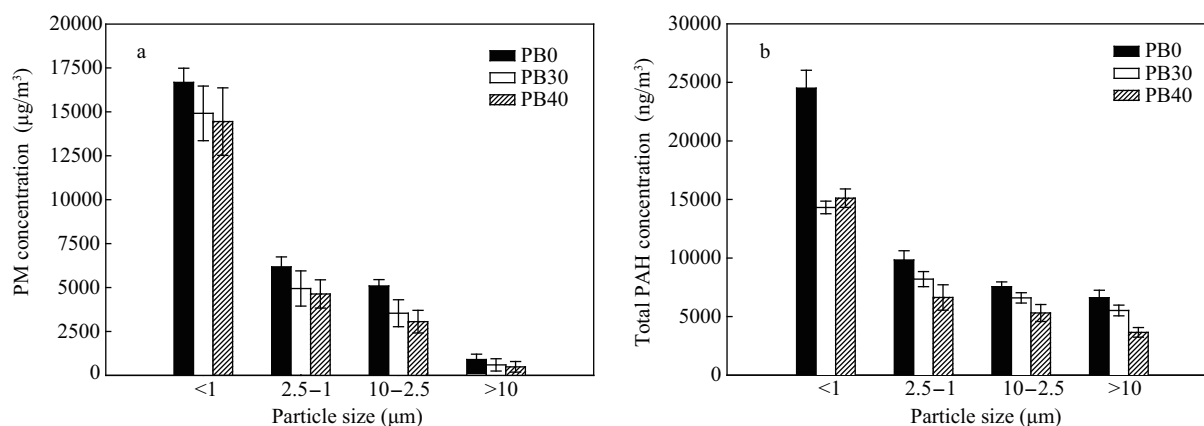
The total PM and associated PAH concentrations for the engine fueled with PB0, PB30 and PB40 were found to increase with the engine operation time as shown in **Fig. 3**. As compared to the same period of engine operation time from 4000 to 5000 hr, the total PM concentration increased by 12.30%, 10.81%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

The MMAD and concentrations of PM and associated

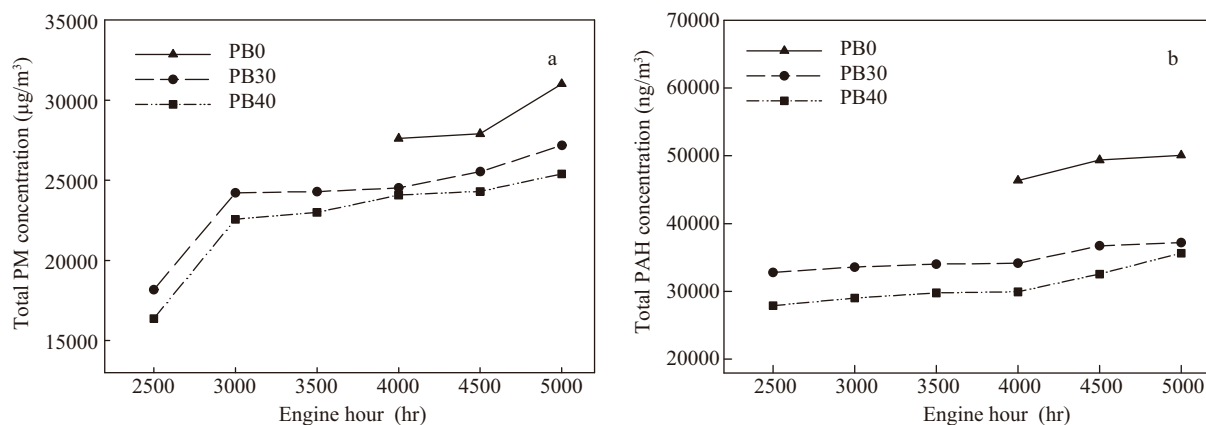
**Table 2** Mass median aerodynamic diameter (MMAD) of PM from agricultural diesel engines

Engine hour (hr)	MMAD ( $\mu\text{m}$ )		
	PB0	PB30	PB40
2500	–	0.61	0.61
3000	–	0.62	0.61
3500	–	0.62	0.62
4000	0.76	0.65	0.63
4500	0.81	0.76	0.69
5000	0.82	0.80	0.70

PB30 and PB40: two different blending mixtures of diesel with crude palm oil 30% and 40% by volume of crude palm oil.



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



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

PAHs, however, increased when the operating time of the engine was increased. This could be a result of the engine wear after running for a long period of time (500 hr of the endurance test is equivalent to two years of distance) which can cause a greater degree of incomplete combustion and a larger portion of PM is generated when compared to a new engine. Weighing the parts of the engine at the beginning of the test and after each 500 hr of running was a way to evaluate engine wear. It was found that the compression rings of the engine had the most significant weight loss and this weight loss increased with engine usage.

### 2.3 Effect of palm oil blends on PM and PAH emissions

As can be seen in **Fig. 3**, the total PM and PAH concentrations were reduced when the fraction of blended palm oil was increased. At the end of 5000 hr, the total PM was reduced by 12.38% and 18.09% when using PB30 and PB40 and contained less PAHs than when using PB0 by 25.73%–28.85%. This indicates that palm oil blends can be more combustible compared to commercial petroleum diesel. This desirable result agrees with many previous investigations (Bagley et al., 1998; Jung et al., 2006). The more oxygen content of palm oil blends most likely enables more complete combustion than diesel fuel, causing a reduction in PM emission and the particulate-associated PAHs should be reduced as well (Kalam and Masjuki, 2004; Leevijit and Prateepchaikul, 2011). In addition, the less aromatic content of palm oil blends could contribute to the reduction of particulate-phase PAHs.

The reduction percentage ( $\eta$ ) of PM and PAH emissions can be calculated by the following Eq. (1) (Chien et al., 2009);

$$\eta = \frac{(E_{PB0} - E_{\text{palm oil blend}})}{E_{PB0}} \times 100\% \quad (1)$$

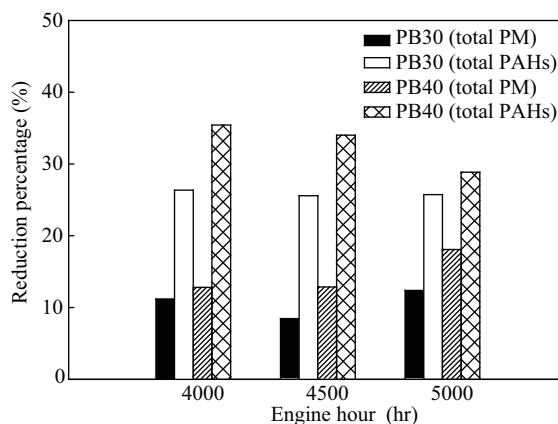
where,  $E_{PB0}$  is the emission with PB0 and  $E_{\text{palm oil blend}}$  is the emission with palm oil blend.

**Figure 4** clearly shows that as the blending ratio of palm

oil was increased, the reduction percentages of PM and PAH emissions increased. The reduction of PAH emission was actually higher than that of PM emission; i.e., the emissions of palm oil blends (PB30 and PB40) contained much lower PAH contents.

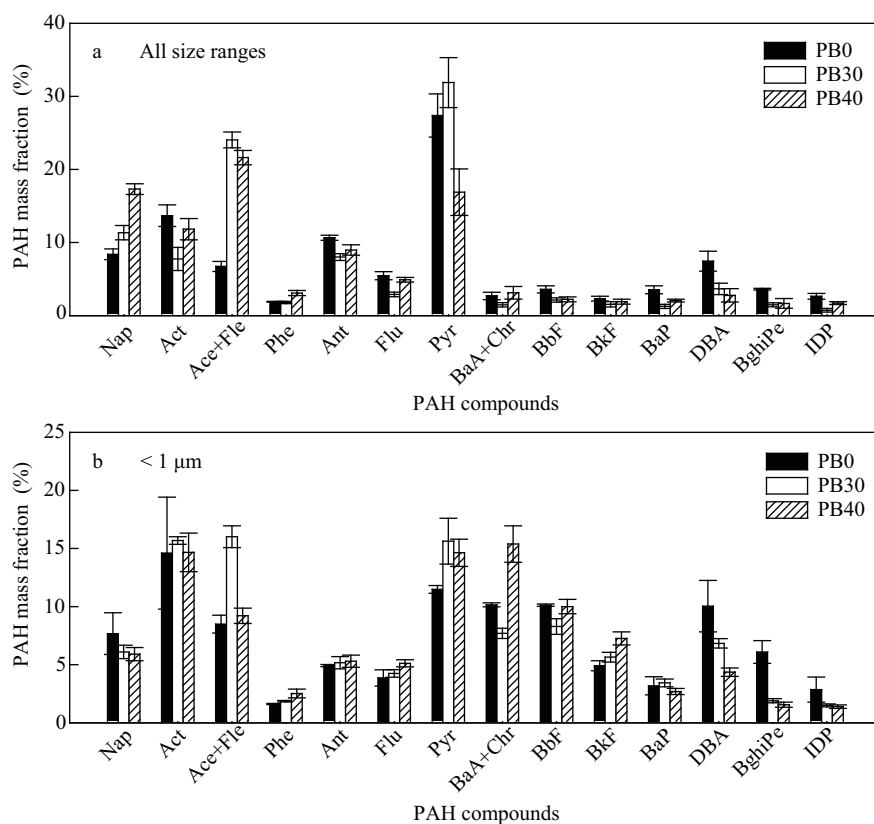
### 2.4 Concentration of 16-PAH compounds

The average mass fraction of individual PAH in PM generated from combustion of PB0, PB30 and PB40 are presented in **Fig. 5a**. It can be seen that the contribution of Pyr compound was dominant. The fractions of 2–3 ring PAH compounds (Nap, Act, Ace+Fle, Phe and Ant) contributed to more than 41% of the total PAHs for PB0, and 53% and 63% of the total PAHs for PB30 and PB40, respectively. These results indicated that the PAH emission from the palm oil blend combustion was primarily dominant by the low molecular weight compounds (Lin et al., 2006). However, when the fine-particles ( $<1 \mu\text{m}$ ) were taken into account, the mass fraction of associated PAHs, shown in **Fig. 5b**, indicated that the larger molecule PAHs (4–6 aromatic rings) which have high toxicity and carcinogenicity were predominant.



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





**Fig. 5** Mass fraction of each PAH bound on (a) all size range particles and (b) fine particles (<1  $\mu\text{m}$ ) emitted from agricultural diesel engines using PB0, PB30 and PB40.

### 2.5 Evaluation of PAH corresponding carcinogenicity

The toxic equivalent factors (TEFs) have been devised as a way of comparing the carcinogenic potency of the individual PAH, using BaP as a reference value of 1 (Nisbet and LaGoy, 1992). The benzo[a]pyrene equivalent (BaP<sub>eq</sub>) can be calculated from Eq. (2).

$$\text{BaP}_{\text{eq}} = \sum_{i=1}^n (\text{TEF}_i \times [\text{PAH}_i]) \quad (2)$$

where,  $\text{TEF}_i$  is the toxic equivalent factor for PAH congener  $i$  (Nisbet and LaGoy, 1992) and  $[\text{PAH}_i]$  is the concentration of PAH congener  $i$ . **Table 3** shows the total BaP<sub>eq</sub> calculated for different experimental conditions. When compared to the same engine operating time, PB0 emitted much higher BaP<sub>eq</sub> than PB30 and PB40. As the palm oil blending ratio was increased, the BaP<sub>eq</sub> emission decreased gradually. The BaP<sub>eq</sub> emission was also found to increase with engine hours.

### 3 Conclusions

The size distribution of particulate matters emitted from the agricultural diesel engine fueled with commercial petroleum diesel (PB0) and degummed-deacidified mixed crude palm oil blends of 30% (PB30) and 40% (PB40)

**Table 3** Concentration of each BaP<sub>eq</sub> measured from emissions of agricultural diesel engines

Engine hour (hr)	$\Sigma\text{BaP}_{\text{eq}}$ ( $\mu\text{g}/\text{m}^3$ )		
	PB0	PB30	PB40
2500	–	2.43	2.04
3000	–	2.58	2.17
3500	–	2.86	2.30
4000	5.77	2.82	2.29
4500	7.43	3.23	2.84
5000	8.56	3.34	3.21

showed in the accumulation mode and the MMAD was dependent on both the blending ratio and engine hour. Increasing the blending ratio caused a reduction of MMAD while increasing the operation time caused an increase of MMAD. The size distribution and concentration of PAHs also displayed the same behaviors as PM. The results indicate that lower molecular weight PAHs predominate in agricultural diesel engine exhaust. For PAH compounds associated with fine-particles (< 1  $\mu\text{m}$ ) indicated a dominance of larger molecular PAHs (4–6 aromatic rings). The most dominant compound was pyrene (Pyr). Overall, the results demonstrated clear reduction of PM, total PAHs and PAH corresponding carcinogenic potency emissions as the blending ratio of palm oil was increased. Because, palm oil contains less aromatic constituent and contains more oxygen amount it most likely enables more complete combustion than commercial petroleum diesel fuel.

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

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