CHAPTER IV

RESULTS AND DISCUSSION

Diesel fuel is a refined petroleum product which is burned in the engines powering most of the world's trains, ships, and large trucks. Petroleum is, of course, a non-renewable resource of finite supply. Acute shortage and dramatic price increases in petroleum and the refined products derived from petroleum have been suffered by industrialized countries during the past quarter-century. Further, diesel engines emit relatively high levels of certain pollutants, especially particulates. Accordingly, extensive research effort is now being directed toward replacing some or all petroleum-based diesel fuel with a cleaner-burning fuel derived from a renewable source such as farm crops.

When pure vegetable oils are used as a fuel source in diesel engines, they often cause excessive engine wear and fuel injector coking, and have high smoke values. Further, their viscosity is much higher than petrolem based diesel fuel.

In an effort to overcome some of the problems associated with using pure vegetable oils, several attempts have been made to use fatty acid methyl esters. These esters are typically prepared by completely transesterifying triglycerides, the major component in fats and oils, with methanol, in the presence of an acid calalyst.

4.1 Identification of Palm Oil Methyl Ester

In the transesterification of crude palm oils, a triglyceride reacts with methanol in the presence of sulfuric acid, producing a mixture of fatty acids alkyl esters, mainly methyl palmitate and methyl oleate, and glycerol. The overall process was shown in Figure 4.1.

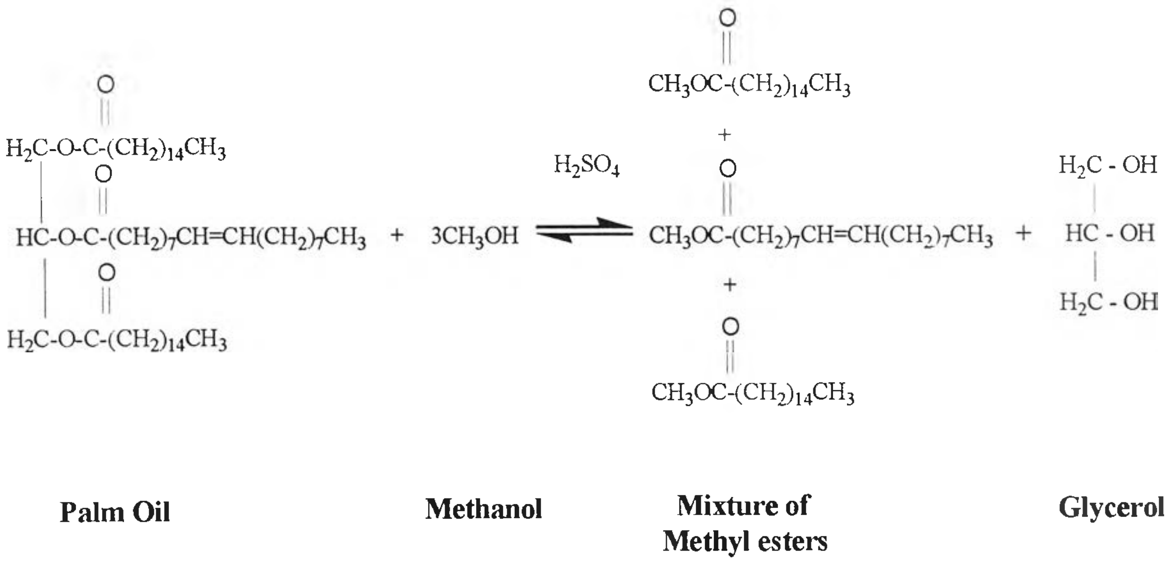

Figure 4.1 Transesterification of palm oil.

The fatty acids in palm oil were refluxed with methanol in the presence of sulfuric acid for 6 hours. Methanol for transesterification is preferred because of the low costs and the best yield of all alcohols. In this study, the 73-85 % yield of the mixture of methyl esters were obtained.

The transesterified product was characterized by ^{13}C NMR, ^{1}H NMR and FT-IR. The ^{13}C NMR spectrum of methyl esters indicated the signal of carbon atom of methyl ($O-CH_3$) at δ 51.40, 62 and 68 ppm (Figure C-1). From ^{1}H NMR spectrum in Figure C-2, the singlet signal at δ 3.63 ppm indicated the protons of methyl group connected oxygen ($O-CH_3$) of methyl ester.

The FT-IR spectrum of methyl esters (Figure C-3) showed the absorption band of C-H stretching of aliphatic at 2912 and 2850 cm^{-1}, absorption band of C=O stretching at 1739 cm^{-1} and C-O stretching at 1176 cm^{-1}.

From the characterizations of the ester fuel above, it may be confirmed that crude palm oil was transesterified to palm oil methyl ester.

The palm oil methyl ester was honey-colored liquid. Table 4.1 shows properties of palm oil methyl ester and diesel fuel.

Table 4.1 Fuel properties

	Diesel fuel	**Palm oil methyl ester**
API Gravity @ 60°F	35.4	31.2
Specific Gravity @ 60/60°F	0.8478	0.8697
Cetane Index	50.5	55.4
Kinematic Viscosity @ 40°C, cSt	3.748	4.860
Pour Point, °C	+3.0	+6.0
Flash Point, (P.M.), °C	68	167
Distillation (°C) :		
IBP	145	213
10% recovery	220	249
50% recovery	279	300
90% recovery	343	339

Values of the API gravity and the specific gravity in Table 4.1 indicate that palm oil methyl ester has slightly higher density than diesel fuel. The cetane index of the ester fuel is higher than diesel fuel. The ester fuel was found to have 1.1 cSt higher viscosity than diesel. The pour point of the ester fuel higher than diesel was obtained. However, the ester fuel gave a flash point 167 degrees, well above the flash point of diesel fuel. The distillation point of the ester fuel is higher than that of diesel fuel.

4.2 Specifications of Test Fuel

Diesel fuel from Bangchak Petroleum Co., Ltd. was used as base fuel in this study. Test fuels which were used to fuel the diesel test engine consist of five blends, base fuel blended with palm oil methyl ester at 10, 20, and 30 % by volume, refined palm oil and crude palm oil was blended at 20 % by volume, comparing the amount of PAHs from exhaust emission with neat diesel fuel. Thus, diesel fuel properties are important for diesel engine such as driving performance, starting, and emission. Table 4.2 shows the properties of these test fuels which were examined according to the ASTM standard method.

As specific gravity of palm oil methyl ester is higer than that of base diesel, addition of palm oil methyl ester into base diesel fuel resulted in higher specific gravity of blended diesel. The cetane number of blended fuel increased due to an increase in the oxygenated compounds of palm oil methyl ester

When blended diesel fuel with palm oil methyl ester, refined palm oil and crude palm oil, the kinematic viscosity were significantly higher than base diesel fuel. However, the blended fuels had pour point lower than pure diesel fuel due to lower melting point of compounds in palm oil methyl ester.

The flash point of blended fuels was higher than that of diesel fuel. Therefore, the blended fuels are safer than diesel fuel to store, handle, and use. The distillation points indicate the volatility of a diesel fuel, but have no direct effect on power or economy. Thus, the blended fuel had less volatility than base diesel fuel.

Table 4.2 Properties of test fuel

Property	ASTM Method	Value	Test Fuel						
			Diesel Fuel	Palm Oil Methyl Ester	B10[a]	B20[b]	B30[c]	RPO20[d]	CPO20[e]
API Gravity @ 60°F	D 1298	report	35.4	31.2	34.7	34.1	33.2	32.8	32.8
Specific Gravity @ 60/60°F	D 1298	0.81 – 0.87	0.8478	0.8697	0.8514	0.8548	0.8591	0.8612	0.8612
Cetane Index	D976	47 min	50.5	55.4	50.8	50.9	51.4	50.8	50.8
Kinematic Viscosity @ 40°C, cSt	D 445	1.8 – 4.1	3.748	4.860	3.850	4.129	4.465	6.068	5.979
Pour Point, °C	D 97	10 max	+3.0	+6.0	-6.0	-6.0	-6.0	-9.0	-3.0
Flash Point, (P.M.), °C	D 93	52 min	68	167	72	73	76	72	72
Distillation (°C) :	D 86								
IBP		report	145	213	156	168	179	150	148
10% rec.		report	220	249	218	226	231	220	225
50% rec.		report	279	300	285	279	296	294	293
90% rec.		357 max	343	339	324	330	289	330	326

[a] Diesel fuel blended with palm oil methyl ester 10% by volume

[b] Diesel fuel blended with palm oil methyl ester 20% by volume

[c] Diesel fuel blended with palm oil methyl ester 30% by volume

[d] Diesel fuel blended with refined palm oil 20% by volume

[e] Diesel fuel blended with crude palm oil 20% by volume

4.3 Identification of PAHs in Diesel Exhaust

PAHs in the diesel exhaust were identified and quantified using a GC-FID technique according to the EPA 610 method. In this study, standard PAHs from EPA 610 contains 16 components naphthalene, acenaphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene, and benzo(ghi)perylene. They were used as the standard compounds for establishing the calibration curve (Appendix A) for determination of each PAH by comparing the peak area in chromatogram (Appendix B). The retention times of the individual PAH are shown in Table 4.3.

In this study, for all of the test fuels at various engine speeds, PAHs in diesel exhaust consisted of different levels of naphthalene, acenaphthylene, acenaphthene, phenanthrene, fluorene, anthracene, fluoranthene, pyrene, benz(a)anthracene, benzo(k)fluoranthene chrysene and benzo(ghi)perylene were found.

Table 4.3 List of selected PAHs in standard mixture of PAHs according to EPA 610 including molecular weight, formula structure and retention time.

PAHs	M.W.	Formula	Retention time (min)
1. Naphthalene	128	$C_{10}H_8$	7.10
2. Acenaphthylene	152	$C_{12}H_8$	10.24
3. Acenaphthene	154	$C_{12}H_{10}$	10.57
4. Fluorene	166	$C_{10}H_8$	11.56
5. Phenanthrene	178	$C_{14}H_{10}$	13.84
6. Anthracene	178	$C_{14}H_{10}$	14.04
7. Fluoranthene	202	$C_{16}H_{10}$	18.36
8. Pyrene	202	$C_{16}H_{10}$	19.37
9. Benz(a)anthracene	228	$C_{18}H_{12}$	26.42
10. Chrysene	228	$C_{18}H_{12}$	26.66
11. Benzo(b)fluoranthene	252	$C_{20}H_{12}$	33.55
12. Benzo(k)fluoranthene	252	$C_{20}H_{12}$	33.72
13. Benzo(a)pyrene	252	$C_{20}H_{12}$	35.53
14. Indeno(1,2,3-cd)pyrene	276	$C_{22}H_{12}$	42.34
15. Dibenz(a,h)anthracene	278	$C_{22}H_{14}$	42.62
16. Benzo(ghi)perylene	276	$C_{22}H_{12}$	43.70

4.4 Effect of Engine Speed on PAHs in Diesel Exhaust

Engine speed affects the swirl characteristics, ignition timing, and combustion temperature of the engine. At low engine speed, there is less swirl and lower combustion chamber temperature. At mid engine speed, the optimum swirl dynamics and optimum combustion timing give the maximum power band for the engine. High engine speed generates over-swirl and shortens the period over which combustion proceeds [1].

In this study, the effect of engine speed was performed at 800, 1600 and 2400 rpm. The value of 800 rpm is the engine speed during traffic congestion while the values of 1600 and 2400 rpm are the engine speeds during medium and high running conditions, respectively. The types and amounts of PAHs found in diesel exhaust are shown in Appendix D. Figure 4.2 shows the total concentrations of PAHs emission from diesel test engine at various speeds.

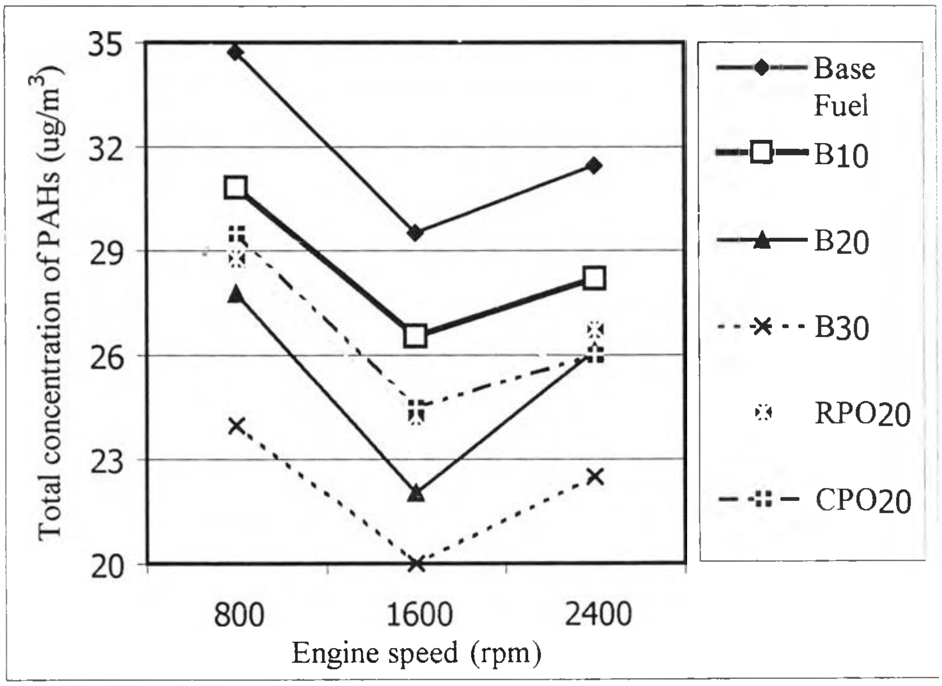

Figure 4.2 Effect of engine speed on total PAHs in diesel test engine exhaust emission.

The amount of PAHs decreases when the engine speed was varied from 800 rpm to 1600 rpm and increases at 2400 rpm. At the engine speed of 800 rpm, the amount of PAHs is the highest emission because there is a low combustion chamber temperature, leading to low oxidation. Whereas at 1600 rpm, there was greater turbulence and swirl, higher flame speed, and optimum combustion timing. Consequently, the fuel and air were mixed more homogeneously and burnt more completely. At the engine speed of 2400 rpm, the total concentrations of PAHs increased because the higher speed may restrict the kinetics of the reaction in such a way that there is insufficient time for complete combustion, so that the pyrosynthetic reactions are more favoured.

At the engine speeds of 1600 and 2400 rpm, the amount of PAHs in the diesel exhaust is lower than 800 rpm because the combustion temperature is higher. These results indicate that at the lowest engine speed of 800 rpm, there is the highest emission of PAHs. Therefore, during traffic congestion, it is expected that the high emissions of PAHs would be obtained.

Classification of polycyclic aromatic hydrocarbons (PAHs) in diesel exhaust. PAHs found in diesel exhaust in this study may be divided into three classes. The first class [PAH(1)] is major PAHs such as naphthalene, acenaphthylene and acenapthene, which are found approximately 90 % of the total PAHs. Therefore, faulty measurements (sampling) of these three PAHs contribute most to errors in total PAHs. The second class [PAH(2)] is carcinogenic PAHs [4,27,30,31] such as phenanthrene, fluoranthene, pyrene, chrysene, benzo(k)fluoranthene and benz(a)anthracene, which are found approximately 3 %. The third class [PAH(3)] is minor non-carcinogenic PAHs such as fluorene, anthracene and benzo(ghi)perylene.

Figures 4.3-4.5 show the amount ratio of classes of PAHs emissions measured at various speeds and blended fuels. In previous work [27] found the low level of higher molecular weight PAHs than pyrene. As well as, in 1998, Buravannint [29] found that naphthalene, acenaphthylene and acenaphthene are the main components of total PAHs in diesel exhaust.

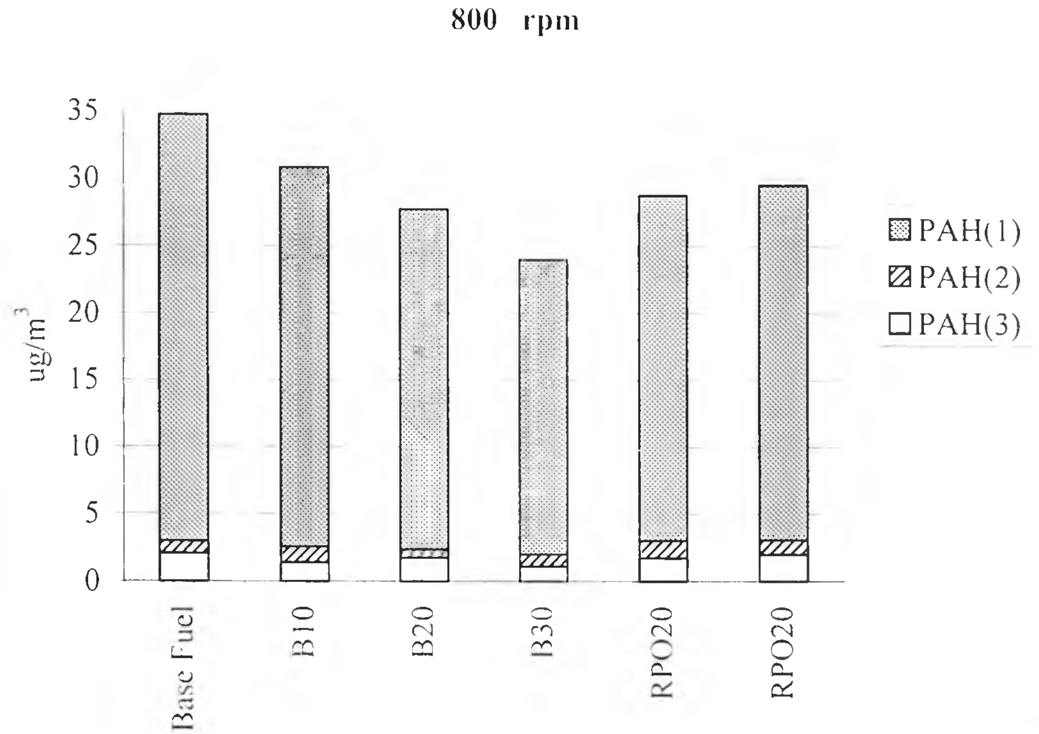

Figure 4.3 Polycyclic aromatic hydrocarbons emissions at engine run 800 rpm.

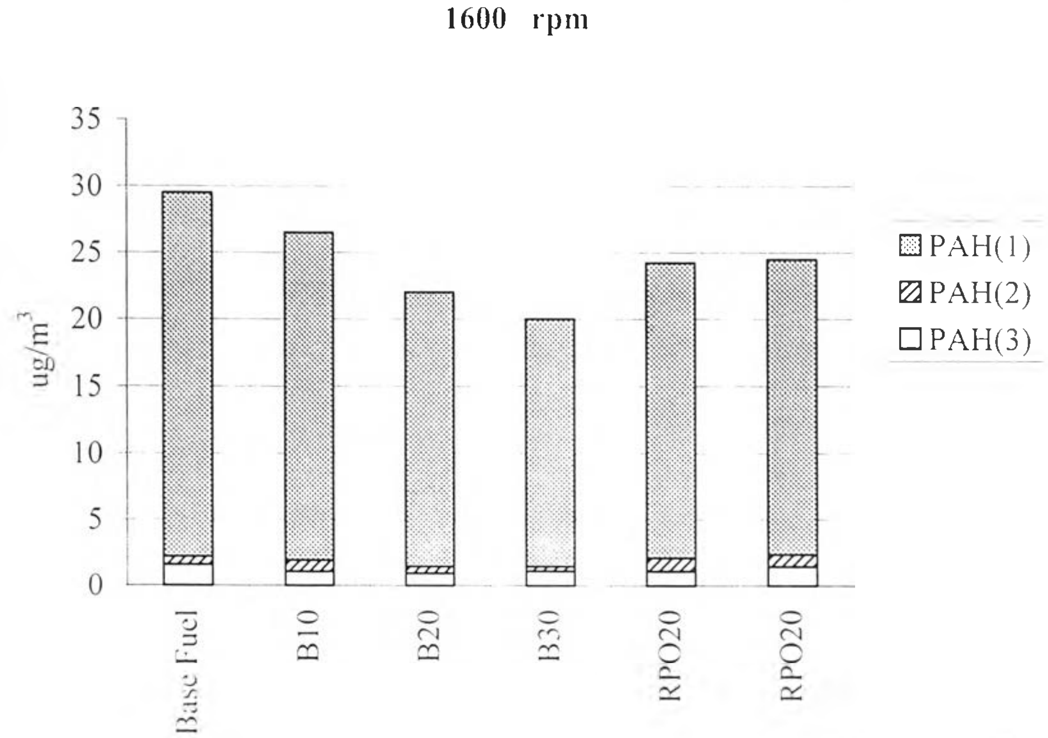

Figure 4.4 Polycyclic aromatic hydrocarbons emissions at engine run 1600 rpm.

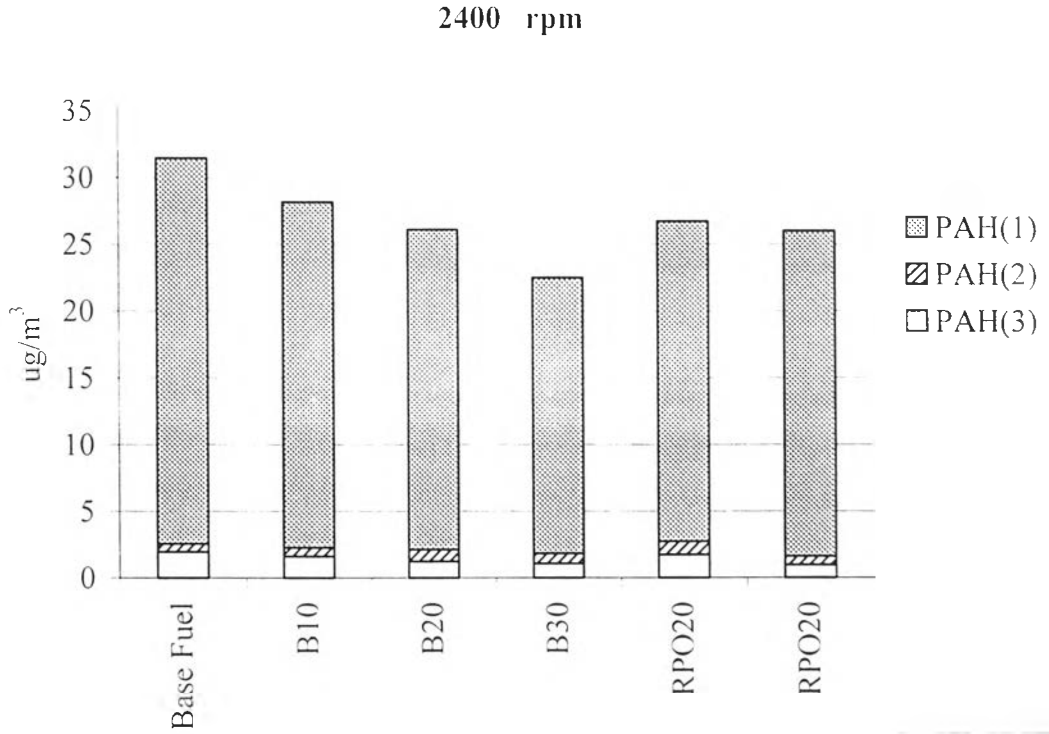

Figure 4.5 Polycyclic aromatic hydrocarbons emissions at engine run 2400 rpm.

4.5 Effect of Concentration of Palm Oil Methyl Ester on PAHs in Diesel Exhaust

In this research, the effect of the amount of palm oil methyl ester in blended diesel fuel on PAHs in diesel exhaust was investigated. Throughout this experiment, only one diesel fuel was used to blend with the ester fuel varying at 10, 20 and 30 % by volume (referred to B10, B20 and B30, respectively). The amount of PAHs in the exhaust gas was analyzed by GC-FID. The concentration of total PAHs in the diesel exhaust is shown in Figure 4.6. Figure 4.7 shows a percentage decrease of the total PAHs concentration as a function of the amount of palm oil methyl ester in blended fuel.

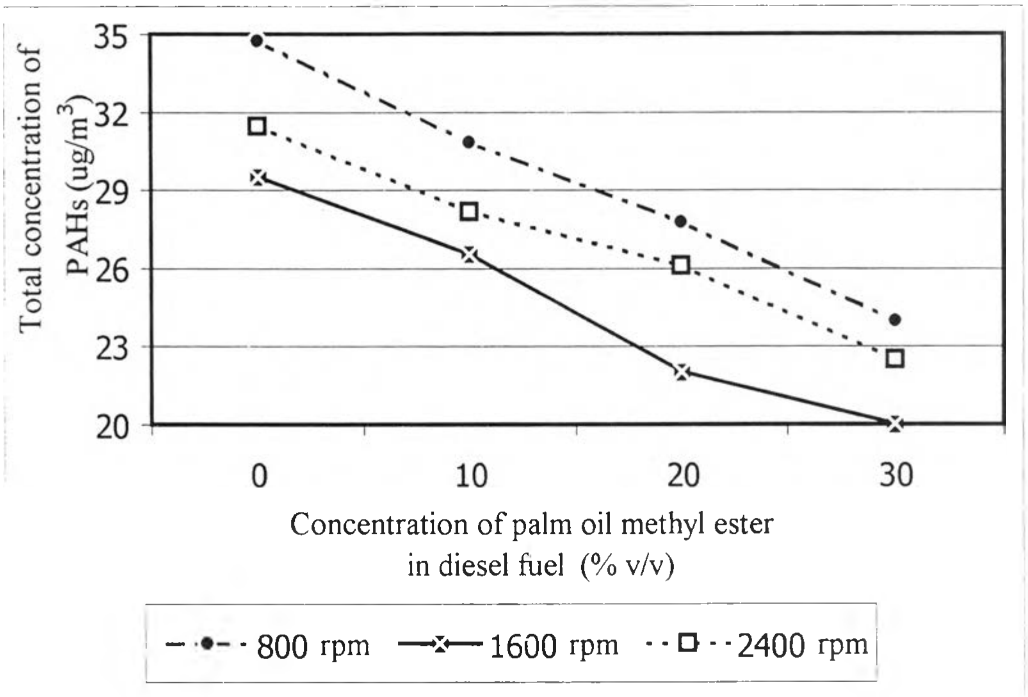

Figure 4.6 Effect of concentration of palm oil methyl ester on total PAHs in diesel exhaust at different engine speeds.

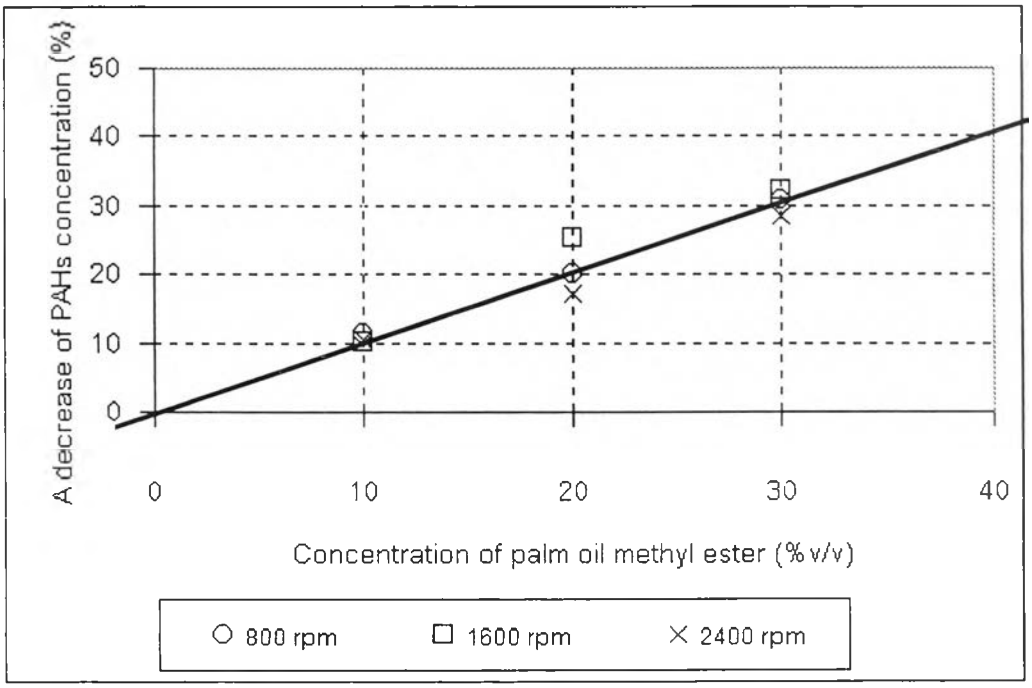

Figure 4.7 Relationship between concentration of palm oil methyl ester and the percentage decrease of total PAHs concentration. A solid line indicates the expected values of the percentage decrease of PAHs.

From Figure 4.6, the amount of PAHs in diesel exhaust was found to decrease with increasing the amount of palm oil methyl ester. The amount of total PAHs emission is highest with base diesel fuel, and lowest with 30 % of palm oil methyl ester blended. Figure 4.7 shows that the percentage decrease of total PAHs concentration is approximately equal to the percentage increase of palm oil methyl ester or the percentage decrease of PAHs in blended diesel fuel. This indicates that palm oil methyl ester should not generate PAHs.

Consideration is now focused on a comparison of the amount of total PAHs in diesel exhaust obtained from use of B20, RPO20 and CPO20, which are blended diesel fuel with palm oil methyl ester, refined palm oil and crude palm oil at 20 % v/v, respectively.

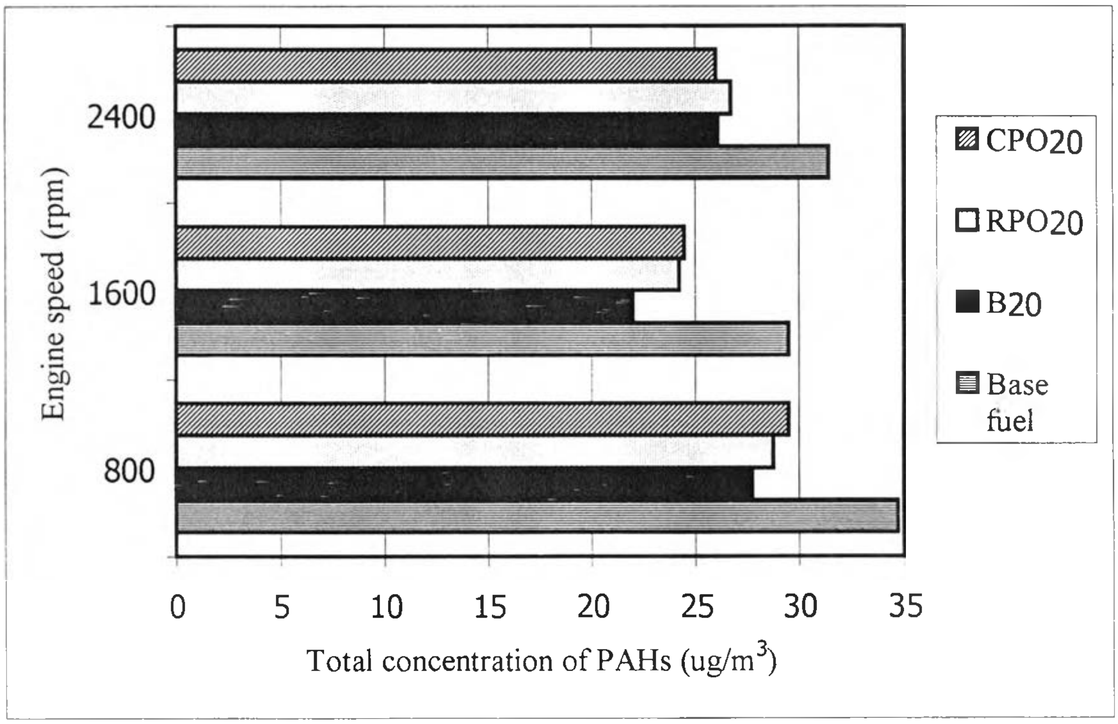

Figure 4.8 Comparison of Total PAHs emissions among three blends, B20, RPO20 and CPO20, at various speeds.

Figure 4.8 shows total PAHs emission from use of blended diesel B20, RPO20 and CPO20. It can be seen that at engine speeds of 800 and 1600 rpm, B20 gives less amount of PAHs in diesel exhaust than do RPO20 and CPO20. At engine speed of 2400 rpm, insignificant difference of PAHs was obtained for all three types of blended diesel fuel.

The RPO20 and CPO20 blended fuel gave a decrease of total PAHs concentration less than do B20 because the viscosities of RPO20 and CPO20 of 6.068 and 5.979 cSt, respectively, are higher than the value of specified limit for using in diesel engine. Previous work [32,33] reported that the high viscosity causes excessive carbon deposits, ring sticking and plugging of injector orifices, in particularly, combustion efficiencies. The lower combustion efficiency may be caused by improper injection and atomization characteristics, due to the difficulty of spraying the viscous fuel.

Moreover, the CPO20 blended fuel were obviously not compatible with diesel fuel. It has many saturated deposits colloided in the blend of them, therefore it may affect on long-term use of diesel engine. Currently, non-transesterified palm oil blended with kerosene is practically used for the agricultural diesel engine, such as water pump.