CHAPTER IV

RESULTS AND DISCUSSION

Identification of Hydrocarbons Exhaust Emission

As mentioned in chapter III, the CBP-1 capillary column with an average liquid film thickness of 0.25 μm. was used for analysis of diesel exhaust emissions. The compositions were identified by comparing with the chromatogram of a typical gasoline obtained by the same condition of GC analysis. The example of chromatograms of hydrocarbon exhaust emissions is presented in Figure 4.1. In the chromatogram, many types of hydrocarbons were indicated and from these the total of 62 peaks were identified, shown in Table 4.1. Their compositions can be classified into 4 groups, paraffins, olefins, napthenes, and aromatics of all of these, the aromatics group is the dominant group. The concentrations of individual groups are about 15-25% for the paraffins, 1-5% for the olefins and napthenes, and 65-85% for the aromatics. The number of carbon atoms in these molecules ranges from C_4-C_{11}, with C_9 and C_{11} being the major compositions.

The hydrocarbon portion of diesel exhaust includes both original fuel components and products that result from thermal cracking during the combustion process. The exhaust contains molecules with higher molecular weight than the fuel, as well as lighter molecules and molecules with significantly different structures from the fuel molecules. In general, the hydrocarbons of diesel includes molecules with 1 to 24 carbon atoms(28).

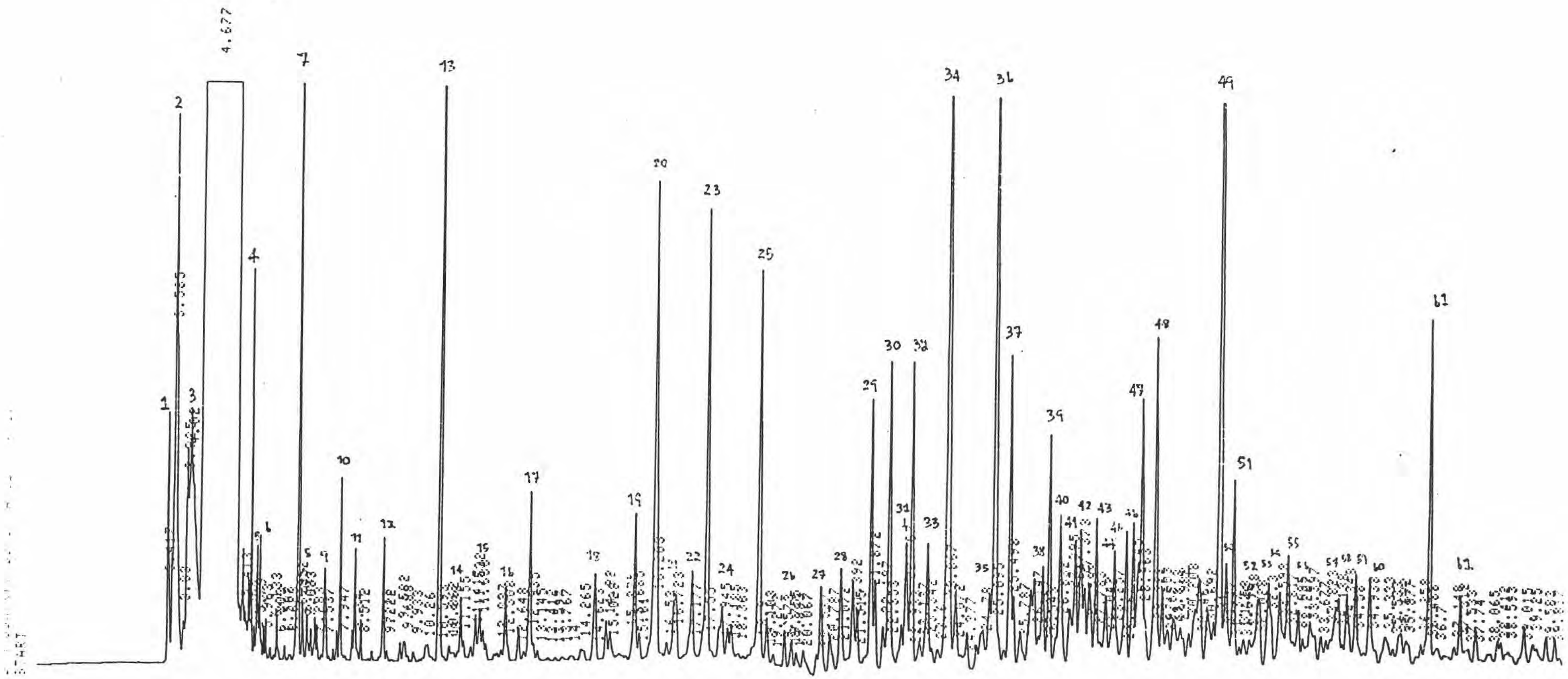

Figure 4.1 GC Chromatogram of hydrocarbons exhaust emission

Table 4.1 Identification of hydrocarbons exhaust emission

Peak No.	Rt. time (min)	Compound name	MW	Type and carbon number			
				P	O	N	A
1	3.4	i-Butane	58	4			
2	3.6	n-Butane	58	4			
3	4.0	cis-2-Butene	56		4		
4	5.9	n-Hexane	86	6			
5	6.1	cis-3-Hexene	84		6		
6	6.2	trans-3-Hexene	84		6		
7	7.1	Benzene	78				6
8	7.2	Cyclohexane	82			6	
9	7.7	3-Methylhexane	100	7			
10	8.1	3-Dimethylcyclopentane	98			7	
11	8.5	n-Heptane	100	7			
12	9.2	Methycyclohexane	98			7	
13	10.6	Toluene	92				7
14	10.9	2-Methyheptane	114	8			
15	11.5	3-Methylheptane	114	8			
16	12.3	1-methyl-3-ethylcyclopentane	112			8	
17	12.9	n-Octane	114	8			
18	14.6	Ethylcyclohexane	112			8	
19	15.6	Ethylbenzene	106				8
20	16.1	m,p-Xylene	106				8
21	16.6	4-Methyloctane	128	9			
22	17.2	3-Methyloctane	128	9			
23	17.4	o-Xylene	106				8
24	17.9	1-Ethyl-3-methylcyclohexane	126			9	
25	18.7	i-Propylbenzene	120				9

Table 4.1 (continued)

Peak No.	Rt. time	Compound name	MW	Type and carbon number			
	(min)			P	O	N	A
26	19.4	2,3,5-Trimethyheptane	142	10			
27	20.3	2,5-Dimethyloctane	142	10			
28	20.9	3,6-Dimethyloctane	142	10			
29	21.7	1-Methyl-3-ethylbenzene	120				9
30	22.2	1,3,5-trimethylbenzene	120				9
31	22.5	5-Methylnonane	142	10			
32	22.6	1-Methyl-2-ethylbenzene	120				9
33	23.2	2-Methylnonane	142	10			
34	23.7	1,2,4-Trimethylbenzene	120				9
35	24.6	n-Decane	142	10			
36	24.9	1,2,3-Trimethylbenzene	120				9
37	25.3	Indane	118				9
38	26.1	C_{11} paraffin	156	11			
39	26.4	1,3-Diethylbenzene	134				10
40	26.6	1-Methyl-3-n-propylbenzene	134				10
41	27.0	1,3-Dimethyl-5-ethylbenzene	134				10
42	27.1	n-Butylbenzene	134				10
43	27.2	1-Methyl-2-n-propylbenzene	134				10
44	28.1	C_{11} paraffin	156	11			
45	28.4	C_{11} paraffin	156	11			
46	28.6	1,4-Dimethyl-2-ethylbenzene	134				10
47	28.8	1,2-Dimethyl-4-ethylbenzene	134				10
48	29.1	1,2-Dimethyl-4-ethylbenzene	134				10
49	30.5	1,2,4,5-Tetramethylbenzene	134				10
50	31.1	1,2,3,5-Tetramethylbenzene	134				10

Table 4.1 (continued)

Peak No.	Rt. time (min)	Compound name	MW	Type and carbon number			
				P	O	N	A
51	31.4	4-Methylindane	132				10
52	31.8	1,1-Dimethyl-n-Propylbenzene	148				11
53	32.1	2-Methyl-butylbenzene	148				11
54	32.4	1-Methyl-butylbenzene	148				11
55	32.7	1,2,3,4-Tetramethylbenzene	134				11
56	33.6	C_{11} aromatic compound	148				10
57	33.8	C_{11} aromatic compound	148				11
58	34.3	C_{11} aromatic compound	148				11
59	34.5	C_{11} aromatic compound	148				11
60	34.9	C_{11} aromatic compound	148				11
61	36.2	Naphthalene	128				10
62	37.1	2-methylundecane	170	12			

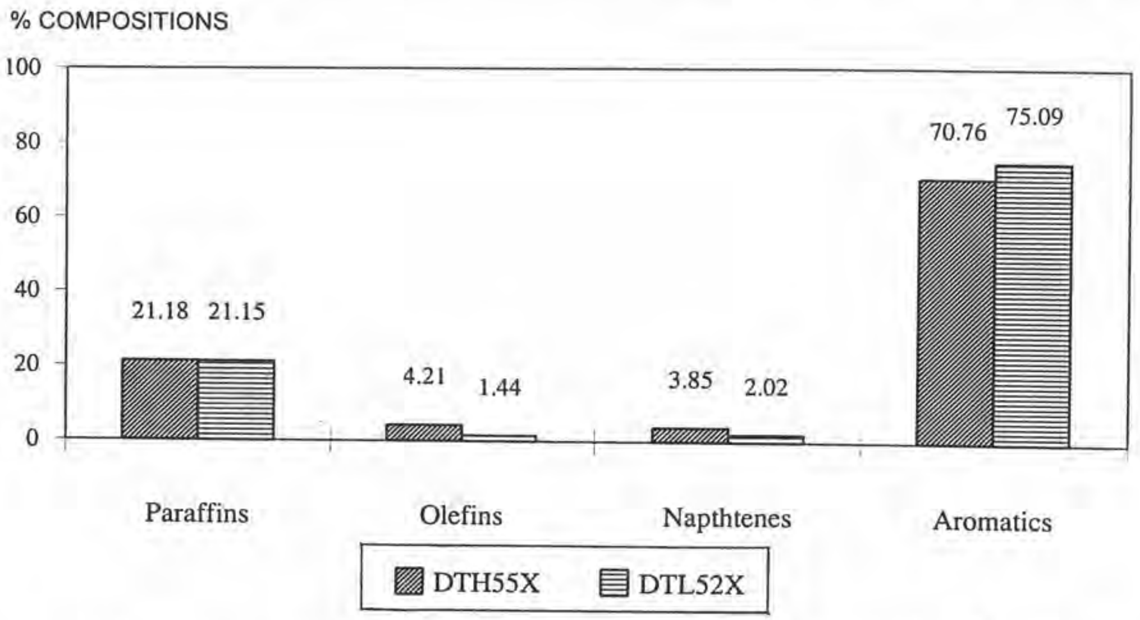

Figure 4.2 Percent compositions of 4 groups hydrocarbon in the exhaust emissions (2500 rpm, no load)

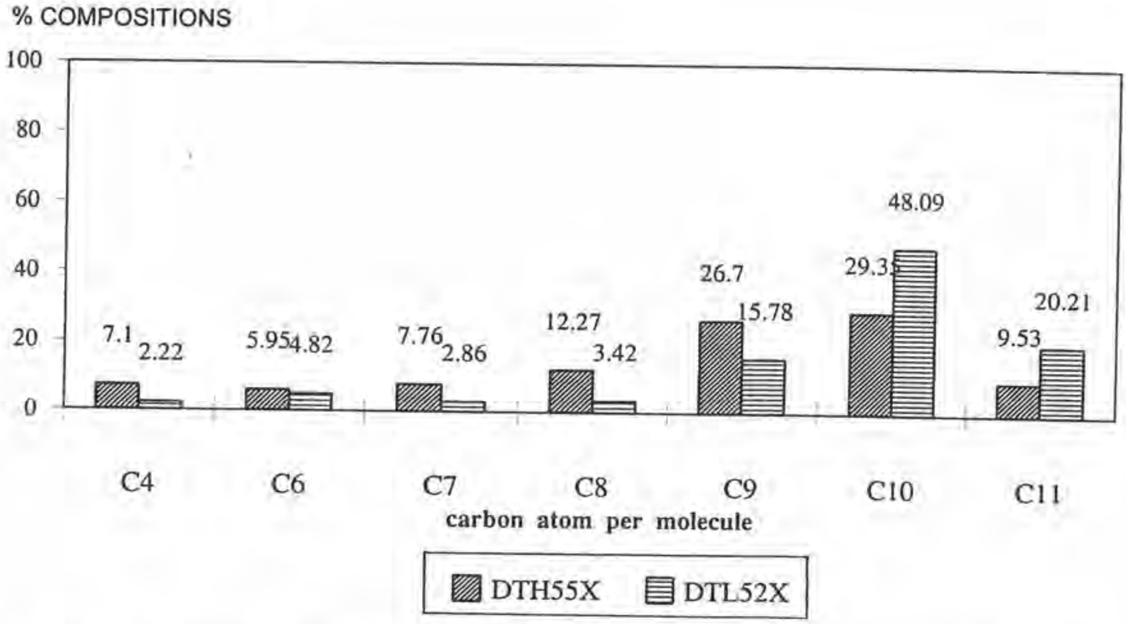

Figure 4.3 Distribution of exhaust hydrocarbons as a function of number of carbon atoms in the molecules (2500 rpm, no load)

The percent hydrocarbon compositions and the distribution of hydrocarbons which having the same number of carbon atom of exhaust emissions from base fuels were shown in Figures 4.2- 4.3, DTH55X having 90% distillation point of 350°C and 55 cetane number while DTL52X having 90% distillation point of 332°C and 52 cetane number. Raw data are presented in Table C1 and C2, in Appendix C.

Figure 4.2 shows that the percentage of Paraffins, Olefins, Napthenes, and Aromatics groups in the exhaust of both fuels are very similar. The aromatics are the major group. The percent hydrocarbon of individual carbon numbers are not different between DTH55X and DTL52X . The percentages of light molecules (C4-C8) are rather low while higher molecules (C9-C11) are higher.

Studies of Various Effect on Exhaust Emissions

1. Effect of Engine Parameters

The two engine parameters, speed and load, effecting the exhaust emissions were studied in this research. DTH55X, base fuel which high 90% distillation point and 55 cetane number, and DTH59N, DTH61N, DTH62N, additized fuels which treated with 0.05-0.30% of EHN, were chosen to investigate these two parameters.

1.1 Effect of Engine Load

In studying the effect of load on exhaust emissions, the engine speed was fixed at 2500 rpm. and load was varied to be 0%, 50%, and 80%. The amount of NO_X, HC, CO, and BTX in the exhaust gas were analyzed. The results from Tables D3, D10-D12 (Appendix D) were plotted to give the histograms in Figures 4.4-4.7.

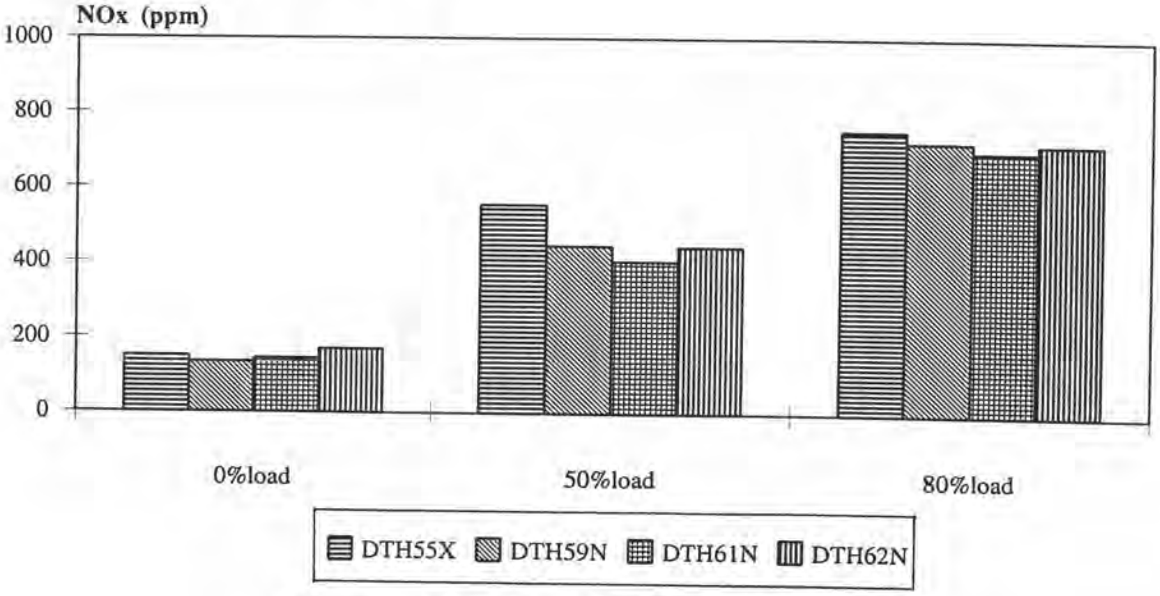

Figure 4.4 Effect of load on NO_X emission

It was found in Figure 4.4 that NO_X emissions of each fuel were significantly increased with increasing load. This can be explained. Increasing load results in a decreasing air-fuel ratio and increasing exhaust temperature, as shown in Table 4.2. Thus more fuel is injected prior to the start of combustion. The rates of pressure rise, cylinder pressures, and temperatures are higher. Locally high temperatures and locally high concentrations of oxygen are required for the production of NO_X(28). For this reason, increasing load can cause higher NO_X production rates.

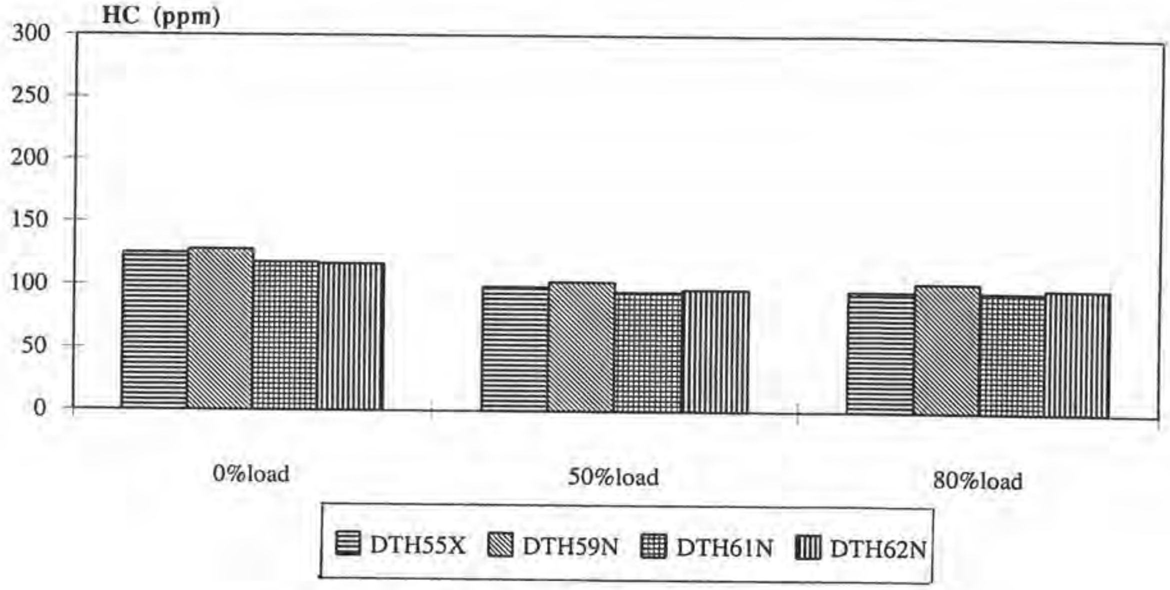

Figure 4.5 Effect of load on HC emissions

Figures 4.5 and 4.6 show the effect of load on HC and CO emissions, respectively. HC and CO emissions were slightly reduced with increasing load from 0% to 50%. As the load continued to increase to 80% the concentrations were rather constant, as the air-fuel ratio was little changed from 50% to 80% load. At light load, the emissions are high because the gas temperature is low and very little oxidation takes place. An increase in load, or rich mixtures, results in lower emissions because of the increased gas temperature and elimination reactions (28).

Table 4.2 The results of engine operating conditions on air-fuel ratio, equivalence ratio (∅) and exhaust temperature.

(∅ < 1 = lean mixture, ∅ > 1 = rich mixture)

Speed(rpm)	%load	A/F ratio	∅	$T_{exhaust}$(°C)
1500	0%	138.91	0.10	110
	50%	47.88	0.30	233
	80%	32.72	0.44	322
2500	0%	123.10	0.12	137
	50%	39.42	0.37	311
	80%	25.63	0.54	431
3500	0%	87.07	0.17	192
	50%	36.23	0.40	369
	80%	26.40	0.55	474

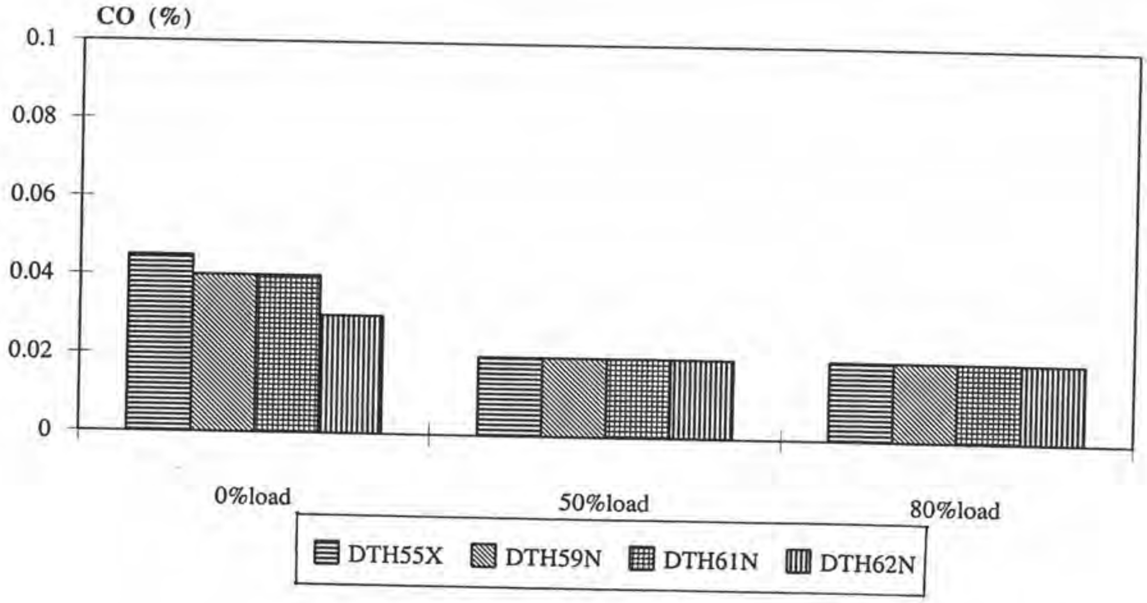

Figure 4.6 Effect of load on CO emissions

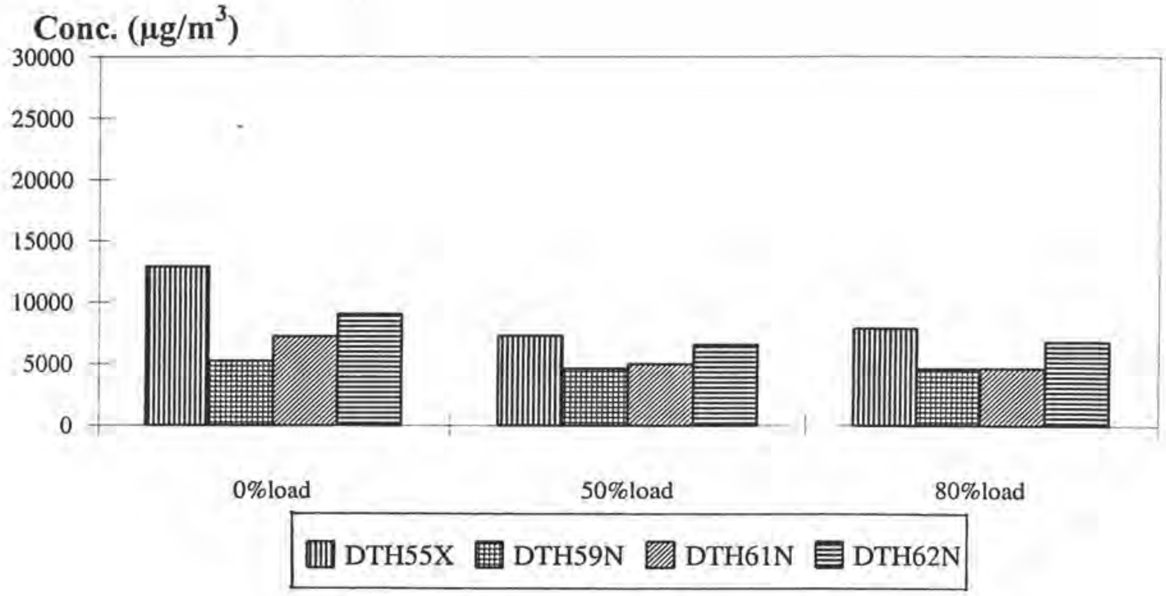

Figure 4.7 Effect of load on BTX emissions

Figure 4.7 presents the emissions of BTX (total benzene, toluene, *m,p*-xylene, and *o*-xylene) as a function of load. It appears to be slightly decreased as the load increased from 0% to 50%. At 80% load the emissions are rather constant. The emissions of benzene, toluene and xylene are shown in Figure B1-B3(Appendix B). The trends were similar with BTX.

The unburned hydrocarbons in the diesel exhaust consist of either original or decomposed fuel molecules, or recombined intermediate compounds. The relative contributions of the original fuel compounds and the products may vary significantly as a function of operating conditions.

At light load the hydrocarbon emissions are mainly composed of the original fuel molecules. This is because the molecules have little chance to decompose. At high loads the temperature is fairly high, so that the medium size molecules are decomposed to lighter molecules and the intermediate compounds recombine to form heavier molecules (28).

1.2 Effect of engine speed

The effect of engine speed on exhaust emission was studied with various engine speed ; 1500, 2500 and 3500 rpm. while the load was fixed at 80%. The amount of NO_X, HC, CO, and BTX in the exhaust gas was analyzed. The results obtained are shown in Tables D3, D10-D12 (Appendix D) and the data are plotted to show the relationship between engine speed and emissions in Figures 4.8-4.11.

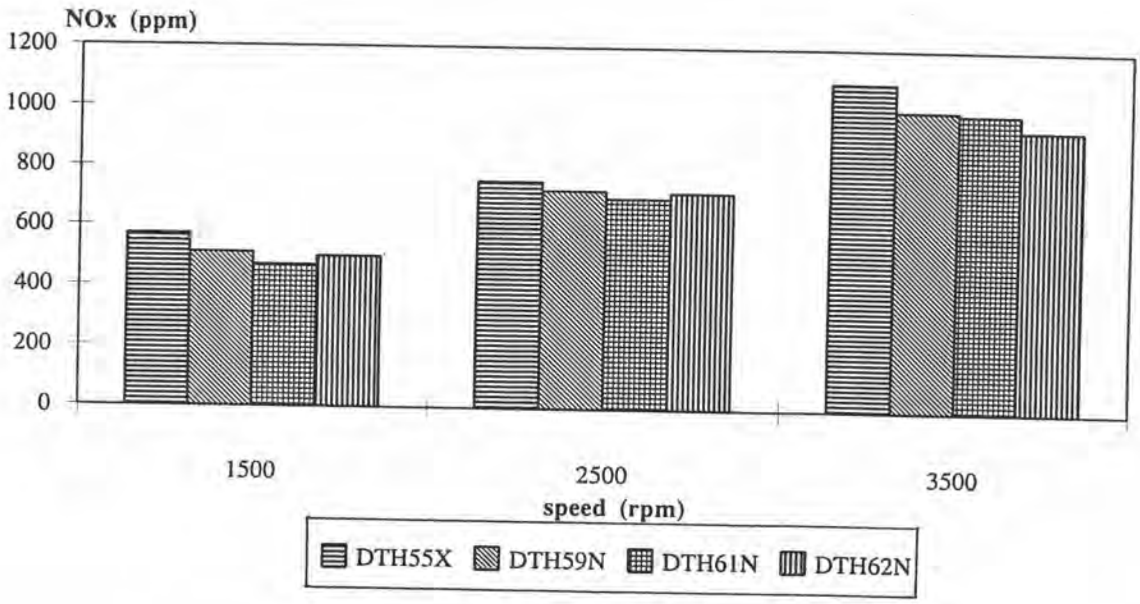

Figure 4.8 Effect of speed on NO_X emissions

Figures 4.8-4.11 show the variation in the NO_X, HC, CO, and BTX emission, at various speeds. The NO_X was significantly increased with increasing engine speed while HC, CO and BTX were rather constant. It is noticed that the %volume of CO emission is low and seems show no clear trend.

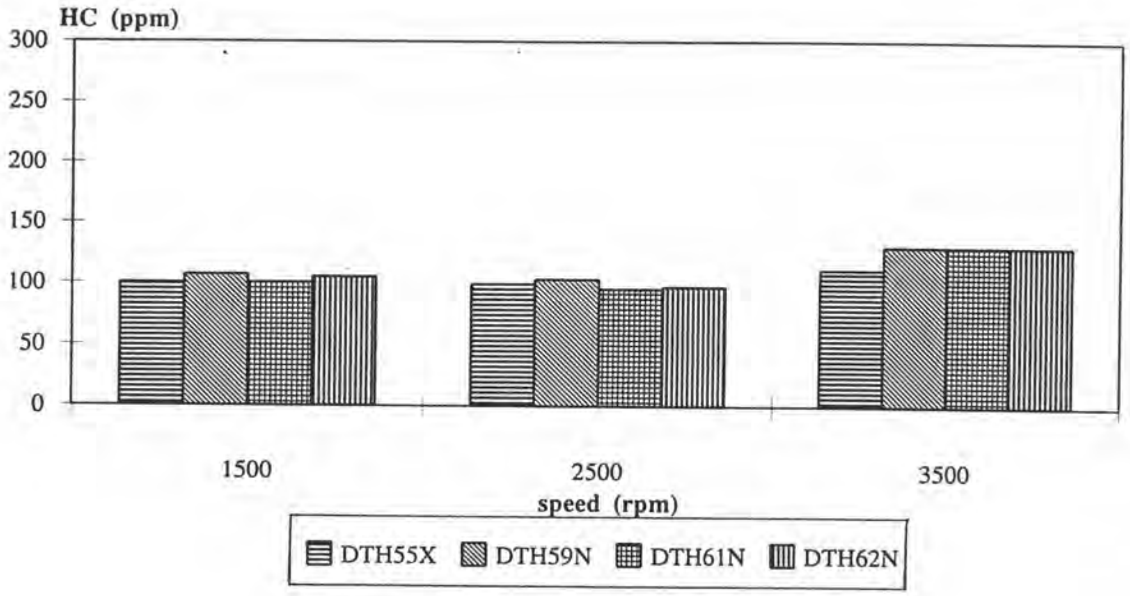

Figure 4.9 Effect of speed on HC emissions

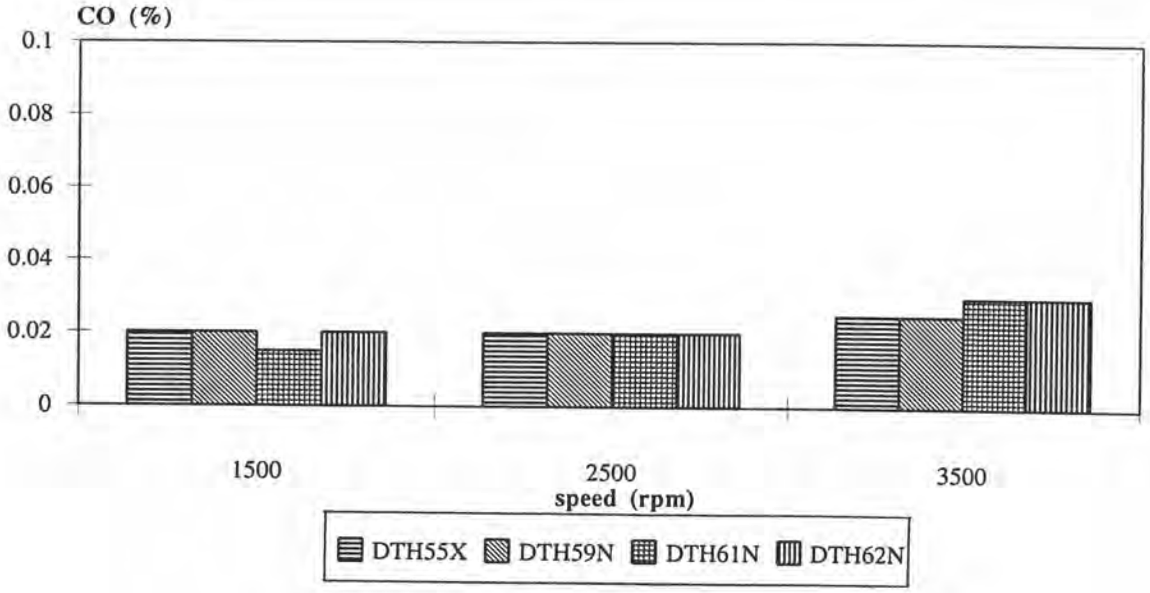

Figure 4.10 Effect of speed on CO emissions

At higher speed, more fuel is injected per cycle to account for the decrease in mechanical efficiency. At such speed the rate of injection are higher, and in spite of the shorter delay period, the amount of fuel injected before top dead center (TDC) is larger. All these factors result in higher temperatures in the chamber. Therefore, the increase in speed is expected to improve the elimination reactions to reduce the hydrocarbons and CO, and to increase the NO_X concentration (28). In this study, engine speed had little effect on emission, because the range of speed from 1500 to 3500 rpm. resulting in little change of the air-fuel ratio (32.72-25.63), as shown in Table 4.2.

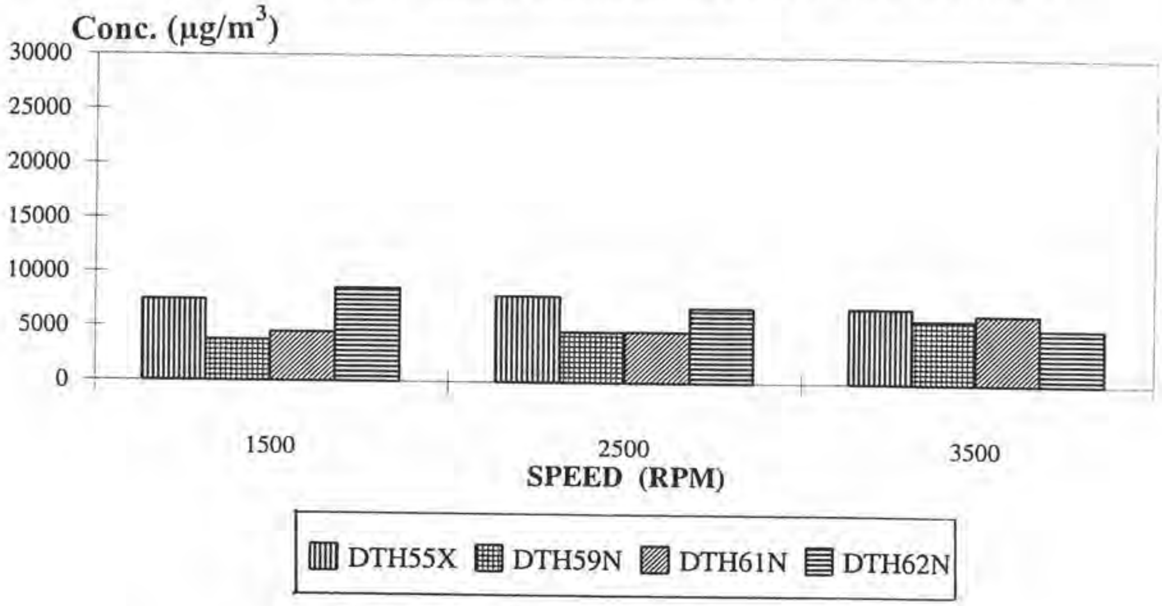

Figure 4.11 Effect of speed on BTX emissions

2. Effect of Fuel Properties

Several diesel fuel properties have been identified as having significant effects on diesel engine emissions. For this study, the fuel properties of 90% distillation point (T90), cetane number, and cetane improver were examined at an engine speed of 2500 rpm.

2.1 Effect of 90% distillation point(T90)

In order to investigate the effects of T90 on emissions, a comparison was made among the two base fuels with the same natural 52 cetane number and different T90 : DTL52X and DTH52X. The 90% distillation point is 332°C for the DTL52X and 345°C for the DTH52X fuel. It should be noted that even at constant cetane number, effects of T90 could not be completely isolated from the other properties. The results from D1 and D6 (Appendix D) were plotted to give the histograms, as shown in Figures 4.12-4.15.

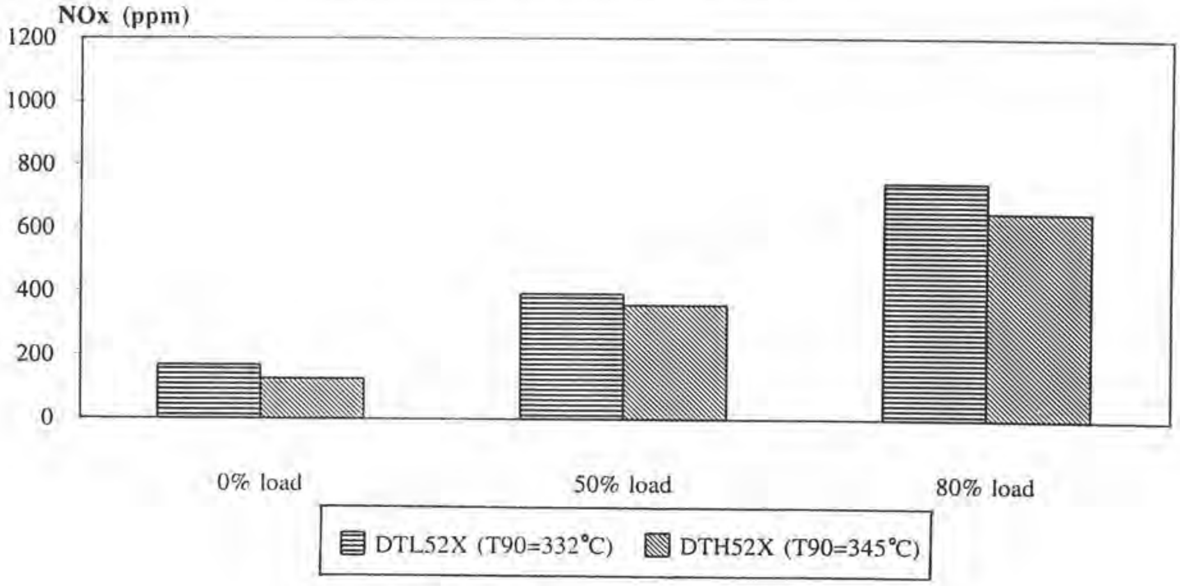

Figure 4.12 Effect of T90 on NO_X emissions

Figures 4.12-4.15 present measurements of NO_X, HC, CO, and BTX emitted using DTL52X and DTH52X fuels. Figure 4.12 shows that DTL52X produces NO_X rather more than DTH52X does. It can be explained in terms of increasing 10% boiling point. The 10% boiling point is 199°C for the DTH52X and 224°C for the DTL52X fuel, as shown in Table 3.2 (Chapter III).

An elevation of the 10% boiling point causes a delay in the progression of combustion, allowing more pressure rise near top dead center. This effect is believed to be similar to the ignition delay effect, in that it results in higher peak temperatures which increases the amount of NO_X formation(17).

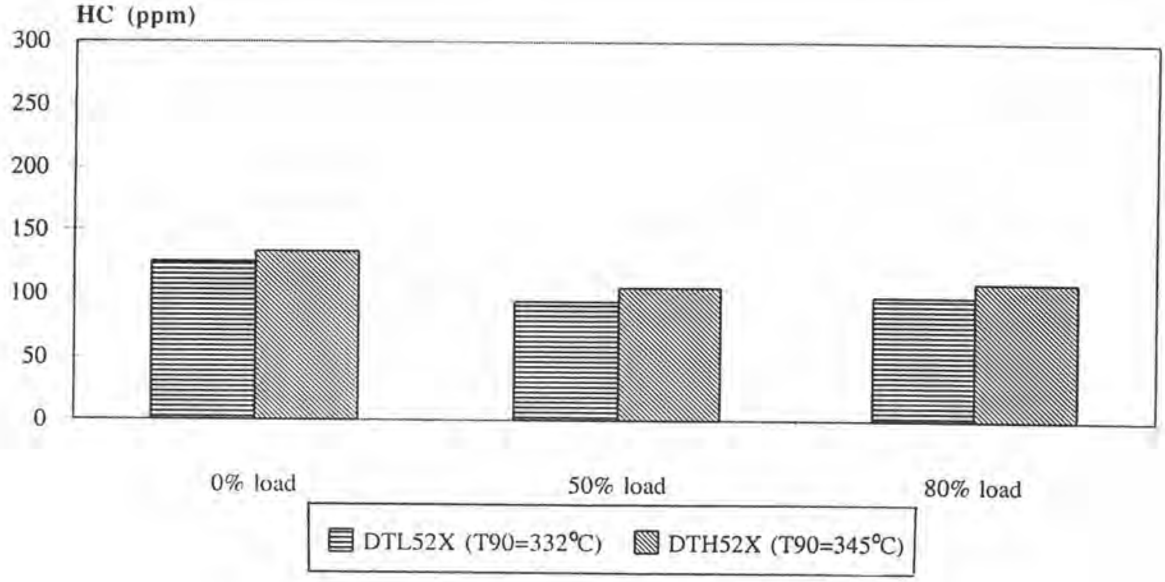

Figure 4.13 Effect of T90 on HC emissions

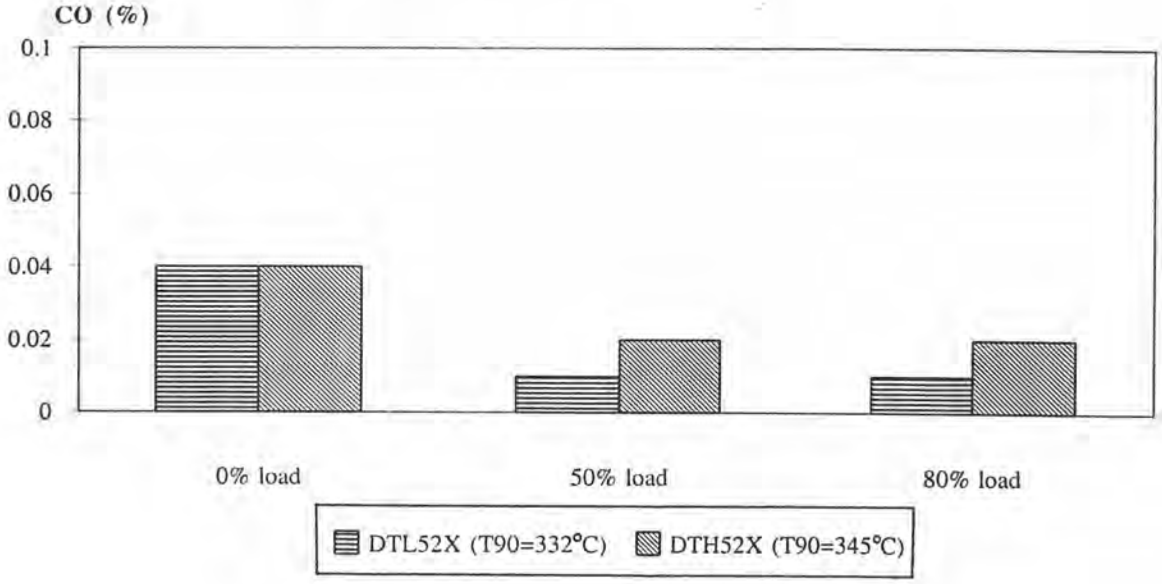

Figure 4.14 Effect of T90 on CO emissions

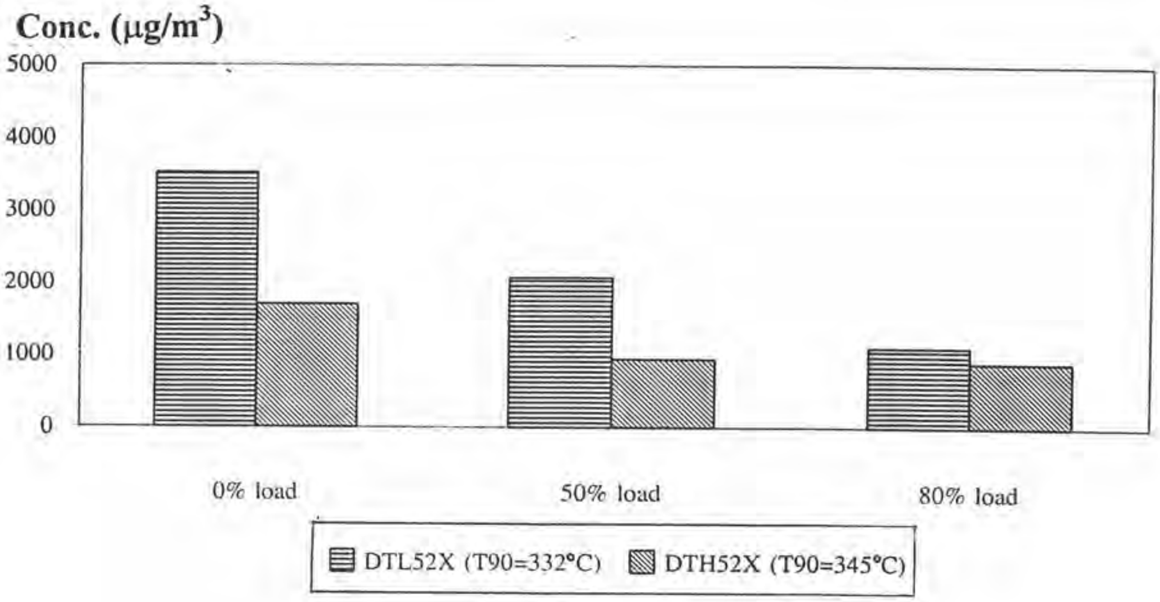

Figure 4.15 Effect of T90 on BTX emissions

The effect of T90 on CO and HC emissions is shown in Figures 4.13-4.14. HC and CO emissions are almost constant as T90 increased from 332 to 345 °C. BTX emissions slightly decreased with increasing T90, as shown in Figure 4.15. This may be related to composition of aromatics in the original fuel that differs in 10% and 90% distillation point.

Early emissions work led to the conclusion that reduction of T90 helps reduce particulates in the exhaust. The reason for this is believed to be that the highest molecular weight portion of the fuel, the fraction which is most difficult to ignite and burn, gives rise to particulates. Its effects on gaseous emissions were of secondary importance compared with the cetane number (19,29).

2.2 Effect of cetane number

Five base fuels with 90% distillation points of 350°C, varying in natural cetane number, were chosen to study the effect of cetane number on emissions. The natural cetane number of the fuel varied from 52 to 58. The specification of these diesel fuels are shown in Table 3.2 (Chapter III). The testes were performed at an engine speed of 2500 rpm. The results from Tables D1-D5 (Appendix D) were plotted to give the histograms as shown in Figures 4.16- 4.19.

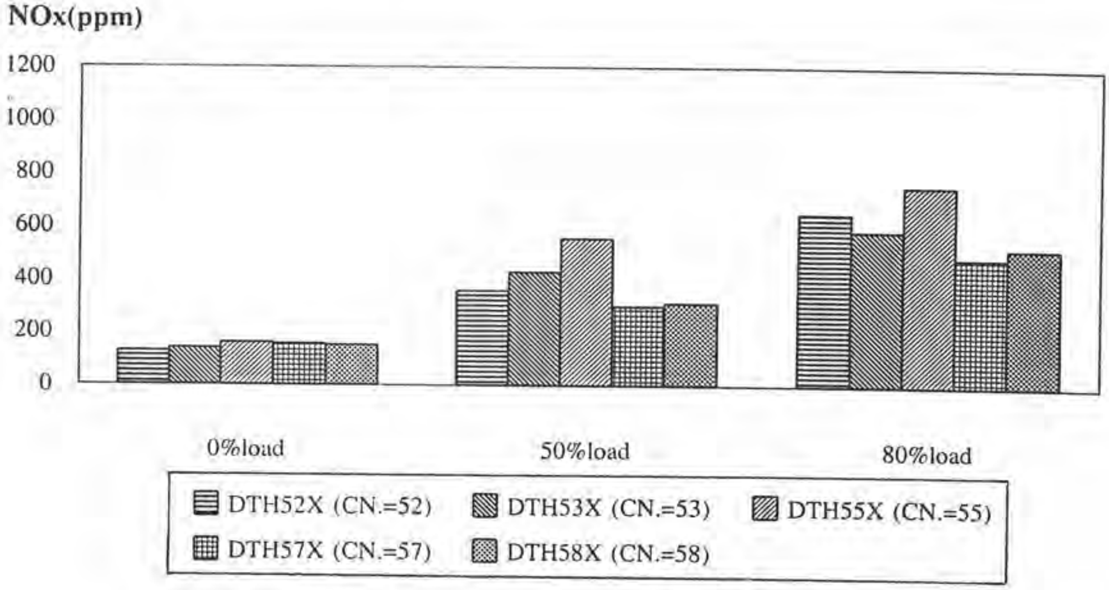

Figure 4.16 Effect of cetane number on NO_X emissions

Figure 4.16 shows the effect of cetane number on NO_X emissions. It can be seen that at 0% load, the NO_X levels were rather small and rather constant with increasing cetane number. While at heavy engine conditions, 50% and 80% load, three fuels with 52, 53, and 55 cetane number showed higher NO_X levels than fuels with 57 and 58 cetane number.

This can be explained in terms of aromatics content. From Table 4.3, fuels with 52-55 cetane number were composed of 22-26 % aromatics and fuels with 57-58 cetane number were composed of 14-16% aromatics. The lower aromatics content tended to reduce NO_X emission.

Table 4.3 % Aromatics of base fuels (T90 = 350 °C) at various cetane number

Cetane Number	% Aromatics
52	25.9
53	25.1
55	21.8
57	15.8
58	14.0

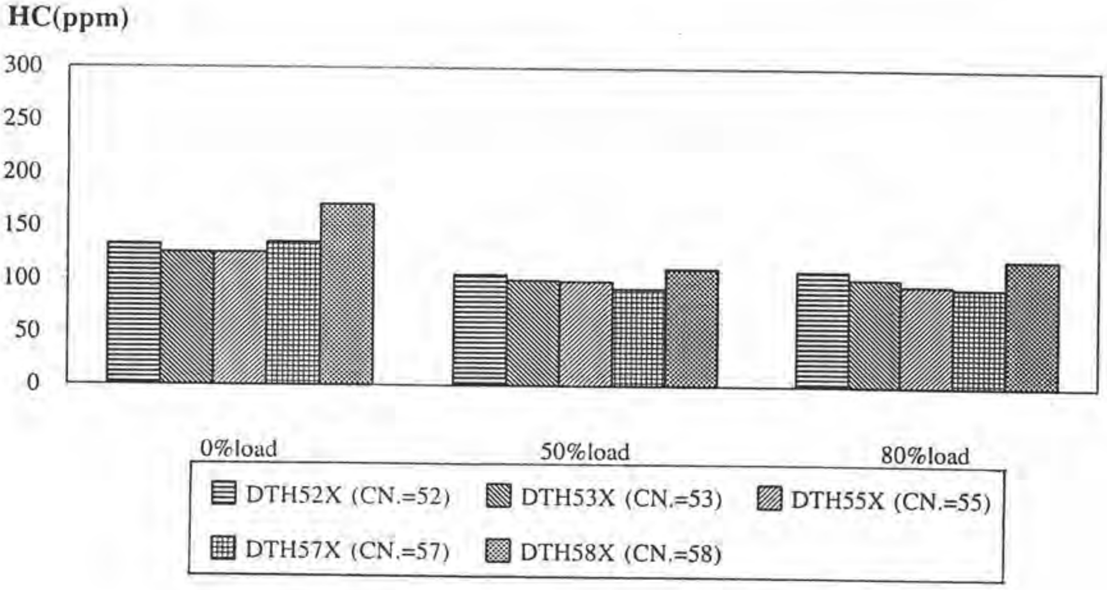

Figure 4.17 Effect of cetane number on HC emissions

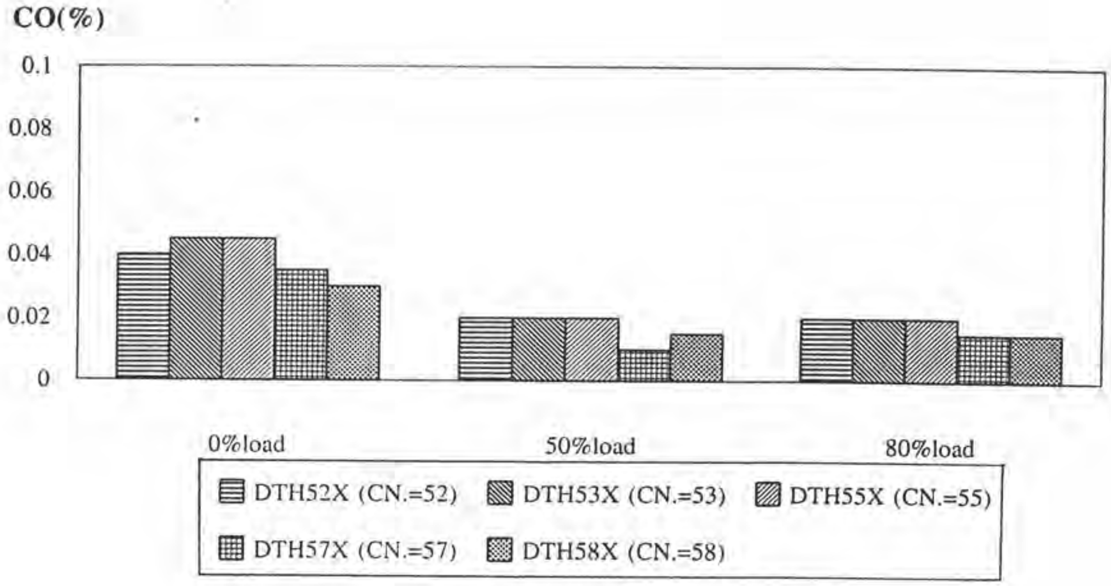

Figure 4.18 Effect of cetane number on CO emissions

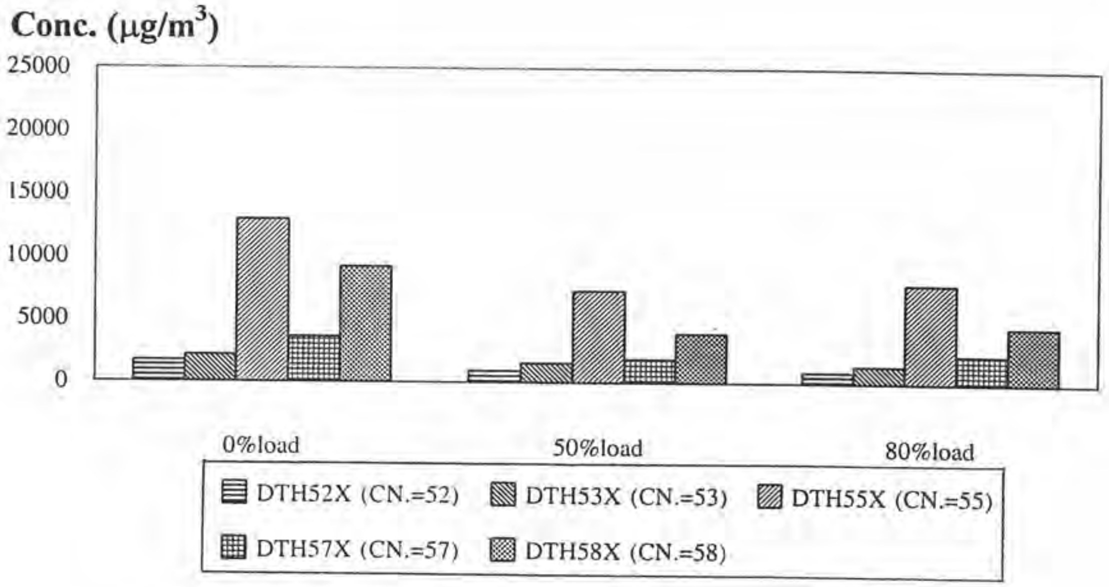

Figure 4.19 Effect of cetane number on BTX emissions

Figure 4.17 shows the relationship between HC emissions and cetane number. The concentration of HC slightly decreased with increasing cetane number from 52 to 57. At the 58 cetane number, HC emissions were increased. However raising, cetane number trended to reduce HC emissions. It was found in Figure 4.18 that CO emissions trended to decrease with increasing cetane number.

Figure 4.19 shows the effect of cetane number on BTX emissions. It can be seen that cetane number and BTX emissions are not correlated. Any analysis of these relationships is complicated on the basis of the data, fuel variables. No firm conclusions can be drawn regarding the dependence of BTX emissions on cetane number. Figure A7 (Appendix A) shows the chromatogram of diesel fuel. The portions of benzene, toluene and xylene are very little. Almost of the BTX emissions results from combustion process.

In the study effect of cetane number, it should be noted that the correlations between cetane number, density, and aromatics contents are difficult to break. There has been much debate over the influence of aromatics on diesel emissions. Previously, many researchers had concluded that a reduction in fuel aromatics led to a reduction in NO_X and PT emissions, but had no effect on HC or CO emissions (18).

However, aromatics content is a general term which refers to a wide range of chemical compounds. The recent Shell studies show that reductions in fuel total aromatics or mono-aromatics actually have no influence at all on particulate emissions, but any influence being very engine-dependent and, indeed, zero in some engines (30).

Further work is required to look at the influence of individual sub-classes of aromatics, such as polyaromatics, on both gaseous and particulate emissions before a definitive conclusion can be reached (2).

2.3 Effect of cetane improver

One base fuel of cetane number 55 and T90 350°C was used for this investigation, to which cetane improver was added progessively. The cetane improver, EHN or DTBP, was added to the base fuel so as to produce DTH-N and DTH-P groups of fuel blends, as shown in Table 4.4, with cetane numbers ranging from 55 to 62. It can be seen that EHN was rather more effective in increasing cetane number than the DTBP additive at the same total volume. The study was performed at an engine speed of 2500 rpm, no load. The results in Appendix D were plotted to show the relationship between cetane number and emissions in Figures 4.20-4.23.

Table 4.4 Increase in cetane number of additional fuel blends

Group	base fuel + %additive	Increase in CN.
DTH-N	DTH55X + 0.05%EHN	4.3
	DTH55X + 0.14%EHN	6.8
	DTH55X + 0.30%EHN	7.5
DTH-P	DTH55X + 0.05%DTBP	1.6
	DTH55X + 0.14%DTBP	4.7
	DTH55X + 0.30%DTBP	7.2

Figures 4.20-4.23 show the effect of addition of cetane improver on NO_X, HC, CO and BTX emissions, respectively. Results show that NO_X, HC, CO and BTX emissions decreased little or remained fairly flat as cetane number increased. There was no different between EHN and DTBP cetane improver. It should be noted that, additive treat rates of 0.05-0.30% and base fuel cetane number 55, EHN and DTBP were similarly effective in reducing the emissions.

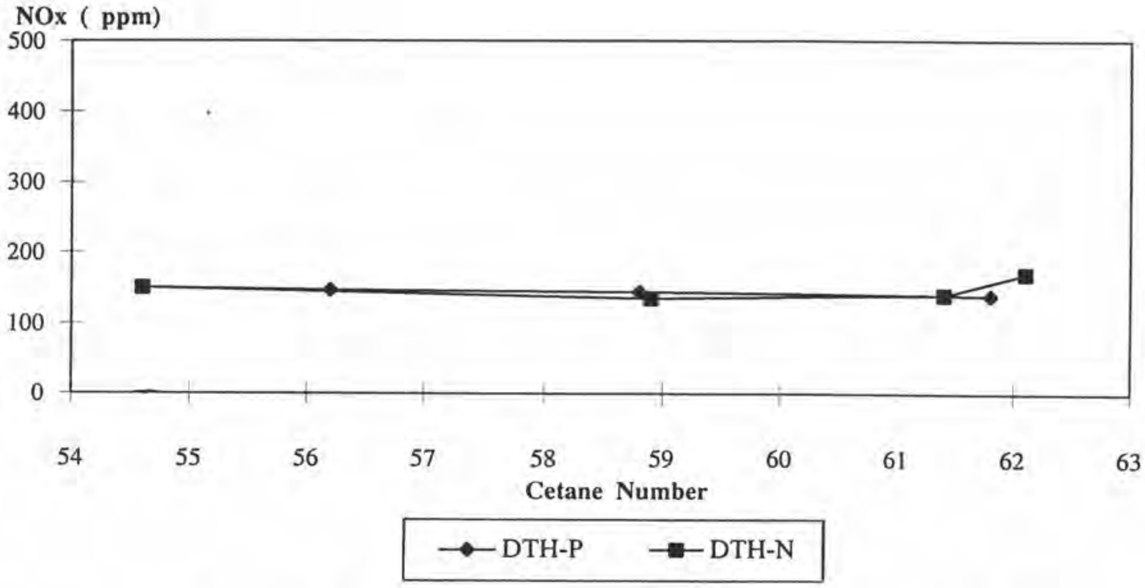

Figure 4.20 Effect of cetane improver on NO_X emissions

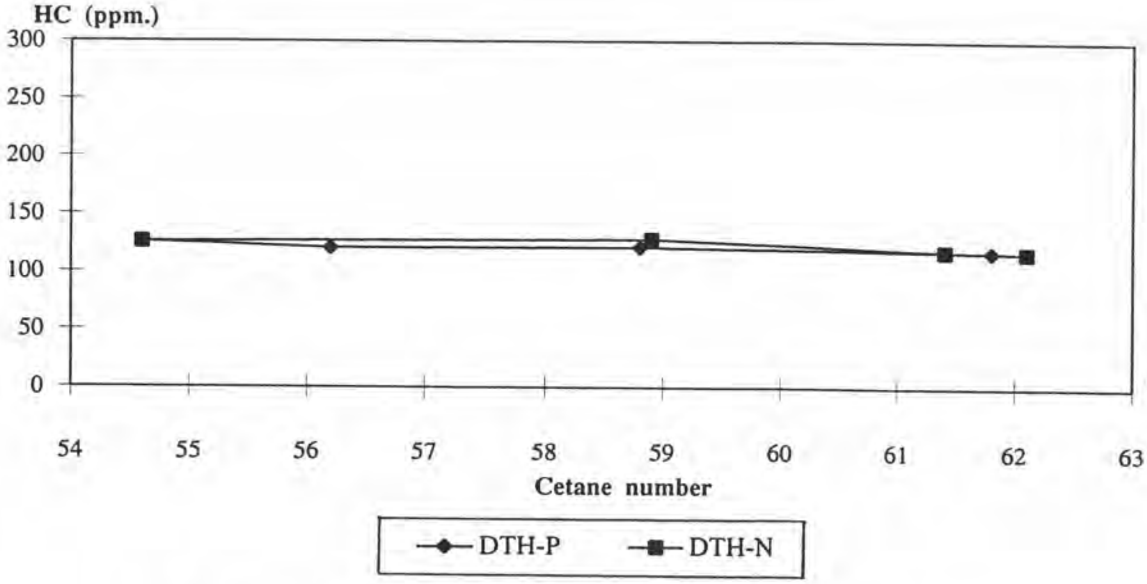

Figure 4.21 Effect of cetane improver on HC emissions

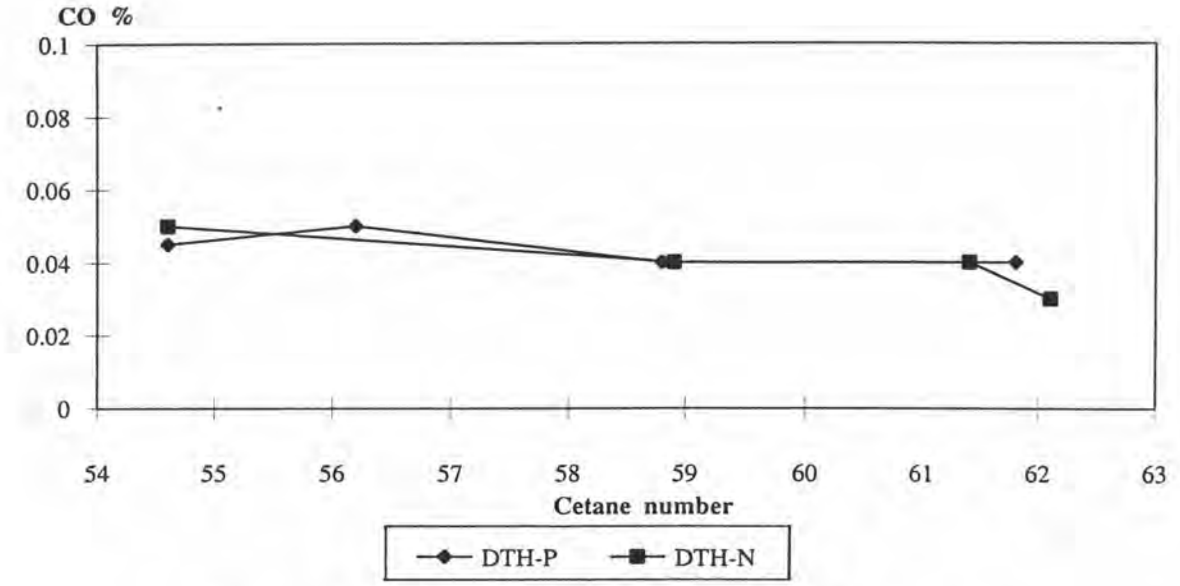

Figure 4.22 Effect of cetane improver on CO emissions

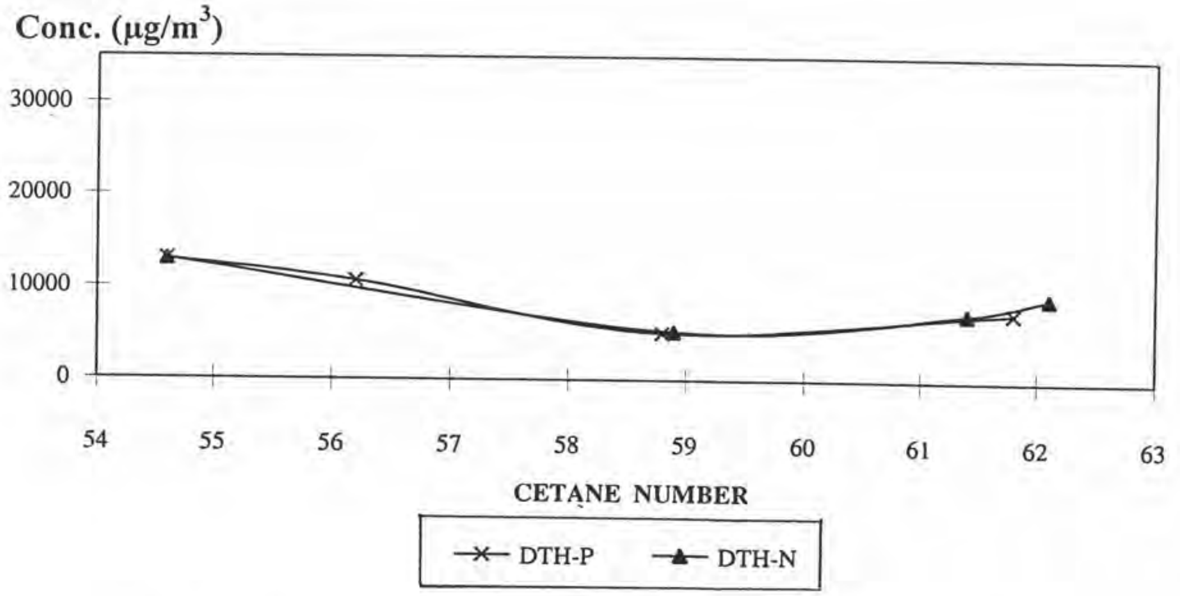

Figure 4.23 Effect of cetane improver on BTX emissions

Cetane improvers reduce the ignition delay of a fuel, hence the increase in measured cetane number. It has been hypothesized that a reduction in HC and CO emissions is a result of a decrease in premixed combustion and a reduction in lean flame-out regions in the fuel spray. A reduced ignition delay would also allow for additional time to complete combustion during the cycle, allowing for additional reductions in HC and CO emissions. As the ignition delay of the fuel is reduced, maximum rates of pressure rise occur farther away from top dead center, resulting in lower peak cylinder pressures and temperatures. NO_X formation is a function of temperature: the higher the peak temperature, the greater the amount of NO_X formed. For this reason, the use of cetane improvers can lower NO_X production rates.(17)

Wong and Steere of Imperial Oil Ltd. have shown that the relationship between ignition delay and cetane number is nonlinear, and that lowering the cetane number will have more and more effect on ignition delay with each successive decrease. For example; decreasing the cetane number from 50 to 40 will only result in 0.4 ms increase in ignition delay whereas a further decrease from 40 to 30 cetane number results in 1.1 ms increase in ignition delay (31). For this reason, the results of the study of the effect of cetane number on emissions were fairly flat with increasing cetane number. Fuels with higher cetane number (55-62) were used in this study.