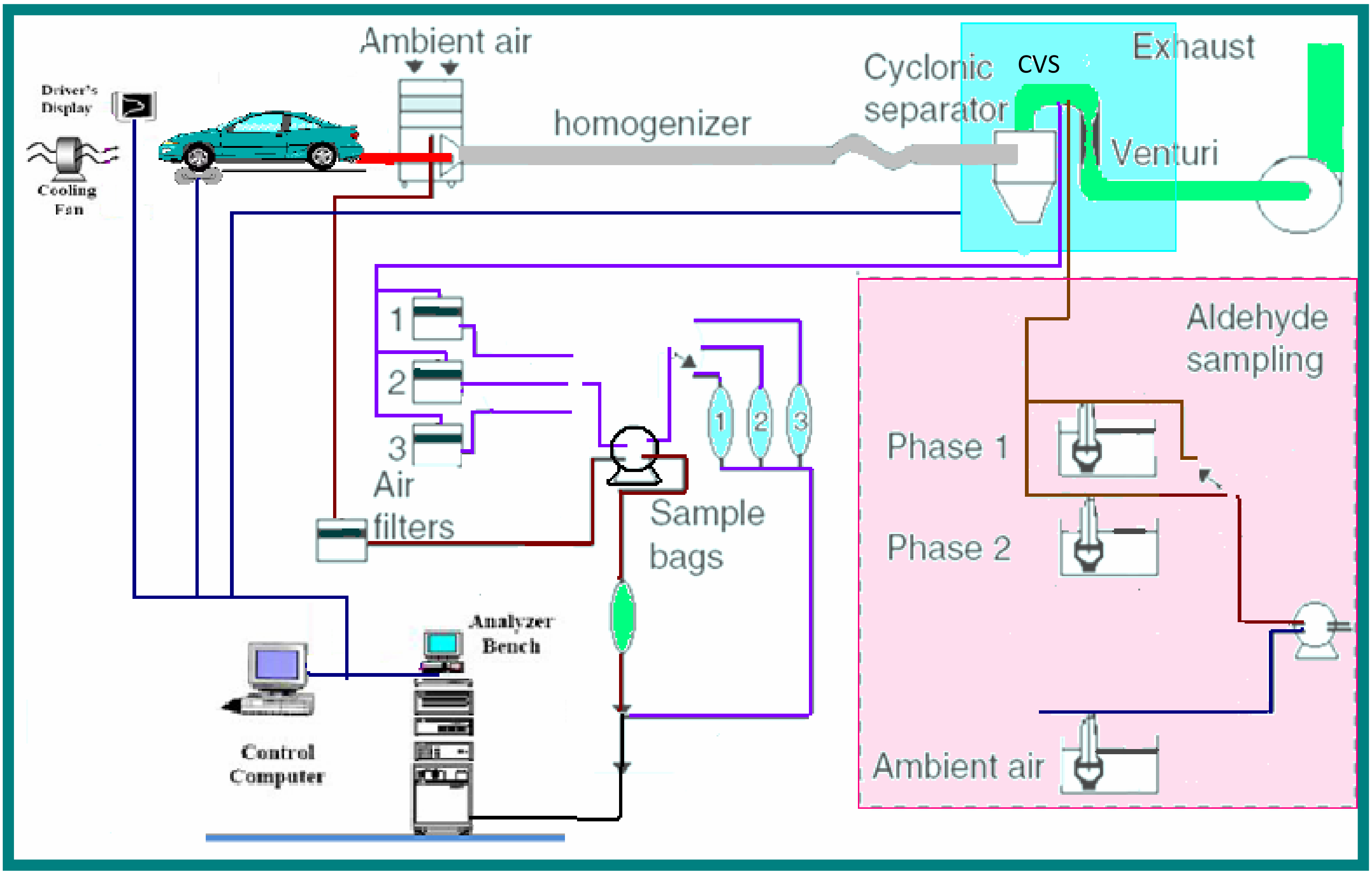
Control of Urban Pollution Series:
CUPS/ / 2010-11

Study of the Exhaust Gases from different fuel based vehicles for Carbonyls and Methane Emissions



CVS –Constant Volume Sampler

Central Pollution Control Board
(Ministry of Environment & Forests)
Website: cpcb.nic.in; email: cpcb@nic.in
(November, 2010)

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FOREWORD

Air Pollution is caused by a number of pollutants emanated from various sources. Under sound air pollution control strategy the detailed analysis and assessment of all the pollutants having detrimental effects on human health and environment is required. Modern Research and Development (R&D) initiatives lead to addition of new air pollutants which require standards formulation for their regulatory control.

Vehicular emissions are one of the predominant sources of carbonyls in the ambient air. Recently Carbonyls consisting of aldehydes and ketones have been identified as precursors of severe secondary pollutants and themselves also are harmful, thus needs detailed study.

The Central Pollution Control Board has undertaken a project on, Assessment and characterization of aldehyde, ketone and methane emissions in vehicle exhaust using different fuels with the help of International Centre of Automotive Technology (ICAT) Manesar.

The project envisaged evaluation and characterization of aldehydes, ketones and methane emissions from different vehicle category exhausts using different fuels.

The assistance extended by ICAT Scientists for conducting the study is gratefully acknowledged. Thankful acknowledgement for Ms. Meetu Puri JSA, Sh. R. C. Saxena Scientist 'D' and Dr. R. S. Mahwar Scientist 'E' for preparing the document under the supervision of Sh. J. S. Kamyotra Member Secretary.

I hope, that this document will be useful to the Regulatory Authorities, Policy makers and all the concerned for controlling vehicular emissions.

November, 2010 (S. P. Gautam)

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ABBREVIATION

DNPH	-	Dinitrophenylhydrazine
MEK	-	Methyl ethyl ketone
ABR	-	Air Resource Board
FTP	-	Federal Test Procedure
Dyno	-	Dynamometer
CVS	-	Control Volume Sampler
CFR	-	Code of Federal Regulations
SHED	-	Sealed Housing Evaporative Determination
HPLC	-	High Performance Liquid Chromatography
UV/VIS	-	Ultraviolet Visible Spectrographic detector
SLB	-	Southern Laboratory Branch
LOD	-	Limit of Detection
PCM	-	Pump Controller Module
TCM	-	Temperature Control Module
LC	-	Liquid Chromatography
ACN	-	Acetonitrile
RF	-	Response factor
THC	-	Total Unburned Hydrocarbons
US EPA	-	United States Environment Protection Agency
IARC	-	International agency for research on cancer
LOAEL	-	Lowest-Observed-Adverse-Effect-Level
LPG	-	Liquefied Petroleum Gas
CNG	-	Compressed Natural Gas
E5	-	Ethanol 5% by Volume
IDC	-	Indian Driving Cycle
MIDC	-	Modified Indian Driving Cycle
LCV	-	Light Commercial Vehicle
HCV	-	Heavy Commercial Vehicle
GVW	-	Gross Vehicle Weight

PC	-	Passenger Car
DT	-	Dilution Tunnel
CFO	-	Constant Flow Orifice
LCG	-	Low Cold Gas Chromatograph
RSD	-	Relative Standard Deviation
AU	-	Astronomical Unit
HPLC	-	High Performance Liquid Chromatography
EPA	-	Environmental Protection Agency
CARB	-	California Air Resource Board
FIA	-	Flame Ionization Analyzer
MEK	-	Methyl Ethyl Ketone

1. INTRODUCTION

1.1 Preamble

The rapid and seemingly unending increase in vehicle population, limited road space and carrying capacity and emissions from different intersectorial activities and study/investigation/monitoring of the Urban Ambient Air Quality is not limited to few parameters such as NO_x, SO_2, CO etc… The study of hazardous air pollutants such as ozone, volatile organic compounds (VOCs), Ketones and aldehydes have acquired new dimensions for obvious reasons, which include their adverse effects on human health, vegetation (ex: crops) and materials. The findings of source apportionment studies conducted by CPCB have revealed that the release of PM_{10} from the transport sector is 20.5% in Delhi and as high as 48.3% in Chennai. The other major sources of PM_{10} emissions in Indian urban environment are garbage burning, road dust, DG sets, construction activities etc.

The CPCB has also carried out a study of the urban air quality in Kolkata for source identification and estimation of ozone, carbonyls, NO_x and VOC emissions. The study details and its findings which have been published by CPCB in its document Control of Urban Pollution Series CUPS/72/2010-11, include cigarette smoke as one of the source of VOC emissions in urban ambient air. The keeping of the Ambient Air Quality from the point of sustainability not only requires ensuring of a sustainable growth of the vehicle population and sustainable siting of developmental activities but also the sustainability of the use of fuels for various purposes including as automotive fuel. The sustainability of automotive fuels includes the type, affects and acceptability of the HAPs that are released from different fuel based vehicles. The CPCB therefore has undertaken a project to study the exhaust gases from different fuel based vehicles for Carbonyls and Methane emissions.

The selection of the target carbonyl compound was based on the documented research in regard to the type of such compounds formed in the combustion of different automotive fuels. The report gives details of the studies conducted including the type of test fuel, vehicle selected, the methodology, the findings and the recommendations.

1.2 Objective of the work

- To characterize Aldehydes, Ketones and Methane Emissions from different category vehicle exhaust using variance in fuels by conducting exhaust mass emission tests and HPLC analysis

1.3 Scope of the work

- Collection of Aldehydes and Ketones of the exhaust gas collected in cartridges during mass emission tests on various category vehicles & fuels
- Determination of the amount of Aldehyde and Ketone present in the cartridges by High Performance Liquid Chromatographic (HPLC) analysis.
- Measurement of methane emissions during bag collection in “mg/km” on various vehicles using various fuels.

2. LITERATURE REVIEW

2.1. Formation and release of carbonyls and methane

2.1.1 Overall Process

Aldehydes and Ketones are characterized by the presence of carbonyl groups. In order to study the oxidation of hydrocarbons, the complex engine system is divided into two parts: (a) the combustion chamber and (b) the exhaust system. Inside the cylinder a fraction of hydrocarbons is oxidized during the expansion and exhaust process and the products are carbon dioxide, carbon monoxide and "hydrocarbons containing oxygen" like Aldehydes, Ketones, Ethers and Alcohols etc. The general mechanism for the formation of Hydrocarbon (HC) is that fuel or fuel-air mixture escapes the primary combustion process to the exhaust system. This fuel (containing HC) then survives the expansion processes and passes through the exhaust system without oxidation and end up in the atmosphere as HC emissions. With the use of catalysts or a thermal reactor in the exhaust system, substantial reductions in HC emission levels can be achieved. The exhaust system temperature might be sufficient for partial oxidation, but not high enough for complete combustion. Cylinder-left-out gases are subjected to oxidation in the exhaust manifold. The engine parameters that influence on oxidation process are speed, spark timing, mixing composition, compression ratio, air / fuel ratio, load and heat losses (J.B.Heywood, 1988).

Factors which influence the engine conditions on hydrocarbon emissions are as follows:

(a) Fuel/Air Ratio:HC emission increases rapidly as the fuel and air mixture becomes fuel rich (Slone et al (1989), Quader et al (1989), Grimm et al (1988). For example, the hydrocarbon mass emitted under rich condition (Φ =1.15) was twice that of lean condition (Φ =0.90). The relative abundance of methane and acetylene increased during fuel-rich operation.

The presence of excess oxygen or excess hydrocarbons during combustion has a significant effect on the relative concentration of the various oxygenated hydrocarbon species emitted. As the availability of oxygen increases, the emission of hydrocarbon partial oxidizing products increases.

(b) Temperature: The combustion rate of hydrocarbons increases rapidly with temperature. Fundamental studies using combustion bombs and spectroscopic measurement of excited species in flames have shown that the combustion rate of hydrocarbons increases rapidly with temperature (Slone et al., 1989). In general, olefins produce higher flame temperatures than aromatics and both are higher than paraffin's (Quader et al., 1989). Spark retardation leads to reduced peak temperature but increased temperature late in the cycle and in the exhaust. NO_x decreases because of the lower peak temperature while HCs decrease because of the increased burn-up resulting from higher late cycle and exhaust temperature. An increase in engine speed usually results in increased combustion chamber temperature and increased catalyst temperature depending upon the thermal heat transfer properties of the particular engine and exhaust system.

Fuel parameters that influence hydrocarbon emissions are as follows:

(a) Fuel Molecular weight: The studies of single cylinder engines revealed that the total engine-out emission is increased as the average molecular weight of the fuel increased.

(b) Fuel Volatility: The change in the distillation temperature can change the engine exhaust gas. In some of the fuels, the decrease in HC emissions (approximately 23%) due to change in there distillation temperature from 360ºC to 138 ^{o}C. The higher HC emissions observed using a higher T_{90} fuel were probably because of the combined effects of the increased absorption of the heavier hydrocarbons ion oils films, on metal surfaces and in cylinder deposits (Siegl et al .1992, Kaiser et al., 1991).

(c) Paraffin content in fuel: When simple paraffin's are substituted for olefins in the fuel, the atmospheric reactivity of exhaust pipe emissions decreases and the non-methane hydrocarbon increases.

(d) Aromatic content in fuel: A decrease in aromatics and olefins and replacement by paraffins will result in an increased production of molecular hydrogen during combustion. The H/C ratio of fuel aromatics and olefins are lower than those of the normal and iso-paraffins. The decrease in aromatics and/or olefins helps in reduced HC emissions, assuming all other important variables remain constant.

(e) Oxygenated compound in fuel: The addition of oxygenated fuel components has the effect of leaning –out the air/fuel ratio, which results in reduced HC and CO emissions.

Presently, only NO_x (Oxides of Nitrogen), CO (Carbon Monoxide), THC (Total Unburned Hydrocarbons) particulates and visible smoke are those emissions which are legislated for the respective type of fueled vehicles. In addition to ongoing regulated parameters, the impact of increasing traffic density on the environment and public health demands need the limits for Aldehydes, Ketones and Methane emissions. A study on these parameters in vehicle/ engine exhaust provides inputs for emission regulations thereby providing scope for reducing pollution levels and consequently improving public health in the country.

Formaldehyde and Acetaldehyde are the most common non methane Carbonyl compounds found in vehicular exhaust.

(i) Formaldehyde is formed due to incomplete combustion of both gasoline and diesel fuel and accounts for 1 to 4% of Total Organic Gas (TOG) emissions, depending on control technology and fuel consumption.

(ii) Vehicle emissions do not only contribute primary formaldehyde but also responsible formaldehyde formed from photo oxidation of the VOC.

(iii) Acetaldehyde is a saturated aldehyde found in vehicle exhaust due to incomplete combustion of fuel.

(iv) Acetaldehyde constitute 0.4 to 1 % of exhaust total organic Gas (TOG), depending on control technology and fuel composition.

(v) Mobile sources contribute to both primary and secondary emissions of acetaldehyde.

(vi) Aldehydes get involved in chemical reaction in the atmosphere, generating other compounds, some of which leads to photochemical smog formation that mostly produces oxidizing gases, especially ozone gas.

(vii) Oxidizing gases formed due to chemical reaction in atmosphere also damage materials like rubber.

2.2 Process chemistry Release/Mechanism.

2. 2.1 Aldehyde and Ketone formation

Aldehydes and ketones found in exhaust gases are formed in the engine and exhaust system. In the basic aldehyde formation reactions, the important carriers of the chain reaction in the combustion of hydrocarbons are the alkyl radicals (R), which are formed by cleavages of C-C or C-H bonds of hydrocarbons. At high temperatures, dehydrogenation by oxygen and presence of other combustion related radicals influence the cleavages processes.

Regarding the higher aldehydes, the general mechanism is based on the formation of the alkyl radicals ($RO_2^{\cdot}$)

$R+O_2 = RO_2^{\cdot}$ -- (1)

This alkyl radical is the precursor for the further reactions, including intra-molecular hydrogen abstractions and decomposition. Finally leading to the following aldehyde formation reactions:

$RCH_2OO^{\cdot} \longrightarrow RC^{\cdot}\ HOOH \longrightarrow RCHO+^{\cdot}OH$ ----------------------- (2)

$$RCH_2O + O_2 \longrightarrow RCHO + HO_2^{\cdot}$$ -- (3)

$$RCH{=}CH_2 + {}^{\cdot}O \longrightarrow RCHO$$ --- (4)

An ambient temperature range in an engine exhaust system of 300-2000 K, the temperature has the large effect on the aldehyde formation.

Aldehydes are formed by oxidation during the combustion and by oxidation of unburnt hydrocarbons. Sources of unburnt hydrocarbons are given below (J.B.Haywood, 1988).

Flame quenching

Flame quenching at the cool combustion chamber walls, which results in a thin layer of unburned fuel/air mixture close to the wall after flame passage.

Crevices mechanism

Crevices in the combustion chamber wall which are too narrow for flame to enter leads to the fuel/air mixture escaping from the primary combustion processes.

Absorption and desorption of fuel vapor in the oil layer and deposits

The oil layer present on the combustion chamber wall and deposits formed on the combustion chamber absorb fuel vapor during intake and compression processes, and this fuel is desorbed during the expansion and exhaust processes.

Gas-phase quenching

It has been created when the engine is operating under extreme conditions of equivalence ratio and spark timing.

Leakage of unburnt mixture through the valve

Valve leakage can occur which leads to a small fraction of fuel/air mixture escaping the primary combustion processes.

Unevaporated liquid fuel in the cylinder

For liquid fuels, an important process which could contribute to hydrocarbon emissions is the liquid fuel within the cylinder which fails to evaporate and mix with sufficient air to burn before the end of combustion, particularly during the engine starting and warm-up process.

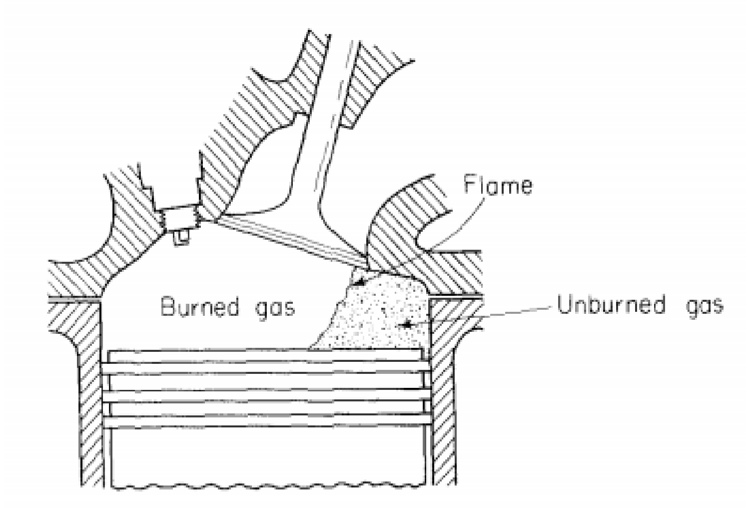


Figure 2.1 In-cylinder burned gas and unburned gas formation

The ketone formation also starts from the alkyl-peroxy radicals RO_2 (Miller et al, 1990)**.**The ketone reaction equation as follows:

$$RR'CHOO^{\cdot} \rightarrow RR'C^{\cdot}OOH \rightarrow RR'CO + {}^{\cdot}OH \quad \text{--------------------------------} \qquad (5)$$

2.2.2 Methane Formation

Methane is emitted from light duty vehicles due to the incomplete combustion of fuel from the engine and the incomplete oxidation of engine-out methane in current catalytic after treatment systems. It is important to recognize, that current vehicles produce and emit substantially less methane than their older counterparts.

2.2.3 Carbonyl Emission

The selective carbonyl and methane emission literature study has been done on the engines using various fuels. The literature given below is the resources which have been used many times in the study of carbonyl emission on engines using various fuels. Very less studies are being available in the public domain.

Gasoline fueled engines

Numerous studies have been conducted on gasoline fueled engine for analyzing carbonyl emissions.

Yao et al. (2008) suggested that reduction in aromatic content in Gasoline increases aldehyde emission. Karl-Erik Egebäck et al (2005) said that, the emissions of aldehydes (especially acetaldehyde and formaldehyde) from vehicles running on ethanol/gasoline blends are expected to increase. Wigg et al, (1973) reported that increasing the aromatic content in fuel reduces formaldehyde emissions from the exhaust. Oberdorfer et al, (1967) denoted that, in gasoline the presence of different groups like (Aromatics, Naphthene, Paraffin, Olefins) have different effect of carbonyl emissions (aldehyde & ketone). The increasing order of carbonyl emission based on the groups is given below:

Aromatic < Naphthene < Paraffin < Olefin

Diesel fueled engines

Wagner et.al, 1996 described that, the higher cetane number fuel (BS III diesel) emits higher carbonyl emissions than lower cetane number fuel (BS II diesel). The other important property like higher sulfur content in BS II Diesel also one of the parameter to emit lower aldehyde emissions (Yung-chen yao et.al, 2008). Yacoub et al. (1996) mentioned that aldehyde emissions increase as the cetane number of the fuel is increased (lower fuel density and aromatic content). Weidmann et al. (1988) investigated that the emissions of aldehyde from diesel engine were slightly lower for lower cetane number and higher for higher cetane number.

Natural gas engines

Natural gas largely consists of methane and ethane. The use of natural gas as a fuel in engines is reviewed by Meeks Jr et al. (1992) and reported that, a reaction between a single methane and oxygen molecule can directly produce formaldehyde as a stable intermediate combustion product. Quenching the formaldehyde molecule before it can be acted upon by oxygen can leave formaldehyde in the exhaust. Similarly, acetaldehyde and acrolein are stable compounds that can be produced from partial combustion of ethane. Weaver et al (1989) described that, the carburetor-based technology vehicle gave high non-regulated hydrocarbons levels, with ethane (732mg/km), acetaldehyde (150mg/km).

Liquefied Petroleum Gas (LPG)

The vehicles run by LPG gives less formaldehyde than normal gasoline engine (Anonymous, 2000). Emissions of aldehydes from LPG vehicles nearly always generates lower than diesel's and often lower than petrol's (Anonymous, 2009).

Ethanol blended gasoline engines

The main effects of ethanol blending were increased acetaldehyde emissions (30-44 times for pure ethanol), reduced emissions of all other carbonyls except formaldehyde and acrolein (which showed a more complex relation to the ethanol content), reduced carbon monoxide (CO) and nitrogen oxide (NO) emissions, and increased hydrocarbon (HC) and nitrogen dioxide (NO_2) emissions (R Magnusson, 2002).

As ethanol has lower heating value, high octane number and lower energy content than gasoline there is a significant increase in aldehydes and formaldehyde emissions from ethanol added gasoline (Magnusson Roger et al, 2002).

Biodiesel blended diesel engine

C. He et al., 2009 experimental results indicate that biodiesel-fueled engine almost has triple carbonyls emissions of diesel-fueled engine. Biodiesel, as an alternative fuel, has lower specific reactivity (SR) caused by carbonyls compared with diesel. When fueled with biodiesel, carbonyl compounds make more contribution to total hydrocarbon emission.

Correa S M et al, 2008 experimental work stated that, the seven carbonyl emissions (formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, butyraldehyde, and benzaldehyde) were evaluated by a heavy-duty diesel engine fueled with pure diesel (D) and biodiesel blends (v/v) of 2% (B2), 5% (B5), 10% (B10), and 20% (B20). Using average values for the heavy duty engines, benzaldehyde showed a reduction on the emission (−3.4% for B2, −5.3% for B5, −5.7% for B10, and −6.9% for B20) and all other carbonyls showed a significant increase: 2.6, 7.3, 17.6, and 35.5% for formaldehyde; 1.4, 2.5, 5.4, and 15.8% for acetaldehyde; 2.1, 5.4, 11.1, and 22.0% for acrolein+acetone; 0.8, 2.7, 4.6, and 10.0% for propionaldehyde; 3.3, 7.8, 16.0, and 26.0% for butyraldehyde.

2.2.4 Methane emission:

Increases in ethanol percentage in gasoline enhances the methane emission in the exhaust may be due to increase in octane number of the gasoline which has the probability of knocking (Anonymous, 2008). Due to the incomplete combustion inside the engine and the incomplete oxidation of methane at exhaust develop higher methane emission (RE Hayes, 2004). The recommended emission factors for highway vehicles are given in table 2.1.

Table 2.1 Recommended emission factors for on highway vehicles

Vehicle type/ Control Technology	CH_4 (g/mi)	CH_4 (g/km)
Gasoline Passenger Cars:		
Low Emission Vehicles	0.013	0.008
EPA Tier 1 [a]	0.02	0.012
EPA Tier 0 [a]	0.066	0.041
Oxidation Catalysts	0.133	0.083
Non-Catalyst	0.162	0.101
Uncontrolled	0.171	0.106
Diesel Passenger Cars:		
Advanced	0.001	0.001
Moderate	0.001	0.001
Uncontrolled	0.001	0.001
Diesel Light Duty Trucks:		
Advanced	0.001	0.001
Moderate	0.001	0.001
Uncontrolled	0.002	0.001

Diesel Heavy Duty Vehicles:		
Advanced	0.004	0.002
Moderate	0.004	0.002
Uncontrolled	0.004	0.002

Motorcycles:		
Non Catalysts Control	0.067	0.042
Uncontrolled	0.09	0.056

(The categories “EPA Tier 0” and “EPA Tier 1” were substituted for the early three-way catalyst and advanced three-way catalyst categories, respectively, as defined in the Revised 1996 IPCC Guidelines)

Advanced: EGR and modern electronic control of the fuel injection system are designated as advanced control technologies.

Moderate: Improved injection timing technology and combustion system design for light- and heavy-duty diesel vehicles (generally in place in model years 1983 to 1995) are considered moderate control technologies.

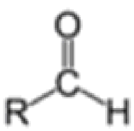
Uncontrolled: Not controlled over the combustion properties

Note: Light and Heavy duty vehicles were tested on Heavy duty Chassis Dynamometer.

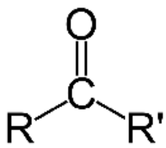
(Source: Anonymous, 2004, Update of Methane and Nitrous Oxide Emission Factors for On Highway Vehicles, Assessment and Standards Division Office of Transportation and -Air Quality, U.S. Environmental Protection Agency.)

2.3 Properties of Aldehydes, Ketones and Methane:

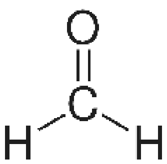
Aldehydes and ketones are partially oxygenated organic compounds containing carbonyl group. An Aldehyde functional group consists of a carbon atom bonded to a hydrogen atom and double-bonded to an oxygen atom (O=CH-). Whereas a **ketone** functional group contains a carbonyl group (C=O) bonded to two other carbon atoms in the form shown below



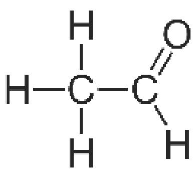
Aldehyde



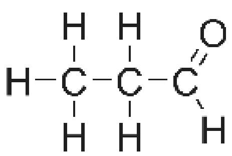
Ketone



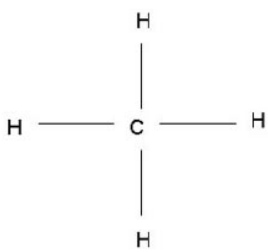
Formaldehyde



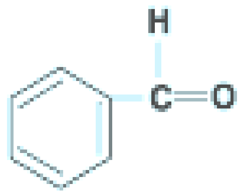
Acetaldehyde



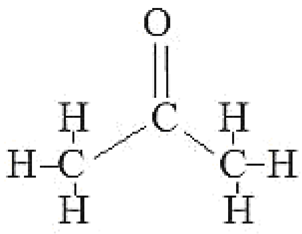
Propionaldehyde



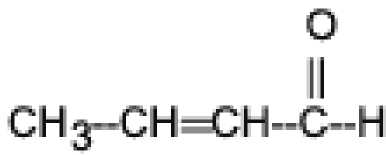
Methane



Benzaldehyde



Acetone



Crotonaldehyde

Figure 2.2 Chemical Formulae for Aldehydes and Ketones

The word aldehyde seems to have arisen from alcohol dehydrogenated. The physiochemical properties of the most common aldehyde and ketones found in engine exhaust emissions are given in Table 2.2.

Table 2.2 Physiochemical properties of carbonyl compounds

Number	IUPAC name	Synonym	C No.	Formula	Molecular Weight	Density	Melting Point	Boiling point
Aldehyde					kg/mol	kg/m^3	ºC	ºC
1	Methanal	Formalydehyde	1	HCHO	30.03	815	-92	-21
2	Ethanal	Acetaldehyde	2	CH_3CHO	44.05	778	-123	20
3	Propanal	Propionaldehyde	3	CH_3CH_2CHO	58.08	797	-81	48
4	Butanal	n-Butylraldehyde	4	$CH_3(CH_2)_2CHCHO$	72.11	803	-97	75
5	Pentanal	n-Valeraldehyde	5	$CH_3(CH_2)_3CHO$	86.13	808	-91	103
6	Hexanal	n-capronaldehyde	6	$CH_3(CH_2)_4CHO$	100.16	814	-56	128
7	Propenal	Acrolein	3	CH_2CHCHO	56.07	841	-86	53
8	Trans-2-Butenal	Crotonaldehyde	4	$CH_3CHCHCHO$	70.09	852	-74	102
9	2Methyl 2propenal	Methacrolein	4	CH_2CCH_3CHO	70.09	843	-81	68
10	Benzenecarbonal	Benzaldehyde	7	C_2H_5CHO	106.13	1046	-26	179

11	3Benzenene carbonal	m-Tolualdehyde	8	$CH_3C_6H_4CHO$	120.15	1020	-35	197
12	2 Propanone	Acetone	3	CH_3COCH_3	58.08	792	-95	57
13	2 Butanone	Methylethylketone	4	$CH_3COCH_2CH_3$	72.11	805	-86	80

2.4 Health Effects of Aldehydes and Ketones:

The health effects of Aldehydes and Ketones are given at Annexure I

3. METHODOLOGY

The project had two major components of execution
1. Vehicle Selection
2. Vehicle testing

3.1 Vehicle selection

The vehicles selected for the testing were depending on high population of the specific vehicle on the Indian market and also depending on the availability at ICAT (Annexure-III). The vehicle models were sourced from retro fitment agencies, dealerships, etc. Normally about three vehicle models of the same vintage and categories were taken for testing.

3.2. Vehicle Testing

The vehicles as selected above were brought to ICAT for testing. Initially, the vehicle was subjected to the minimum check list like exhaust leak check, rectified if there was any exhaust leak. The fuel in the vehicle tank was drained off and test fuel was topped up after necessary flushing. After the minimum check vehicle was subjected to exhaust mass emission test on the chassis dynamometer. The standard vehicle exhaust mass emission tests were performed on the chassis dynamometer. The test procedures used for different vintages were as per the prevalent emission test procedure applicable for that category and model of the vehicle. The test cycle on the different categories of vehicles is given in Table 3.1.

Table 3.1 Vehicle category test cycles

Test Cycles	
Vehicle Category	**Test Cycle**
2/3 Wheeler vehicles	Indian Driving Cycle (IDC)
Post 2000 Model year 4 Wheeled vehicle with Gross Vehicle Weight (GVW) less than or equal to 3500 kgs	Modified Indian Driving Cycle (MIDC)
Gross Vehicle Weight (GVW) more than 3500 kgs	13 Mode Cycle

During the mass emission test, the exhaust methane emission was measured for all the vehicles (2 and 3 wheelers) tested at the running time (648 sec) by the use of Constant Volume Sampler (CVS) bag and the methane emission is mentioned in g/min. Additionally the cartridge sample for Aldehydes and Ketones has been taken at the same running time by the use of Impinger System. The method SOP MLD 104 was used to determine aldehyde and ketone compounds in automotive source samples by High Performance Liquid Chromatography (HPLC). Measuring pollutants are collected based on the test cycle used and vehicle/engine category is given in Table 3.2.

Table 3.2 Measuring pollutants from vehicle category

Measuring pollutants		
Vehicle Category	**Testing Cycle**	**Measuring Pollutants**
2 & 3 Wheeler	IDC	Methane, Aldehydes and Ketones
3 Wheeler	IDC	Methane, Aldehydes and Ketones
4 Wheeler Passenger cars	MIDC	Methane, Aldehydes and Ketones
4 Wheeler LCV	13 Mode Cycle	Methane, Aldehydes and Ketones
4 Wheeler HCV	13 Mode Cycle	Methane, Aldehydes and Ketones

3.2.1 Inertia Setting For Different Categories of Vehicles

For the purpose of mass emission test, the following inertia setting for the dynamometer was used.

2 wheelers: ULW (Unladen Weight) + 75 kg

3 wheeler gasoline: ULW + 150 kg (2 passengers X 75)

3 wheeler Diesel: GVW

Passenger Cars: ULW+150 kg (2 passengersX75)

Multi Utility Vehicles: ULW+450 kg (6 passengersX75)

LCV: GVW & HCV: GVW

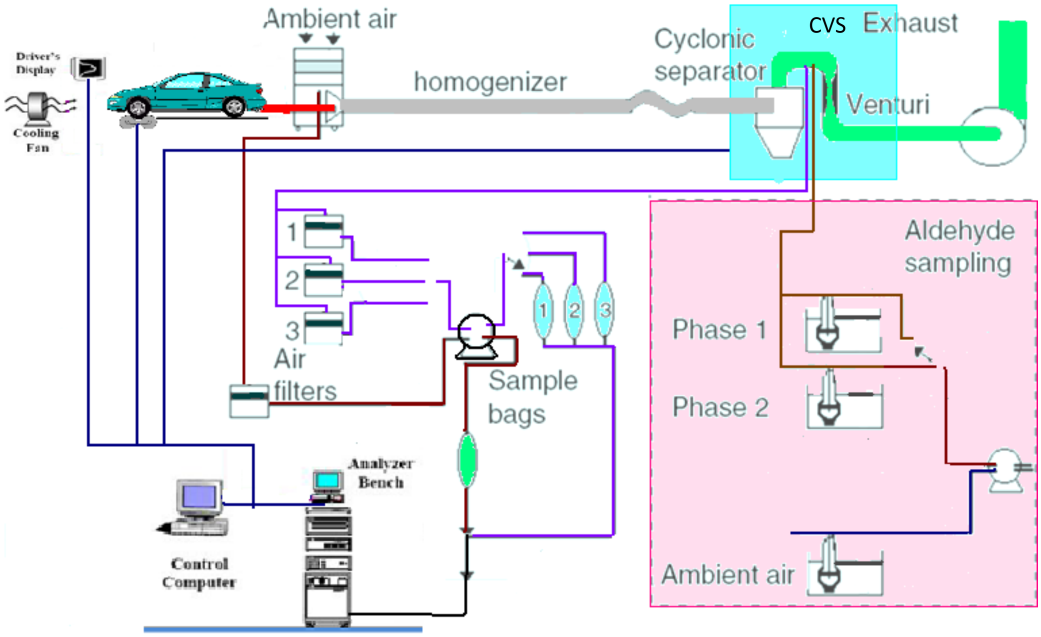
The coast down equation for the dynamometer tests was used as per the available data with ICAT.

3.3 Test procedure and equipment details

Equipment details for mass emission testing are given at Annexure VIII. Mass Emission Test Procedure for Methane emissions are given at Annexure V.

Emission cycles were a sequence of speed and load conditions performed on an engine dynamometer. Emissions measured on vehicle (chassis) dynamometers were expressed in grams of pollutant per unit of travelled distance, expressed in g/km. In a transient cycle such as the one used for the chassis dynamometer testing, the vehicle followed a prescribed driving pattern, which included accelerations, decelerations, changes of speed and load, etc. The final test results were obtained by analyzing exhaust gas samples collected in polyurethane bags over the duration of the cycle. In order to determine the emission of a vehicle, the vehicle was tested in ICAT’s emissions test cell, under conditions which accurately simulated the driving cycle as applicable to the vehicle category under test.

Each test vehicle was mounted with its drive wheels on the rollers of the test bed whose rotational resistance was adjusted to simulate friction and aerodynamic drag. Inertial masses were added to simulate the weight of the test vehicle as per the category of the vehicle. A variable speed, vehicle cooling blower mounted at a short distance in front of the vehicle provided the necessary cooling. The test vehicle was then soaked (i.e., cooled to bring it to ambient temperature and conditions and maintained in that state till the commencement of the test) on the chassis dynamometer to get the vehicle and the engine conditions in line with the test cell ambient conditions.



CVS –Constant Volume Sampler

Figure 3.1 Schematic Test Cell Layout

(*The used test procedures in this project for variable speed, vehicle cooling mechanism, etc are as per the standard method followed in CMVR-126 and TAP 115/116, part-II of chapter 1, 2, 3, 4. It may be noted that these procedures are followed in India for any type approval and homologating testing by govt. agencies.)

The ambient air flow rate for diluting exhaust is mentioned below:

1. Two wheelers ------- 2 m^3/min
2. Three wheelers ------- 3 m^3/min
3. Four wheelers ------- 8 m^3/min

Before starting the test, the chassis dynamometer was warmed up for 30 minutes with the vehicle mounted on the chassis dynamometer and the engine in OFF condition. After the warm up chassis dynamometer was calibrated to compensate for frictional losses and then the test was performed on the vehicles. A highly skilled driver was enlisted to drive the test vehicles on the chassis dynamometer. The driver strictly followed the test cycle by maintaining the speed, changing the gears and accelerating and decelerating the vehicle in tandem with the driving instructions displayed on the monitor.

After ensuring the calibration of the test cell, the driver started the engine and remained in the idling condition for a period prescribed as per the applicable regulatory test procedure depending upon the vintage and category of the vehicle. Thereafter, the exhaust gases produced by the test vehicle were diluted with fresh air using a DT (dilution tunnel) and a critical flow venturi-type CVS (constant volume sampler). For gaseous emission measurement, a constant proportion of the diluted exhaust gas was extracted for collection in one sample bag. The pollutant concentration in the sample bag at the end of the test corresponded exactly with the mean concentration in the total quantity of fresh air/exhaust mixture that was extracted. As the total volume of the fresh air/mixture could be defined, the pollutant concentrations were used as the basis for calculating the pollutant masses produced during the vehicles, the diluted exhaust gas was measured continuously by using a heated FID THC analyzer. The exhaust gas emission analyzers were calibrated before the gas analysis. The gas analysis of each sample bag was done immediately after each test. The gases in the sampling bag was analyzed for concentrations of CO (carbon monoxide), NOx (nitrogen oxides), THC (gasoline) and CO_2 (carbon dioxide), CH_4 (Methane) and the emissions were expressed in g/km. Diluted exhaust gas and ambient air was collected in individual cartridges for analyzing carbonyl emission from vehicular exhaust. The time duration for the cartridge collection is same as like bag collection time of regulated emission (CO, NOx &HC). After completion of cartridge collection, was stored in a temperature of 4 ^{0}C till HPLC analysis, as per SOP MLD 104 (Annexure VI).

3.3.1. Test Conditions

During the test, the test cell temperature was maintained between 293 K and 303 K (20 and 30°C). The absolute humidity (H) of either the air in the test cell or the intake air of the engine was maintained between 5.5 and 12.2 g H_2O/kg dry air. For post 2000 vehicles, the soak period was maintained for a minimum of 6 hours and up to a maximum of 30 hours at 20-30 degree Celsius.

3.3.1.1 Mass emission Calculations

The mass emission of pollutants was calculated by means of the following equation:

$$M_i = \frac{V_{mix} \times Q_i \times k_H \times C_i \times 10^{-6}}{d}$$

M_i = Mass emission of the pollutant in g/km

V_{mix} = Volume of the diluted exhaust gas expressed in m^3 and corrected to standard conditions 293 K and 101.33 kPa

Q_i = Density of the pollutant in kg/m^3 at normal temp & pressure (293 K and 101.33 kPa)

k_H = Humidity correction factor used for the calculation of the mass emission of oxides of nitrogen. There is no humidity correction factor for HC, CO and CH_4.

C_i = Concentration of the pollutant in the diluted exhaust gas expressed in ppm and corrected by the amount of the pollutant contained in the dilution air

d = Distance covered in km

3.3.2 Exhaust methane gas measurement:

Flame Ionization Detector – Low Cold Gas chromatography (FID 4000-LCG)

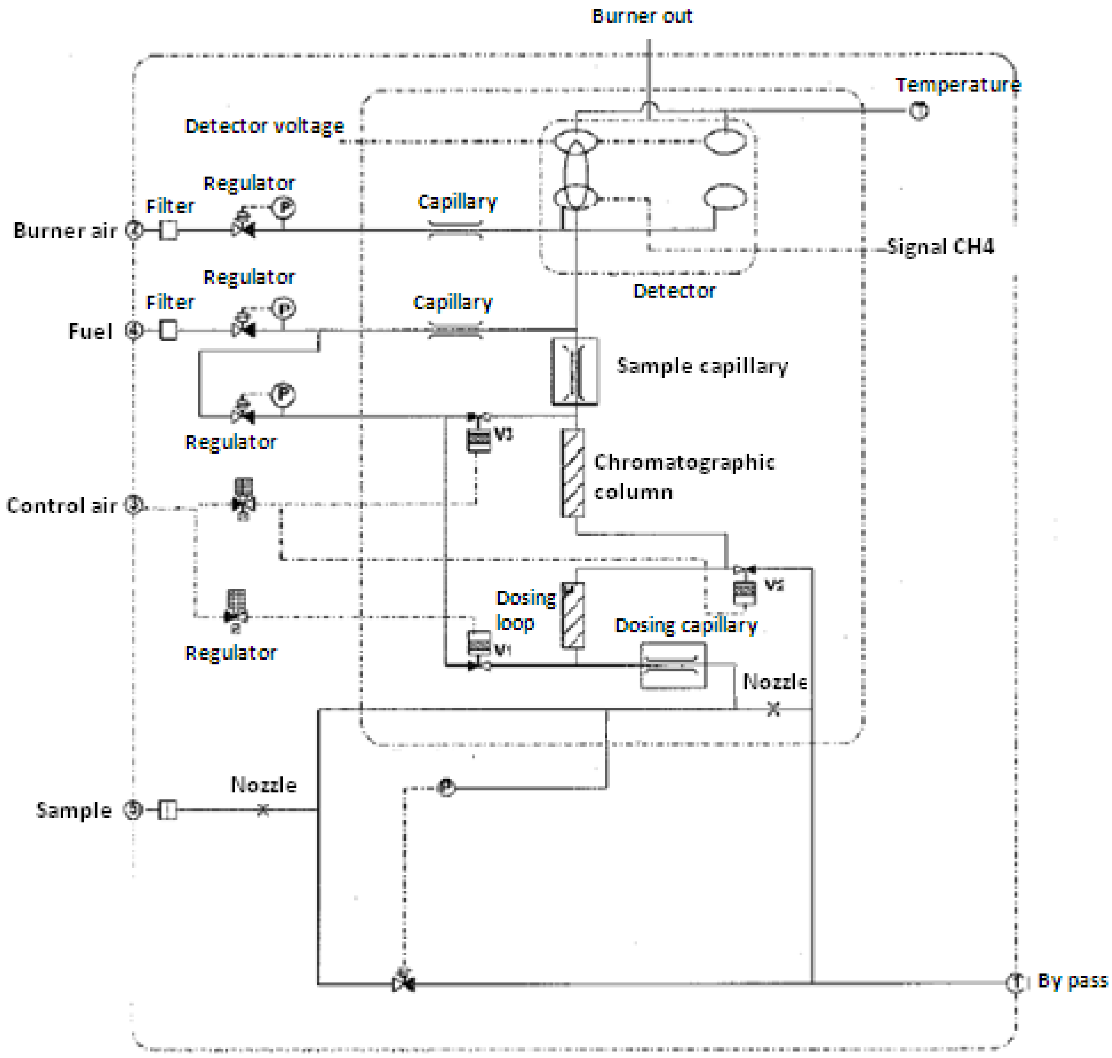


Figure 3.2 Flow diagram of FID 4000 LCG measurement system

3.3.2.1 Measuring system (FID 4000):

An Emission measurement system (AMA 4000) has been developed, designed and manufactured in accordance with the EU guidelines 89/336/EWG (EMC) and 93/68/EWG (low voltage)

The following harmonization standards have been used:

DIN EN 983	**:**	Pneumatic safety
DIN EN 55 011 Class A	**:**	Limits and measuring processes for radio interface of industrial, scientific and medical high frequency equipment (ISM equipment)
DIN EN 61000-6-2	**:**	Electromagnetic compatibility (EMC), basic technical standard, interface resistance
DIN EN 61010-1	**:**	Safety requirements for electrical equipment for

		measurement, control and laboratory use
BGV A3	**:**	Electric systems and operating material

Table 3.3 Description of FID 4000 LCG equipment

Parts	Description	Operation
Burner air	Synthetic air	Assisting for burning
Fuel	Hydroge:Helium (60:40)	Burning fuel to burn CH_4
Control air	Compressed air	To operate regulating valves
Dosing capillary		Sample gas pass through small passage
Dosing loop		Acts like filter
Detector voltage		To ignite the Fuel+Burn air+CH_4

3.3.2.2 Method of Operation:

IN FID 4000 LCG is used to characterize the methane (CH_4) gas from vehicle exhaust. The sample gas is passing through filter, nozzle, Dosing capillary, Dosing loop and Chromatographic column. Dosing capillary is a passage with small cross sectional area which passes uniform flow of gas. After Dosing capillary, the gas is send to Dosing loop where filtering operation take place. Then filtered sample gas is passing through Chromatographic column. In chromatographic column segregate the CH_4 from sample gas. Segregated CH_4 is mixed with fuel (Hydrogen (60%) + Helium (40%)) and burn air (Synthetic air). The mix is drive into detector area. In detector area, the gas mix is burnt out with use of spark from detector voltage. The burnt gas produces ions and it attracted by anode. Ions are converted into current and it amplified. After amplification it is digitalized.

3.3.3. High-performance liquid chromatography analysis

High-performance liquid chromatography (or High pressure liquid chromatography, HPLC) is a form of column chromatography used frequently in biochemistry and analytical chemistry to separate, identify and quantify compounds. HPLC utilizes a column that holds chromatographic packing material (stationary phase), a pump that moves the mobile phase(s) through the column, and a detector that shows the retention times of the molecules. Retention time varies depending on the interactions between the stationary phase, the molecules being analyzed, and the solvent(s) used.

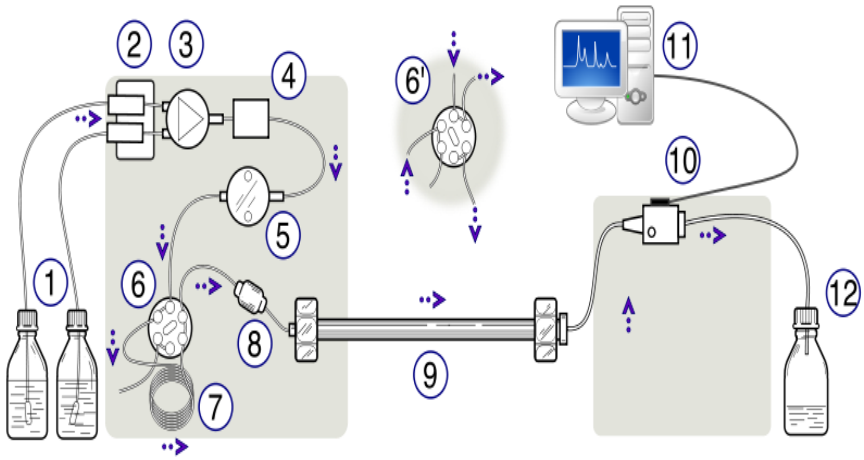


Figure 3.3 Schematic representation of an HPLC unit

(1) Solvent reservoirs,

(2) Solvent degasser,

(3) Gradient valve,

(4) Mixing vessel for delivery of the mobile phase,

(5) High-pressure pump,

(6) Switching valve in "inject position",

(6') Switching valve in "load position",

(7) Sample injection loop,

(8) Pre-column (guard column),

(9) Analytical column,

(10) Detector (i.e. IR, UV),

(11) Data acquisition, and

(12) Waste or fraction collector.

3.3.3.1 Theory of operation

The sample to be analyzed is introduced in small volume to the stream of mobile phase. The analyte's motion through the column is slowed by specific chemical or physical interactions with the stationary phase as it traverses (passes through) the length of the column. The amount of retardation depends on the nature of the analyte, stationary phase and mobile phase composition. The time at which a specific analyte elutes (comes out of the end of the column) is called the retention time; the retention time under particular conditions is considered a reasonably unique identifying characteristic of a given analyte. The use of smaller particle size column packing (which creates higher backpressure) increases the linear velocity (speed) giving the components less time to diffuse within the column, leading to improved resolution in the resulting chromatogram. Common solvents used include any miscible combination of water or various organic liquids (the most common are methanol and Acetonitrile). Water may contain buffers or salts to assist in the separation of the analyte components, or compounds such as Trifluoroacetic Acid which acts as an ion pairing agent.

A further refinement to HPLC has been made to vary the mobile phase composition during the analysis; this is known as gradient elution. A normal gradient for reversed phase chromatography might start at 5% methanol and progress linearly to 50% methanol over 25 minutes; the gradient chosen depends on how hydrophobic the analyte is. The gradient separates the analyte mixtures as a function of the affinity of the analyte for the current mobile phase composition relative to the stationary phase. This partitioning process is similar to that which occurs during a liquid-liquid extraction but is continuous, not step-wise. In this example, using a water/methanol gradient, the more hydrophobic components will elute (come off the column) when the mobile phase consists mostly of methanol (giving a relatively hydrophobic mobile phase). The more hydrophilic compounds will elute under conditions of relatively low methanol/high water.

The choice of solvents, additives and gradient depend on the nature of the stationary phase and the analyte. Often a series of tests are performed on the analyte and a number of trial runs may be processed in order to find the HPLC method which gives the best separation of peaks.

3.3.3.2 Quality Control of HPLC analysis

The analysis of carbonyl compound by HPLC analysis was performed by the international standard method CARB, SOP MLD-104. The details of the method are given at Annexure VI.

A. Extraction Efficiency:

As per standard method, each cartridge contains an absorbing compound (2, 4-DNPH) which complexes with the carbonyl compounds to form their Dinitro-phenylhydrazone derivatives (called carbonyl-DNPH). The cartridges are then extracted with 5.0 milliliters (mL) HPLC grade Acetonitrile. (Tejada, 1986b).

B. Calibration regression coefficient:

The instrument was calibrated and regression coefficient (r^2) for each component (13 numbers) was found more than 0.99, which shows the evidence of standardized and calibrated the instrument conditions. Regression coefficient of different carbonyl components are given in table 3.4.

Table 3.4 Regression coefficient of different carbonyl components

Component Name	Regression Coefficient (r^2)
Formaldehyde	0.99
Acetaldehyde	0.99
Acrolin	0.99
Actone	0.99
Propionaldehyde	0.99
Crotonaldehyde	0.99
Methacrolein	0.99
Methyl ethyl ketone	0.99
Valeraldehyde	0.99
Butyraldehyde	0.99
Benzaldehyde	0.99
M-tolunaldehyde	0.99
Hexanal	0.99

C. Method of Detection Limit (MDL)

This is based on the standard concentration limit, lower than this limit of a sample cannot be detected/ analyzed by the HPLC. This value is also term as LOD (limit of detection limit). As per SOP-104, the limit should be lower than 0.0075 µg/ml. In our standard method, the LOD values were found lower than this standard limit, which shows that the instrument is in perfect. Minimum detection limit of various components are given in table 3.5.

Table 3.5 Minimum detection limit of various components

Component Name	LOD	Maximum Std Limit
Formaldehyde	0.00271	0.0075
Acetaldehyde	0.00577	
Acrolin	0.00591	
Actone	0.00525	
Propionaldehyde	0.00436	
Crotonaldehyde	0.00602	
Methacrolein	0.00319	
Methyl ethyl ketone	0.00487	
Valeraldehyde	0.00486	
Butyraldehyde	0.00648	
Benzaldehyde	0.00569	
M-tolunaldehyde	0.00402	
Hexanal	0.00425	

All the data represented in the above tables are showing the quality control analysis of carbonyl components for HPLC system.

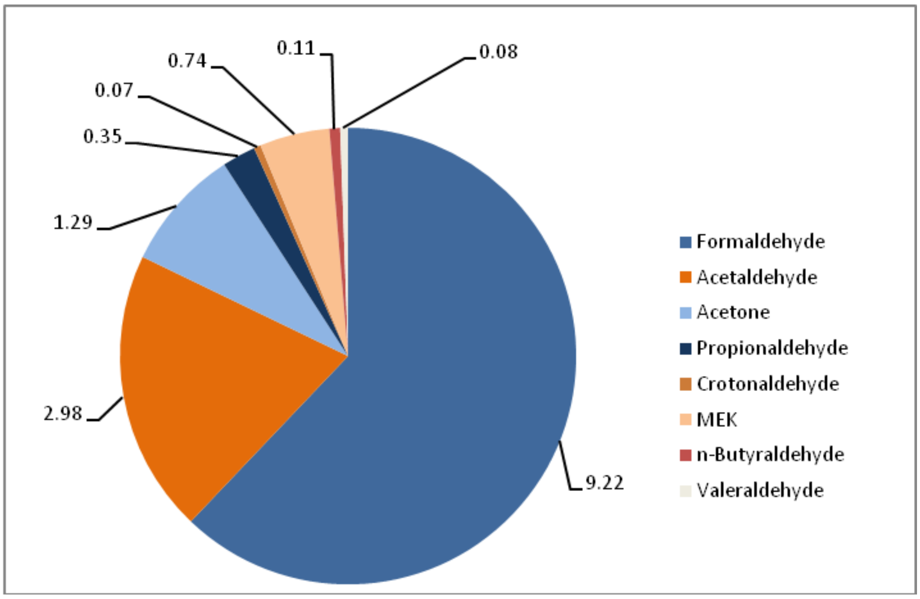
4. RESULTS

This chapter gives the details of Aldehyde, Ketone and Methane emission results from various fuel (BS II Petrol, BS III Petrol, E5+BS III Petrol, BS II Diesel, BSIII Diesel, B10+BS III Diesel, CNG and LPG) engines based on the vehicle categories as discussed in Methodology.

Carbonyl (aldehyde and ketone) emissions from two wheeler, three wheeler and four wheeler passenger car in "µg/km" for each of three vehicles per vehicle category and fuel used specified in section 4.1 and the same way methane emission were specified in section 4.2. Aldehyde, ketone and methane emissions from Light commercial vehicle and heavy commercial vehicle/engine categories also quantified in terms of "mg/kW hr" and it has mentioned in section 4.1 and 4.2 respectively. Summary of average carbonyl emission from two wheeler category with BS II Petrol, BS III Petrol and BS III Petrol+E5 are given in table 4.1. Summary of other category with respect to fuels are mentioned in Annexure IV.

4.1 Carbonyl emission (2W, 3W, 4W, LCV & HCV)

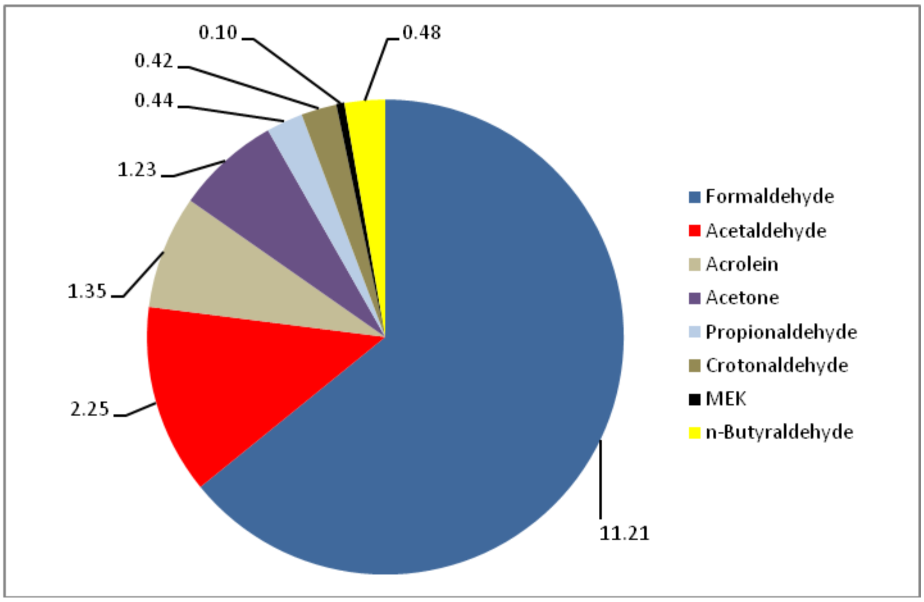
4.1.1 Two wheelers



* MEK: Methyl Ethyl Ketone

Figure 4.1 Carbonyl emissions from BS II Petrol fueled two wheeler (µg/km)

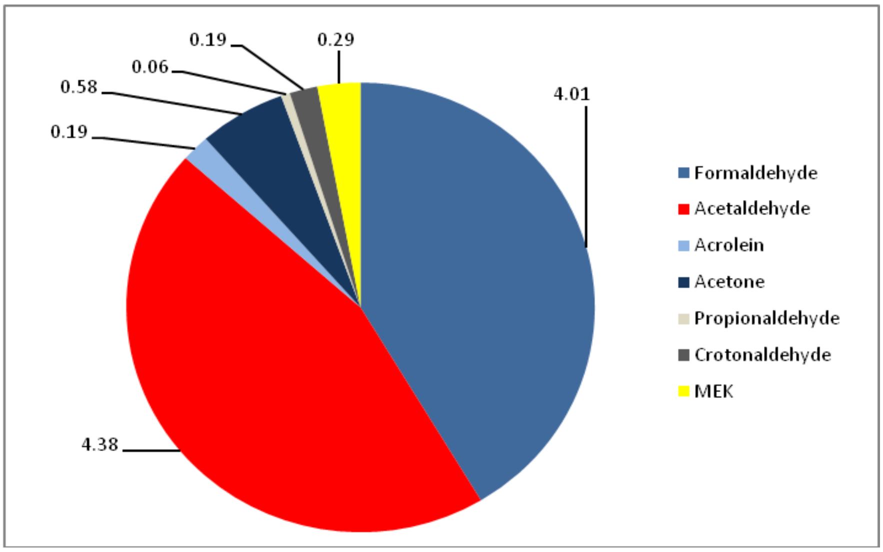
The above chart shows the carbonyl emissions from two wheeler vehicles run by BS II Petrol. Formaldehyde is the major aldehyde from BS II Petrol which amounts to 62.1% of the total carbonyl emission (14.84 µg/km). Other major Aldehydes are acetaldehyde and acetone from BS II Petrol fueled vehicle.



* MEK: Methyl Ethyl Ketone

Figure 4.2 Carbonyl emissions from BS III Petrol fueled two wheeler (µg/km)

The above chart shows the carbonyl emissions from two wheeler vehicle run by BS III Petrol. Formaldehyde is the major aldehyde from BS III Petrol which amounts to 64% of the total carbonyl emission (17.49 µg/km). Other major Aldehydes are acetaldehyde, Acrolein and acetone from BS III Petrol fueled vehicle.



* MEK: Methyl Ethyl Ketone

Figure 4.3 Carbonyl emissions from BS III Petrol + E5 fueled two wheeler (µg/km)

The above chart shows the carbonyl emissions from two wheelers which are run by 5% ethanol blended BS III Petrol. Acetaldehyde & formaldehyde accounts for 45% and 41.3%, respectively of the total aldehyde emission (9.72 µg/km). Other aldehydes emission includes acrolein, methyl ethyl ketone and acetone from 5% ethanol blended BS III Petrol fueled vehicle.

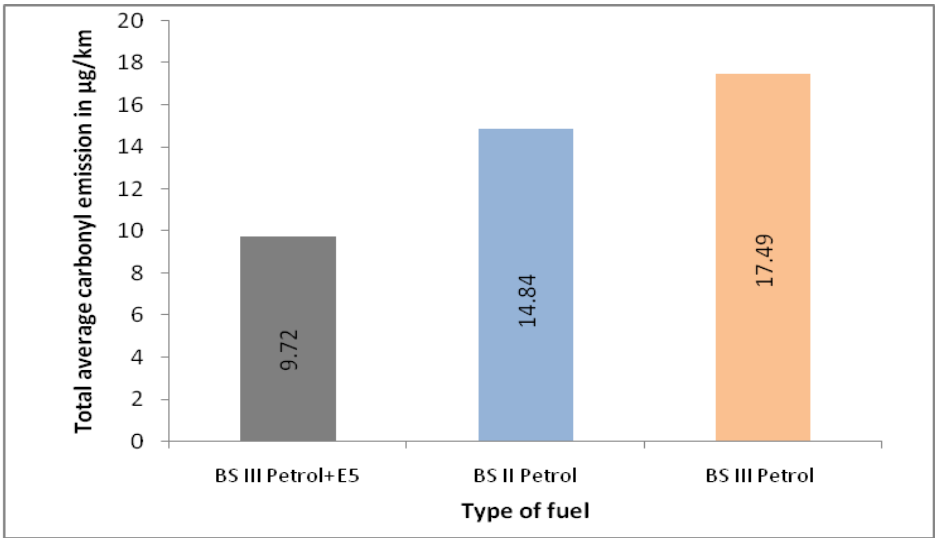


Figure 4.4 Comparison of Total carbonyl compound emissions using various fuels in two wheeler category

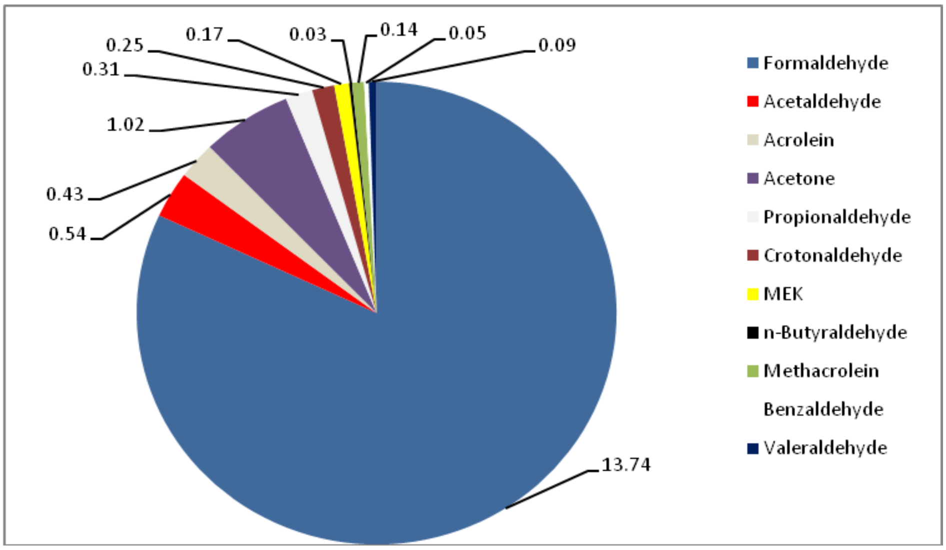
The graph above gives the comparison of total aldehyde emission from two wheelers which are run by BS II Petrol, BS III petrol and BS III Petrol+E5 fuels. BS III Petrol fueled two wheeler vehicles emit 15% and 47% more total carbonyl emission than BS II Petrol and BS III Petrol+E5 fueled vehicles respectively.

Table 4.1 Results of Carbonyl emissions from two wheeler vehicle Category

	Fuel used					
	BS II Petrol		**BS III Petrol**		**BS III Petrol (Ref) + E5**	
Name of the carbonyl compound emission	**Range** µg/km	**Mean** µg/km	**Range** µg/km	**Mean** µg/km	**Range** µg/km	**Mean** µg/km
Formaldehyde	7.88-10.09	9.22	6.31-15.61	11.21	3.61-4.79	4.01
Acetaldehyde	2.20-3.87	2.98	1.33-3.48	2.25	3.77-4.91	4.38
Acrolein	Nd	Nd	0-2.29	1.35	0-0.56	0.19
Acetone	0.63-1.67	1.29	0.92-1.73	1.23	0.18-0.81	0.58
Propionaldehyde	0.25-0.44	0.35	0.06-0.23	0.44	0-18	0.06
Crotonaldehyde	0-0.22	0.07	0-0.15	0.42	0-0.36	0.19
MEK	0.51-0.87	0.74	0-024	0.10	0.26-0.34	0.29
n-Butyraldehyde	0.08-0.14	0.11	0-0.16	0.48	Nd	Nd
Methacrolein	Nd	Nd	Nd	Nd	Nd	Nd
Benzaldehyde	Nd	Nd	Nd	Nd	Nd	Nd
Valeraldehyde	0-0.25	0.08	Nd	Nd	Nd	Nd
m-Tolualdehyde	Nd	Nd	Nd	Nd	Nd	Nd
Hexanal	Nd	Nd	Nd	Nd	Nd	Nd
Total Avg emission	**14.84 µg/km**		**17.49 µg/km**		**9.72 µg/km**	

Nd-Not Detectable

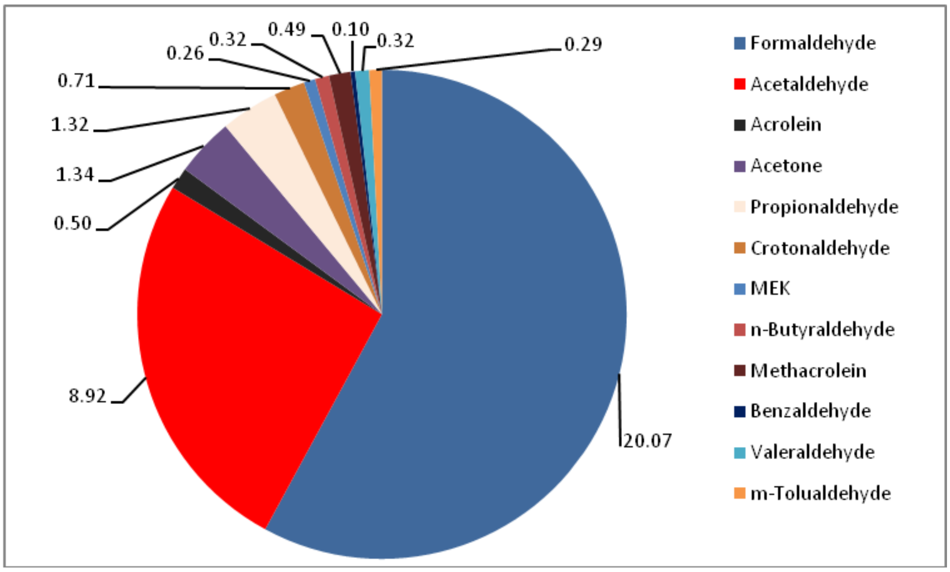
4.1.2 Three wheelers



* MEK: Methyl Ethyl Ketone

Figure 4.5 Carbonyl emissions from BS II Diesel fueled three wheeler (µg/km)

The above chart shows the carbonyl emissions from three wheelers run by BS II Diesel. Formaldehyde is the major aldehyde from BS II Diesel which amounts to 81.2% of the total carbonyl emission (16.77 µg/km). Other major aldehydes are acetaldehyde, acrolein and acetone from BS II Diesel fueled vehicle.



* MEK: Methyl Ethyl Ketone

Figure 4.6 Carbonyl emissions from BS III Diesel fueled three wheeler (µg/km)

The above chart shows the carbonyl emissions from three wheeler vehicles run by BS III Diesel. Formaldehyde is the major aldehyde from BS III Diesel which amounts to 57.9% of the total carbonyl emission (34.65 µg/km). Other major Aldehydes are Acetaldehyde, Acetone and Propionaldehyde from BS III Diesel fueled vehicle.

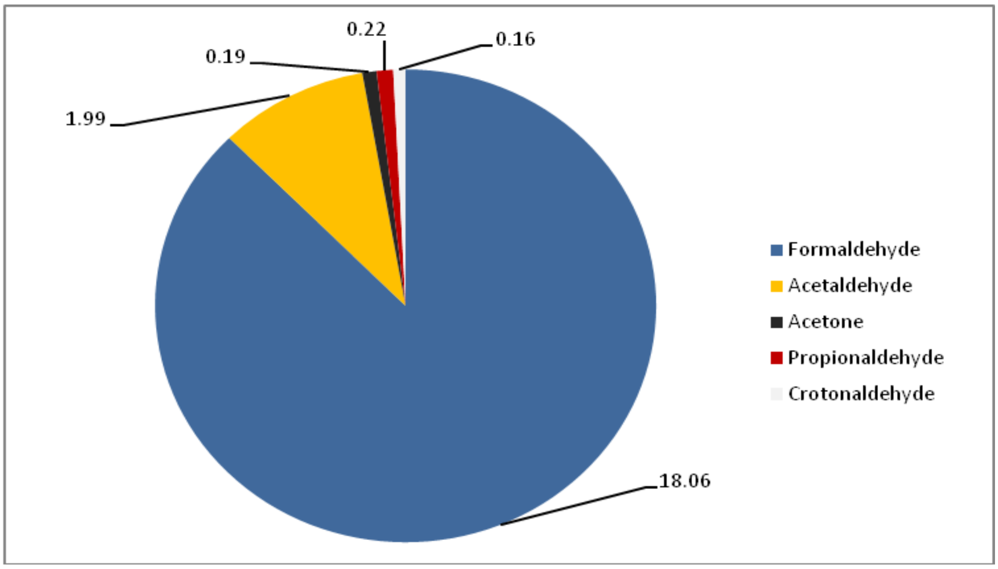


Figure 4.7 Carbonyl emissions from CNG fueled three wheeler (µg/km)

The above chart shows the carbonyl emissions from three wheeler vehicles run by Compressed Natural Gas (CNG). Formaldehyde is the major aldehyde from CNG which amounts to 88% of the total carbonyl emission (20.62 µg/km). Other major aldehyde is acetaldehyde from CNG fueled vehicle.

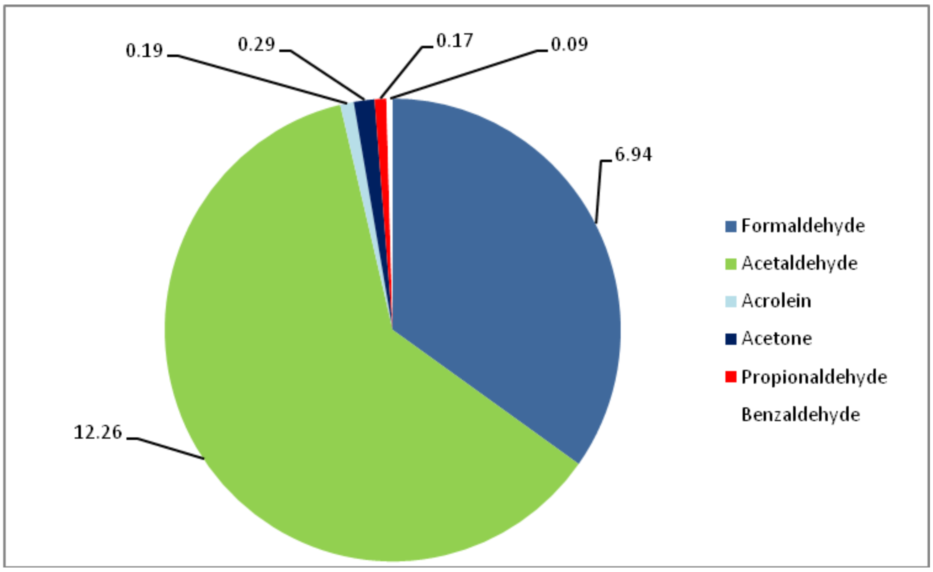
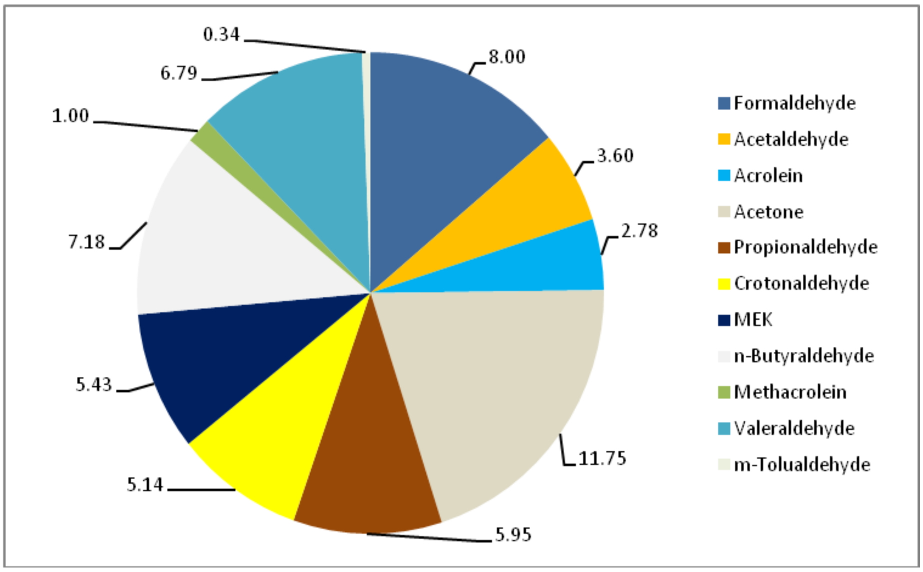


Figure 4.8 Carbonyl emissions from BS III Diesel+B10 fueled three wheeler (µg/km)

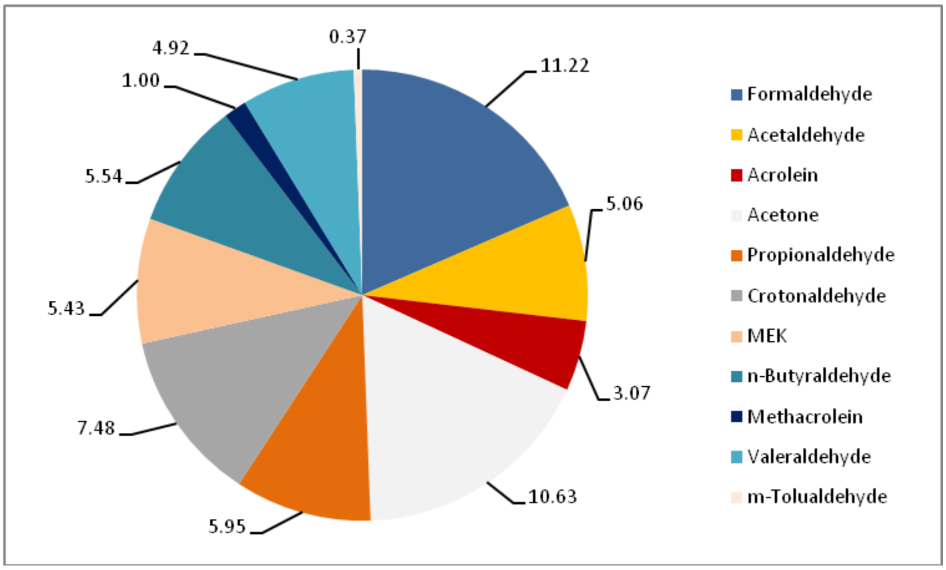
The above chart shows the carbonyl emissions from three wheeler vehicles run by 10% biodiesel blended with BS III Diesel. Acetaldehyde is the major aldehyde from BS III Diesel+B10 which amounts to 61% of the total carbonyl emission (19.94 µg/km). Other major aldehyde is formaldehyde from BS III Diesel+B10 fueled vehicle.



* MEK: Methyl Ethyl Ketone

Figure 4.9 Carbonyl emissions from BS II Petrol fueled Three wheeler (µg/km)

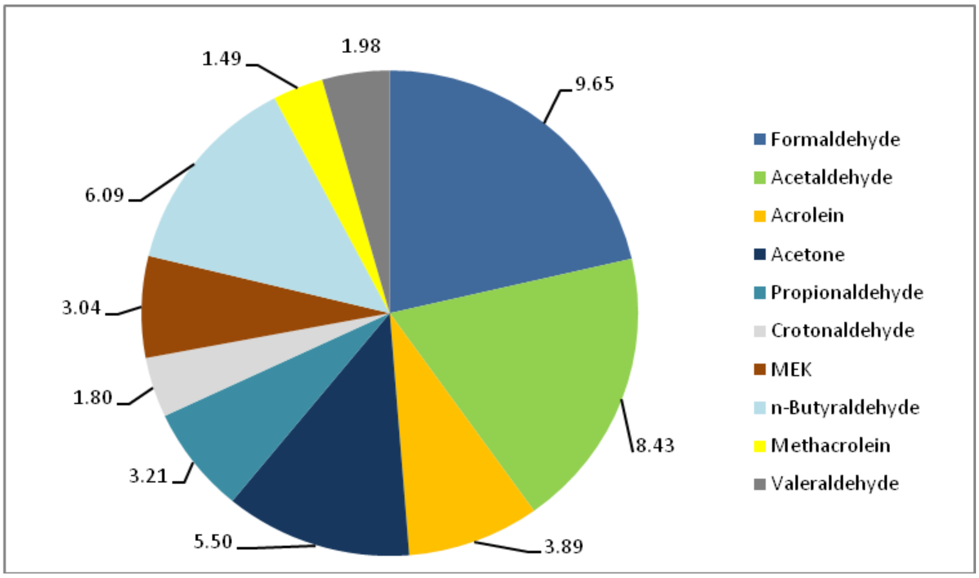
The above chart shows the carbonyl emissions from three wheeler runs by BS II Petrol. Acetone is the major aldehyde from BS II Petrol which amounts to 20.3% of the total carbonyl emission (57.96µg/km). Other major aldehydes are Formaldehyde, Acetaldehyde, Acrolein, Propionaldehyde, n-Butyraldehyde, Valaraldehyde and Acetone from BS III Petrol fueled vehicle.



* MEK: Methyl Ethyl Ketone

Figure 4.10 Carbonyl emissions from BS III Petrol fueled three wheeler (µg/km)

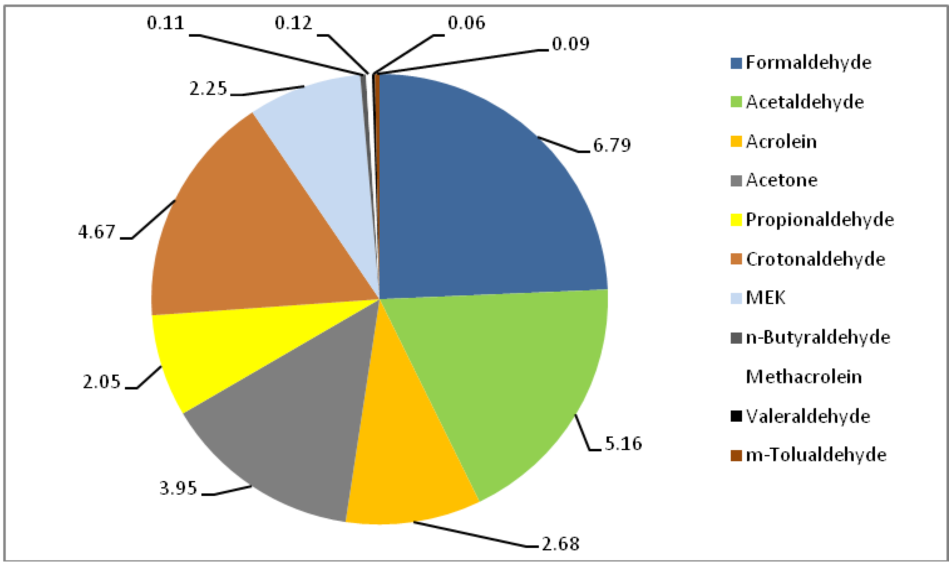
The above chart shows the carbonyl emissions from three wheeler run by BS III Petrol. Formaldehyde and acetone are the major aldehydes from BS III Petrol which amounts to 18.5% and 17.5% of the total carbonyl emission (60.66 µg/km). Other major aldehydes are formaldehyde, acetaldehyde, Acrolein, Propionaldehyde, Crotonaldehyde, Methyl Ethyl Ketone, n-Butyraldehyde, Valaraldehyde and Acetone from BS III Petrol fueled vehicle.



* MEK: Methyl Ethyl Ketone

Figure 4.11 Carbonyl emissions from BS III Petrol+E5 fueled three wheeler (µg/km)

The above chart shows the carbonyl emissions from three wheeler vehicles run by 5% ethanol blended BS III Petrol. Formaldehyde and acetaldehyde are the major aldehydes from BS III Petrol+E5 which are 21.4% and 18.7% of the total carbonyl emission (45.08 µg/km). Other major aldehydes are acetone and n-butyraldehyde from BS III Petrol+E5 fueled vehicle.



* MEK: Methyl Ethyl Ketone

Figure 4.12 Carbonyl emissions from LPG fueled three wheeler (µg/km)

The above chart shows the carbonyl emissions from three wheelers run by Liquefied petroleum gas (LPG). Formaldehyde and acetaldehyde are the major aldehydes from LPG which amounts to 24.3% and 18.5% of the total carbonyl emission (27.93 µg/km). Other major aldehydes are acetone and Crotonaldehyde from LPG fueled vehicle.

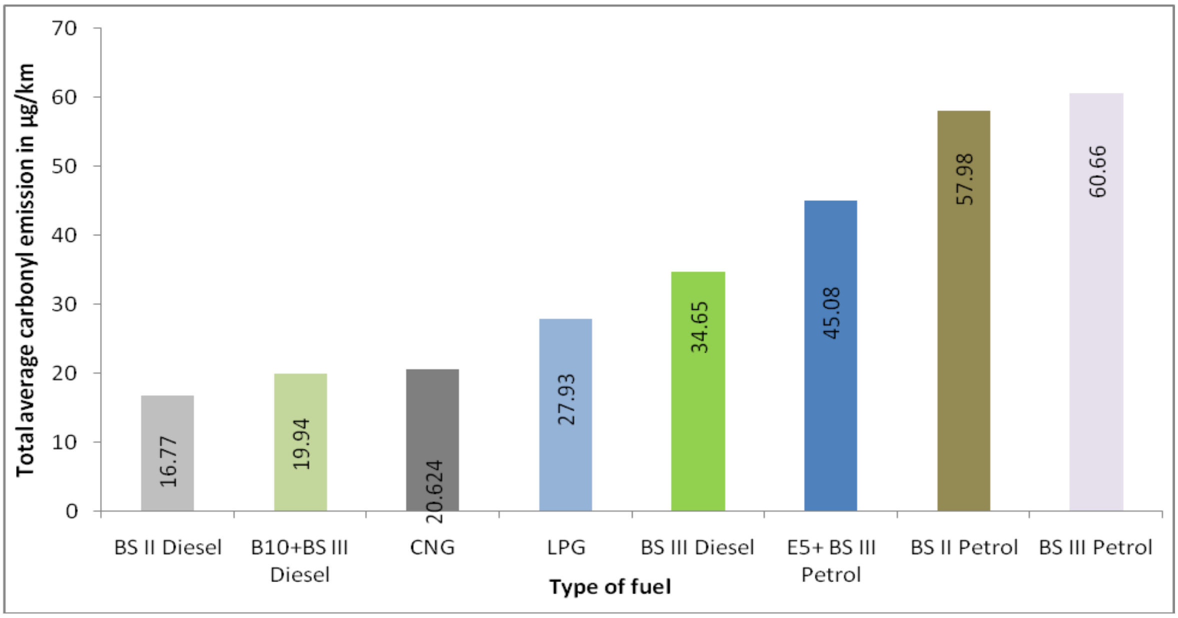


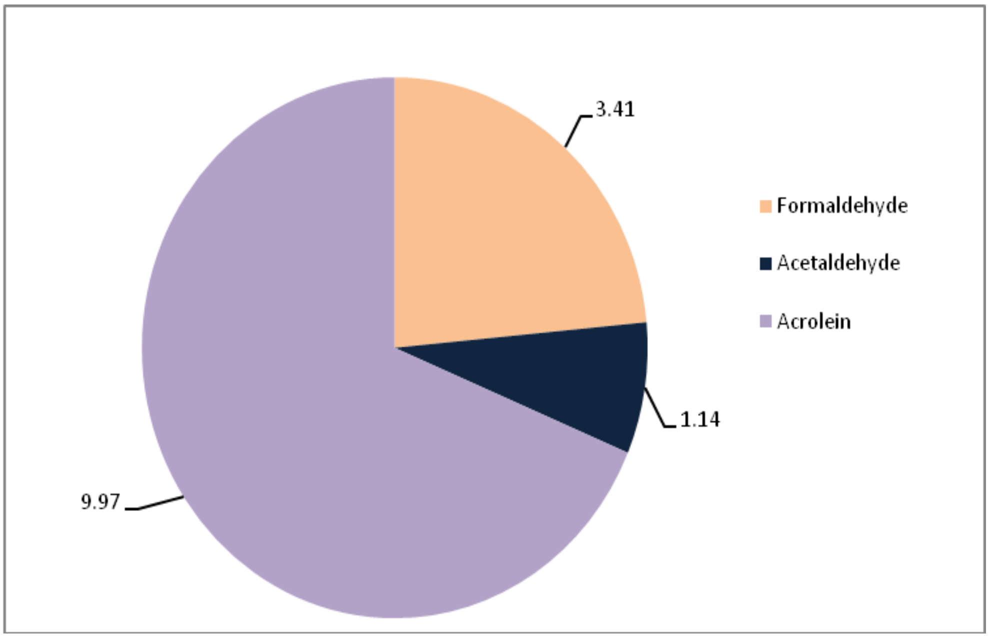
Figure 4.13 Comparison of Average total carbonyl compound emissions using various fuels in three wheeler category

The graph above gives the comparison of total carbonyl emissions from three wheeler passenger car runs by BS II Petrol, BS III Petrol, 5% ethanol blend BS III Petrol, Liquefied Petroleum Gas, BS II Diesel, BS III Diesel, BS III Diesel+B10 and CNG. The total carbonyl emission from BS III Petrol fueled vehicle accounts 54%, 72%, 43%, 67% and 66% more total carbonyl emission than LPG, BS II Diesel, BS III Diesel, BS III Diesel+B10 and Compressed natural gas fuels respectively.

The result shows that the carbonyl emissions from 2, 3-wheeler with BS III petrol is higher than the petrol blended ethanol fuel. The reason behind this can be described as the presence of oxygenated molecule in ethanol fuel helps for complete combustion inside the cylinder. This may be main cause for the less emission with blended ethanol with BS III petrol over normal petrol or blended diesel with biodiesel over reference diesel. (Magmusson et.al, 2002)

4.1.3 Four wheeler passenger cars

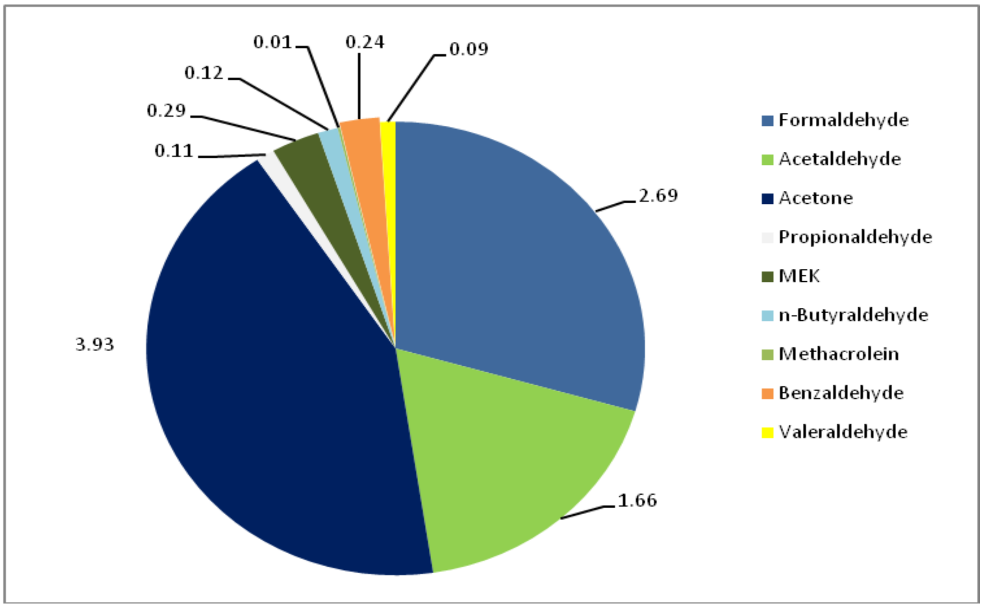
The individual composition of total average carbonyl emissions from BS II Petrol, BS III Petrol, BS III Petrol+E5, CNG, LPG, BS II Diesel, BS III Diesel, and BS III Diesel+ B10 fueled vehicles are graphically represented in Figures 4.14, 4.15, 4.16, 4.17, 4.18, 4.19, 4.20 and 4.21 respectively.



* MEK: Methyl Ethyl Ketone

Figure 4.14 Carbonyl emissions from BS II Petrol fueled in four wheeler passenger cars (µg/km)

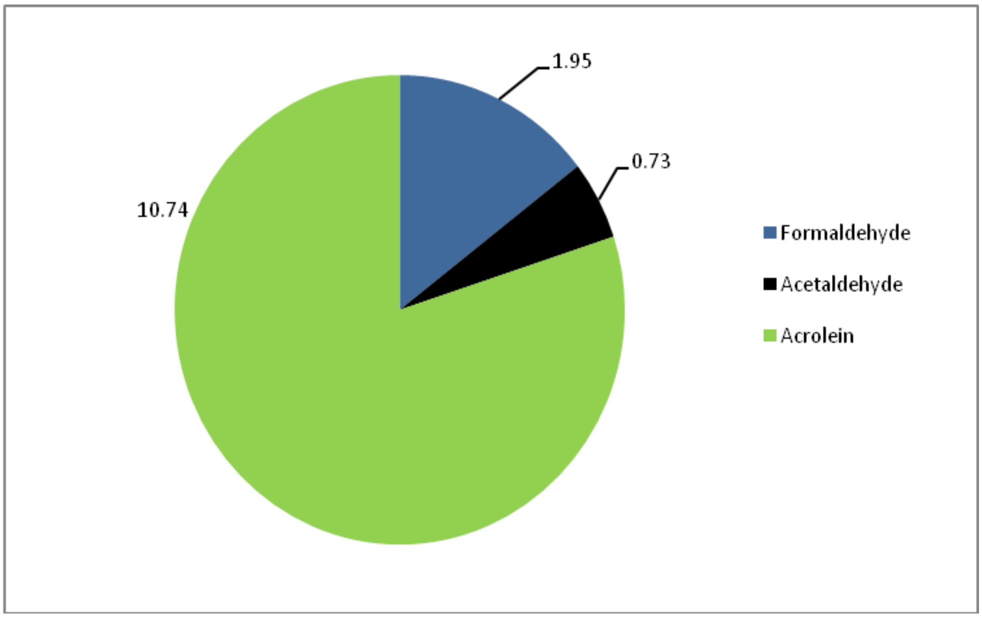
The above chart shows the carbonyl emissions from four wheeler passenger car run by BS II Petrol. Acrolein is the major aldehyde from BS II Petrol which amounts to 68.7% of the total carbonyl emission (14.52 µg/km). Other major Aldehydes are Formaldehyde and Acetaldehyde from BS II Petrol fueled vehicle.



* MEK: Methyl Ethyl Ketone

Figure 4.15 Carbonyl emissions from BS III Petrol fueled in four wheeler passenger cars (µg/km)

The above chart shows the carbonyl emissions from four wheeler passenger car run by BS III Petrol. Acetone is the major aldehyde from BS II Petrol which amounts to 43% of the total carbonyl emission (9.14 µg/km). Other major aldehydes are formaldehyde and acetaldehyde from BS III Petrol fueled vehicle.



* MEK: Methyl Ethyl Ketone

Figure 4.16 Carbonyl emissions from BS III Petrol+ E5 fueled in four wheeler passenger cars (µg/km)

The above chart shows the carbonyl emissions from four wheeler passenger car run by 5% ethanol blended BS III Petrol. Acrolein is the major aldehyde from BS III Petrol+E5 which amounts to 80% of the total carbonyl emission (13.41 µg/km). Other major aldehydes are formaldehyde and acetaldehyde from BS II Petrol fueled vehicle.

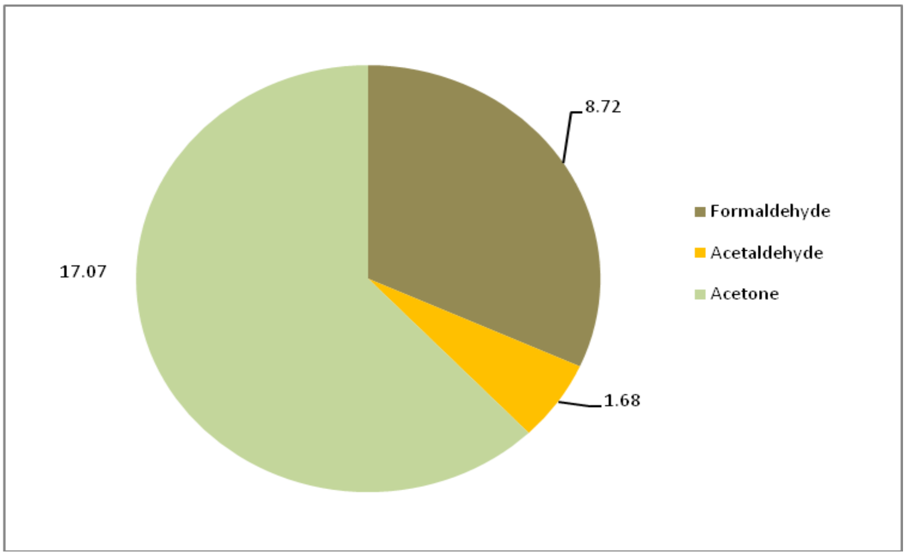
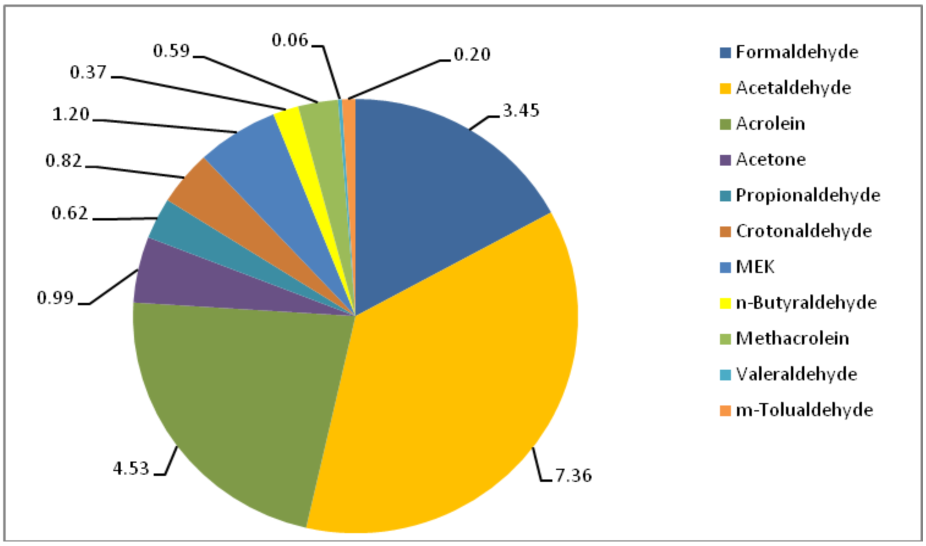


Figure 4.17 Carbonyl emissions from Compressed Natural Gas fueled in four wheeler passenger cars (µg/km)

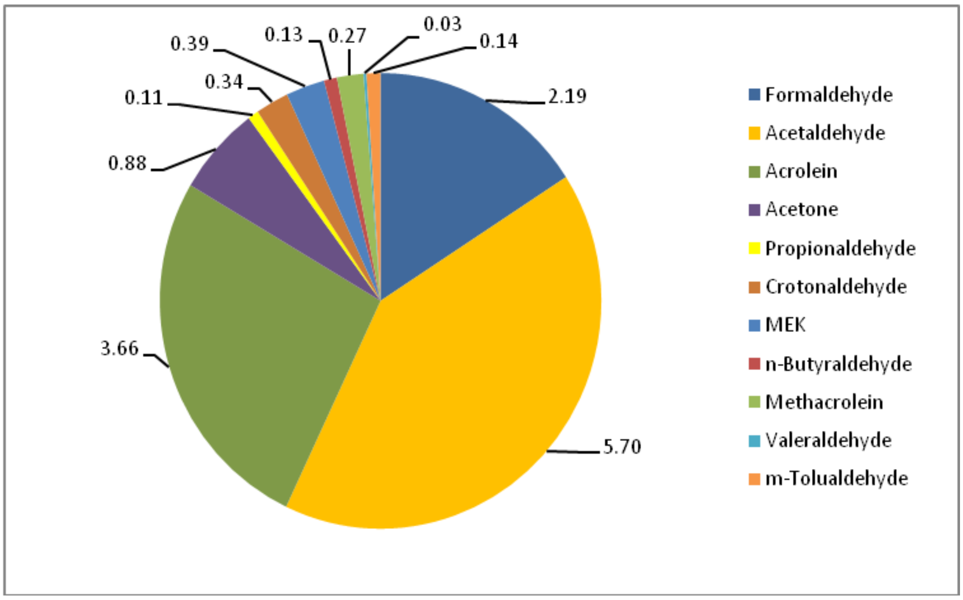
The above chart shows the carbonyl emissions from four wheeler passenger car run by CNG. Acetone is the major aldehyde from CNG which amounts to 62.2% of the total carbonyl emission (27.47 µg/km). Other major aldehydes are formaldehyde and acetaldehyde from BS II Petrol fueled vehicle.



* MEK: Methyl Ethyl Ketone

Figure 4.18 Carbonyl emissions from LPG fueled in four wheeler passenger cars (µg/km)

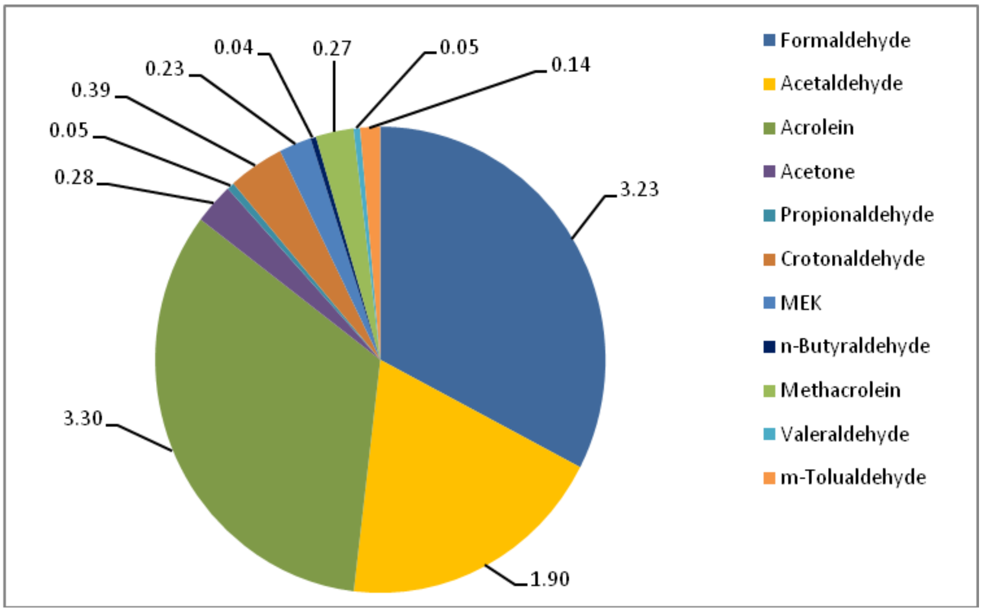
The above chart shows the carbonyl emissions from four wheeler passenger car run by Liquefied petroleum gas (LPG). Acetaldehyde is the major aldehyde from LPG which amounts to 36.5% of the total carbonyl emission (20.18 µg/km). Other major aldehydes are formaldehyde and acrolein from LPG fueled vehicle.



* MEK: Methyl Ethyl Ketone

Figure 4.19 Carbonyl emissions from BS II Diesel fueled in four wheeler passenger cars (µg/km)

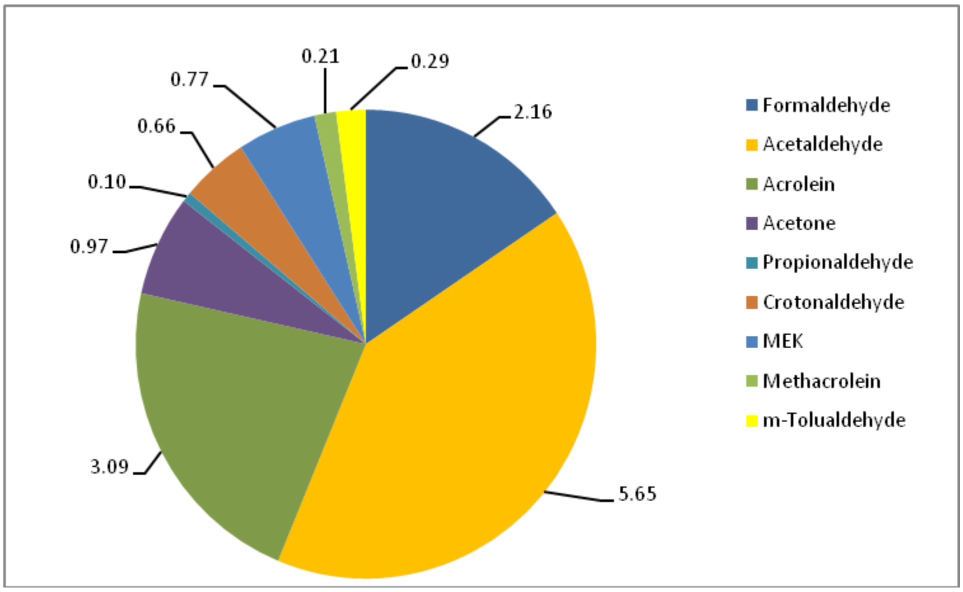
The above chart shows the carbonyl emissions from four wheeler passenger car run by BS II Diesel. Acetaldehyde is the major aldehyde from BS II Diesel which amounts to 41.2% of the total carbonyl emission (13.83 µg/km). Other major aldehydes are formaldehyde and acrolein from BS II Diesel fueled vehicle.



* MEK: Methyl Ethyl Ketone

Figure 4.20 Carbonyl emissions from BS III Diesel fueled four wheeler passenger cars (µg/km)

The above chart shows the carbonyl emissions from four wheeler passenger car run by BS III Diesel. Formaldehyde and acrolein are the major aldehydes from BS III Diesel which amounts to 33.4% and 32.6% of the total carbonyl emission (9.89 µg/km). Other major aldehyde is Acetaldehyde from BS III Diesel fueled vehicle.



* MEK: Methyl Ethyl Ketone

Figure 4.21 Carbonyl emissions from BS III Diesel +B10 fueled four wheeler passenger cars (µg/km)

The above chart shows the carbonyl emissions from four wheeler passenger car run by 10% biodiesel blend with BS III Diesel. Acetaldehyde is the major Aldehydes from BS III Diesel+B10 which amount to 40.7% of the total carbonyl emission (13.88 µg/km). Other major Aldehydes are Formaldehyde and acrolein from BS III Diesel+B10 fueled vehicle.

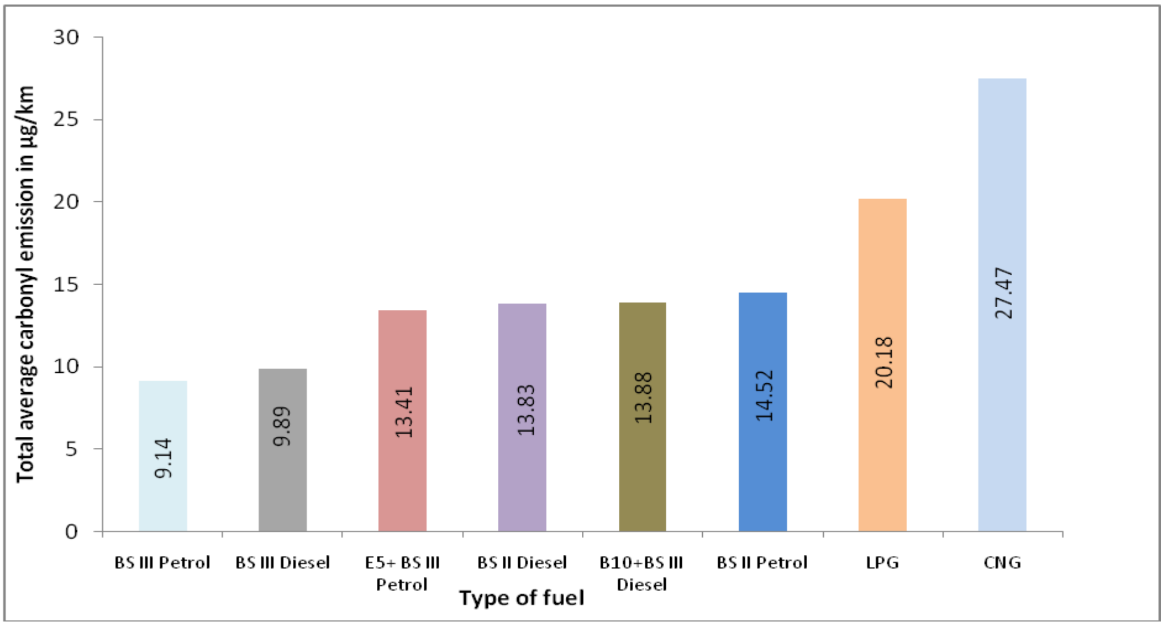


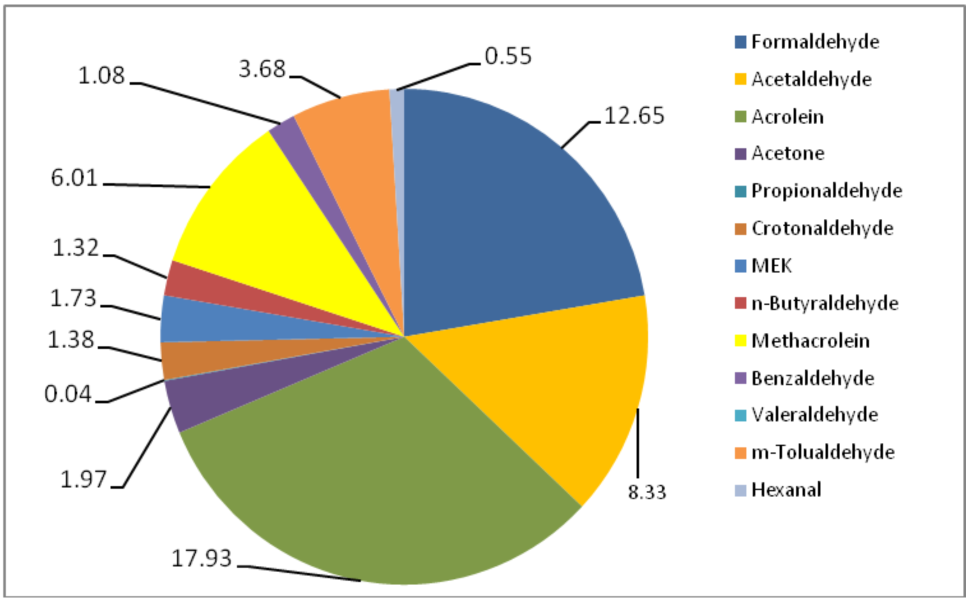
Figure 4.22 Comparison of Average total carbonyl compound emissions using various fuels in four wheeler passenger car category

The above graph gives the comparison of total carbonyl emissions from four wheeler passenger car runs by BS II Petrol, BS III Petrol, 5% ethanol blend BS III Petrol, Liquefied Petroleum Gas, BS II Diesel, BS III Diesel, BS III Diesel+B10 and Compressed Natural Gas (CNG). The total carbonyl emission from CNG fueled vehicle accounts 26.5%, 47%, 51%, 49.6% and 49.4% more total carbonyl emission than Liquefied petroleum gas, BS II Petrol, BS III Petrol+E5, BS II Diesel, BS III Diesel+B10 fuels respectively. Vehicles run by BS II Petrol and BS II Diesel emit minimum carbonyl emissions.

It is inferred from the results that emission from the 4-wheeler are showing reverse to the 2,3-wheeler vehicle. The probable cause for this emission aspect is may be due to the use of carbureted engine in 2 & 3 wheeler, where proper mixing (Quantity governing method) is not done. Where, in 4-wheeled vehicles multi point injection systems for SI engines and Common rail direct injection for CI engines (Quality governing method) were used for this experiment. That may be the probable reason for which the 4-wheeler emits less emission with blended fuel over 2,3-wheeler engine.

4.1.4 Light Commercial Vehicle (LCV): (Tested on engines)

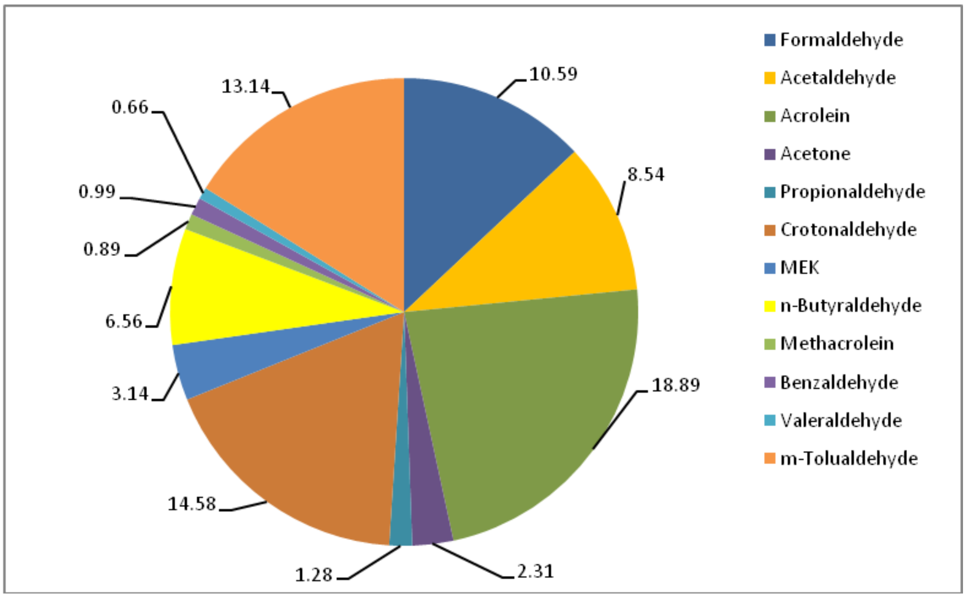
In this category, light commercial vehicle engines were tested and emission collected as per 13 mode test procedure. Carbonyl emissions of BS II Diesel, BS III Diesel, BS III Diesel+B10 and Compressed Natural Gas fueled engines results are represented in figures 4.23, 4.24, 4.25 and 4.26 respectively. For Compressed Natural Gas (CNG), retro-fitment engines have been used due to unavailability of dedicated engine in the market. Total average carbonyl compound emissions comparison chart represented in figure 4.27.



* MEK: Methyl Ethyl Ketone

Figure 4.23 Carbonyl emissions from BS II Diesel fueled LCV (mg/kW.hr)

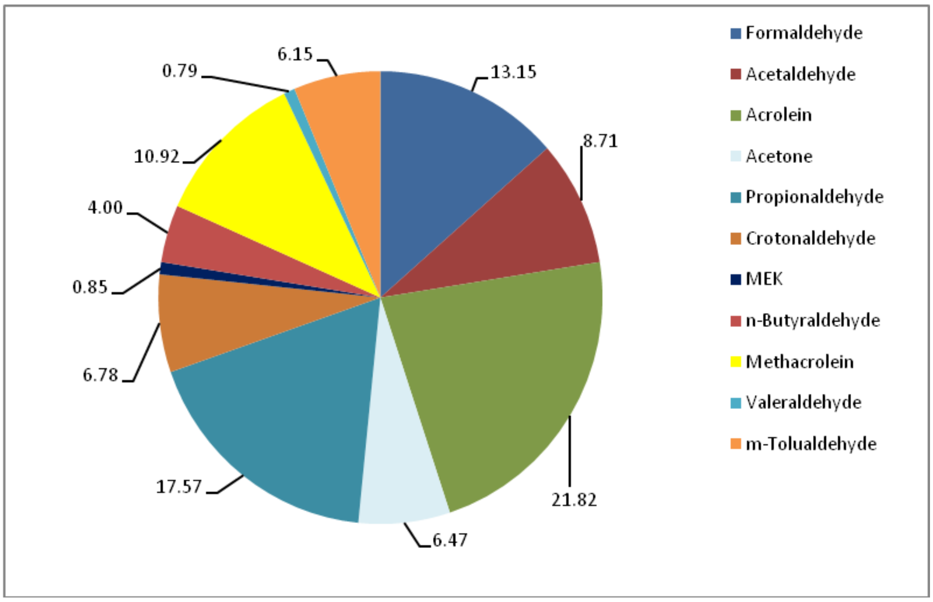
The above chart shows the carbonyl emissions from Light commercial vehicle run by BS II Diesel. Acrolein is the major Aldehyde from BS II Diesel which amounts to 31.6% of the total carbonyl emission (56.66 mg/kW.hr). Other major Aldehydes are Formaldehyde, Acetaldehyde and Methacrolein from BS II Diesel fueled vehicle.



* MEK: Methyl Ethyl Ketone

Figure 4.24 Carbonyl emissions from BS III Diesel fueled LCV (mg/kW.hr)

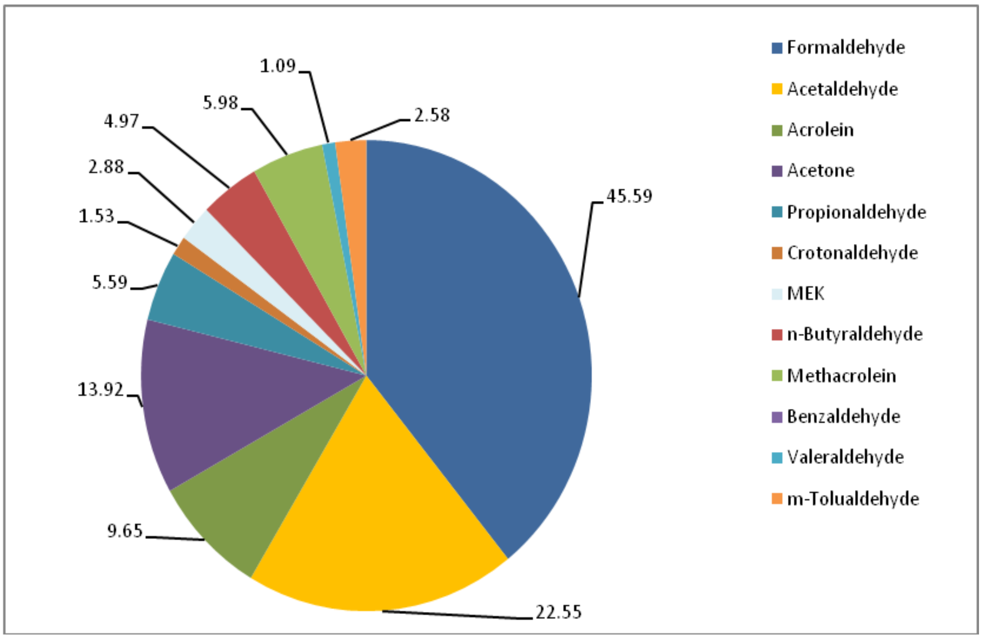
The above chart shows the carbonyl emissions from Light commercial vehicle run by BS III Diesel. Acrolein is the major aldehyde from BS II Diesel which amounts to 23.1% of the total carbonyl emission (81.56 mg/kW.hr). Other major aldehydes are Formaldehyde, Crotonaldehyde and m-Tolualdehyde from BS III Diesel fueled vehicle.



* MEK: Methyl Ethyl Ketone

Figure 4.25 Carbonyl emissions from BS III Diesel +B10 fueled LCV (mg/kW.hr)

The above chart shows the carbonyl emissions from Light commercial vehicle run by 10% Biodiesel blended BS III Diesel. Acrolein is the major aldehyde from BS II Diesel+B10 which amounts to 22.4% of the total carbonyl emission (97.22 mg/kW.hr). Other major aldehydes are Formaldehyde, Propionaldehyde and Methacrolein from BS III Diesel+B10 fueled vehicle.



* MEK: Methyl Ethyl Ketone

Figure 4.26 Carbonyl emissions from CNG fueled LCV (mg/kW.hr)

The above chart shows the carbonyl emissions from Light commercial vehicle run by compressed natural gas. Formaldehyde is the major aldehyde from CNG which amounts to 39.2% of the total carbonyl emission (116.34 mg/kW.hr). Other major aldehydes are Acetaldehyde and Acetone from CNG fueled vehicle.

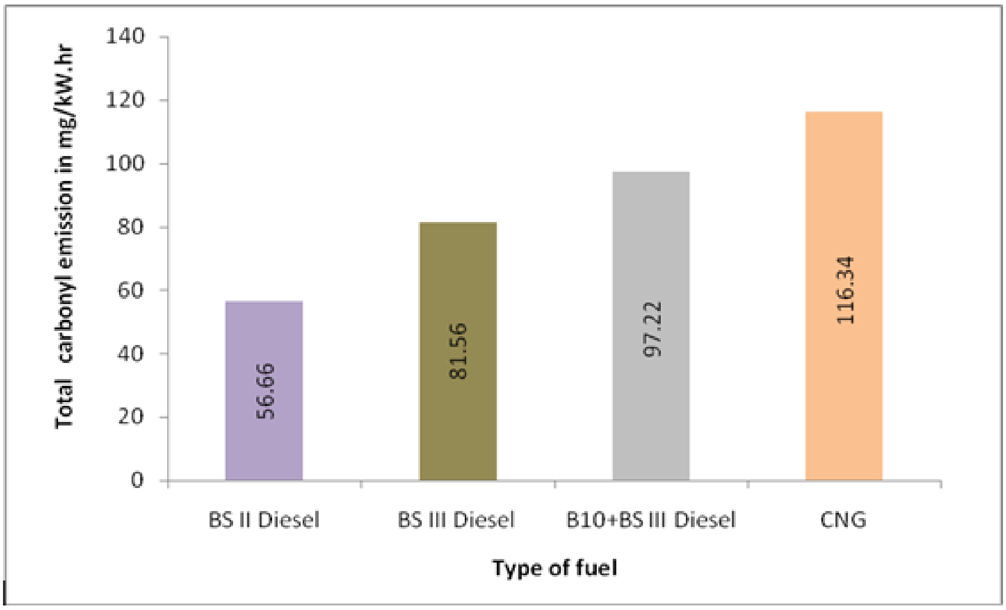


Figure 4.27 Comparison of total carbonyl compound using various fuels in LCV category

The above graph shows the comparison of total carbonyl emissions from Light commercial vehicle runs by BS II Diesel, BS III Diesel, BS III Diesel+B10 and Compressed Natural Gas (CNG). The total carbonyl emission from CNG fueled vehicle accounts 51%, 30% and 16% more than carbonyl emission from BS II Diesel, BS III Diesel, BS III Diesel+B10 fuels respectively.

4.1.5 Heavy Commercial Vehicles (HCV): (Tested on engines)

In this category, heavy commercial vehicle engines were tested and emissions collected as per 13 mode test procedure. Carbonyl emissions of BS II Diesel, BS III Diesel, BS III Diesel+B10 and Compressed Natural Gas fueled engines results are represented in figures 4.28, 4.29, 4.30 and 4.31 respectively. The comparison of total average carbonyl emission are combined and mentioned in figure 4.32.

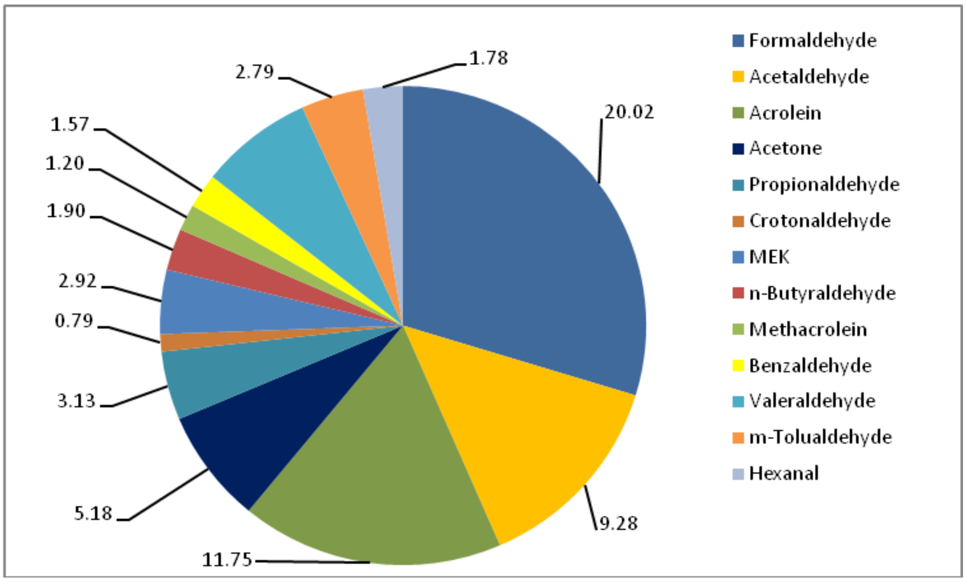


Figure 4.28 Carbonyl emissions from BS II Diesel fueled in HCV (mg/kW.hr)

The above chart shows the carbonyl emissions from Heavy commercial vehicle run by BS II Diesel. Formaldehyde is the major aldehyde from BS II Diesel which amounts to 29.7% of the total carbonyl emission (67.37 mg/kW.hr). Other major aldehydes are acetaldehyde and acrolein from BS II Diesel fueled vehicle.

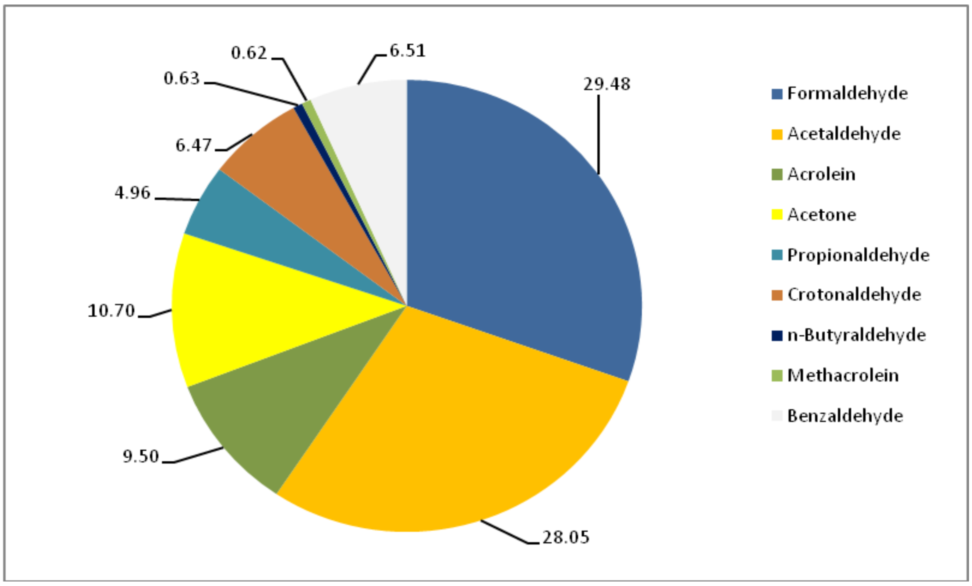
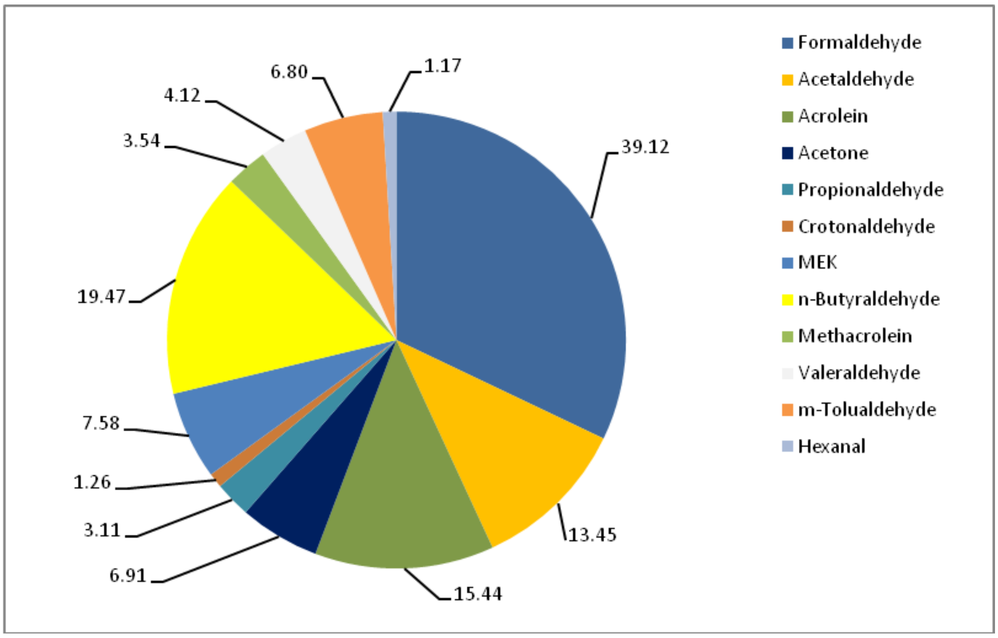


Figure 4.29 Carbonyl emissions from BS III Diesel fueled in HCV (mg/kW.hr)

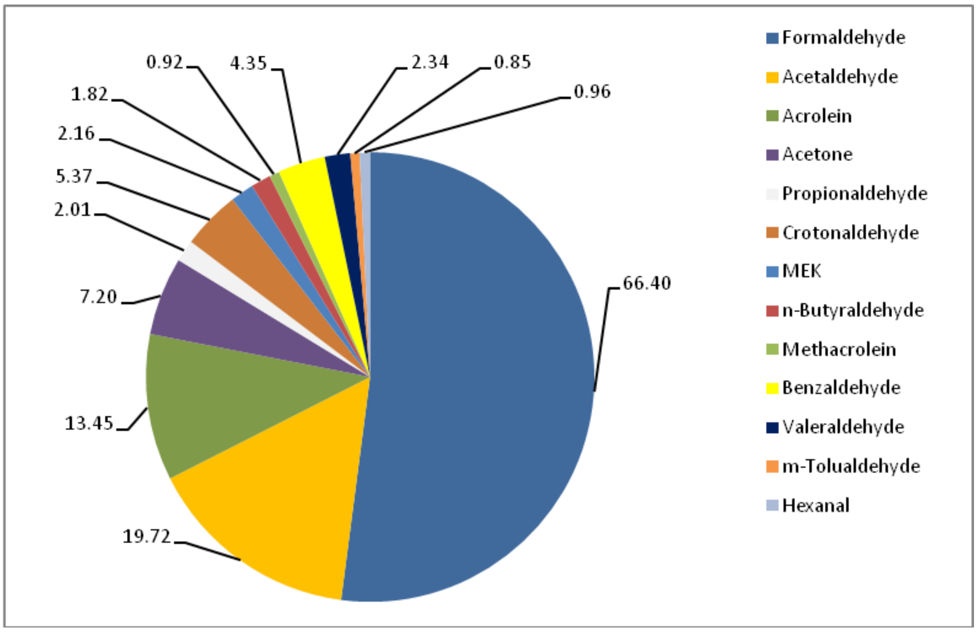
The above chart shows the carbonyl emissions from Heavy commercial vehicle run by BS III Diesel. Formaldehyde is the major aldehyde from BS III Diesel which amounts to 30.4% of the total carbonyl emission (96.93 mg/kW.hr). Other major aldehydes are acetaldehyde, acetone and acrolein from BS II Diesel fueled vehicle, apart from formaldehyde.



* MEK: Methyl Ethyl Ketone

Figure 4.30 Carbonyl emissions from BS III Diesel +B10 fueled in HCV (mg/kW.hr)

The above chart shows the carbonyl emissions from Heavy commercial vehicle run by 10% Biodiesel blended BS III Diesel. Formaldehyde is the major aldehyde from BS III Diesel+B10 which amounts to 32% of the total carbonyl emission (121.97 mg/kW.hr). Other major aldehydes are n-Butyraldehyde, Acrolein and Acetaldehyde from BS III Diesel+B10 fueled vehicle, apart from formaldehyde.



* MEK: Methyl Ethyl Ketone

Figure 4.31 Carbonyl emissions from Compressed Natural Gas fueled in HCV (mg/kW.hr)

The above chart shows the carbonyl emissions from Heavy commercial vehicle run by CNG. Formaldehyde is the major aldehyde from CNG which amounts to 52% of the total carbonyl emission (127.52 mg/kW.hr). Other major aldehydes are acetaldehyde and acrolein from CNG fueled vehicle, apart from formaldehyde.

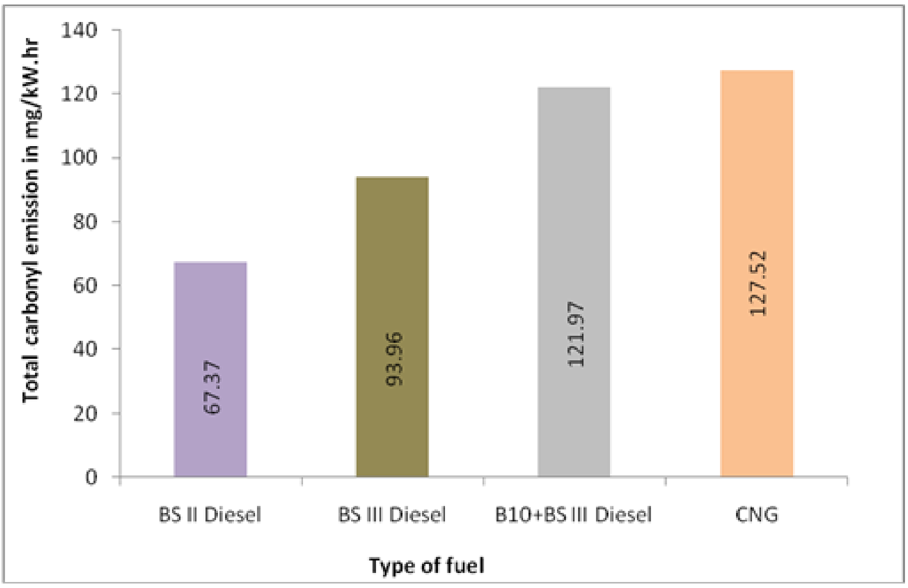


Figure 4.32 Comparison of total carbonyl compound emissions using various fuels in HCV

From the above figure it can be seen that the comparison of total carbonyl emissions from Light commercial vehicle runs by BS II Diesel, BS III Diesel, BS III Diesel+B10 and Compressed Natural Gas (CNG). The total carbonyl emission from CNG fueled vehicle accounts 47%, 26% and 4% more total carbonyl emission than BS II Diesel, BS III Diesel, BS III Diesel+B10 fuels respectively.

4.2 Methane emission (2W, 3W, 4W, LCV &HCV)

Comparison of total average methane emission of each fuel with respect to vehicle category are graphically represented in figures 4.33, 4.34, 4.35, 4.36 and 4.37 respectively.

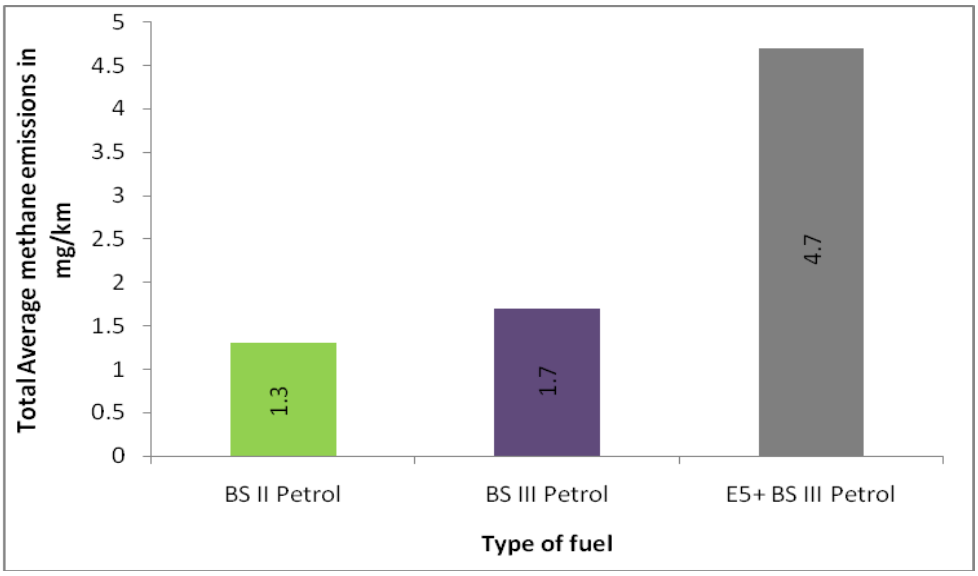


Figure 4.33 Comparison of methane emissions using various fuels in two wheeler category

The Figure above shows the comparison of methane emission from two wheeler vehicle runs by BS II petrol, BS III Petrol and BS III Petrol +E5. The methane emission from BS III Petrol +E5 fueled vehicle accounts 72.3% and 63.8% more than BS II Petrol and BS III Petrol, fuels respectively.

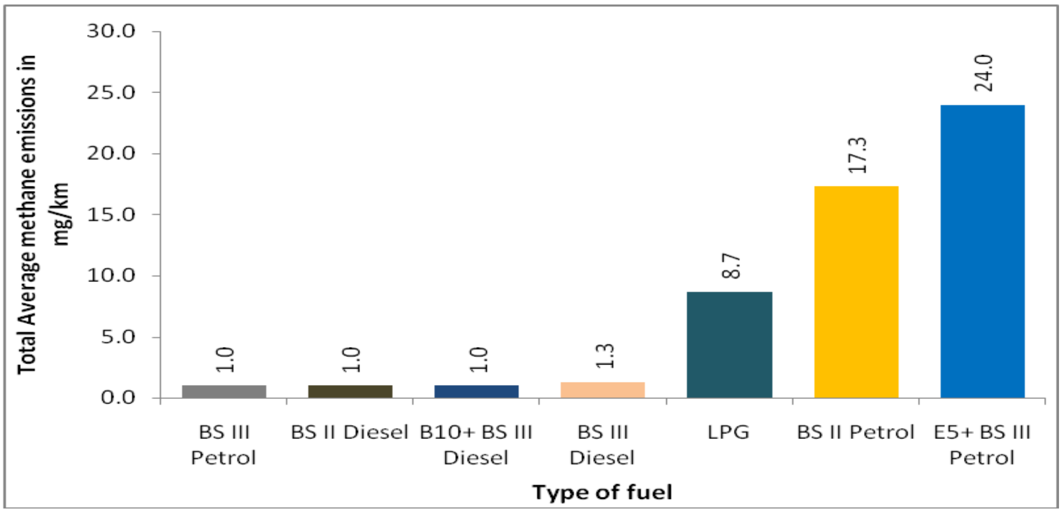


Figure 4.34 Comparison of Average methane emissions using various fuels in three wheeler category

The above figure shows the comparison of methane emission from three wheeler vehicle category runs by BS II Petrol, BS III Petrol, BS II Petrol+E5, Liquefied petroleum gas, BS II Diesel, BS III Diesel, BS III Diesel+B10 and Compressed Natural Gas. In the three wheeler vehicle category, the methane emission from CNG is more compared to other fuels. (** Three wheeler **CNG vehicle emits 2852** mg/km amount of methane emission)

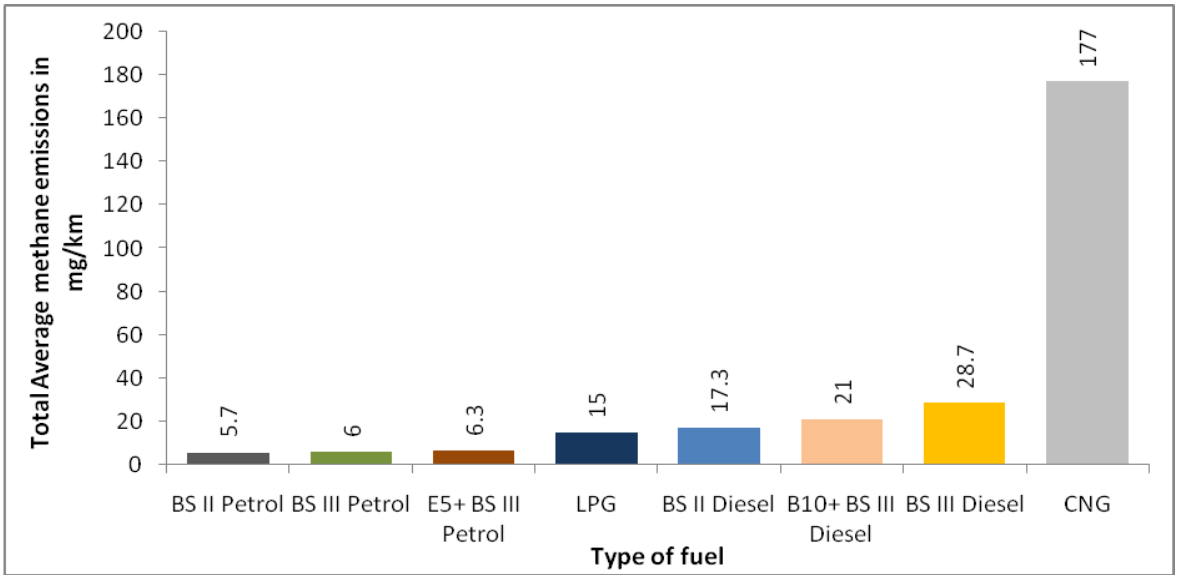


Figure 4.35 Comparison of Average methane emissions using various fuels in four wheeler category

From the above figure it can be inferred that the methane emission from CNG fueled vehicle accounts approximately 5 times more than other fuels.

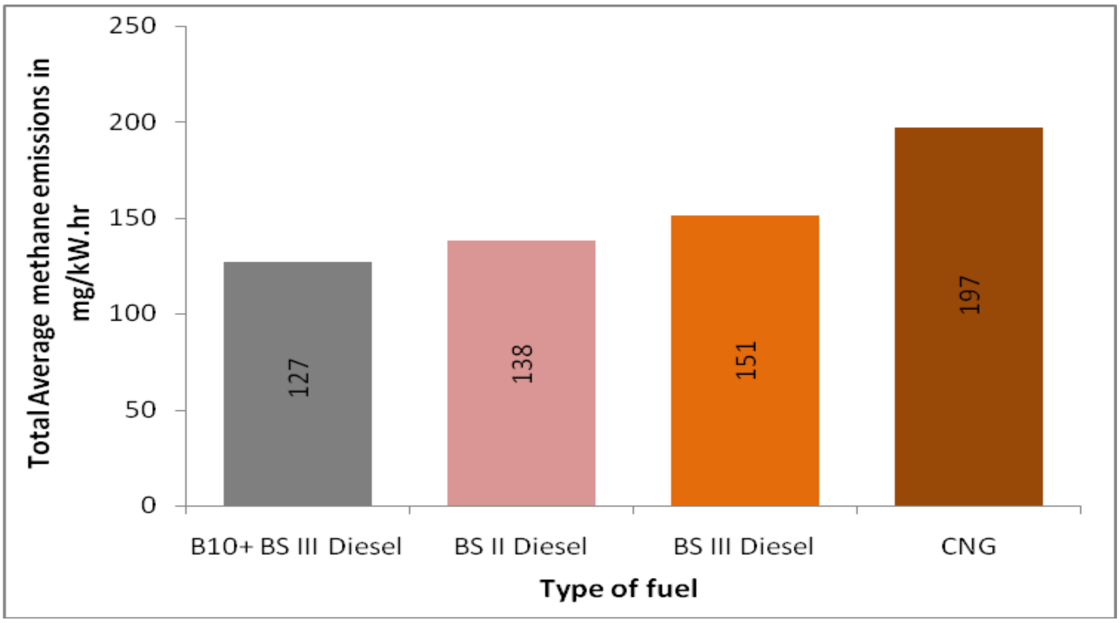


Figure 4.36 Comparison of Average methane emissions using various fuels in LCVs

The figure above shows the comparison of methane emission from Light commercial vehicle runs by BS II Diesel, BS III Diesel, BS III Diesel+B10 and Compressed Natural Gas (CNG). The methane emission from CNG fueled vehicle accounts 30%, 23.3% and 35.5% more than BS II Diesel, BS III Diesel, and BS III Diesel + B10 fuels respectively.

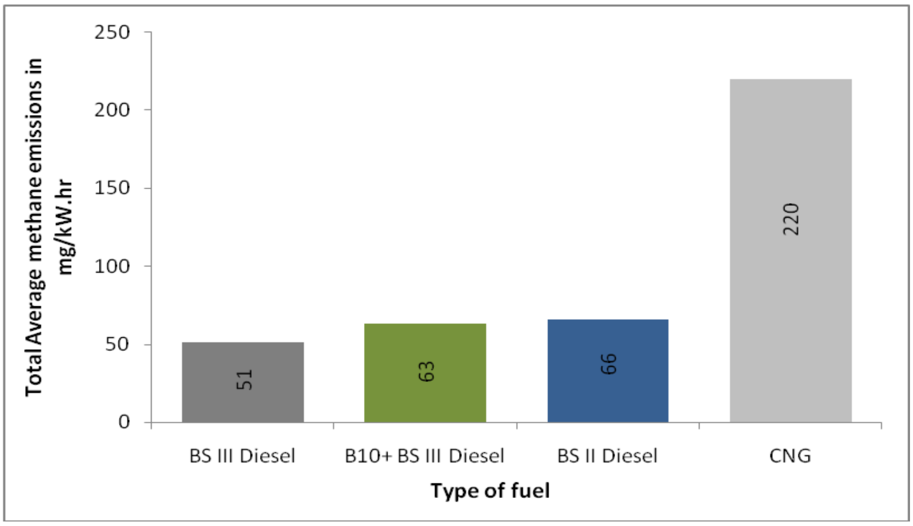


Figure 4.37 Comparison of methane emissions using various fuels in HCVs

The figure above shows the comparison of methane emission from Heavy commercial vehicle runs by BS II Diesel, BS III Diesel, BS III Diesel+B10 and Compressed Natural Gas (CNG). The methane emission from CNG fueled vehicle accounts 70%, 77% and 71% more methane emission than BS II Diesel, BS III Diesel, BS III Diesel + B10 fuels respectively.

4.3 Formaldehyde emission (2W, 3W, 4W, LCV &HCV):

Comparison of average formaldehyde emission of each fuel with respect to vehicle category are graphically represented in figures 4.38, 4.39, 4.40, 4.41 and 4.42 respectively.

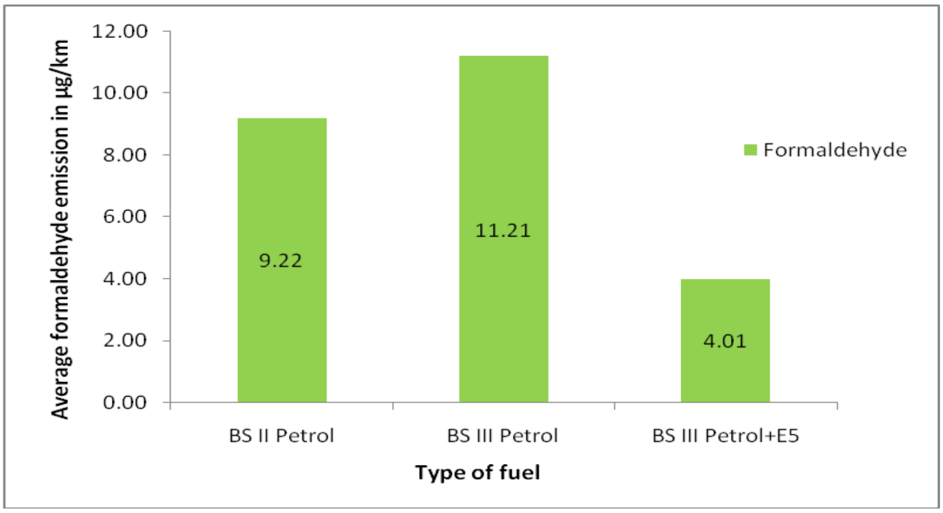


Figure 4.38 Comparison of formaldehyde emission from various fuels in two wheeler.

The figure above shows the comparison of Average formaldehyde emission from two wheeler vehicle runs by BS II petrol, BS III Petrol and BS III Petrol +E5. The Average formaldehyde emission from BS III Petrol fueled vehicle accounts 17.8% and 64.2% more total carbonyl emission than BS II Petrol and BS III Petrol +E5 fuels respectively.

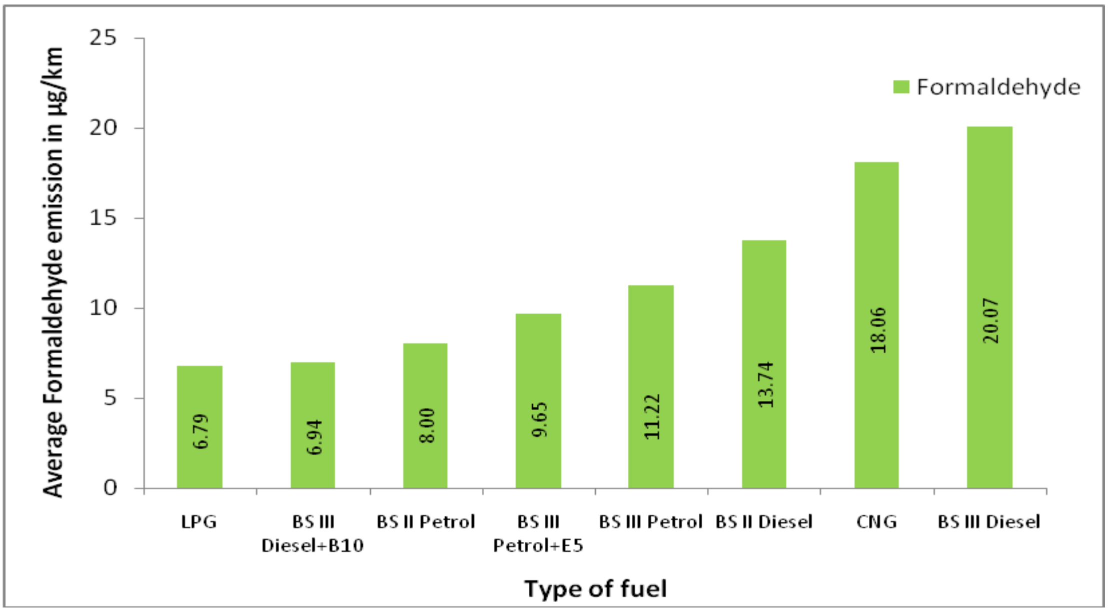


Figure 4.39 Comparison of formaldehyde emission from various fuels in three wheeler

The figure above shows the comparison of Average formaldehyde emission from four wheeler passenger cars runs by BS II Petrol, BS III Petrol, BS II Petrol+E5, Liquefied petroleum gas, BS II Diesel, BS III Diesel, BS III Diesel+B10 and Compressed Natural Gas (CNG). In the three wheeler vehicle category, major formaldehyde emitting fuel is BS III Diesel fuel. Other major formaldehyde emission emitting fuels are BS III petrol, BS II Diesel and CNG.

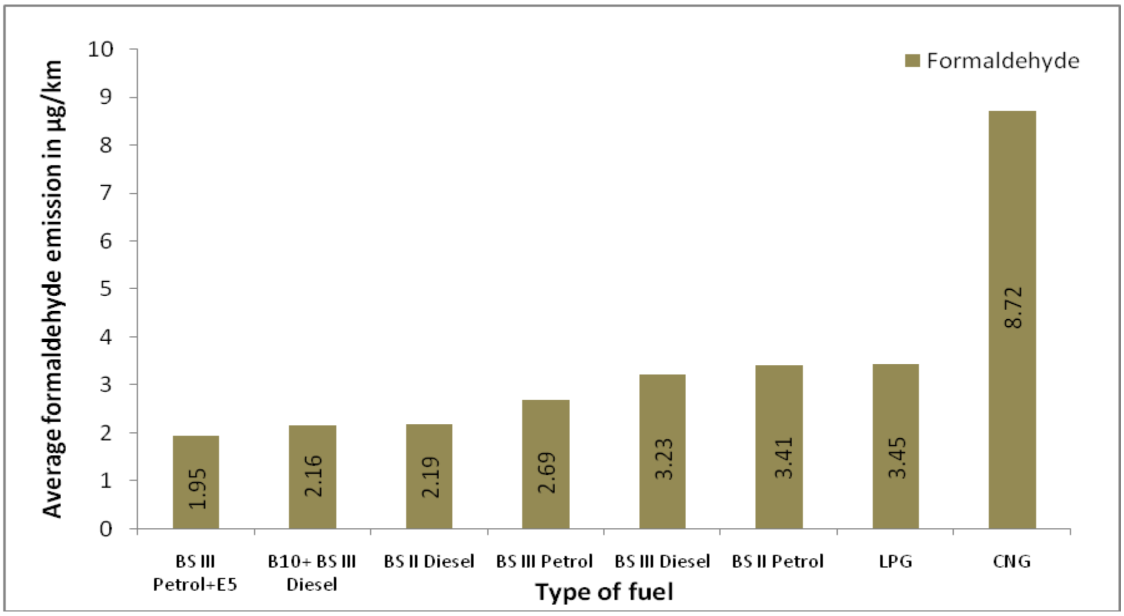


Figure 4.40 Comparison of formaldehyde emission from various fuels in four wheeler

The figure above shows the comparison of Average formaldehyde emission from three wheeler vehicles runs by BS II Petrol, BS III Petrol, BS II Petrol+E5, Liquefied petroleum gas, BS II Diesel, BS III Diesel, BS III Diesel+B10 and Compressed Natural Gas (CNG). The Average formaldehyde emission from LPG fueled vehicle accounts approximately 2.5 times more emission than other fuels run by vehicle. Other major methane emission emitting fuels are BS III Diesel, BS III Petrol and LPG from four wheeler passenger cars, apart from CNG.

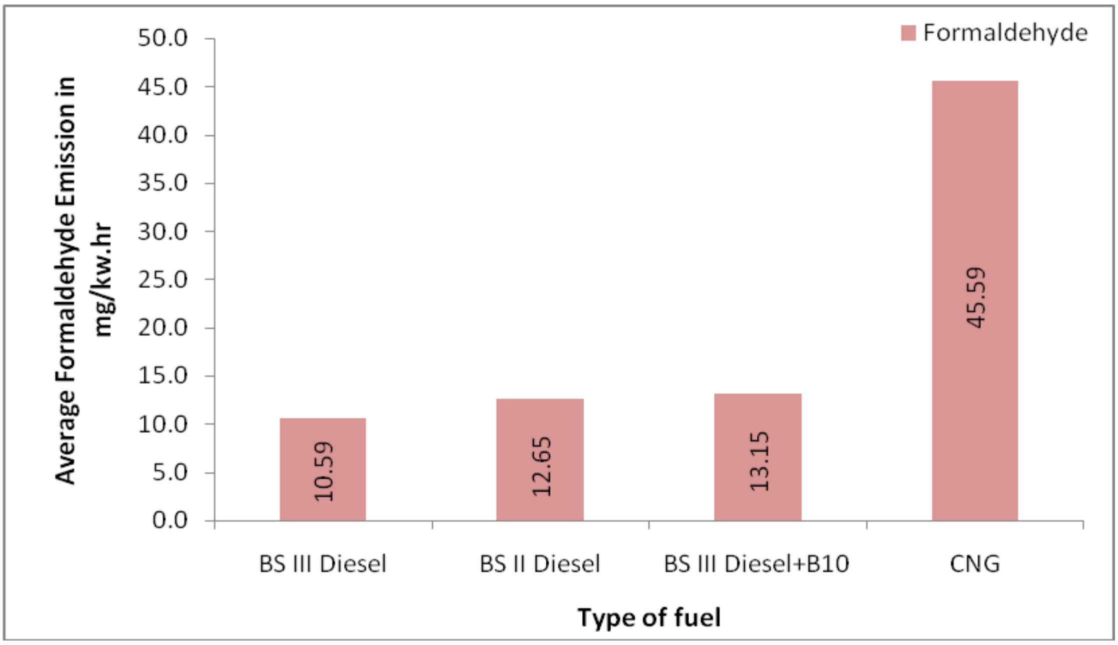


Figure 4.41 Comparison of formaldehyde emission from various fuels in LCVs

The figure above shows the comparison of average formaldehyde emission from Light commercial vehicle runs by BS II Diesel, BS III Diesel, BS III Diesel+B10 and Compressed Natural Gas (CNG). The average formaldehyde emission from CNG fueled vehicle accounts 76.8%, 72.3% and 71.2% more methane emission than BS III Diesel, BS II Diesel and BS III Diesel+B10 fuels respectively.

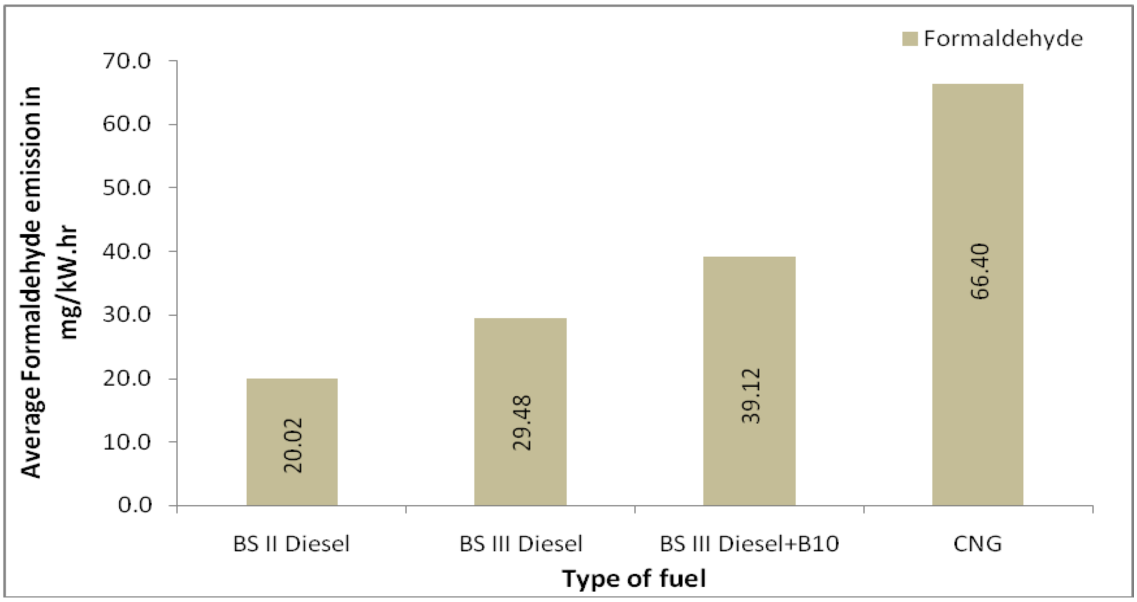


Figure 4.42 Comparison of formaldehyde emission from various fuels in HCVs

The figure above shows the comparison of average formaldehyde emission from Heavy commercial vehicle runs by BS II Diesel, BS III Diesel, BS III Diesel+B10 and Compressed Natural Gas (CNG). The average formaldehyde emission from CNG fueled vehicle accounts 69.8%, 55.6% and 41.1% more methane emission than BS II Diesel, BS III Diesel and BS III Diesel + B10 fuels respectively.

5. DISCUSSIONS

The results are discussed in terms of Carbonyl emissions and methane emissions respectively

5.1 Carbonyl emissions

The discussions of results in terms of carbonyl emissions per kilometer for three major vehicle categories (i.e..two wheelers, three wheelers and four wheeler Passenger cars) and carbonyl emissions per mg/kW.hr for two vehicle categories (i.e..LCVs and HCVs) with various fuels. Pie-charts are plotted for each vehicle categories viz. two wheeler, three wheeler, four wheeler passenger car, Light commercial vehicle and Heavy commercial vehicle respectively with respect to fuel used. Tabulation of carbonyl emissions are presented in Annexure IV (in terms of Range, Mean and Standard deviation).

As per mass emission test procedure (CMVR-Type Approval Procedure), vehicle category of two wheeler, three wheeler and four wheeler passenger cars were tested on chassis dynamometer. Emission collection bag (for methane) and DNPH (2,4-Dinitrophenylhydrazine) sample cartridges collection (for aldehyde and ketones) was done. Both the collection time period was same. Collected cartridges were analyzed in High performance Liquid Chromatography (HPLC) for aldehyde and ketone measurement values.

Figures 4.1 to 4.32 show carbonyl emissions apportionment for each fuel and comparative data based on vehicle category. Charts are plotted with average individual carbonyl compound emissions. Eleven type of aldehydes and two type of ketones values are shown (μg/km) in each figure for two wheeler, three wheeler and four wheeler passenger cars and for Light commercial vehicle and Heavy commercial vehicles in mg/kW.hr.

5.1.1 Two wheelers

Figure 4.1 to 4.3 shows the distribution of carbonyl compounds in the total emission as result of usage of various fuels (BS II Petrol, BS III Petrol, and BS III Petrol+ E5) in two wheeler category. Formaldehyde is dominating in the emission of carbonyl compounds from conventional BS II & BS III petrol fueled two wheeler vehicles. In detail formaldehyde emission is 1.9% more in lower aromatic and sulfur content (BS III petrol) fueled vehicles compared to slightly higher aromatic and sulfur content (BS II petrol) fueled vehicles in respect to respective total carbonyl emission. Acetaldehyde, Acetone, Acrolein, Crotonaldehyde are next to the formaldehyde emission level. Acetaldehyde is major carbonyl emission in the oxygenated (BS III petrol+5% ethanol) blended fuel vehicles.

Two wheeler vehicles run by 5% ethanol blended fuel, emitted 40% and 53% average more Acetaldehyde, comparing with BS II Petrol and BS III Petrol. Increase in acetaldehyde emission for BS III petrol + E5 run vehicle may be due to partial oxidation of ethanol during combustion. Karl-Erik Egebäck et al (2005) found similar observation for ethanol blended petrol fuel.

Conventional fuels (i.e. BS II Petrol & BS III Petrol) emit higher formaldehyde, acetone, acrolein, propionaldehyde, n-valeraldehyde than Ethanol blended fuel (BS III Petrol+E5) gasoline. This may be due to complete combustion and oxidation in the presence of oxygenated fuel in BS III Petrol.

The total average aldehyde and ketone emission results revealed that vehicles run by lower aromatic content petrol (i.e. BS III Petrol) produced 17.7% and 80.2 % more total carbonyl emission than higher (than BS III petrol) aromatic content petrol (BS II petrol) and 5% ethanol blended BS III Petrol (BS III+E5), respectively. (Yao et al. 2008) suggested that reduction in aromatic content in Gasoline increases aldehyde emission. The higher aldehyde emissions may be the result of increased fraction of the paraffin and olefins (Oberdorfer et al, 1967) and Wigg et al, 1973).

Another most important findings is that blending of 5% ethanol with BS III petrol reduces the total carbonyl emission to almost half (44.4% reduction) compared to total carbonyl emission coming from BS III petrol. This tremendous reduction may be due to the presence of ethanol in BS III petrol which supplies more free oxygen, resulting in more complete combustion.

5.1.2 Three wheeler

Figure 4.5 to 4.8 shows the carbonyl emissions from three wheeler vehicle categories for BS II Diesel, BS III Diesel, Compressed Natural Gas (CNG) and 10% Bio-diesel blend with BS III Diesel fuels. The order of increasing formaldehyde emissions corresponds to BS III Diesel+B10, BS II Diesel, BS III Diesel and Compressed Natural gas. Higher cetane number fuel (BS III diesel) emits higher carbonyl emissions than lower cetane number fuel (BS II diesel) (Wagner et.al, 1996). The other important property is higher sulfur content in BS II Diesel also one of the parameter to emit lower aldehyde emissions (Yung-chen yao et.al, 2008).

Figures 4.9 to 4.12 show that the carbonyl compound emissions from BS II petrol, BS III Petrol, BS III Petrol+E5 and Liquefied Petroleum Gas (LPG) fueled vehicles. Based on experimental results, increasing order of carbonyl emissions from above mentioned fuel are given below:

CNG < LPG < BS III Petrol+ E5 < BS II Petrol < BS III Petrol

(20.624 μg/km) < (27.928 μg/km) < (45.077 μg/km) < (57.978 μg/km) < (60.664 μg/km)

The carbonyl emission is less in LPG, may be due to cylinder combustion. In LPG vehicles, improved and smoother acceleration, reduced combustion chamber and spark plug deposit leads (due to gaseous state) to less carbonyl emissions. Emissions of aldehydes from LPG vehicles nearly always generate lower than diesel and often lower than petrol (Anonymous, 2009).

Major aldehydes emitted by ethanol blended fueled (BS III Petrol+E5) vehicles are acetaldehyde and formaldehyde compared to other aldehydes. In cylinder combustion ethanol produces acetaldehyde emission (Magnusson Roger et al, 2002).

The total carbonyl emission from BS III Petrol fueled vehicle accounts 54%, 72%, 43%, 67% and 66% more than Liquefied petroleum gas, BS II Diesel, BS III Diesel, BS III Diesel+B10 and Compressed natural gas fuels respectively. Conventional fuels (BS II Petrol and BS III Petrol) generate higher aldehydes emission than LPG and ethanol blend fuel. Considering

Conventional fuels, BS II petrol (sulfur content: 500 mg/kg) vehicle gives slightly less aldehyde (carbonyl) emissions than BS III petrol (sulfur content: 350 mg/kg) vehicle due to reduction of aromatic content and sulfur content. Reduction of maximum aromatic content in BS III petrol is less than BS II petrol may resulted in increased aldehydes emission for BS III petrol vehicles. Yao et al. (2008) also showed that reduction in aromatic content increased aldehydes emission.

5.1.3 Four wheeler passenger car

Figure 4.14 shows Carbonyl emissions from BS II Petrol fueled vehicles majorly emit acrolein, acetaldehyde, formaldehyde and methyl ethyl ketone. With BS III Petrol fueled vehicles, acetone is dominating from other carbonyls followed by formaldehyde and by acetaldehyde. The emissions from four wheeler vehicle are less than two wheeler category because of exhaust treatment processes (warmed-up catalyst results in reduction in aldehyde emission). As per Bharat stage emission norms, four wheeler category norms are stringent than two wheeler and three wheeler norms.

The average total carbonyl emissions from BS III petrol (figure 4.15) and 5% ethanol blend (BS III petrol+E5) fueled four wheeler (figure 4.16) are more than BS II petrol fueled four wheeler may be due to fuel aromatics, olefins, paraffin, sulfur and benzene contents. Particularly, decreasing the amount of aromatic content, benzene content and sulfur content increases aldehyde emissions. In the total carbonyl compound emissions of four wheelers (three vehicles), the increase in the individual carbonyl compound emissions correspond to following order of the BS II Petrol fuel (Figure 4.14):

Methyl ethyl ketone < Acetaldehyde < Formaldehyde < Acrolein

BS II Petrol and ethanol blend fueled vehicles emit majorly the above mentioned emissions because of advanced injection technology and catalytic converter design parameters (i.e cell density, percentage change in catalyst, etc.,) the carbonyl emissions are less when compared to three wheeler category.

Considering the total average carbonyl emissions from BS III Petrol (figure 4.15) fueled passenger car gives less (37%) than BS II Petrol may be due to increased percentage of complete combustion in engine in-cylinder compared with BS II Petrol.

In the total carbonyl compound emissions of four wheelers (three vehicles), increase in the individual carbonyl compound emissions correspond to following order of the 5% ethanol blended BS III Petrol fuel (Figure 4.16):

Acetaldehyde < Formaldehyde < Acrolein

Figure 4.17 shows the comparison of average total carbonyl compound emissions using various fuels. In India, now only the automobile manufacturers start to produce dedicated CNG engine vehicles. While doing this project the testing has been done on retro-fitment vehicle due to un-availability of dedicated CNG vehicle in the market. As far as the emission point of concern, the Compressed Natural gas (CNG) vehicles emitted more amounts of total carbonyl emission compared to other seven fuels. This may be due to older engine technologies and poor exhaust treatment process which emits higher aldehyde emission. Newkirk M.S et al, 1995 explained that formaldehyde emissions from CNG engines without catalyst could be rather high.

Figure 4.18, 4.19, 4.20 and 4.21 represents the total average carbonyl emissions from Liquefied Petroleum Gas (LPG), BS II Diesel, BS III Diesel and B10 blended BS III Diesel respectively. Vehicle mass emission test has been done with same vehicle model, vintage and fuels (BS II Diesel, BS III Diesel and BS III Diesel+B10). The results show that, formaldehyde, acetaldehyde and acrolein emissions dominated by all three fuels (BS II Diesel, BS III Diesel and B10 blended BS III Diesel) because of improper air fuel ratio and insufficient combustion air result in improper combustion and it leads to aldehyde emissions. Bio diesel blend fuel vehicle emits higher acetaldehyde emission than other carbonyl emission (i.e formaldehyde, acrolein, acetone etc.)

Figure 4.22 shows the comparison of total average carbonyl emission from different fuels. The Conventional fuels emit less carbonyl emissions than LPG and CNG fuels. BS II Petrol, BS III Petrol, Ethanol blend fuels releases less emission because petrol engine vehicles are having new and effective treatment devices (Catalytic converter) compared with retro-fitment vehicles (two years older below 10000 km).

Considering BS II Diesel, BS III Diesel and B10 blended fuel vehicles where the oxidation catalysts are used. Both catalytic converter and oxidation catalyst are reduced the amount of total carbonyl emission.

5.1.4 Light commercial vehicle (LCV)

Figure 4.23, 4.24, 4.25 and 4.26 shows that the average carbonyl emissions by Light Commercial Vehicle engines run by BS II Diesel, BS III Diesel, BS III Diesel+B10 and Compressed Natural Gas respectively. Out of three fuels (BS II Diesel, BS III Diesel and B10+BS III Diesel), engine run by BS III Diesel+B10 gives more carbonyl emission (97.224 g/kW.hr) than BS II Diesel (56.663 g/kW.hr) and BS III Diesel (81.562 g/kW.hr). Correa S M et al. (2008) experimental study shows that Formaldehyde, Acrolein, Crotonaldehyde, Propinaldehyde, Methacrolein, acetone and Butyraldehyde are major emission from B10+ BS III Diesel fuel is higher than conventional diesel fuels (BS II Diesel and BS III Diesel).

C. He et al, 2009 experimental results indicates that biodiesel-fueled engine almost have triple carbonyls emissions of diesel-fueled engine.

Figure 4.26 explained that CNG fueled LCV engine gives higher carbonyl emission (116.343 g/kW.hr) than other three fuels. Meeks Jr., N.N et al (1995) explained that a single methane and oxygen molecule can directly produce formaldehyde as a stable intermediate combustion product. Quenching the formaldehyde molecule before it can act on oxygen molecule can leave formaldehyde in the exhaust. Similarly, acetaldehyde and acrolein are stable compounds that can be produced from partial combustion of ethane. Because natural gas largely consists of methane and ethane, aldehyde testing was limited to their direct analogs: formaldehyde, acetaldehyde, and acrolein (Meeks et al, 1992).

Figure 4.27 shows various fuels average total carbonyl compound emissions comparison from the light commercial vehicles. Carbonyl emissions are in the increasing order of the following:

BS II Diesel < BS III Diesel < B10+BS III Diesel< CNG

5.1.5 Heavy commercial Vehicle (HCV)

Figure 4.28, 4.29 and 4.30 shows that the average carbonyl emissions emitted by Heavy Commercial Vehicle engines which is run by BS II Diesel, BS III Diesel, BS III Diesel+B10 and Compressed Natural Gas respectively. The average total carbonyl emission results revealed that vehicles run by Bio-diesel blended fuel (121.97 mg/kW.hr) produced 45% and 23% more emission than BS II Diesel (67.37 mg/kW.hr) and BS III diesel (93.96 mg/kW.hr). Bio-diesel blended fueled engine releases high carbonyl emission because bio-diesel itself contains some appreciable amount of carbonyl compounds. Bio-diesel inheriting oxygen atoms are basically an ester mixture of saturated and non-saturated fatty acids which may include secondary oxidation products (like volatile and non volatile carbonyl compounds). Yacoub et al. (1996) mentioned that aldehyde emissions increase as the cetane number of the fuel is increased (lower fuel density and aromatic content). Weidmann et al. (1988) investigated that the emissions of aldehyde from diesel engine were slightly lower for lower cetane number and higher for higher cetane number.

Figure 4.31 show that the total average carbonyl emissions emitted by Compressed Natural Gas fueled (CNG) Heavy Commercial Vehicle engines. It explained that CNG fueled HCV engine gives higher carbonyl emission (127.52 mg/kW.hr) than other three fuels (BS II Diesel, BS III Diesel and BS III Diesel+B10). The reason for higher carbonyl emissions are same as mentioned in Light Commercial Vehicle engine. In Both Light Commercial Vehicle and Heavy commercial Vehicle CNG engines were converted from diesel engines so that combustion inside the cylinder is not perfect while comparing with diesel fueled (BS II Diesel, BS III Diesel and BS III Diesel+B10) engines. Figure 4.32 show that the comparison of total average carbonyl emission emitted by four fuels.

5.2. Methane Emissions

This section presents methane emissions per kilometer results for each fuel of three vehicle categories analyzed. Methane emissions were estimated by the use of bag collection at that time of testing (Mass emission Test). The bag collection time can vary with respect to vehicle category and fuels. A summary of the results are provided in Annexure IV.

The Methane emissions from BS II Petrol and BS III Petrol fueled two wheeler vehicle category is almost same level. Both fuels were tested in same model and same vintage vehicles. Due to the incomplete combustion inside the engine and the incomplete oxidation of methane at exhaust develop higher methane emission (RE Hayes, 2004).

The ethanol blended petrol fueled vehicle (4.7 mg/km) releases 3.61 times and 2.76 times more methane emissions than conventional fuels (1.3 mg/km & 1.7 mg/km for BS II & BS III petrol respectively. Results showing in figure 4.33 describes the vehicles with 5% ethanol blended BS III Petrol are giving more methane emission than using BS II & BS III Petrol. In the experiment catalytic converter efficiency was taken as same for all. This concludes, increase in ethanol percentage in gasoline enhances the methane emission in the exhaust may be due to increase in octane number of the gasoline which has the probability of knocking (Anonymous, 2008).

In three wheeler category, vehicle model used for testing is same for BS II Diesel, BS III Diesel and 10% bio-diesel blended BS III diesel fuels (figure 4.34). The emission level of methane (F) from Compressed Natural Gas fueled vehicles is more due to presence of methane in compressed natural gas emits more methane than other fuels.

Figure 4.35 shows the comparison of average methane emission from BS II Petrol, BS III Petrol, E5+ BS III Petrol, LPG, BS II Diesel, BS III Diesel and B10+BS III Diesel and CNG fueled four wheeler category passenger cars. Retrofitted CNG vehicle emits more methane than conventional, blended and alternative fuels (Annexure VI). The advancement in exhaust after treatment technology gives fewer amounts of HC emissions but average methane emission level is increasing may be because of cylinder combustion characteristics or due to catalytic converter not attaining peak conversion temperatures.

Figure 4.36 shows that CNG fueled engine emits more methane (197 mg/kW.hr) than BS II Diesel (138 mg/kW.hr) and BS III Diesel (151 mg/kW.hr) and B10+BS III Diesel (127 mg/kW.hr) due to higher methane content (Min 87% methane) (Annexure VI).

Figure 4.37 shows the comparison of average methane emission from BS II Diesel, BS III Diesel, B10+BS III Diesel and CNG fuels. Due to un- availability of dedicated CNG, HCV engines retro fitment CNG engines has been tested. Figure 4.37 shows that CNG engine (706 g/kW.hr) emits higher amount of methane than BS II Diesel (0.066 g/kW.hr), BS III Diesel (51 g/kW.hr) and B10 blended BS III Diesel (0.063 g/kW.hr) fuels.

6. CONCLUSION

For two wheeler category

- The average of total aldehyde and ketone emission results revealed that vehicles run by BS III Petrol (17.47 µg/km) produced 15% and 44 % more emission than BS II petrol (14.84 µg/km) and 5% ethanol blended BS III (BS III+E5) Petrol (9.72 µg/km), respectively. Reduction of maximum aromatic content in BS III petrol as compared to BS II petrol may have resulted in increased aldehyde emission for BS III run vehicles.
- Two wheeler vehicles, run by 5% ethanol blended BS III Petrol, emitted 40% and 53% average more Acetaldehyde (4.91 µg/km), comparing with BS II Petrol (2.97 µg/km) and BS III Petrol (2.26 µg/km). Increase in Acetaldehyde emission for BS III+E5 run vehicle may be due to partial oxidation of ethanol during combustion.
- Conventional fuels (BS II Petrol & BS III Petrol) emit higher formaldehyde, acetone, acrolein, propionaldehyde, Valeraldehyde compared to alternative fuel (E5 + BSIII Petrol). Michelle Heath reported that conventional fuels can also be modified to a reformulated gasoline to help reduce toxic emissions. The oxygen content of ethanol fuels used in properly modified vehicles results in increased energy efficiency and engine performance. Extended spark-plug life and lower carbon deposits are also expected because ethanol burns cleaner than gasoline.
- The ethanol blended petrol (4.7 mg/km) emits more methane i.e 3.61 times and 2.76 times more than conventional fuels (1.3 mg/km & 1.7mg/km) for BS II & BS III petrol respectively.

For three wheeler category

- The average total aldehyde and ketone emission results revealed that vehicles run by BS III diesel (34.65 µg/km) emits 51.5% , 42.4% and 40.4 % more than BS II Diesel (16.77 µg/km), 10% bio diesel blended BS III Diesel (19.94 µg/km) and CNG (20.62 µg/km), respectively. Yacoub et al. (1996) mentioned that aldehyde emissions increase as the cetane number of the fuel increased (lower fuel density and aromatic content).
- Three wheeler vehicles run by 10% biodiesel blended BS III Diesel, emitted 95%, 27% and 83% more Acetaldehyde (12.26 µg/km) compared to BS II Diesel (0.54 µg/km) BS III Diesel (8.92 µg/km) and CNG (1.99 µg/km) respectively.
- Based on experimental results, increasing order of carbonyl emissions from BS II petrol, BS III Petrol, E5+BS III Petrol and LPG fueled vehicles is as follows:

  LPG < E5+BS III Petrol < BS II Petrol < BS III Petrol

  (27.93 µg/km) < (45.08 µg/km) < (57.98 µg/km) < (60.66 µg/km)

- Three wheeler vehicles run by CNG emits more methane (2852 mg/km) compared to BS II Diesel (1 mg/km), BS III Diesel (1.3 mg/km), 10% biodiesel blended BS III Diesel (1 mg/km), BS II Petrol (17.3 mg/km), BS III Petrol (1 mg/km), E5+ BS III Petrol (2.4 mg/km) and LPG (8.7 mg/km).

- Major aldehydes emissions emitted by 5% ethanol blended petrol fueled vehicles are acetaldehyde and formaldehyde compared to other aldehydes.
- Conventional fuels (BS II Petrol and BS III Petrol) generate higher aldehydes emission than LPG and E5 petrol. Considering Conventional fuels, BS II petrol vehicle gives slightly less emissions than BS III petrol vehicle due to reduction of aromatic content. Reduction of maximum aromatic content in BS III petrol than BS II petrol may have resulted in increased aldehydes emission for BS III run vehicles.

For four wheeler category

- The average total aldehyde and ketone emission results revealed that vehicles run by CNG (27.49 µg/km) produced 47.1%, 66.7% and 51.2 % more emission than BS II Petrol (14.52 µg/km), BS III petrol (9.14 µg/km), 5% ethanol blended BS III (BS III+E5) Petrol (13.41 µg/km) respectively. Comparing the aldehyde emissions from natural gas fueled vehicle with the gasoline fueled vehicle shows an increase of 20% in the formaldehyde value when the engine is fueled with natural gas while the catalytic converter efficiency for formaldehyde was 96% and 98%. Retro-fitment CNG vehicles gives more aldehyde emission when compared to direct CNG vehicles.
- Acrolein emission is higher in BS II Petrol (9.97 µg/km) and 5% ethanol blended BS III Petrol (10.73 µg/km) run vehicles compared to other aldehydes and ketone emissions (from BS III petrol and CNG vehicle acrolein emission were absent).
- As per the experimental analysis, the Increasing order for formaldehyde emission from gasoline engine are as follows:

  E5+BS III Petrol < BS III Petrol < BS II Petrol < CNG

  (1.95 µg/km) < (2.69 µg/km) < (3.41 µg/km) < (8.72 µg/km)

- The increasing order of average methane emission from conventional, alternative and blended fuel are as follows:

  BS II Petrol < E5+BS III Petrol < BS III Petrol < CNG

  (5.7 mg/km)< (6.3 mg/km) < (10 mg/km) < (181 mg/km)

- Considering Diesel engine fuels, Propionaldehyde, acetone, Crotonaldehyde, Methyl ethyl ketone, n-Butyraldehyde, Methacrolein, Benzaldehyde, m-Tolualdehyde and Hexanal emissions were absent. The complete combustion percentage will be more when compare to older engines and technologies. The aldehyde emissions are absent due to the improved vehicle catalytic converter technologies, location of catalytic converter and better fuel injection technologies.

For Light Commercial Vehicle's

- Out of three fuels (BS II Diesel, BS III Diesel and B10+BS III Diesel), engine run by B10+ BS III Diesel emits more carbonyl (97.22 g/kW.hr) compared to BS II Diesel (56.66 g/kW.hr) and BS III Diesel (81.56 g/kW.hr).
- CNG fueled LCV engine emits more carbonyls (116.34 mg/kW.hr) than BS II Diesel (56.66 mg/kW.hr), BS III Diesel (81.562 mg/kW.hr) and B10+ BS III Diesel (97.22 mg/kW.hr). A single methane and oxygen molecule can directly produce formaldehyde as a stable intermediate combustion product.

❖ CNG fueled engine emits more methane (197 mg/kW.hr) than BS II Diesel (138 mg/kW.hr) and BS III Diesel (151 mg/kW.hr) and B10+BS III Diesel (127 mg/kW.hr) due to higher methane content in the fuel (min 87% methane).

For Heavy Commercial Vehicles

❖ The average total aldehyde and ketone emission results revealed that vehicles run by CNG (127.52 mg/kW.hr) produced 47%, 24% and 4% more emission than BS II Diesel (67.38 mg/kW.hr), BS III diesel (96.93 mg/kW.hr) and 10% bio diesel blended BS III Diesel (121.97 mg/kW.hr) respectively.

❖ BS II Diesel fueled engine emits more methane (66 mg/kW.hr) than BS III Diesel (51 mg/kW.hr) and B10+BS III Diesel (63 mg/kW.hr).

❖ CNG fueled heavy duty engine emits 706 mg/kW.hr methane due to higher methane content (87-93%).

The table 6.1 and 6.2 gives the comparison of best and worse fuel with Carbonyls and Methane emissions in different types of Vehicles.

Table 6.1 Comparison of best & worse fuel with Carbonyl emission in different types of vehicles

Carbonyl emission best and worst fuels			
Sl.No	**Vehicle Category**	**Best Fuel**	**Worst Fuel**
1	Two wheeler	BS III Petro +E5	BS III Petrol
2	Three wheeler	BS II Diesel	BS III Petrol
3	Four wheeler	BS III Petrol	CNG
4	Light Commercial Vehicle	BS II Diesel	CNG
5	Heavy Commercial Vehicle	BS II Diesel	CNG

Table 6.2 Comparison of best & worse fuel with Methane emission for different types of vehicles

Methane emission best and worst fuels			
Sl.No	Vehicle Category	Best Fuel	Worst Fuel
1	Two wheeler	BS II Petrol	BS III Petro +E5
2	Three wheeler	BS III Petrol	CNG
3	Four wheeler	BS II Petrol	CNG
4	Light Commercial Vehicle	BS III	CNG

		Diesel+B10	
5	Heavy Commercial Vehicle	BS II Diesel	CNG

7. RECOMMENDATIONS

A huge database of unregulated carbonyl emission from Indian vehicles with different fuels has been generated in this project. This database in future may work as the preliminary platform for any future norms/guideline for Indian Vehicular Emission Norms. During the course of this project some recommendations have been identified and mentioned below.

- ❖ As an outcome of this project, it has been concluded that retro-fitment CNG fueled vehicle emits significantly more amount of carbonyl emissions, compared with other fueled vehicles. More studies can be done on retro-fitment CNG vehicles which are thrust area of future fuel to improve clean environment.

- ❖ In LCV and HCV categories, Biodiesel blended diesel emits significant amount of carbonyl emission next to CNG category. This significant finding demands future detailed study in this area. A comparative study of gain (power, regulated emission and easy availability) and loss (increased unregulated emissions) from biofuel may be a very interesting area of future research.

- ❖ This study indicates that India may require directive or emission norms for aldehyde and ketone emission for certain category of vehicle and fuel. [In this regard, it is interesting to note that California has already legislated formaldehyde emission norms for Passenger cars (0.015 g/mile) and for Light duty vehicle (0.015 g/mile)]. But, more detailed All India Coordinated Research Project (AICRP) on this area is required before imposing any such directive or emission norms.

GLOSSARY

Compression ratio:

It is the ratio between the volume of the cylinder and combustion chamber when the piston is at the bottom of its stroke, and the volume of the combustion chamber when the piston is at the top of its stroke.

Secondary air injection:

The first systems injected air very close to the engine, either in the cylinder head's exhaust ports or in the exhaust manifold. These systems provided oxygen to oxidize (burn) unburned and partially-burned fuel in the exhaust before its ejection from the tailpipe. There was significant unburned and partially-burned fuel in the vehicle exhaust and so secondary air injection significantly reduced tailpipe emissions. However, the extra heat of re-combustion, particularly with an excessively rich exhaust caused by misfiring or a mal-adjusted carburetor, tended to damage exhaust valves and could even be seen to cause the exhaust manifold to incandesce.

Equivalence ratio:

The equivalence ratio of a system is defined as the ratio of the fuel-to-oxidizer ratio to the stoichiometric fuel-to-oxidizer ratio.

Ignition timing:

In a spark ignition internal combustion engine, the process of setting the time that a spark will occur in the combustion chamber (during the compression stroke) relative to piston position and crankshaft angular velocity.

Inertia Setting:

A physical object's inertia describes the resistance to a change in its state of motion. By varying the inertia setting on the chassis dynamometer the influence of vehicle mass is isolated from the effect this change may have on other vehicle properties, e.g. rolling resistance. An increase in inertia will yield a higher engine load during acceleration but also a less rapid deceleration due to the increased momentum. A reduction in inertia, obviously, has the opposite effect. At constant speed a change in inertia will not affect engine load.

Aromatic content:
Percent aromatic hydrocarbons present in a solvent mixture or in a compound.

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ANNEXURE I

Health effects of Aldehydes and Ketones

Sl.No	Name of aldehyde/ketone	Health effects
1	Formaldehyde	Irritation of the eyes, respiratory tract , nausea, headache, tiredness, and thirst.
2	Acrolein, Acetaldehyde and Crotonaldehyde	Irritation of the eyes, skin, and mucous membranes of the upper respiratory tract.
3	Propionaldehyde, n-Butyraldehyde and Isobutyraldehyde	Eye and respiratory tract irritation
4	Other high-molecular- weight aldehydes such as Chloroacetaldehyde, valeraldehyde, Furfural, the Butyl aldehydes , Glyoxal, Malonaldehyde, Benzaldehyde, Synapaldehyde	less toxic than formaldehyde and Acrolein
5	methyl ethyl ketone	affects nervous system, creates headaches, dizziness, fatigue, narcosis (acts like a narcotic), nausea, vomiting, and passing out ,irritates the eyes, nose, skin and throat, contact with the eyes can permanently damage them. Repeated exposure may damage the nervous system and may affect the brain.

ANNEXURE II

VEHICLE TEST MATRIX

Test matrix of Project activity						
Sl.No	Fuel Consumption	2 Wheelers	3 Wheelers	4 Wheelers Passenger Cars	Light Duty Commercial vehicles	Heavy Duty Commercial vehicles
1	Reference BS II Petrol	3	3	3		
2	Reference BS II Diesel		3	3	3	3
3	Reference BS III Petrol	3	3	3		
4	Reference BS III Diesel		3	3	3	3
5	LPG (retrofitted)		3	3		
6	CNG (retrofitted)		3	3	3	3
7	Ethanol 5% Blend with BS III Petrol	3	3	3		
8	Biodiesel 10% blend with BS III Diesel		3	3	3	3

ANNEXURE III

FUEL SPECIFICATIONS

Gasoline specification

Parameter	**Unit**	**BS II Petrol**	**BS III Petrol**	**Test method**
Research Octane Number (RON)		95	95	EN 25164
Motor Octane Number (MON)		85	85	EN 25163
Density @ 15 C	kg/m3	748-762	740-754	ISO 3675
Reid Vapour Pressure	kPa	56-60	56-60	EN 12 (BS II) Pr EN ISO; 13016-1; (DVPE) (BS III)
Distillation:				
Evaporated @ 100 C	% v/v	49-57	50-58	EN-ISO 3405
Evaporated @ 150 C	% v/v	81-87	83-89	EN-ISO 3405
Final boiling point	C	190-215	190-210	EN-ISO 3405
Residue	% volume	2	2	EN-ISO 3405
Hydrocarbon analysis				
Olefins	% v/v	max 10.0	max 10.0	ASTM D 1319
Aromatics	% v/v	28-40	29-35	ASTM D 1319
Benzene	% v/v	max 1.0	max 1.0	Pr. EN 12177 (BS II) ASTM D 1319 (BS III)
Oxygen content	% m/m	max 2.3	max 1.0	EN 1601
Sulphur content	mg/kg	max 100	max 10.0	Pr. EN ISO/DIS 14596 (BS II) ASTM D 5453 (BS III)
Lead content	mg/l	max 5.0	max 5.0	EN 237
Phosphorous content	mg/l	max 1.3	max 1.3	ASTM D 3231

Source: **GSR 686 (E) (BS II) & GSR 84(E) (BS III))**

Diesel Specification

Parameter	Unit	BS II Diesel	BS III Diesel	Test method
Cetane Number		52-54	52-54	EN-ISO 5165
Density @ 15 ºC	kg/m3	833-837	833-837	EN-ISO 3675
Viscousity @ 40 ºC	mm2/sec	2.5-3.5	2.3-3.3	EN-ISO 3104
Distillation:				
50% point	ºC	min 245	min 245	EN-ISO 3405
95% point	ºC	345-350	345-350	EN-ISO 3405
Final boiling point	ºC	max 370	max 370	EN-ISO 3405
Flash point	ºC	min 55	min 55	EN-22719
CFPP	ºC	max -5	max -5	EN 116
Polycyclic aromatic hydrocarbon	% m/m	3.0-6.0	3.0-6.0	IP 391
Water content	% m/m	max 0.05	max 0.02	EN-ISO 12937
Ash content	% m/m	max 0.01	max 0.01	EN-ISO 6245
Sulphur content	mg/kg	max 300	max 10.0	Pr. EN-ISO/DIS 14596 (BS II) ASTM D 5453 (BS III)

(Source: **GSR 686 (E) (BS II) & GSR 74 (E) (BS III))**

Jatropha Bio-diesel specification

S.No.	Characteristics	Requirement
i.	Density at 15°C, kg/m^3	860-900
ii.	Kinematic Viscosity at 40°C, cSt	2.5-6.0
iii.	Flash point (PMCC) °C, min	120
iv.	Sulphur, mg/kg max.	50
v	Carbon residue (Rams bottom) ,% by mass, max	0.05
vi.	Sulfated ash, % by mass, max	0.02
vii.	Water content, mg/kg, max	500
viii	Total contamination, mg/kg, max	24
ix	Cu corrosion, 3 hrs at 50°C, max	1
x	Cetane No., min	51
xi	Acid value, mg KOH/g, max	0.5
xii	Methanol, % by mass, max	0.2
xiii	Ethanol, % by mass, max	0.2
xiv	Ester content, % by mass, min	96.5
xv	Free Glycerol, % by mass, max	0.02

xvi	Total Glycerol, % by mass, max	0.25
xvii	Phosphorous, mg/kg, max	10
xviii	Oxidation stability, at 110°C hrs, min	6

(Source: Society of Indian Automobile Manufacturers)

Auto Compressed Natural Gas specification

Sl.no	**Constituent**	**Value**	**Tolerance**
1	Wobbe Number	1350	+/- 20
2	Water, lbs/million ft^3	0.5	Maximum
3	Hydrogen Sulphide, grains/100 ft^3	0.1	Maximum
4	Other soluble sulphide, grains/100 ft^3	0.1	Maximum
5	Carbon dioxide, vol.%	3	Maximum
6	Oxygen, vol.%	1	Maximum
Hydrocarbons (% of Total Organic Carbon Present)			
7	Methane	80	Minimum
8	Ethane	10	Maximum
9	C3 and higher HC	5	Maximum
10	C6 and higher HC	1	Maximum
11	Total Unsaturated HC	1	Maximum
Other species (mole %)			
12	Hydrogen	0.1	Maximum
13	Carbon Monoxide	0.1	Maximum

(Source: Haryana City Gas Distribution Ltd, Sector-29, Gurgaon)

Liquid Petroleum Gas specification

S.No.	Characteristic	Requirement
1	Vapour pressure at 40 ^{0}C, KPa gauge	520-1050
2	C5 Hydrocarbons and heavier, mole percent, Max	2
3	Dienes (as 1,3 Butadiene), mole percent, Max	0.5
4	Total volatile sulphur (after stenching), ppm, Max	150
5	Copper strip corrosion at 40 ^{0}C for 1 hour, Max	Class 1
6	Hydrogen sulphide	Pass the test
7	Evaporation residue, mg/kg, Max	100
8	Free water content	Nil
9	Motor Octane Number (MON), Min	88
10	Odour	Unpleasant and distinctive down to 20 percent lower explosive limit (LEL)

Indian fuel ethanol specification

S.N	Absolute (Anhydrous) Alcohol	Special Grade
1	Relative Density @ 15.6/15.6 ^{0}C,	max 0.7961
2	Ethanol content @ 15.6 ^{0}C, vol%, min (excluding denaturant)	99.5
3	Miscibility with water	Miscible
4	Alkalinity	Nil
5	Acidity (CH3COOH), mg/l,	max 30
6	Residue on evaporation, wt%,	max 0.005
7	Aldehydes, as (CH3CHO), mg/l,	max 60
8	Copper, mg/kg,	max 0.1
9	Conductivity, microS/m,	max 300
10	Methyl alcohol, mg/liter,	max 300
11	Appearance	Clear and bright
Note:		
1. For test methods, reference should be made to the Bureau of Indian Standards (IS 15464:2004)		
2. The denaturant to be mixed with ethanol in a proportion which is to be prescribed by law from time to time.		

ANNEXURE IV

Summary of carbonyl and methane emission results

Tabulation results of Carbonyl emissions from two wheeler Category

	Fuel used					
	BS II Petrol		**BS III Petrol**		**BS III Petrol+E5**	
Name of the carbonyl compound emission	**Range** µg/km	**Mean** µg/km	**Range** µg/km	**Mean** µg/km	**Range** µg/km	**Mean** µg/km
Formaldehyde	7.88-10.09	9.22	6.31-15.61	11.21	3.61-4.79	4.01
Acetaldehyde	2.20-3.87	2.98	1.33-3.48	2.25	3.77-4.91	4.38
Acrolein	Nd	Nd	0-2.29	1.35	0-0.56	0.19
Acetone	0.63-1.67	1.29	0.92-1.73	1.23	0.18-0.81	0.58
Propionaldehyde	0.25-0.44	0.35	0.06-0.23	0.44	0-18	0.06
Crotonaldehyde	0-0.22	0.07	0-0.15	0.42	0-0.36	0.19
MEK	0.51-0.87	0.74	0-024	0.10	0.26-0.34	0.29
n-Butyraldehyde	0.08-0.14	0.11	0-0.16	0.48	Nd	Nd
Methacrolein	Nd	Nd	Nd	Nd	Nd	Nd
Benzaldehyde	Nd	Nd	Nd	Nd	Nd	Nd
Valeraldehyde	0-0.25	0.08	Nd	Nd	Nd	Nd
m-Tolualdehyde	Nd	Nd	Nd	Nd	Nd	Nd
Hexanal	Nd	Nd	Nd	Nd	Nd	Nd
Total Avg emission	**14.84 µg/km**		**17.49 µg/km**		**9.72 µg/km**	

Nd-Not detectable

Tabulation results of Carbonyl emissions from three wheeler Category

	Fuel used							
Name of the carbonyl compound emission	**BS II Diesel**		**BS III Diesel**		**B10+ BS III Diesel**		**CNG**	
	Range	**Mean**	**Range**	**Mean**	**Range**	**Mean**	**Range**	**Mean**
Formaldehyde	12.25-	13.74	19.37-	20.07	6.6-7.64	6.94	15.34-	18.06
Acetaldehyde	0.03-0.96	0.54	7.88-9.54	8.92	2.89-18.7	12.26	1.54-2.44	1.99
Acrolein	0-1.20	0.43	0.24-0.97	0.50	0-0.50	0.19	Nd	Nd
Acetone	0.16-1.78	1.02	1.29-1.37	1.34	0-0.55	0.29	0.02-0.34	0.19
Propionaldehyde	0.05-0.77	0.31	0.61-1.86	1.32	0.09-0.26	0.17	0-0.66	0.22
Crotonaldehyde	0.07-0.37	0.25	0.22-1.35	0.71	Nd	Nd	0.02-0.25	0.16
MEK	0-0.3	0.17	0-0.53	0.26	Nd	Nd	Nd	Nd
n-Butyraldehyde	0-0.1	0.03	0.07-0.66	0.32	Nd	Nd	Nd	Nd
Methacrolein	0-0.40	0.14	0.35-0.68	0.49	Nd	Nd	Nd	Nd
Benzaldehyde	0-0.16	0.05	0-0.29	0.10	0-0.27	0.09	Nd	Nd
Valeraldehyde	0-0.27	0.09	0-0.49	0.32	Nd	Nd	Nd	Nd
m-Tolualdehyde	Nd	Nd	0.88-0.32	0.29	Nd	Nd	Nd	Nd
Hexanal	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd
Total Avg Emission	**16.77 µg/km**		**34.650 µg/km**		**19.94 µg/km**		**20.624 µg/km**	

	Fuel used							
Name of the carbonyl compound emission	**BS II Petrol**		**BS III Petrol**		**E5+ BS III Petrol**		**LPG**	
	Range	**Mean**	**Range**	**Mean**	**Range**	**Mean**	**Range**	**Mean**
Formaldehyde	2.46-11.03	8.00	8.29-14.87	11.2	7.18-11.26	9.65	4.17-9.85	6.79
Acetaldehyde	1.62-5.12	3.60	2.9-7.17	5.1	8.05-12.14	8.43	2.76-6.90	5.16
Acrolein	0.94-4.44	2.78	1.81-4.44	3.1	2.95-5.48	3.89	0.68-3.79	2.68
Acetone	8.17-13.84	11.75	8.17-13.24	10.6	4.03-8.17	5.50	2.60-4.90	3.95
Propionaldehyde	4.73-5.59	5.95	4.73-7.51	5.9	2.43-4.73	3.21	1.19-2.79	2.05
Crotonaldehyde	1.37-12.13	5.14	1.37-12.13	7.5	1.31-2.72	1.80	4.27-5.31	4.67
MEK	4.00-7.36	5.43	4.00-7.36	5.4	2.19-4.00	3.04	1.95-2.75	2.25
n-Butyraldehyde	1.82-10.33	7.18	3.31-9.38	5.5	3.44-9.38	6.09	0-0.34	0.11
Methacrolein	0-2.77	1.00	0-2.77	1.0	0-2.77	1.49	0-0.28	0.12
Benzaldehyde	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd
Valeraldehyde	0-15.34	6.79	4.57-5.16	4.9	0-5.04	1.98	0-0.17	0.06
m-Tolualdehyde	0-1.10	0.34	0-1.10	0.4	ab	ab	0-0.14	0.09
Hexanal	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd
Total Avg emission	**57.98 μg/km**		**60.66 μg/km**		**45.08 μg/km**		**27.93 μg/km**	

Nd-Not detectable

Tabulation results of Carbonyl compound emissions from four wheeler Category

	Fuel used							
Name of the Carbonyl compound emission	**BS II Petrol**		**BS III Petrol**		**E5+ BS III Petrol**		CNG	
	Range	**Mean**	**Range**	**Mean**	**Range**	**Mean**	**Range**	**Mean**
Formaldehyde	1.29-6.15	3.41	1.47-3.63	2.69	0.31-3.83	1.95	4.39-13.14	8.72
Acetaldehyde	0.57-1.6	1.14	1.14-2.15	1.66	0.66-0.97	0.73	1.03-2.04	1.68
Acrolein	2.99-20.4	9.97	Nd	Nd	0-16.89	10.74	Nd	Nd
Acetone	Nd	Nd	3.11-4.93	3.93	Nd	Nd	15.60-18.14	17.07
Propionaldehyde	Nd	Nd	0.08-0.15	0.11	Nd	Nd	Nd	Nd
Crotonaldehyde	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd
MEK	Nd	Nd	0-0.65	0.29	Nd	Nd	Nd	Nd
n-Butyraldehyde	Nd	Nd	0-0.30	0.12	Nd	Nd	Nd	Nd
Methacrolein	Nd	Nd	0-0.04	0.01	Nd	Nd	Nd	Nd
Benzaldehyde	Nd	Nd	0-0.36	0.24	Nd	Nd	Nd	Nd
Valeraldehyde	Nd	Nd	0-0.27	0.09	Nd	Nd	Nd	Nd
m-tolualdehyde	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd
Hexanal	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd
Total Avg emission	**14.52 µg/km**		**9.14 µg/km**		**13.41 µg/km**		**27.47 µg/km**	

Nd-Not detectable

	Fuel used							
Name of the Carbonyl compound emission	**BS II Diesel**		**BS III Diesel**		**B10+ BS III Diesel**		**LPG**	
	Range	**Mean**	**Range**	**Mean**	**Range**	**Mean**	**Range**	**Mean**
Formaldehyde	0.46-3.6	2.19	0.46-6	3.23	0.08-3.6	2.16	2.83-3.85	3.45
Acetaldehyde	0.66-10.20	5.70	0-5.05	1.90	0.31-9.90	5.65	5.99-7.65	7.36
Acrolein	3.47-4.01	3.66	1.14-5.28	3.30	0.59-4.62	3.09	2.94-7.65	4.53
Acetone	0-1.78	0.88	0-0.85	0.28	0-1.82	0.97	0.75-1.2	0.99
Propionaldehyde	0-0.16	0.11	0-0.13	0.05	0-0.24	0.10	0.19-1.23	0.62
Crotonaldehyde	0-0.81	0.34	0-1.04	0.39	0-1.51	0.66	0.53-1.05	0.82
MEK	0-0.8	0.39	0-0.56	0.23	0-1.25	0.77	0.8-1.91	1.20
n-Butyraldehyde	0-0.24	0.13	0-0.12	0.04	Nd	Nd	0-0.49	0.37
Methacrolein	0-0.43	0.27	0-0.66	0.27	0-0.51	0.21	0.45-0.67	0.59
Benzaldehyde	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd
Valeraldehyde	0-0.088	0.03	0-0.14	0.05	0	0.00	0-0.17	0.06
m-tolualdehyde	0-0.28	0.14	0-0.52	0.14	0-0.84	0.29	0.13-0.32	0.20
Hexanal	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd
Total Avg emission	**13.83 µg/km**		**9.89 µg/km**		**13.88 µg/km**		**20.18 µg/km**	

Nd-Not detectable

Tabulation results of Carbonyl compound emissions from Light Commercial Vehicle Category

	Fuel used							
Name of the Carbonyl compound	**BS II Diesel**		**BS III Diesel**		**B10+ BS III Diesel**		**CNG**	
	Range	**Mean**	**Range**	**Mean**	**Range**	**Mean**	**Range**	**Mean**
Formaldehyde	4.59-20.88	12.65	2.82-24.13	10.59	1.02-25.85	13.15	43.18-46.87	45.59
Acetaldehyde	7.4-10.16	8.33	2.78-11.56	8.54	4.93-15.046	8.71	13.40-30.79	22.55
Acrolein	9.01-43.94	17.93	7.69-48.73	18.89	2.74-45.66	21.82	9.2-10.48	9.65
Acetone	0-3.95	1.97	1.06-5.82	2.31	3.20-10.2	6.47	6.88-17.28	13.92
Propionaldehyde	0-0.08	0.04	0-2.4	1.28	0-34.36	17.57	3.58-7.91	5.59
Crotonaldehyde	0.05-3.46	1.38	3.08-36.24	14.58	3.47-13.4	6.78	0.85-1.91	1.53
MEK	0.76-2.67	1.73	0-7.52	3.14	0.13-1.34	0.85	1.16-4.16	2.88
n-Butyraldehyde	0.23-3.06	1.32	0.81-17.77	6.56	1.21-8.86	4.00	3.49-6.36	4.97
Methacrolein	0-17.25	6.01	0-2.10	0.89	0-31.34	10.92	3.96-7.68	5.98
Benzaldehyde	0-1.89	1.08	0-2.97	0.99	Nd	Nd	Nd	Nd
Valeraldehyde	Nd	Nd	0-1.98	0.66	0-1.35	0.79	0-3.26	1.09
m-tolualdehyde	2.03-5.61	3.68	4.85-34.57	13.14	0.93-13.89	6.15	1.80-3.67	2.58
Hexanal	0-1.66	0.55	Nd	Nd	Nd	Nd	Nd	Nd
Total Avg emission	**56.66 mg/kW.hr**		**81.56 mg/kW.hr**		**97.22 mg/kW.hr**		**116.34 mg/kW.hr**	

Nd-Not detectable

Tabulation results of Carbonyl compound emissions from Heavy Commercial Vehicle Category

	Fuel used							
Name of the Carbonyl compound	**BS II Diesel**		**BS III Diesel**		**B10+ BS III Diesel**		**CNG**	
	Range	**Mean**	**Range**	**Mean**	**Range**	**Mean**	**Range**	**Mean**
Formaldehyde	14.54-26.61	20.02	27.47-32.7	29.48	17.34-52.46	39.12	45.08-91.35	66.40
Acetaldehyde	6.31-13.95	9.28	22.36-33.24	28.05	11.66-15.76	13.45	11.64-27.89	19.72
Acrolein	7.87-13.99	11.75	6.94-10.83	9.50	6.61-32.76	15.44	10.76-14.87	13.45
Acetone	4.89-5.45	5.18	3.83-14.16	10.70	5.66-9.32	6.91	6.49-7.60	7.20
Propionaldehyde	1.26-5.66	3.13	0-10.27	4.96	1.83-4.50	3.11	0.11-4.24	2.01
Crotonaldehyde	0.27-1.12	0.79	4.89-8.43	6.47	0.09-2.24	1.26	3.72-6.28	5.37
MEK	1.09-5.11	2.92	Nd	Nd	2.37-15.80	7.58	0.20-5.11	2.16
n-Butyraldehyde	0-4.53	1.90	0-1.67	0.63	1.12-55.35	19.47	0.23-3.14	1.82
Methacrolein	0.80-1.52	1.20	0-1.86	0.62	1.82-4.78	3.54	0-1.4	0.92
Benzaldehyde	0-4.7	1.57	0.10-16.97	6.51	Nd	Nd	0-13.05	4.35
Valeraldehyde	3.81-7.01	5.07	Nd	Nd	0-12.35	4.12	0-4.9	2.34
m-tolualdehyde	2.23-3.2	2.79	Nd	Nd	0.36-18.16	6.80	0.76-0.97	0.85
Hexanal	0.73-2.35	1.78	Nd	Nd	0-3.52	1.17	0-0.57	0.96
Total Avg emission	**67.37 mg/kW.hr**		**93.96 mg/kW.hr**		**121.97 mg/kW.hr**		**127.52 mg/kW.hr**	

Nd-Not detectable

Tabulation results of Methane emission from various category vehicles

S.N	Vehicle category	Fuel used	Emissions (mg/km)	
			Range	Mean
1	**Two wheeler**	**BS II Petrol**	1-2	1.3
2		**BS III Petrol**	1-2	1.7
3		**E5+BS III Petrol**	4-5	4.7
4	**Three wheeler**	**BS II Petrol**	14-20	17.3
5		**BS III Petrol**	1-2	1.5
6		**E5+BS III Petrol**	19-32	24
7		**LPG**	8-9	8.7
8		**BS II Diesel**	1	1
9		**BS III Diesel**	1-2	1.3
10		**B10+BS III Diesel**	1	1
11		**CNG (mg/km)**	2014-3303	2852
12	**Four wheeler**	**BS II Petrol**	5-6	5.7
13		**BS III Petrol**	4-7	6
14		**E5+BS III Petrol**	5-7	6.3
15		**LPG**	9-26	15.0
16		**BS II Diesel**	1-50	17.3
17		**BS III Diesel**	16-53	28.7
18		**B10+BS III Diesel**	1-55	21
19		**CNG**	120-280	177

	Vehicle Category	Fuel used	Emissions in mg/kW.hr	
			Range	Mean
20	**Light Commercial Vehicle Engine**	**BS II Diesel**	136-140	138
21		**BS III Diesel**	143-156	151
22		**B10+BS III Diesel**	125-130	127
23		**CNG**	178-217	197
24	**Heavy Commercial Vehicle Engine**	**BS II Diesel**	63-71	66
25		**BS III Diesel**	32-63	51
26		**B10+BS III Diesel**	63-71	65
27		**CNG**	209-237	220

ANNEXURE V

TEST PROCEDURE

13 mode cycles test Procedure:

- Install Engine on the test bed, check alignment with dynamometer & air inlet and exhaust system routing, fuel meter connection.
- Configure the project in TLS software in bridge PC by entering the engine data from AIS 007 as declared by customer submitted through CSC department.
- Crank the engine, warm up cycle will start on defined points as in project.
- After warm up, power check cycle will start, after completion of power check cycle, software calculate the values of A, B, C. Speed, calculation of these values given in (Annexure I).
- After power check, R24 Cycle will start; in this cycle net power will be checked on customer defined speeds at fixed full load fuel injection pump setting.
- After R24 cycle, ESC cycle starts. Details of ESC cycle are given below.

13 mode cycle (ESC Test cycle):

The test cycle consists of a number of speed and power modes which cover the typical operating range of diesel engines. During each mode the concentration of each gaseous pollutant, exhaust flow and power output shall be determined, and the measured values weighted. Test cycle (13 modes) is given below.

Mode Number	Engine Speed	Torque	Weighting Factor	Mode Length (Mins)
1	Idle		0.15	4
2	A	100	0.08	2
3	B	50	0.1	2
4	B	75	0.1	2
5	A	50	0.05	2
6	A	75	0.05	2
7	A	25	0.05	2
8	B	100	0.09	2

9	B	25	0.1	2
10	C	100	0.08	2
11	C	25	0.05	2
12	C	75	0.05	2
13	C	50	0.05	2

INDIAN DRIVING CYCLE: (2/3 Wheelers)

Mass Emission test on 2/3 wheelers (BSII/BSIII)

1. Test Sample preparation (Vehicle):

- Ensure that exhaust system of vehicle is leak proof by blocking the exhaust pipe and see if the vehicle's engines stall.
- If the engine stalls and stops, no leakages in the system.
- Physical verification of the vehicle for any leakages i.e. oil or grease.
- Ensure that the settings of the engine and of the vehicle's control are adequate as prescribed by the manufacturer.
- Ensure that tyre pressure is adjusted to the indicated value by the vehicle manufacturer.
- Appropriate test fuel i.e. BSII & BS III as required by the test standard to be filled in the fuel tank.
- In case of "Type Approval" the 90% of the fuel tank capacity is filled with the fuel.
- Perform the preconditioning of the vehicle.
- After preconditioning keep the vehicle in soak room in which a temperature remains relatively constant between 293 K and 303 K (20 and 30°C). The vehicle soaking shall be carried out for at least 6 hours and continue until the engine oil temperature, if any, are within ± 2°C of the temperature of the room.

2. Pre Test Preparation:

- Ensure that all the instruments are switched on 1 hr before the test for warmup.
- Ensure that the *temperature* of test cell should be in between: 20 and 30°C.
- Ensure that the *absolute humidity* (H) of the test cell or the intake air of the engine should be in between: $5.5 \leq H \leq 12.2$ g H_2O/kg dry air.
- Verify the calibration status of the instruments before the test.

- Weight the particulate filters and record the initial weights of primary and secondary filters for particulate emission measurements for Diesel Vehicles and fit them in the dilution tunnel.
- Ensure that the road load equation is available for coast down

<u>Test procedure:</u>

For Gasoline/Diesel/LPG/CNG Vehicles

Type I:- Emission Measurements

- Push the vehicle on the chassis dynamometer and clamp the non driving wheel without starting the engine.
- Connect vehicle exhaust pipe to the gas sampling system based on the type of fuel used in the vehicle.
- Align the vehicle on the chassis dyno through AVL's dyno software.
- The vehicle shall be approximately horizontal during the test so as to avoid any abnormal distribution of the fuel.
- Set the required inertia on chassis dynamometer as obtained from the road load equation of the vehicle.
- Perform the coast down of the vehicle through software.
- Prepare the AMA by checking the zero and span of the system
- Ready the CVS and FFP (for diesel engines) system by enabling them for remote mode.
- Fill the vehicle data in the GEM software and ready the system for test.
- Check all the systems are in remote mode.
- Start the test and rider will ride the vehicle as per the IDC. The operator is provided with the speed tolerance of ± 1 kmph in driving cycles.(***Annexure I***)
- Bag filling and Sampling will start as per the driving cycle i.e. Indian Driving Cycle.
- After the test, analysis of the exhaust gas collected in the sample bags will be done by AMA and GEM will generate a file for the test.
- Test data is generated and printout is taken of the file.
- Annexure is generated for the test

<u>Abbreviations:</u>

- AMA: - It's an exhaust gas analyzer of AVL Pvt. Ltd.
- CVS:- Constant Volume Sample
- FFP:- Full Flow Particulate(for Diesel)
- IDC: - Indian Driving Cycle.

Annexure I

(Indian Driving cycles)

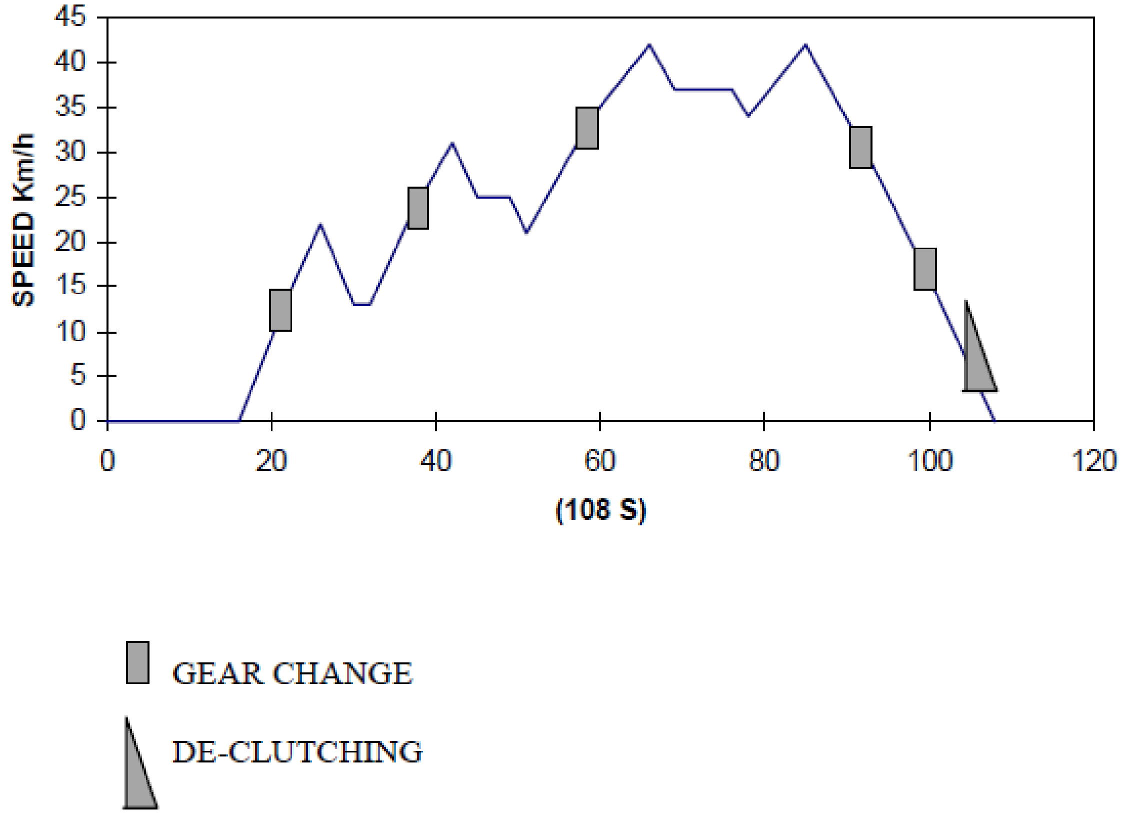


Fig 1 : OPERATING CYCLE WITH RECOMMENDED GEAR POSITION

Test Sample preparation (Vehicle):

- Ensure that exhaust system of vehicle is leak proof.
- Physical verification of the vehicle for any leakages.
- Ensure that the settings of the engine and of the vehicle's control are adequate as prescribed by the manufacturer.
- Ensure that tyre pressure is adjusted to the indicated value by the vehicle manufacturer.
- Appropriate test fuel i.e. BS III or BS IV as required by the test standard to be filled in the fuel tank.
- In case of "Type Approval" the 90% of the fuel tank capacity is filled with the fuel.
- Perform the preconditioning of the vehicle.

- After preconditioning keep the vehicle in soak room in which a temperature remains relatively constant between 293 K and 303 K (20 and 30°C). The vehicle soaking shall be carried out for at least 6 hours and continue until the engine oil temperature, if any, are
  within ± 2°C of the temperature of the room.

Pre Test Preparation:

- Ensure that all the instruments are switched on 1 hr before the test for warmup.
- Ensure that the temperature of test cell should be in between: 20 and 30°C.
- Ensure that the absolute humidity (H) of the test cell or the intake air of the engine should be in between: $5.5 \leq H \leq 12.2$ g H_2O/kg dry air.
- Verify the calibration status of the instruments before the test as per clause 3.
- Precondition the particulate filters and record the initial weights of primary and secondary filters for particulate emission measurements for Diesel Vehicles and fit them in the dilution tunnel.
- Ensure that the road load equation is available for coast down and if in case not available, perform the coast down by power absorption method provided unladen mass is given.

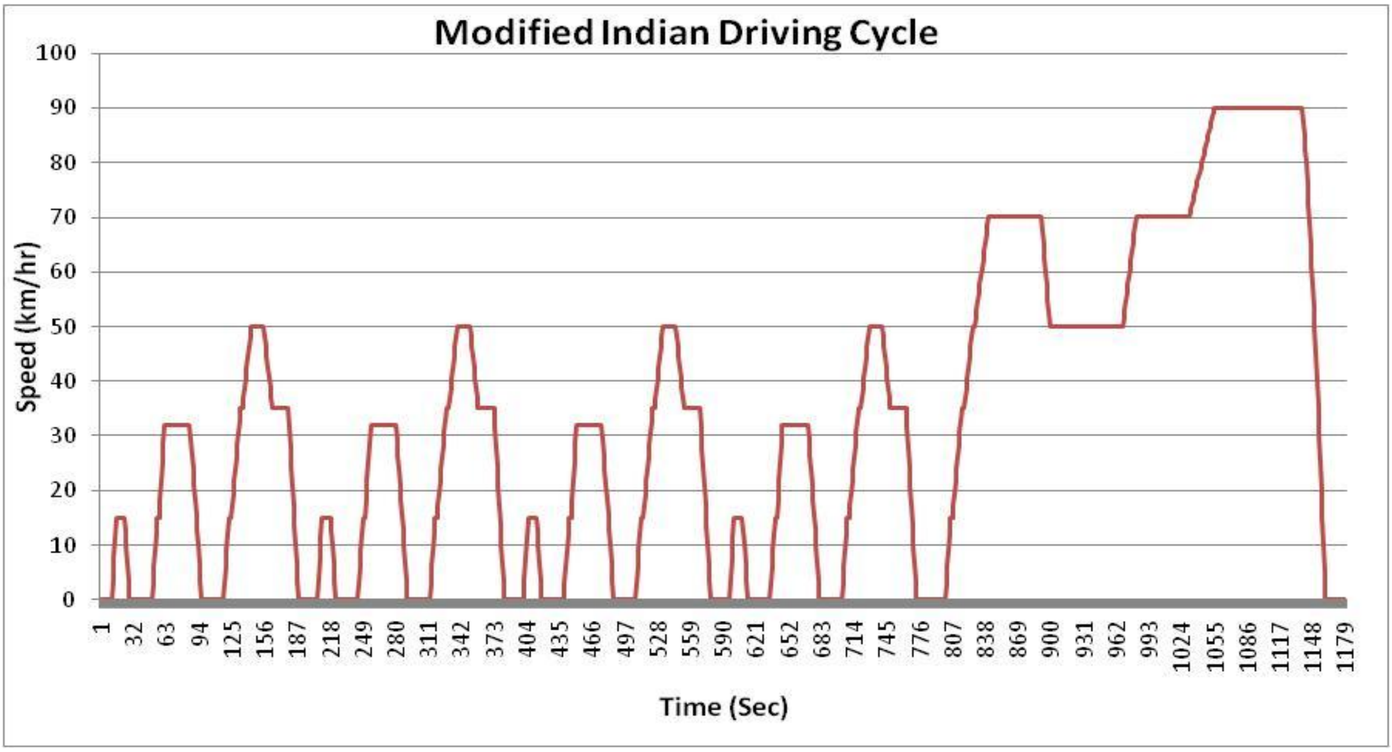
Test procedure:

For Gasoline Vehicles

Type I:- Emission Measurements

- Push the vehicle on the chassis dynamometer and clamp the non driving wheel without starting the engine.
- Connect vehicle exhaust pipe to the gas sampling system based on the type of fuel used in the vehicle.
- Align the vehicle on the chassis dyno through AVL’s dyno software.
- The vehicle shall be approximately horizontal during the test so as to avoid any abnormal distribution of the fuel.
- Set the required inertia on chassis dynamometer as obtained from the road load equation of the vehicle.
- Perform the coast down of the vehicle through software.
- Prepare the AMA by checking the zero and span of the system

- Ready the CVS and FFP (for diesel engines) system by enabling them for remote mode.
- Fill the vehicle data in the GEM software and ready the system for test.
- Check all the systems are in remote mode.
- Start the test and rider will ride the vehicle as per the MIDC. The operator is provided with the speed tolerance of ± 1 kmph in driving cycles.(Annexure I)
- Bag filling and Sampling will start as per the driving cycle i.e. Modified Indian Driving Cycle for the Year 2000(annexure I)
- After the test, analysis of the exhaust gas collected in the sample bags will be done by AMA and GEM will generate a file for the test.
- Test data is generated and printout is taken of the file.
- Annexure is generated for the test



ANNEXURE VI

AUTOMOTIVE SOURCE SAMPLES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY AIR RESOURCE BOARD (SOP MLD 104)

1 Introduction

1.1 The procedure describes a method of sampling and analyzing automotive engine exhaust for aldehyde and ketone compounds (carbonyls) in the range of 0.02 to 200 micrograms (mg) in 2,4-dinitrophenylhydrazine (DNPH) impregnated cartridges. Currently the target compounds analyzed and reported by this method are: formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, Crotonaldehyde, Methacrolein, Butyraldehyde, Methyl Ethyl Ketone (MEK), Benzaldehyde, Valeraldehyde, m-Tolualdehyde, and Hexanal.

1.2 The procedure is derived from a method used by the U.S.EPA (Riggin, 1984; Winberry et. al., 1999) and integrated into Method 1004 of the California Nonmethane Organic Gas Test Procedures (ARB, 2002).

2 Method Summary

2.1 Sample Collection:

2.1.1 For routine motor vehicle testing, the vehicle is tested according to the Federal Test Procedure (FTP), using a dynamometer (dyno) and constant volume sampler (CVS) to dilute the exhaust for sampling (see CFR in the reference section).

2.1.2 Samples are also received from CVS testing using non-FTP driving cycles, Sealed Housing Evaporative Determinations (SHEDs), cartridge samples for round-robin testing and carbonyl-containing samples from other miscellaneous sources.

2.1.3 The automotive test personnel collect the carbonyl samples by flowing dilute exhaust (approximately 1.0 liter/min. flow rate) through cartridges (Tejada, 1986a). The samples are then brought to the laboratory for analysis.

2.2 Extraction and Analysis:

2.2.1 Each cartridge contains an absorbing compound (2,4-DNPH) which complexes with the carbonyl compounds to form their dinitrophenylhydrazone derivatives (called carbonyl-DNPH in this document). The cartridges are then extracted with 5.0 milliliters (mL) acetonitrile and analyzed (Tejada, 1986b).

2.2.2 Separation and analysis is performed using a High Performance Liquid Chromatograph (HPLC) with an ultraviolet (UV/VIS) detector.

3 Interferences and Limitations

3.1 As with any chromatographic method, this method is subject to interference by compounds in the acetonitrile extract having the same retention time as one of the thirteen target compounds and detectable by ultraviolet absorption. Periodic confirmations using an alternative method and/or instrumentation, e.g., alternative HPLC column or mobile phase may be needed to minimize these interferences.

3.2 If samples are not analyzed the same day as received, they must be refrigerated at a temperature below 40°F. Refrigerated samples are stable for up to 30 days.

3.3 The extraction of cartridges with 5.0 mL acetonitrile performed in the laboratory established a statistical average eluted volume of 4.4 mL; the remaining 0.6 mL is retained in the cartridge.

4 Instruments and Apparatus

4.1 The Southern Laboratory Branch (SLB) currently utilizes a modular Waters HPLC analytical system assembled from the components listed below. Equivalent HPLC systems that meet the requirements of this analytical procedure are also acceptable.

4.1.1 Dual high pressure pumps (Waters Model 510). An equivalent HPLC system should consist of pump/pumps with a minimum of two channels and sufficient pulse dampening for meeting the limit of detection (LOD) requirement.

. **4.1.2** Pump controller module (Water PCM/15xx). Typical modern HPLC systems do not require a separate pump controller module.

4.1.3 Liquid autosampler with sample tray at 20°C (Waters Model 717 WISP). An equivalent HPLC system should consist of a sample handling module capable of maintaining 20°C.

4.1.4 Temperature control module (Waters TCM). An equivalent HPLC system should consist of column holding module capable of maintaining 40°C.

4.1.5 Chromatographic Columns: two Supelcosil columns (Supelco, Inc., 4.6 mm inside diameter x 25 cm long) in series and a guard column (2.0 cm long) packed with LC-18 beads of 5 mm particle size. Many vendors supply HPLC columns with similar stationary phase compositions (i.e. C-18). An equivalent column should be able to resolve the DNPH-derivatives of the 13 target compounds into 13 peaks.

4.1.6 UV/VIS Detector (Waters Model 486 tunable absorbance detector). An equivalent HPLC system should consist of a detector able to measure absorbance in the 360-370 nm region and meet the specified LOD requirement.

4.1.7 Computer-based data system for peak integration (Millennium32). An equivalent software package should be able to control the HPLC system and to facilitate peak integration.

5 Reagents and Materials

5.1 For sample collection: DNPH impregnated cartridges (SEP-PAK DNPH Silica cartridges from Waters)

5.2 Acetonitrile (ACN), HPLC grade, VWR Scientific or equivalent

5.3 Purified water, HPLC grade, VWR Scientific or equivalent

5.4 Methanol, HPLC grade, VWR Scientific or equivalent

5.5 Stock solutions – Carbonyl-DNPH standard solution, by Cerilliant Corporation or equivalent, consisting of thirteen compounds (see Table 3.4), each having a concentration of 1.0 mg/mL, 3.0 mg/mL, or 15.0 mg/mL and 99% purity. The concentrations are the amount of carbonyl compound (NOT the carbonyl-DNPH derivative) per mL of solution.

5.6 Working Standard – A typical working standard is prepared as needed by diluting 2.0 mL of the 3.0 mg/mL stock solution to 10 mL (v/v) using ACN for dilution. Current working standard concentration is 0.6 mg/mL.

5.7 Control Standard – A quality control standard, containing all target carbonyl-DNPH derivatives within the typical concentration range of real samples, is analyzed to monitor the precision of the analysis of each target carbonyl. The control standard is prepared by batch mixing old samples and spiking with the stock carbonyl-DNPH standard solution, if needed, to obtain the desired concentration levels of the target analytes. All target compounds except acrolein have been found to be stable in the control standard.

6. Procedure

6.1 DNPH-impregnated cartridges are used to collect carbonyl samples from automotive exhaust. Separate background samples are collected during each of the three test phases, although one composite background may be collected instead.

6.2 Each cartridge is extracted by connecting it to a syringe assembly and applying 5.0 mL of acetonitrile. The liquid containing the carbonyl-DNPH derivatives is allowed to flow by gravity into a glass storage container until the entire yellow color band has been eluted.The plunger is then pressed to expel the excess ACN from the cartridge. Although approximately 0.6 mL of ACN is retained in the cartridge, no carbonyls are retained.

6.3 Approximately 0.75 mL of the extract is transferred into a 1.0 mL autosampler glass vial and sealed with a plastic snap cap. For equivalent HPLCs sample vials of different volume and cap type are acceptable.

6.4 A typical sample run is comprised of:

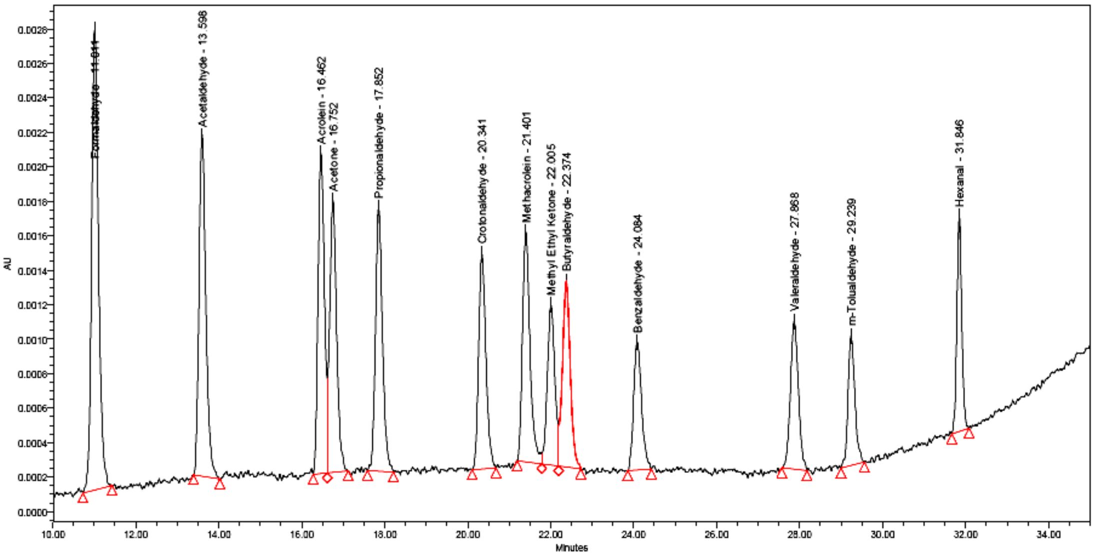
6.4.1 Working standard, control standards, ACN blank, field blank, and samples.

6.4.2 A stock standard solution of an appropriate concentration is loaded within sequence if a sample that exceeds the working standard concentration (0.6 mg/mL) is expected.

6.5 Typical operating conditions for the HLPC system are:

Columns	Analytical column - Supelcosil, 4.6 mm ID x 25 cm long, two columns in series Guard column - 4.6 mm ID x 2.0 cm long packed with LC-18, 5 µm pellicular beads
Column oven temperature	40℃
Detector	UV/VIS at 360 nanometers (nm)
Sample volume	10 µL
Solvent A	Acetonitrile (ACN)
Solvent B	10% (v/v) methanol in water
Flow	1.2 mL/minute (min)
Program	50% A, 50% B; 0 (initial condition)
	60% A, 40% B; 0 to 10 min (linear gradient)
	65% A, 35% B; 10 to 20 min (linear gradient)
	100% A, 0% B; 20 to 30 min (linear gradient)
	100% A, 0% B; 30 to 32 min (hold)
	50% A, 50% B; 32 to 35 min (linear gradient)
	50% A, 50% B; 35 to 45 min (equilibrating)
Data system	PC-controlled data acquisition system

Operating Parameters for the HPLC Analysis.



Elution of profile of the target carbonyl-hydrazone from the supelcosil HPLC Column

6.6 The peaks are identified and quantified by the data system. All chromatograms are checked for proper identification and baseline drift. Any misidentification and drifting in the baseline are manually corrected by the reintegration of the chromatograms

6.7 Only the target carbonyl peaks at or above the LOD are reported.

7 Calculations

7.1 The target carbonyl concentrations, in µg/mL, are calculated by the data system using each carbonyl-DNPH compound (Table 1) as an external standard.

7.2 The mass of each carbonyl compound per cartridge is determined using the following

Calculation:

Mass sample (µg) = Peak Area sample x RF x Volume of Extract (mL)

Where the RF is the response factor calculated from the daily calibration as follows

$$\textbf{RF} = \frac{\text{Concentration (working standard) } \mu\text{g/mL}}{\text{Peak Area (working standard)}}$$

ANNEXURE VII

EQUIPMENT SPECIFICATION

Dynamometer specification

Parameter	Chassis dynamometer		Engine dynamometer
	AVL make 2/3 wheeler	**AVL make 4 wheeler(PC) and LCV**	**HCV**
Type	DC machine	DC machine	Eddy Current
Max. Power	70 kW	140 Kw	550 kW
Max. speed	200 kmph	200 kmph	9000 rpm
Max. Tractive	660 N	1000 N	N/A
Roller diameter	955 mm	1019.2 mm	N/A
No.of rollers	Single roller	Double roller	N/A
Max. Torque	N/A	N/A	2000 Nm
Accuracy	Less than 2%	Less than 2%	1%

Control Volume Sampler specification

Parameter	2/3 wheeler	4 wheeler (PC)
	Horiba	**Horiba**
Venturi	1,2,4,5 m^3/min	6,8,….12 m^3/min
Tunnel diameter	297 mm	297 mm
Filter holder assembly	70-47	70-47
Propane injection	Critical Flow Orifice (CFO)	Critical Flow Orifice (CFO)

Methane analyzer specification

FID 4000 lcg gas chromatograph with FID for CH4 measurement

Dimensions	½ 19" housing 3 height units
Material	PTFE Viton Stainless steel for sample gas conducting components
Weight	12 kg
Voltage supply	115/230 VAC ± 10 % .50/60 Hz
Power draw	max. 400 W
Permissible ambient temperature	5 to 40 °C
Permissible air pressure	700 to 1.100 hPa abs.
Measuring ranges	CH4: 0 - 3.000 ppm C_1 (4 measuring ranges definable)
Process time	< 40s
Detection limit	20 ppbC_1
Drift [a)]	≤ 1,0% of the measuring value + 2x DL/h
Linearity fault	≤ 1.0 % of the measuring value + 1x DL
Noise/reproducibility [b)]	≤ 0.5 % of the measuring value + 2x DL
Sample flow rate	approx. 60 l/h
Properties of sample	Dew point ≤ 30 °C Particles ≤ 5 µm
Connections for inputs and outputs	Zero, span gas (1 input) Control air (1 input) Fuel (1 input) Burner air (1 input) Bypass (1 output) Detector (1 output)
Input pressure for zero and span gas	400 hPa ± 30 hPa rel.
Input pressure for burner air, fuel and control air	1.000 hPa ± -2.000 hPa rel.
Oxygen fault [c)]	≤ 1 % of the measured C_3H_8 value
Digital interface	CAN Bus with CANopen protocol

a) With constant ambient pressure and temperature

b) over 10 successive measurements

c) For all O_2-concentrations between 0 - 21 %

		2/3 wheeler	4 wheeler (PC)	LCV & HCV
CH4	Model	FID 4000 Low Cold Gas chromatograph (LCG)	FID 4000 Low Cold Gas chromatograph (LCG)	Flame Ionization Analyzer (FIA)
	Range	0-250 ….2500ppmc	0-250 ….2500ppmc	0-250 ….2500ppmc

ppmc- Parts per million concentration

High Performance Liquid Chromatography (HPLC) Specifications:

Parts	Parameters	Specification
Gradient Pump	Pump type	quaternary gradient pump
	Flow Rate	0.001 to 10 mL/min in 0.001 steps
	Flow Accuracy	0.05% at 1 mL/min
	Flow Precision	Less than 0.075% RSD
	Pressure Pulsation	$\pm$ 0.5% at 2mL/min
	Max Pressure	0-40 MPa (400 bar)
	Gradient Precision	< 0.20% RSD
	Gradient Composition accuracy	$\pm$ 1% (1mL/min)
	Flow repeatability	better than 0.1%
Variable UV Detector	Detector Type	Double beam photometric
	Wavelength	190 – 900 nm
	Drift	$1x10^{-4}$ AU/h at 230 nm, $3x10^{-4}$ AU/h at 254 nm
	Linearity	Better than 1%, 0.001 to 2A
	Wavelength Accuracy	$\pm$ 1 nm with auto calibration
	Wavelength Precision	$\pm$ 0.1 nm
	Noise	0.6×10^{-5} AU or less at 250 nm
	Light Source	Deuterium lamp
	Band/Slit width	6 nm typical over entire range
Column Oven	Temperature range	1 to 65 ^{0}C
	Temperature stability	0.1 ^{0}C
	Column Capacity	Upto 3, 25 cm (10 mm ID max)
	Heat-up/cool down time	5 min from ambient to 40^{0}C, 10 min from 40 ^{0}C to 20 ^{0}C
	Temperature Accuracy	$\pm$ 0.8 ^{0}C with calibration $\pm$ 0.5 ^{0}C
Degasser	Max Flow Rate	5ml/min
	Number of Channels	4
	Internal Volume	Approx. 7 mL/flow path (not including the tubes connected)
	Max Withstand Pressure	0.2 MPa
Injector	Injector Type	Rheodyne, Manual injection valve, 20 µl sample loop and mounting stand.

ANNEXURE VIII

TEST VEHICLE SPECIFICATION

Specification of Hero Honda Passion Pro (Two wheeler)

Engine	
Type	Air-cooled, 4-stroke single cylinder OHC
Displacement (cc)	97.2 cc
Maximum Power	5.4 kW (7.8 Ps) @ 7500 rpm
Maximum Torque	0.82 Kg-m (8.04 N-m) @ 4500 rpm
Starting	Self & Kick Start
Bore x Stroke	50.0 x 49.5 mm
Compression Ratio	9.0 :1
Ignition	DC – Digital CDI with TCIS – Throttle Controlled Ignition System
Engine Oil Grade	SAE 10 W 30 SJ Grade (JASO MA Grade)
Kerb Weight (Kgs)	116 (Kick) / 119 (Self)
Fuel:	
Tank Capacity	10.3 Ltrs (Min)
Reserve	1.8 Ltrs

Specification of Wagon R vxi BS III (4- wheeler LPG & CNG)

Engine	
Engine Type	In-Line Engine
Engine Description	1.1L 64bhp 4 cyl. In-line, FC engine
Engine Displacement(cc)	1061
No. of Cylinders	4
Maximum Power	64@6,200 (PS@rpm)
Maximum Torque	8.6@3,500 (kgm@rpm)
Valves Per Cylinder	4
Fuel Supply System	MPFI
Bore x Stroke	68.5 x 72 mm
Compression Ratio	9.0:1
Turbo Charger	No
Super Charger	No
Fuel	
Fuel Type	Petrol
Fuel Tank Capacity (litres)	35
Emission Norm Compliance	Bharat Stage III

Specification of Maruti Swift Dzire LDI (4 Wheeler-Diesel)

Engine	
Engine Type	In-Line Engine
Engine Description	1.3L 75PS DDiS engine w/ Common Rail multi injection technology
Engine Displacement(cc)	1248
No. of Cylinders	4
Maximum Power	75 PS at 4,000 rpm
Maximum Torque	190 Nm at 2,000 rpm
Valves Per Cylinder	4
Valve Configuration	DOHC
Fuel Supply System	CRDI
Bore x Stroke	69.6 x 82 mm
Compression Ratio	17.6:1
Turbo Charger	Yes
Super Charger	No
Fuel	
Fuel Type	Diesel
Fuel Tank Capacity (litres)	43
Emission Norm Compliance	Bharat Stage III

Specification Of Maruti Swift Dzire VXI (4 Wheeler-Petrol)

Engine	
Engine Type	In-Line Engine
Engine Description	1.3L 85PS AlTec32 engine
Engine Displacement(cc)	1197
No. of Cylinders	4
Maximum Power	85PS at 6000 rpm
Maximum Torque	113Nm at 45 rpm
Valves Per Cylinder	4
Valve Configuration	SOHC
Fuel Supply System	MPFI
Bore x Stroke	74 x 75.5 mm
Compression Ratio	9.0:1
Turbo Charger	No
Super Charger	No
Fuel Type	Petrol
Fuel Tank Capacity (litres)	43
Emission Norm Compliance	Bharat Stage III

Specification of JSA 1360D II Load Carrier (Petrol / CNG Variant- 3 wheeler)

Engine	
Type	Air Cooled , Four Stroke
No. Of cylinders	Single
Bore	85mm
Stroke	90mm
Cubic capacity	510cc
Max output	11BHP @ 3000 rpm
Max. Torque	29.0 Nm
Capacities	
Fuel tank	10.25 ltr.
Engine oil	1.75 ltr
Gear oil	1.0 ltr.
Gross vehicle weight	1359.5 Kg
Seating capacity	1+1 6+1

Specification of TATA 709 (HCV)

Make:	Tata
Model:	709
Variant:	LPT
Type:	Truck
Application:	For Goods Transport
Engine	
Displacement:	2956cc
Engine Type:	TATA 497 TC
Gear Box:	GBS-27 synchromesh
Maximum Power:	67.5 @ 2800
Maximum Torque:	261 @ 1800
Cylinders:	4-in-line DI Turbo
Bore & Stroke:	97x100
Kerb Weight:	2820kgs
Gross Vehicle Weight:	7500 kgs

Specification of TATA 407 (LCV)

Model	TATA 497 SP
Type	High speed, water cooled, naturally aspirated, high pressure direct injection diesel engine with dry liners.
No of cylinders	4 in line
Bore/Stroke	97/100 mm
Capacity	2356cc turbo
Maximum engine output	75 PS@ 2800rpm
Maximum operating speed	3500 rpm
Idling speed	600 rpm
Maximum torque	225Nm @ 1250-1800rpm
Firing order (From F.W end)	1-3-4-2
Compression Ratio	17. :1
Air filter	Oil bath type
Oil filter	Full flow paper type
Fuel filter	Single stage find filteration
Fuel injection pump	Inline type– MICS
Governor	Centrifugal type variable speed RSV
Fuel injection begins	15 degree before TDC
Cooling water temperature	850 C to 950 C
Cooling system pressure	0.5 bar
Max permissible GVW (kg)	5700
Maximum Payload (kg)	3626