CHAPTER IV

RESULT AND DISCUSSION

Diesel engine emission contains thousands of chemical substances. These are ejected partly in the gas phase, and partly in the particulate phase of the exhaust. Due to different vapor pressures, temperatures, and concentrations of the individual species, these substances form particles or contribute to the gas phase of emission. PAH emission contributes to the particulate phase at low temperature but low molecular weight PAHs contribute to semivolatile phase. For that reason, PUF and GF were used as filter for collecting particulate and semivolatile phase from diesel exhaust.

Properties of Diesel Fuel

Diesel fuel properties are important for diesel engine such as driving performance, starting, and emission. The results were shown in Table 4.1-4.2. Table 4.2 shows cetane number, cetane index and T90 and new code for the further discussion. These results are different cetane number, cetane index and T90 that were expected in the experiment.

Table 4.1 Properties of Base Diesel Fuel

TEST ITEM	METHOD ASTM D	LIMITS	DTH52X	DTH53X	DTH55X	DTH57X	DTH58X	DTL52X
API Gravity @ 60°F	1298	report	38.0	37.9	37.0	38.2	38.7	37.6
Specific Gravity @60/60°F	1298	0.81-0.87	0.8348	0.8353	0.8398	0.8338	0.8314	0.8368
Calculated Cetane Index	976	47 min	52	52	54	56	56	53
Viscosity Kinetic @ 40°C cSt	445	1.8-4.1	2.8	2.8	3.4	3.4	3.3	3.0
Pour Point °C	97	10 max	-9	3	-6	3	3	-3
Sulphur Content, %wt	4294	0.25 max	0.15	0.10	0.21	0.19	0.19	0.08
Copper Corrosion (3 hr. @ 50°C)	130	No.1 max	No 1	No 1	No 1	No 1	No 1	No 1
Carbon Residue, %wt	4530	0.05 max	0.01	0.01	0.01	0.01	0.01	0.01
Water & Sediment, %wt	2709	0.05 max	Traces	Traces	Traces	Traces	Traces	Traces
Ash, %wt	482	0.01 max	0.004	0.005	0.006	0.005	0.005	0.005
Flash Point, (P.M.), °C	93	52 min	72	72	69	72	66	83
Distillation :	86							
Initial Boiling Point, °C		report	170	182	170	177	176	197
10% vol recovered °C		report	199	207	211	219	214	224
50% vol recovered °C		report	267	267	284	282	280	271
90% vol recovered °C		357 max	345	349	350	349	348	332
Colour ASTM	1500	4.0 max	L 0.5	1.0	L 1.0	L 1.5	L 1.5	2.0
Aromatic Content,%wt			25.9	25.1	21.8	15.8	14.0	16.3

Table 4.2 Comparing Cetane index, Cetane Number and T90

DIESEL FUEL (new code)	Cetane Index (CI)	Cetane Number(CN)	T90 °C
DTH52X	52	51.8	345
DTH53X	52	52.6	350
DTH55X	54	54.6	350
DTH57X	56	57.4	349
DTH58X	56	57.7	348
DTL52X	53	52.2	332
DTH59N	54	58.9	350
DTH61N	54	61.4	350
DTH62N	54	62.1	350
DTH56P	54	56.2	350
DTH58P	54	58.8	350
DTH60P	54	61.8	350
DTL56N	53	55.8	332
DTL58N	53	58.0	332
DTL60N	53	59.8	332

PAHs in Diesel Exhaust

In this study, for all of the diesel fuels and for all of the engine conditions, it was found that PAHs in diesel exhaust consisted of the different levels of Naphthalene, Methylnaphthalene, Dimethylnaphthalene, Acenaphthene, Phenanthrene, Methylphenanthrene, Fluoranthene, and Pyrene. In this experiment, there were no reference standards for all of the alkyl PAHs, such as Methylnaphthalene, Dimethylnaphthalene, and Methylphenanthrene. Therefore, alkyl PAHs were identified by comparing their mass spectra with the standard mass spectra in NIST library or with other research. For example, the isomers of Methylphenanthrene are 2-methylphenanthrene, 3-methylphenanthrene, 9+4-methylphenanthrene, and 1-methylphenanthrene, as shown in Figure B7.

The chemical and biological reactions of alkyl PAHs may be substantially different from those of the parent PAHs. For example, it has been

suggested that a greater tendency for aromatic molecules with alkyl side chains to form larger condensed aromatic structures during pyrolysis[9].

The carcinogenicities of alkyl PAHs may also differ from those of their parent PAHs. Some workers have proposed that certain alkylated PAHs may be as potent as, or even more mutagenic and carcinogenic than the corresponding parent molecules.

Many workers found low level of the higher molecular weight PAHs than pyrene. In this study, they could not be detected because their concentration was lower than detection limit as shown in Table 4.4. However, PAHs in the further discussion are Phenanthrene, Fluoranthene, and Pyrene because they are PAHs regulated by several states in USA as shown in Table 4.8.

The two-ringed PAHs were emitted into the semivolatile phase rather than into the particulate phase because over 90 percent of PAHs in semivolatile phase were trapped in PUF. Mainly higher molecular weight PAHs were trapped in GF as shown in Table 4.3. Some of the low molecular weight PAHs contaminated the blank of the PUF.

Table 4.3 PAHs in glass fiber filter, polyurethane foam and blank

PAHs	GF (%)	PUF (%)	Blank,GF (ppm)	Blank,PUF (ppm)
Naphthalene	4.3	95.7	0.00	1.16
Methylnaphthalene	3.7	96.3	0.00	1.18
Dimethylnaphthalene	1.1	92.3	0.00	1.50
Acenaphthene	8.8	91.2	0.00	1.07
Phenanthrene	38.7	61.3	0.00	0.00
Methylphenanthrene	50.8	49.2	0.00	0.00
Fluoranthene	63.3	36.7	0.00	0.00
Pyrene	60.3	39.7	0.00	0.00

Detection Limits

From the results in Table 4.4 it was concluded that the detection limit of the low molecular weight PAHs was lower than that of the high molecular weight PAHs.

Table 4.4 MolecularWeight, Retention Time and Detection Limits of Standard PAHs

PAHs	MW.	Retention time (min)	Detection limits (ppm)
Naphthalene	128	4.611	0.25
Acenaphthylene	152	6.689	0.25
Acenaphthene	154	7.026	0.25
Fluorene	166	8.158	0.25
Phenanthrene	178	10.994	0.25
Anthracene	178	11.155	0.25
Fluoranthene	202	14.898	0.25
Pyrene	202	15.546	0.25
Benz[a]anthracene	228	21.117	0.50
Chrysene	228	21.210	1.00
Benzo[b]fluoranthene	252	25.063	nd
Benzo[k]fluoranthene	252	25.143	nd
Benzo[a]pyrene	252	26.091	1.00
Indeno[1,2,3-cd]pyrene	276	29.189	2.00
Dibenzo[a,h]antracene	278	29.309	2.00
Benzo[ghi]perylene	276	29.569	1.00

nd = not determined

Recovery and Repeatability

Repeatability of the analytical method indicates a good precision. It was found that high molecular weight PAHs had better precision than low molecular weight PAHs because the low molecular weight PAHs could easily be lose during sampling, extracting and sample storage.

Table 4.5 Repeatability of Analytical Method

PAHs	Repeatability (ppm)			SD
	1	2	3	
Naphthalene	15.47	14.44	15.63	0.645
Methylnaphthalene	19.30	14.67	19.17	2.636
Dimethylnaphthalene	14.86	12.89	14.31	1.016
Acenaphthene	11.08	11.25	10.35	0.478
Phenanthrene	1.06	1.06	1.07	0.005
Methylphenanthrene	3.08	3.17	2.97	0.100
Fluoranthene	0.35	0.37	0.33	0.175
Pyrene	1.66	1.63	1.65	0.015

Table 4.6 Recovery of Extraction Method

PAHs	First Extraction (ppm)	Second extraction (ppm)	Recovery %
Naphthalene	15.47	2.88	81.38
Methylnaphthalene	19.30	0.57	97.04
Dimethylnaphthalene	14.86	1.34	90.98
Acenaphthene	11.08	0.00	100
Phenanthrene	1.06	0.00	100
Methylphenanthrene	3.08	0.00	100
Fluoranthene	0.35	0.00	100
Pyrene	1.66	0.00	100

Table 4.7 Recovery of Sampling Method

PAHs	GF+PUF[1] (ppm)	PUF[2] (ppm)	Recovery %
Naphthalene	9.96	1.4	85.94
Methylnaphthalene	14.45	0.38	97.28
Dimethylnaphthalene	14.80	0.00	100
Acenaphthene	10.20	0.00	100
Phenanthrene	1.13	0.00	100
Methylphenanthrene	1.84	0.00	100
Fluoranthene	0.32	0.00	100
Pyrene	0.66	0.00	100

[1] first PUF in filter holder, [2] second PUF in filter holder

By considering the recovery of extraction method and sampling method shown in Tables 4.6-4.7 were concluded that only naphthalene and naphthalene derivatives was poorly recovery because most of them had a high concentration in the PUF and there were difficulties in extraction. Therefore, the amount of phenanthrene, fluoranthene and pyrene were used to the following discussion and also they were harmful than the other PAH.

In the combustion process, more than 99% of fuel-related PAHs are decomposed. In the diesel exhaust, the ratio of uncombusted fuel related to the sum of PAHs varies from about 1% to 80% depending on the fuel and engine conditions.[12,13,16]. Therefore in this research, the amount of PAHs in diesel exhaust was sum of PAHs from some of the original diesel fuel without combustion, called uncombusted PAHs, and from combustion process called synthetic PAHs. However, the amount of PAHs in diesel exhaust also depended on the temperature in the combustion chamber, air to fuel ratio and other diesel fuel properties.

Filter Characteristics

The results in Figures 4.1-4.2 show that the characteristics of GF and PUF containing particulate and semivolatile phase of diesel exhaust differ with of engine load. At 80% of engine load, the color of GF was strongly black and the color of PUF was slightly yellow. It can be indicated that a lot of PAHs in the particulate phase may be PAHs from combustion process. In contrast, at no load, the color of GF was slightly gray and the color of PUF was strongly yellow. It can be indicated that a lot of PAHs in semivolatile phase may be PAHs from uncombustible PAHs.

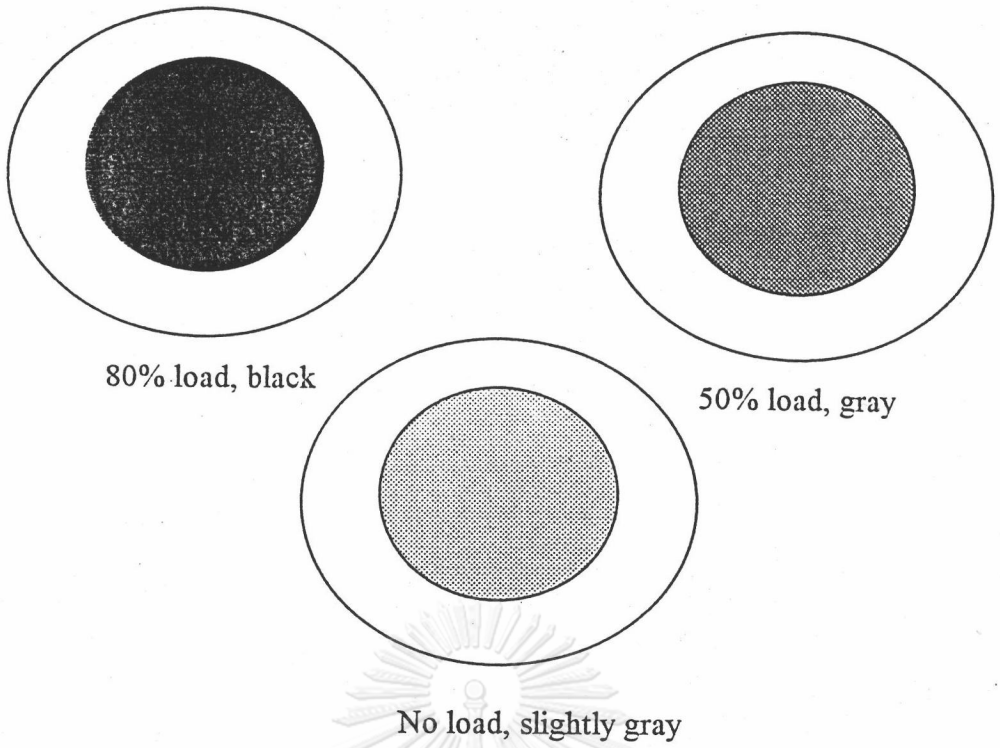

Figure 4.1 Particulate Phase were trapped with Glass Fiber Filter in Exhaust Emission, at 2500 rpm

Figure 4.2 Semivolatile Phase were trapped with Polyurethane Foam in Diesel Exhaust, at 2500 rpm

Effect of Engine Load

Engine load is strongly correlated with combustion chamber temperature. At low combustion chamber temperatures, fuel impinges on the piston bowl walls and, contained within the residual sac volume of the injector, tends to survive combustion. Low engine load also gives rise to hydrocarbon emissions by 'quenching' of the flame front in the clearance between the piston top and the cylinder head near top dead center[12].

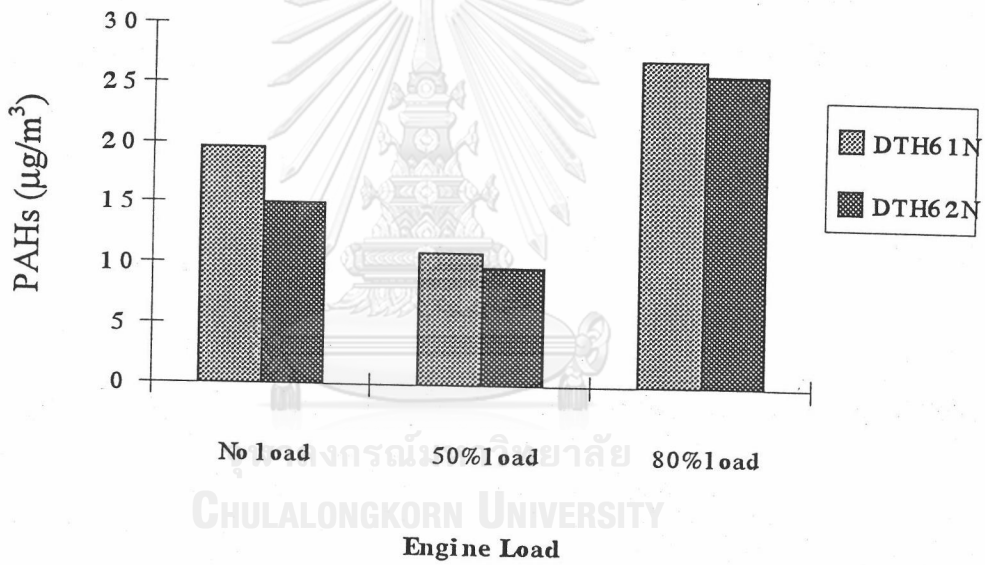

Figure 4.3 The Effect of Engine Load on PAHs in Diesel Exhaust.

Figure 4.3 shows the amount of PAHs at different engine load when two types of diesel fuel-DTH61N and DTH62N, were used. It was noticed that when the engine load was changed from no load to 50% load, the amount of PAHs decreased. However, the amount of PAHs at 80% load was more than the amount of PAHs at both 50% load and no load. This can be explained by

considering that when the engine is operated at no load, the temperature of combustion would be low. This results in a low efficiency of combustion, and the uncombusted PAHs are released in diesel exhaust. When the engine was operated at 50% load, the temperature of combustion would increase. This resulted in the increase of combustion efficiency and low level of uncombusted PAHs. Therefore the amount of PAHs at 50% load was less than the amount of PAHs at no load. However, when the engine was operated at 80% load, the efficiency of combustion was high, but the higher temperature of the combustion chamber leads to an increase in synthetic PAHs.

However, Air to Fuel ratio may be an important factor that affects the amount of PAHs in diesel exhaust. The variation of air to fuel ratio is shown in Table D3. It indicated that fuel consumption was increased when load increased.

Effect of Engine Speed

Engine speed affects the swirl characteristics, injection timing and combustion temperature of the engine. At low speed, there is less swirling and lower combustion chamber temperature. At mid-speed, the optimum swirl dynamics and optimum combustion timing develop the maximum power band for the engine. High engine speed generates over-swirl and shortens the period over which combustion proceeds[12].

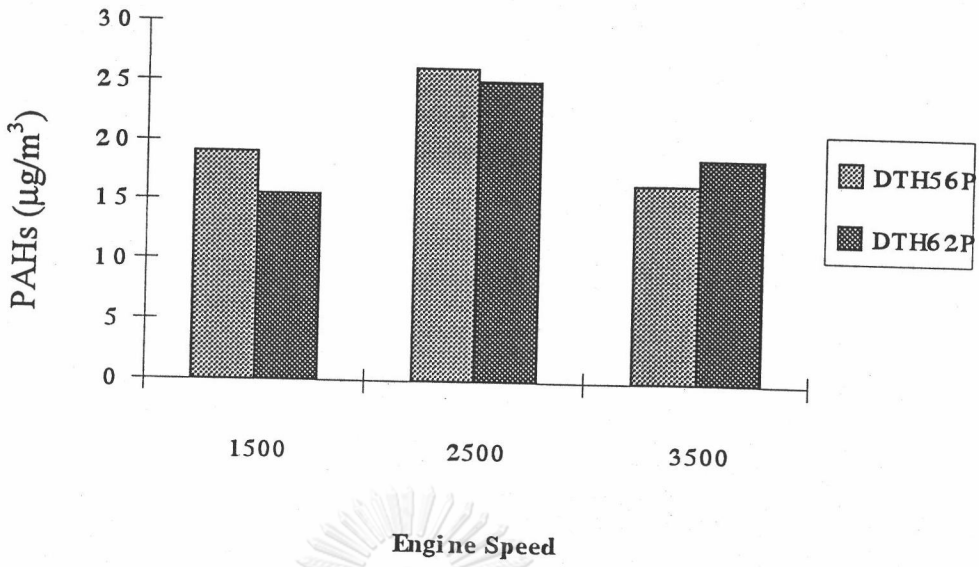

Figure 4.4 The Effect of Engine Speed on PAHs in Diesel Exhaust.

The increase of engine speed may be explained in term of different rates of combustion of PAHs. The higher speed will limit the time of combustion reactions, allowing sufficient combustion time for some PAHs, but not for others[12]. The results show that PAHs increased when engine speed was changed from 1500 rpm to 2500 rpm and decreased at 3500 rpm (Figure 4.4.). The engine speed of 1500 rpm, the low combustion chamber temperature leads to a smaller amount of uncombusted PAHs in diesel exhaust. At the engine speed 2500 rpm, the amount of PAHs was higher because of the high temperature in the combustion chamber. On the other hand, at the engine speed of 3500 rpm., the temperature in the combustion chamber was higher but the amount of PAHs was lower. Limitation of reaction time for synthetic PAHs may be a reasonable explaination.

Effect of Cetane Number

A different distillation process for diesel fuel affects physical and chemical properties, especially a change in the aromatic content that can affect the cetane number and exhaust emission. Aromatic compounds in diesel fuel, especially benzene derivatives such as ethylbenzene and xylene are an important precursor for synthetic PAHs in combustion process[3]. In this experimental section, the cetane improvers were not added to diesel fuel. However, the other fuel properties that may effect the amount of PAHs in diesel exhaust such as aromatic content and sulfur content are considered.

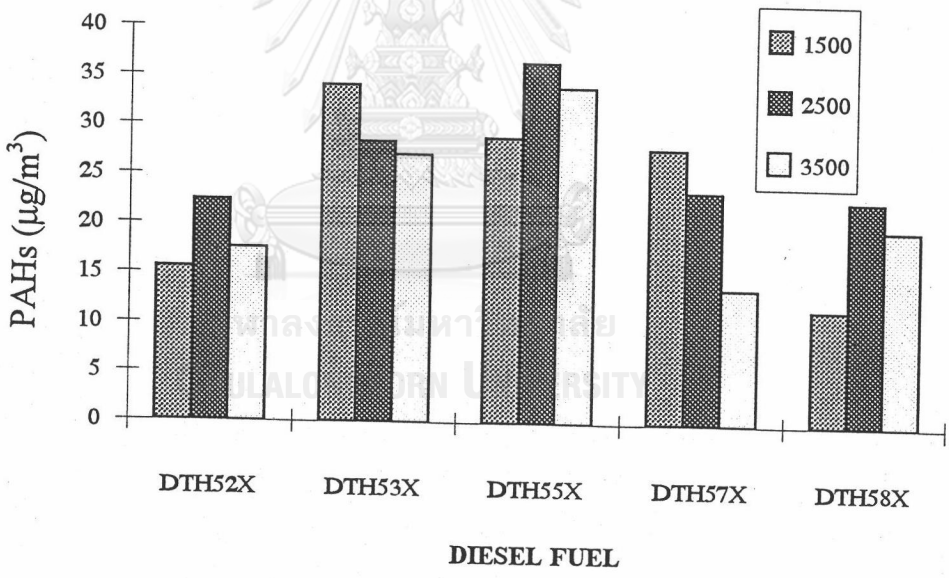

Figure 4.5 The Effect of Cetane Number on PAHs in Diesel Exhaust at 80% load and Different Engine Speeds.

In this experiment, when the cetane number increased from 52 to 55, the amount of PAHs in diesel exhaust increased, and when cetane number

increased from 55 to 58 the amount of PAHs in diesel exhaust decreased. This result indicated that the aromatic content may affect PAHs in diesel exhaust, but only diesel fuel with cetane number 55 to 58.

Effect of Cetane Improver

The important chemistry contributed to the spontaneous ignition process by the cetane improver additives takes place exclusively in the gas phase. There is no single generic mechanism by which these additives reduce the ignition delay : both iso-octyl nitrate and di-t-butyl peroxide may accelerate the ignition of ordinary diesel fuel about equally[18].

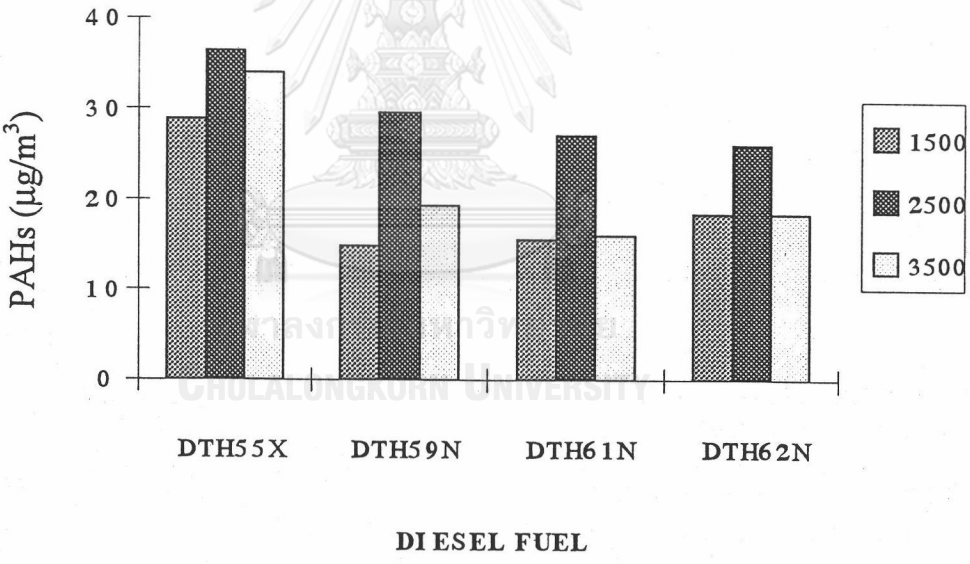

Figure 4.6 The Effect of Adding 2-Ethylhexyl Nitrate to DTH55X on PAHs in Diesel Exhaust at 80% load and Different Engine Speeds.

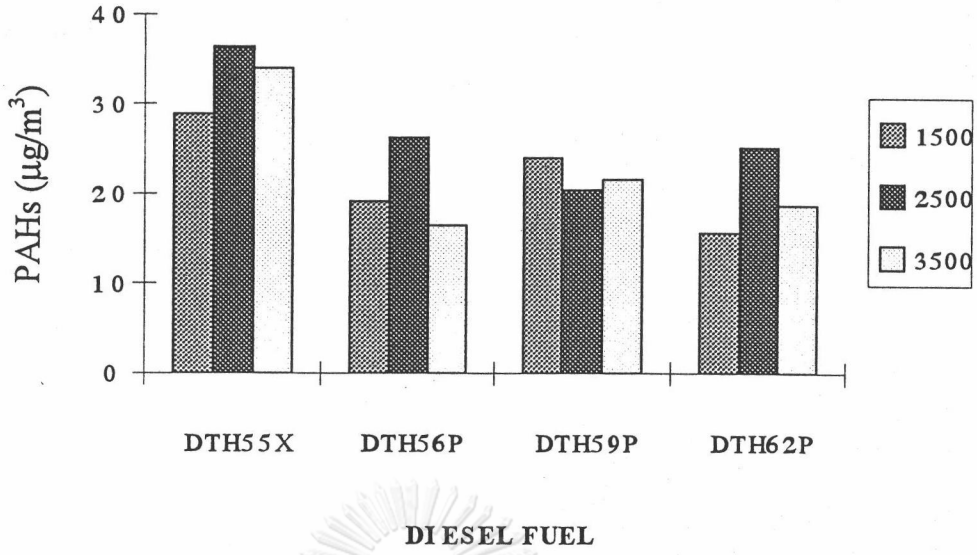

Figure 4.7 The Effect of Adding Di-t-butyl Peroxide to DTH55X on PAHs in Diesel Exhaust at 80% load and Different Engine Speeds.

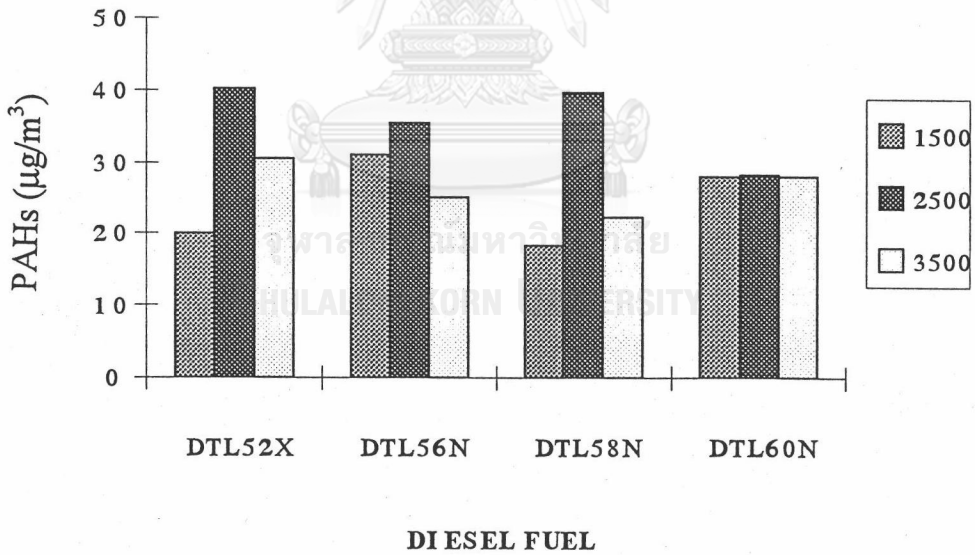

Figure 4.8 The Effect of Adding 2-Ethylhexyl Nitrate to DTL52X on PAHs in Diesel Exhaust at 80% load and Different Engine Speeds.

The cetane improver, 2-ethyl hexyl nitrate, was added to diesel fuel of cetane number 55. The cetane number of this diesel fuel increased from 55 to 59, 61 and 62 respectively. The results are shown in Figure 4.6. It was found that when the cetane number increased from 55 to 59, the amount of PAHs in the diesel exhaust decreased and when the cetane number increased to 61 and 62, the amount of PAHs in diesel exhaust only slightly changed.

Addition of di-t-butyl peroxide into the same base diesel fuel led to the cetane number increasing from 55 to 56, 59 and 62 respectively. The results are shown in Figure 4.7.They indicate that addition of di-t-butyl peroxide has the same trend as addition of 2-ethyl hexyl nitrate.

The result in Figure 4.8 shows that when 2-ethyl hexyl nitrate was added into DTL52X, it led to the cetane number increasing from 52 to 56, 58,and 60 but it could not reduce PAHs in diesel exhaust.

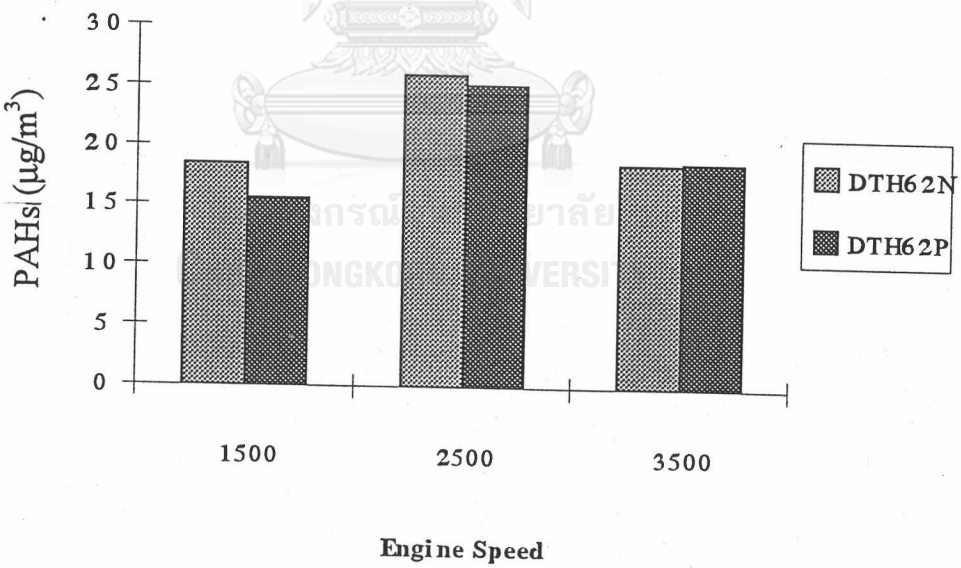

Figure 4.9 Comparison of 2-Ethylhexyl Nitrate and Di-t-butyl Peroxide with the amount of PAHs in Diesel Exhaust

Comparison of the two types of cetane improver with decreasing PAHs in diesel exhaust showed that the amount of PAHs in diesel exhaust decreased equally. The results are shown in Figure 4.9.

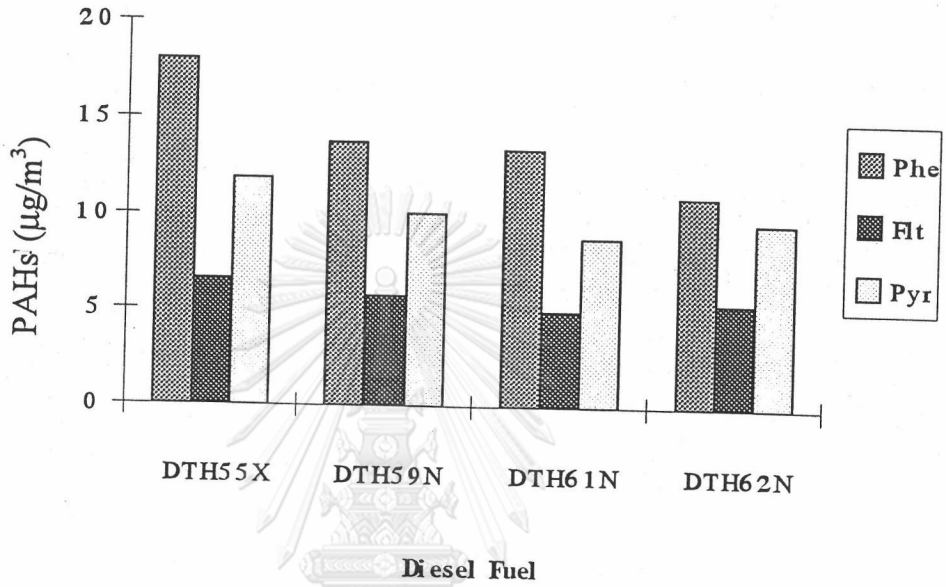

Figure 4.10 Effect of 2-Ethylhexyl Nitrate on Each PAH in DieselExhaust at 80% load 2500 rpm.

The results in Figure 4.10 show that the ratio of the amount of individual PAHs was slightly different in each diesel fuel. Therefore, the total amount of PAHs was used in the discussion above.

Toxicity of Individual PAHs

There are many species of PAHs reported, but in this work, it was found that five species of PAH were important, Naphthalene, Acenaphthene, Phenanthrene, Fluoranthene, and Pyrene. These are important carcinogenic and mutagenic PAHs. In the regulation of many states of USA., these are limited in air and water pollution.

Table 4.8 Regulation and Guideline to PAHs in Air Pollution

State	Description	Information	References
Connecticut			NATICH 1992
(Fluorene)	8-hour average	50.000μg/m^3	
(Naphthalene)	8-hour average	1000.00 μg/m^3	
Louisiana			
(Fluorantene)	Annual	0.060μg/m^3	
Vermont			
(B[a]P)	Annual	3.0x10^{-4}μg/m^3	
(Phenanthrene)	Annual	1.30μg/m^3	
(Pyrene)	Annual	3.40μg/m^3	