

CHAPTER III

EXPERIMENTAL

Apparatus and Chemicals

1. Apparatus

1. Gas Chromatography-Flame ionization detector
Shimadzu. model GC-14A
2. Personal Sample Pumps
SKC model 224-PCXR4
3. Pump Calibrators
SKC model UltraFlo™
4. Pump Chargers and Battery Packs
SKC model Master Charger
5. Coconut-Base Active Charcoal, sorbent sample Tubes
SKC Cat. No. 226-09 (400/200 mg.)
6. CO non-dispersive infrared (NDIR) analyzer
SERVOMEX model 1490 (Range: 0-2.00% and 0-10.0%)
7. HC flame ionization detector (FID) analyzer
SERVOMEX model 3000 (Range: 0-10,000 ppm.)
8. NO_x chemiluminescence analyzer
SERVOMEX model 4000 (Range: 0-10,000 ppm.)

9. Eddy current dynamometer

NSDK NISHISHIBA model NEDD-130H

10. Dynamometer control desk

NSDK NISHISHIBA model HM-640 B

2. Chemicals

1. Magnesium perchlorate

Analysis grade (83%); Merck

2. Carbon disulphide

Analytical grade (99.9%); Merck

3. Benzene

Analytical grade (99.9%); BDH England

4. Toluene

Analytical grade (99.7%); WAKO Japan

5. Xylene

Analytical grade (96.0%); Merck

6. Pentane ; C₅

Standard grade; Japan

7. Hexane ; C₆

Standard grade; Japan

8. Heptane ; C₇

Standard grade; Japan

9. Octane ; C₈

Standard grade; Japan

10. Nonane ; C₉

Standard grade; Japan

11. Decane ; C₁₀

Standard grade; Japan

12. 2-Ethylhexyl nitrate (EHN)
CAS No.27247 96-7 ; Octel, United Kingdom
13. Di-tert-Butyl Peroxide (DTBP)
CAS No.110-05-4 ; ARCO, U.S.A.

Test Engine

Table 3.1 Characteristics of ISUZU engine (model 4JA1)

Bore	93 mm
Stroke	92 mm
Displacement	2.499 liters
Compression Ratio	18.4:1
Number of Cylinders	4
Injection	Direct injection
Rated power, hp./rpm.	87/4000
Peak Torque, kg-m./rpm.	17.5/2000
Low Idle Speed	750 rpm.

The test engine used in this study was a ISUZU 4-cylinder, 2500 cc. DI. Full engine details are shown in Table 3.1. The engine was installed on a test bed connected to an eddy current dynamometer. In addition, the engine was connected to the equipment for the measurement of conventional gaseous emissions (NO_x , HC, CO) as shown in Figure 3.1.

The engine was run at several constant speeds and at each speed the test conditions were conducted to cover a range of engine loads. (Increasing engine load corresponds to increased equivalence ratio. Equivalence ratio is defined as the ratio of the stoichiometric air-fuel ratio to the actual air-fuel ratio.)

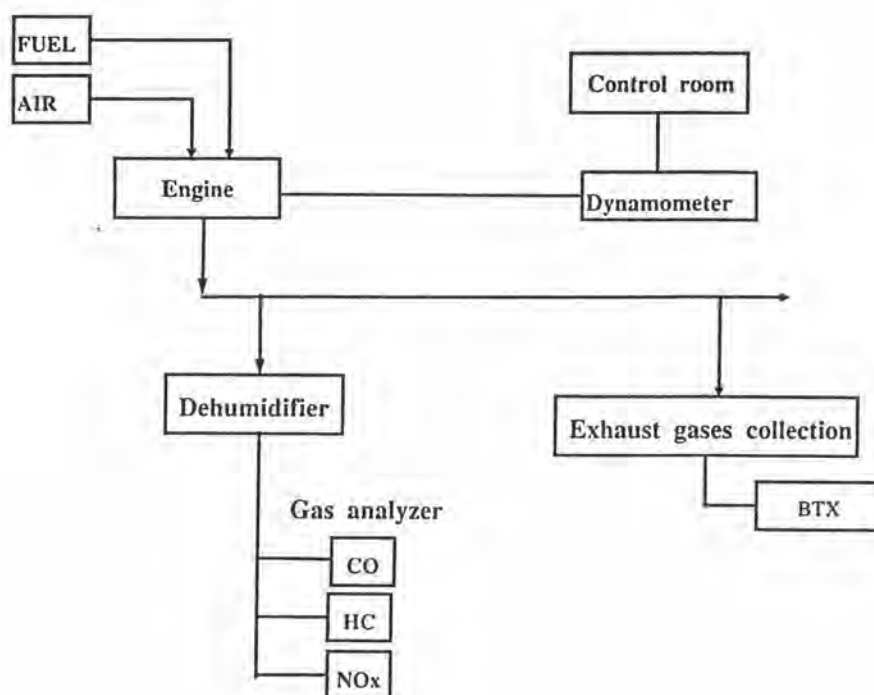


Figure 3.1 Engine layout

Whenever a fuel was changed, new fuel was introduced into the fueling system, new fuel filters were installed, and the fuel lines were flushed by running the engine at idle for about 30 minutes. Then, the engine was operated for sampling exhaust emissions.

Test Fuels

Six different diesel fuels, varying in 90% distillation point (T90) and cetane number, were used as base fuels for this test. Physical and chemical characterization data for each fuel are described in Table 3.2.

Table 3.2 Physical and chemical properties of base fuels

TEST ITEM	methods ASTM D	LIMITS	DTH52X	DTH53X	DTH55X	DTH57X	DTH58X	DTL52X
Cetane number	613	Report	51.8	52.6	54.6	57.4	57.7	52.2
Aromatics, wt %	2549	Report	25.9	25.1	21.8	15.8	14.0	16.3
API Gravity @ 60 °F	1298	Report	38.0	37.9	37.0	38.7	38.2	37.6
Specific Gravity @ 60/60°F	1298	0.81-0.87	0.8348	0.8353	0.8398	0.8314	0.8338	0.8368
Calculated Cetane Index	976	47 min	52	52	54	56	56	53
Viscosity Kinematic @ 40°C,cSt	445	1.8-4.1	2.8	2.8	3.4	3.3	3.4	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, %vol	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	66	72	83
Distillation:	86							
Initial Boiling Point, °C		Report	170	182	170	176	177	197
10% vol recovered, °C		Report	199	207	211	214	219	224
50% vol recovered, °C		Report	267	267	284	280	282	271
90% vol recovered, °C		357 max	345	349	350	348	349	332
Colour,ASTM	1500	4.0 max	L0.5	1.0	L1.0	L1.5	L1.5	2.0

Both the additives, 2-Ethylhexyl nitrate (EHN) and Di-tert-butyl peroxide (DTBP), were added to the base fuels (DTH55X and DTL52X). Treat rates were varied at 0.05, 0.14, and 0.30 % by volume so as to produce nine additional fuel blends with cetane numbers ranging from 55 to 62. Supplemented base fuels were used to compare the emissions reduction potential of the two cetane improvers. Fifteen types of fuels were investigated in this study, as shown in Table 3.3.

Table 3.3 Properties of fuel/additive mixtures

Fuel code	Additive (volume %)	T90(°C)	Cetane No.	Cetane index
DTH 52X	-	345	51.8	52
DTH 53X	-	349	52.6	52
DTH 55X	-	350	54.6	54
DTH57X	-	348	57.4	56
DTH 58X	-	349	57.7	56
DTH 59N	DTH55X + EHN 0.05%	350	58.9	54
DTH 61N	DTH55X + EHN 0.14%	350	61.4	54
DTH 62N	DTH55X + EHN 0.30%	350	62.1	54
DTH 56P	DTH55X + DTBP 0.05%	350	56.2	54
DTH 59P	DTH55X + DTBP 0.14%	350	58.8	54
DTH 62P	DTH55X + DTBP 0.30%	350	61.8	54
DTL 52X	-	332	52.2	53
DTL 56N	DTL52X + EHN 0.05%	332	55.8	53
DTL 58N	DTL52X + EHN 0.14%	332	58.0	53
DTL 60N	DTL52X + EHN 0.30%	332	59.8	53

Exhaust Emissions Testing Procedures

The exhaust emissions were tested at steady state conditions. The engine was operated at three constant speeds (1500, 2500, 3500 rpm.) and at each speed tests at 0%, 50%, and 80% engine load were included for each type of fuel. Gaseous emissions measurements were made using non-dispersive infrared analysis for CO, heated flame ionization detector for HC, and chemiluminescence for NO_x. All instruments were manufactured by Servomex. The composition of hydrocarbons was analyzed by gas chromatography. In this study, the sample exhaust gases, which were collected on activated charcoal sorbent tube and desorbed with carbon disulphide, were analyzed by GC/FID capillary column for identification of individual hydrocarbons. There are many compounds and four of them, benzene, toluene, *m,p*-xylene, and *o*-xylene, were selected for quantitative determination.

1. Collection of Samples (22,23)

Exhaust emissions were collected on a charcoal tube by a personal sampling pump, shown in Figure 3.2. Sample flow was maintained at rates 2 L/min.; collection times were 15 min. The charcoal tube consists of two sections of 20/40 mesh activated charcoal. The front section of 400 mg. is retained by a plug of glass wool, and the back section of 200 mg. is retained by urethane foam. Both ends of the tube are flame-sealed (Figure 3.3).

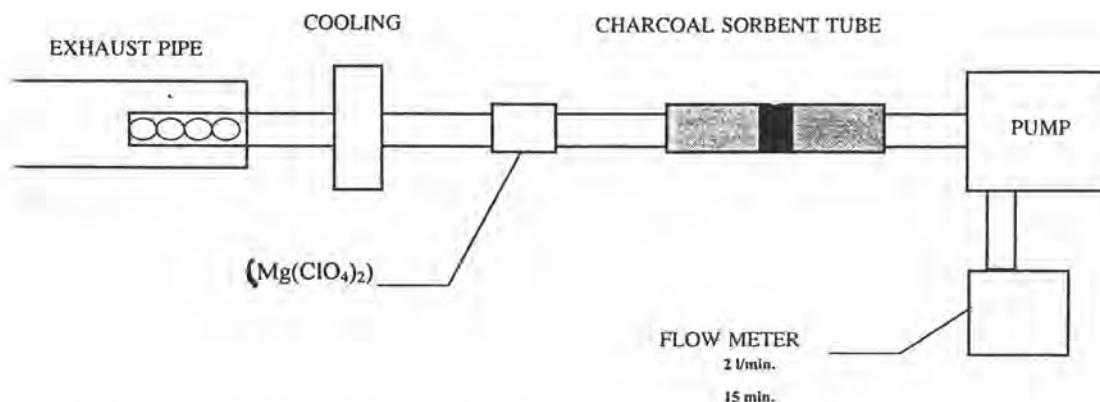


Figure 3.2 Schematic of exhaust gases collection for analysis by GC

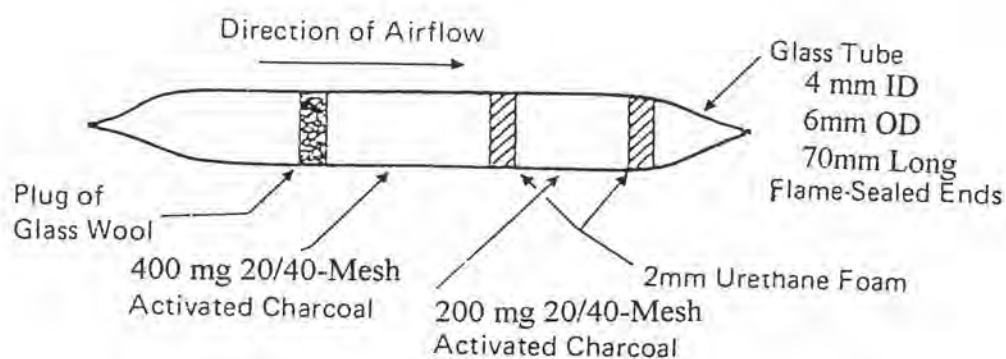


Figure 3.3 Details of Activated Charcoal Adsorption Sampling Tube

Immediately before sampling, the ends of the tube were broken to provide openings. The back section of the charcoal sorbent tube was positioned connected to the sampling pump with tubing. The inlet end of the tube in the tubing connected to the exhaust pipe so that the front section of the tube was exposed to the exhaust emissions. The power switch for the pump was turned on and the sampling began. When complete, the pump was turned off. Immediately after sampling, the charcoal sorbent tubes were removed from the

tubing, detached from the pump, capped with plastic caps and taken to the laboratory for analysis.

2. Analysis of Samples (24)

2.1 Preparations of Samples.

In preparation for analysis, each charcoal tube was scored with a file in front of the first section of charcoal and broken open. The glass wool was removed and discarded. The charcoal in the front section was transferred to a 2 ml stoppered sample container. The separating section of foam was removed and discarded; the back section was transferred to another stoppered container. These two sections were analyzed separately.

2.2 Desorption of Samples.

Prior to analysis, 2.0 and 1.0 ml of carbon disulphide were pipetted into the front and back sections, respectively. The sample vials were capped as soon as the solvent was added to minimize volatilization and agitated occasionally for 30 minutes for desorption of samples.

2.3 Gas Chromatography conditions.

The GC analyses were performed on GC-14A gas chromatography (Shimadzu, Japan), equipped with flame-ionization detector. Capillary column was made of fused silica (Shimadzu) with an I.D. of 0.22 mm. CBP-1 dimethylsilicone fluid liquid phase was used and the coated film thickness was approximately 0.25 μm . Nitrogen was used as the carrier gas.

The instrument conditions are reported in Table 3.4 and the GC chromatogram of exhaust emissions from front and back sections of charcoal sorbent tube are shown in Figure A1-A2 (Appendix A).

Table 3.4 Summary of Gas Chromatography Conditions

Column:	
Dimensions	50 M x 0.22 mm I.D.
Material	Fused silica
Liquid phase	CBP-1 methylsilicone fluid
Film thickness	0.25 μm
Column temperature:	
Initial isothermal temperature	40 °C
Initial isothermal period	5 min
program	3 °C/min to 150 °C
Final isothermal temperature	150 °C
Final isothermal period	to the end of the analysis
Carrier gas	Nitrogen
Carrier gas flow rate	1 ml/min
Injector temperature	150 °C
Sample volume injected	1 μl
Split ratio	1:5
Detector	Flame ionization
Detector temperature	250 °C

3. Compound Identification (25)

The individual hydrocarbons were identified by comparing their retention times with those obtained from known hydrocarbon standards. Six of the paraffin group (n-pentane, n-hexane, n-heptane, n-octane, n-nonane and n-decane) and three of the aromatic group (benzene, toluene and xylene) were used. In addition, compounds for which could not be obtained standards were identified by comparison with the chromatograms of a typical gasoline sample obtained under the same condition of GC analysis. The GC Chromatograms of hydrocarbon standards and typical gasoline are shown in Figure A3-A4 (Appendix A). The identification of its compositions is presented in Table 4.1 (Chapter IV).

Table 3.5 Dilution for preparation of standards

Hydrocarbon* Conc. in ppm.(v/v).	Aliquot of Hydrocarbon	Final dilution volume in ml
10000	1 ml Pure Hydrocarbon	100
200	2 ml of 10000 ppm standard	100
100	5 ml of 200 ppm standard	10
50	5 ml of 100 ppm standard	10
20	2 ml of 100 ppm standard	10
10	1 ml of 100 ppm standard	10

* Hydrocarbon was Benzene, Toluene or Xylene.

4. Calibration and Standards

Standards preparation (benzene, toluene, and xylene) is shown in Table 3.5. Standard solutions were analyzed, under the same GC conditions and during the same time period as the samples, to construct the calibration curve (Figure A5 in Appendix A). All standards were stored in a freezer when not in use.

The concentrations of standards in ppm (v/v) were converted into $\mu\text{g/ml}$ by using the density of the analyte. Calibration curves were established by plotting concentration in $\mu\text{g/ml}$ versus peak area as shown in Figure A6 (Appendix A).

5. Determination of Desorption Efficiency (D.E.) (26)

The procedure for determining desorption efficiency is as follows. The end of the front section of charcoal tube was broken and capped with parafilm. A known amount of a carbondisulphide solution of hydrocarbon standard (benzene, toluene, xylene) containing 10,000 ppm (v/v) was injected directly into the activated charcoal with a microliter syringe, and the tube was capped with more parafilm. Volume of hydrocarbons standard solution, 1, 2, and 5 μl , were injected into three charcoal sample tubes at each of volume. Sample tube was allowed to stand overnight to assure complete adsorption of the analyte on to the charcoal. Then the sample was desorbed and analyzed.

The desorption efficiency equals the weight in μg recovered from the tube divided by the weight in μg added to the tube.

$$\text{D.E.} = \text{weight recovered} / \text{weight added}$$

Table 3.6 Desorption efficiency of benzene, toluene and xylene

standard	weight added ($\mu\text{g/ml}$)	weight recovered ($\mu\text{g/ml}$)	D.E.
Benzene	43.9	43.74	1.00
	17.56	17.74	1.01
	8.78	8.86	<u>1.01</u>
			1.01
Toluene	43.4	42.76	0.99
	17.36	17.01	0.98
	8.68	8.51	<u>0.98</u>
			0.98
Xylene	43.0	35.69	0.83
	17.20	14.45	0.84
	8.60	7.40	<u>0.86</u>
			0.84

6. Calculation of Hydrocarbons Concentrations (27)

The weight of hydrocarbons (benzene, toluene, *m,p*-xylene, *o*-xylene) were read in μg corresponding to each peak area from the standard curve. No. volume corrections are needed, because the standard curve is based on $\mu\text{g/ml}$ carbon disulphide, and the volume of sample injected is identical to the volume of the standards injected.

Corrections were made for the blank for each sample with the following equation:

$$\mu\text{g} = \mu\text{g sample} - \mu\text{g blank}$$

where :

$\mu\text{g sample} = \mu\text{g found in front section of sample tube}$

$\mu\text{g blank} = \mu\text{g found in front section of blank tube}$

A similar procedure was followed for the backup section. The weights found in the front and backup section were added to get the total weight in the sample.

$\text{Total weight in the sample } (\mu\text{g}) = \mu\text{g front section} + \mu\text{g back section}$

The total weight were divided by desorption efficiency to obtain the corrected $\mu\text{g/sample}$

$\text{Corrected } \mu\text{g/sample} = \text{Total weight} / \text{D.E.}$

The concentration of the analyte in the exhaust gas can be expressed in $\mu\text{g/m}^3$ by the following equation:

$\mu\text{g/m}^3 = \text{corrected } \mu\text{g} \times 1000(\text{L/m}^3) / \text{air volume sample (L)}$

$\text{Air volume sample} = 30 \text{ L.}$