1.1 HISTORY & IMPORTANCE OF AUTOMOTIVE EMISSIONS

Evolution of Worldwide Emission Regulations started since world war-II when the use of automobile increased in public domain. First time the California state observed changes in the ambient air quality due to automotive pollution and in 1958 California Ambient Resource Board (CARB) has enforced world’s first emission regulation in the California state. Later on Environmental Protection Agency (EPA) was established to bring a national regulation for the United State of America in 1960 covering old vehicle models. Further, Europe, Japan and other Asian countries have formulated and adopted emission standards in their countries. In the beginning emission regulations covered only gaseous pollutants like carbon monoxide (CO), un-burnt total hydrocarbons (THC) and oxides of nitrogen (NOx), however, first time in 1985 CARB has introduced new regulatory pollutant as particulate matter specifically for diesel vehicles. In Europe till July, 1988 emission regulation was only for gaseous pollutants and from 1988 onwards PM$_{10}$ was introduced for diesel vehicles. Similarly, in India first time whole country was covered by emission regulation under central motor vehicle rule (CMVR) No. 15 which was only for idling emissions and the mass emission standards for gaseous pollutants was introduced from 1991 for gasoline light duty vehicles and in 1992 for diesel vehicles, however, like Europe PM standard came into force since April, 2000 with India Stage-I norms. Since inception emission regulations were tightened drastically as shown in Figure 1.1 to get the improvement in the ambient air quality. Indian emission regulations are in harmonization with European regulations. Emission road map is directly associated with fuel road map. Currently, India is practicing Bharat Stage IV norms with 50 ppm sulfur level which shows drastic reduction in diesel sulfur from 5000 ppm since 1996. Currently, Europe is with
Euro 6 norms with 10 ppm sulfur level which were introduced since, 2014 and it includes PM$_{2.5}$ and particle numbers both for diesel as well as for gasoline direct injection vehicles.

![Graph showing emission norms](image)

**Figure 1.1** Evolution of Emission norms for passenger cars and light duty vehicles

In India as per the latest information Bharat Stage VI norms are likely to get introduced by the year 2020, which will also need diesel with ultralow sulfur below 10 ppm. Stringency of the emission norms shows that almost all the pollutants are tightened near to 90% from their baseline norms since they were introduced. For the passenger cars and LDV’s particulate emission norms have been tightened until Euro 6 to the level of 98.2% from it’s base line norms. Vehicle manufacturers can meet these very high stringent norms by using advanced engines and exhaust after treatment technologies. Tightening of the emission norms since it’s inception till date by 98% couldn’t show proportionate effectiveness in ambient air quality. This can be observed from the increased rate of mortality due to air pollution specifically ultrafine particles which causes various kinds of diseases like asthma, bronchitis, and hardening of blood veins, cardiovascular diseases and spread of cancers of different organs in both old and young generations.

Till Euro-4 emission standards (i.e. equivalent Bharat Stage IV in India) the regulations are based on gravimetric measurement method to measure PM$_{10}$ i.e. total mass of the particulates up to 10 µm size. In the recent international studies, health implications of ultrafine particle emissions from vehicles have been investigated. Apart from particulate
mass other metrics like particle number, size and surface area of ultrafine particles found to play an important role adversely affecting human health. Compared to large or coarse particles, ultrafine and nano particles cause severe health effects. Present method of PM10 measurement is gravimetric where, chloro-fluro carbon glass fiber filter paper having the porosity of 0.3 µm is used to collect the particulate matter at a temperature below 52°C. Thus current PM measurement by gravimetric method using filter paper method doesn’t capture the ultrafine and nanoparticles which are below 0.3 µm.

Typically, diesel exhaust shows nucleation mode particles below 50 nm and they contribute around 90% of total PN. Similarly, accumulation mode contributes maximum towards particle mass around 80% and to particulate number around 8 to 10%. These accumulation particles are typically in the size range above 50 nm up to 1 µm. Understanding the seriousness of increased rate of mortality and severe impacts on the human health and environment, UNECE formed a separate sub group known as PMP (Particulate Measurement Program) under WP 29 - GRPE to study ultrafine and nanoparticles and to formulate new measurement test procedure and equipment setup to measure both particulate mass of PM$_{2.5}$ and the particle number (PN). The UNECE-GRPE PMP program was realized by Great Britain, Germany, France, Sweden, Netherlands and Switzerland, with the focus on future regulation on nanoparticle emissions from light duty vehicles and heavy duty engines (Reference record notes on www.unece.org of GRPE). Japan has also joined this PMP program. GRPE-PMP group experts have taken lot of efforts to finalize the test methodology and the equipment setup to overcome the challenges to measure the particle number and PM$_{2.5}$ mass with good accuracy and reliability. This measurement methodology is adopted by European commission to amend ECE Regulation No.83 to make PN and PM$_{2.5}$ measurement mandatory in the Euro-5b/ Euro-6 emission regulations. First time in the world Europe has introduced the emission norms for particle number and PM$_{2.5}$ as $6 \times 10^{11}$ and 4.5 mg/km respectively, both for diesel and gasoline direct injection passenger cars, for which details are given below in Table-1.1(E/ECE/324/Rev.1/Add.82/Rev.5 and E/ECE/TRANS/505/Rev.1/Add.82/Rev.5, Regulation No. 83 Revision 5, Emission Limits from Table 1, pp19).
Table 1.1 Euro 5b Emission Norms for Passenger Cars

<table>
<thead>
<tr>
<th>Category</th>
<th>Class</th>
<th>Reference mass Vehicle Reference Mass (kg)</th>
<th>Limit values</th>
<th>Limit in mg/km</th>
<th>PM (#/km)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>CO</td>
<td>THC</td>
<td>NMHC</td>
</tr>
<tr>
<td>M</td>
<td>—</td>
<td>All</td>
<td>1000500</td>
<td>100</td>
<td>68</td>
</tr>
<tr>
<td>N_{1}</td>
<td>I</td>
<td>RM ≤ 1,305</td>
<td>1000500</td>
<td>100</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>1,305 &lt; RM ≤ 1,760</td>
<td>1810630</td>
<td>130</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>1,760 &lt; RM</td>
<td>2270740</td>
<td>160</td>
<td>108</td>
</tr>
<tr>
<td>N_{2}</td>
<td>—</td>
<td>All</td>
<td>2270740</td>
<td>160</td>
<td>108</td>
</tr>
</tbody>
</table>

Here, PI means positive ignition and CI means compression ignition.

*Positive ignition particulate mass and number limits shall apply only to vehicles with direct injection engines.

1.2 CHALLENGES IN MEASURING PARTICLE NUMBER AND PM_{2.5}

There are real challenges in measuring PM_{2.5} from the advanced technology vehicles which are fitted with diesel particulate filter (DPF) and continuously regenerative trap (CRT) by using gravimetric method. This is due to very less amount of coarse particulates available in the exhaust sample getting collected on the filter paper. These issues and challenges are resolved by the new Euro-5b/ Euro-6 regulatory test procedure by recommending the following.

- Till Euro-4 PM_{10} is measured by using microbalance having readability of 1 µg.
  The new Euro-5b/ Euro-6 regulatory test procedure to measure PM_{2.5} recommends use of micro balance having readability of 0.1 µg for better sensitivity & accuracy.
- For the better stability of particulates new procedure recommends to control the temperature of diluted exhaust within 47±5 °C inside the dilution tunnel and also near particulate filter holder, earlier till Euro IV this temperature was required to be anything below 52°C.
- In order to measure PM2.5 pre-classifier is required before particulate filter holder so that it will remove the particles above 2.5 µm.
To measure particle number Euro-5b/ Euro-6 standard recommends use of equipment like volatile particle remover (VPR) and condensation particle counter (CPC). VPR is used to remove all the volatile and semi-volatile particles in the exhaust sample so as to measure only solid particles after conditioning and stabilizing by passing the sample through two stage of dilution viz. hot and cold dilution. Accurate control on dilution ratios and dilution temperature at both the stages of dilution is necessary to stabilize the particles before measurement in terms of number and size. CPC measures the particle number of solid particles by optical method.

1.3 CLASSIFICATION OF ENGINE EXHAUST PARTICLES

Particle is a small body having definite internal structure but negligible mass. Based on the size particles are classified into three categories. Nano size particles are all below 50 nm, particles above 50 nm and up to 100 nm are ultrafine particles, particles above 100 nm and up to 2.5 µm are fine particles and rest of the particles above 2.5 µm are coarse particles. Just to get comparative understanding about particle size, a thickness of the normal paper is 0.1mm and size of the human hair is between 40 to 120 µm. This means we can have more than 1000 such nanoparticles sitting on the tip of hair, which are mainly responsible for adverse health effects. Generally, automotive particle emissions are categorized as accumulation mode particles and nucleation mode particles. Accumulation mode particles form a lognormal size distribution with a median above 30 nm and they are mainly consists of carbonaceous particles. Nucleation mode particles, generally below 30 nm and they consists predominantly condensed volatile material; mainly sulfate and heavy hydrocarbons. Presence of nucleation mode particles in the exhaust depends on the concentration of carbon in the accumulation mode particles. Generally, volatile sulfates and different species of hydrocarbons in the exhaust tend to condense on these nucleation mode particles causing change in their morphology. Hydrocarbons and sulfates tend to get condensed independently when carbon emission found reduced. This leads to the formation of large number of very small nucleation mode particles. These particles are below 30 nm size and are customarily called as nanoparticles. Normally, a separate lognormal distribution is observed for the nucleation mode particles having size median below 30 nm, which gets superimposed on the distribution of accumulation mode particles.
1.4 DISTRIBUTION OF ENGINE EXHAUST PARTICLE SIZE, NUMBER AND MASS

The extent of the nucleation mode formation is dependent on various parameters like engine and fuel technology, use of exhaust after-treatment devices, operating conditions and also strongly linked with sampling and measurement conditions.

Figure 1.2 Typical distribution of particulate number, mass and surface area for diesel engine exhaust

Figure 1.2 shows diesel aerosol number and mass weighted size distributions. The distributions are tri-modal and lognormal in the form. The concentration of particles for any size range is proportional to the area under the corresponding curve in that range. Accumulation mode particles in the size range from 0.05 to 1 μm contributes maximum towards particulate mass which cover ultrafine and fine particles. Whereas, nano particles are found within size range up to 50 nm. Kittleson et al. (2002) found that the nuclei mode and the accumulation mode get formed at different times and they have varieties of compositions in the form of carbonaceous agglomerates and associated adsorbed materials. The nuclei mode particles usually consist of volatile organic and sulfur compounds which get formed during exhaust cooling and dilution. Nuclei mode particles may contain solid carbon and metal compounds. The nuclei mode particles contribute approximately, 1-20 % towards total particulate mass and more than 90 % of the particle number. The coarse mode particles contain 5-20 % of the total particulate mass and size above 1 μm. Coarse
mode particles are the accumulated particles comes from re-entrained exhaust and found on the surfaces of cylinder and exhaust system. Velimir et al. (2008) observed that diesel engines mostly emit particles in the nano size range which is also true for gasoline engines. Nanoparticles are formed by nucleation during dilution and cooling of the exhaust and they generally consist of hydrocarbons or sulfates. Accumulation mode particles are formed directly by combustion and they consists mainly carbonaceous materials and soot agglomerates. Ultrafine and nanoparticle emissions are important from both human health environment points of view.

1.5 EFFECTS OF ULTRAFINE AND NANOPARTICLES ON HUMAN HEALTH

Recent studies have showed that adverse health effects are dependent on total particulate mass, and also on the other metrics like size, number and surface area. Smaller particles have been claimed to cause more adverse effects than larger particles. Hence, Air Quality Standard in the USA has been revised to incorporate new parameter to measure fine particles PM$_{2.5}$ in addition to PM$_{10}$, to bring the effectiveness to ambient air quality which is the best for the worldwide air quality standard. European Air Quality standards have also adopted PM$_{2.5}$ under the CAFÉ (Clean Air for Europe) program. Ultrafine and nanoparticles are mainly related to health concern because they can reach into the deep races of the lungs called alveoli. Health effects of these particles include asthma, difficult or painful breathing, chronic bronchitis, especially in children and the elderly people, lung cancer, cardiovascular diseases, birth defects, and premature deaths. Particulate emissions were examined and identified in early 1970’s itself as vulnerable, causing deaths and other severe health concerns. PM pollution is estimated to cause 22,000 to 52,000 deaths per year in the United States (from 2000) and 200,000 deaths per year in Europe. The coarse size particles up to 3.3 µm get arrested into nostrils & pharynx because of cilia and mucus. Further, particles up to 1.1 µm travels up to secondary bronchi and they causes the problems like cough and aggravates asthma and lung problems. But the particles below 1.1 µm penetrate up to alveoli and rest there, where exactly the gas exchange process occurs and causes lung cancers (Ref. Figure 1.3 below).
During the gas exchange process some of the particles of nano size can directly enter into the blood stream as they can easily pass through the lung membrane which is having a porosity of approximately 50 nm, these particles then travel to various organs of the body and they directly affect the body cells. In particular, a study published in the Journal of the American Medical Association reported that vascular inflammation and atherosclerosis which leads to hardening of arteries is due to deposition of PM$_{2.5}$ in the form of plaques. This reduces elasticity of arteries leading to heart attacks and other severe cardiovascular problems which may occur even at short term exposure with elevated concentration. Brook et al. reported that PM$_{2.5}$ generally have been associated with increased risks of stroke, myocardial infarction (MI), arrhythmia, and heart failure exacerbation depends on the period of exposure and individual health condition. Most recent studies conclude that the overall absolute risk for mortality due to PM exposure is greater due to cardiovascular compared to pulmonary diseases for both short as well as for long term exposures (Brook et al.). Several new studies have also demonstrated that residing in locations with higher long-term average PM levels elevates the risk for cardiovascular morbidity and mortality. As per the study in The Lancet around 7.4% of heart attacks in the general public are due to the traffic exhaust. The ultrafine particles (≤ 100 nm) may cause severe damage to the cardiovascular system. Some of the threatening facts includes, the lifetime cancer risk caused by air pollution due to diesel particulate matter (DPM) is responsible for 70% - 89% of the total cancer risk caused by air pollution in the U.S. Similarly, in Canada it is
estimated that exposure to DPM could cause up to 13,600 Canadians to develop cancer over their lifetimes. European commission has identified a social need and taken bold steps to bring the new regulation for particle number from Euro-5b onwards and also the particulate mass measurement standard changed from PM$_{10}$ to PM$_{2.5}$ with new procedure.

1.6 EFFECTS OF ULTRAFINE AND NANOPARTICLES ON CLIMATE CHANGE

Effect of particles on the climate can be in two different ways as direct and indirect effects. In direct effect, particles absorb infrared and solar radiations whereas, indirect effects of particles on climate is complex and difficult to assess. Particulate matters are well known to impair the visibility and affects the monuments and scenic area. Fine particles which are major cause of haze can travel with air currents for long distances. Cloud albedo which influences precipitation, increases when the water gets condensed on to the particulates resulting in large number of droplets in the clouds and this suppresses the precipitation, causing large amount of water to remain in the atmosphere. Climate change due to air pollution particularly due to increased greenhouse gas (GHG) emissions results in an increase in global average temperature. GHG traps the heat in the earth’s atmosphere causing warming up of earth’s surface. Main source of airborne particulate matter is due to increased industrialization and urbanization without proper planning and measures causing more serious threat in densely populated areas. Climate change is directly related to health which are mainly causing premature deaths due to several reasons like respiratory problems, cardiovascular diseases and cancer etc. (Ahlvik et al.,1998).

1.7 NEED TO STUDY NANO AND ULTRAFINE PARTICLE EMISSIONS

Considering the above explained dreaded effects of ultrafine and nanoparticle emissions new European regulations have covered diesel and gasoline direct injection engines/vehicles for PM$_{2.5}$ and particle number under Euro-5b/ Euro-6 emission norms for these advanced technology vehicles. However, old vehicles up to Euro 4 & Euro 5 technology which are major in population and plying on the road are the real concerns which need to be evaluated considering social concerns. Several researchers have reported about the vulnerable effects of nano and ultrafine particles particularly coming out from compression ignition and spark ignition engines. Based on the reports from international health
institutes and also recent reports from WHO confirmed toxicity of diesel exhaust, a social need is felt in the public health interest to assess the old technology and in-use vehicles. In this context study need to be conducted specifically in terms of particulate mass, size and their number concentration for developing countries having major population of vehicles with old technologies and running on road with conventional gasoline, diesel fuels and alternate fuels like CNG particularly when there is no in-service compliance or inspection and maintenance program in the country like India.

1.8 LAYOUT OF THE THESIS

The thesis includes total seven chapters which are organized below.

Chapter 1: Introduction

The background introduction includes history and importance of automotive emissions and evolution of emission regulations particularly for particulates, PM$_{2.5}$, particle number and the challenges in measuring them. This chapter also covers significance of ultrafine and nano particles from health and environment point of view. An overview of particulate and it’s various metrics like size and distribution pattern which are studied in the present work are explained. This chapter also covers layout of research work undertaken.

Chapter 2: Literature Review

A comprehensive literature review report in the area of ultrafine and nanoparticle emissions from light duty vehicle exhaust of diesel, gasoline and CNG is presented. The literature review conducted can be categorized in 4 main areas Viz. A) Fundamentals of particulate emissions which include: particles and their classification, mechanism of formation of ultrafine & nanoparticles, factors influencing particulate formation and typical particle size distribution for different technology vehicle & their health effects. B) Literature reviews include particulate Emissions from different categories of vehicles viz. light duty diesel engines and vehicles, gasoline direct injection (GDI) and port fuel injection engines, hybrid vehicles and alternate fuel vehicles. C) Literature studied on the various technologies to control ultrafine and nanoparticles has provided information on the
exhaust after treatment technologies used and their constraints and the specific research ongoing. D) Fourth area of literature Survey carried out was useful to finalize the strategy to develop theoretical model which has helped to understand the data type, steps to be followed to establish simplified and good regression model. The important remarks from literature reviewed, research gaps and constraints in the work carried out and the problems identified are highlighted. Understanding the thrust at the national and international level and considering the future need the objectives, scope and the contributions of this research are also highlighted in this chapter.

Chapter 3: Experimental Test Setup and Methodology

Experimental test set up recommended by the new European regulation for particle number measurement was ensured for the standard regulatory requirements and was augmented for measurement of particle size and to collect the sample for chemical speciation is explained in this chapter. Details of test matrix and test methodology are also presented here.

Chapter 4: Data Configuration and Novel Approach of Analysis

Here, the constraints identified from the nanoparticle measuring equipment which provide huge raw data output files, finding difficulty to draw the useful inferences is explained. The novel approach of stepwise data analysis technique along with data configuration presented here to draw important inferences which will be useful for development engineers as it provides the vital information to the engine researcher, transmission designer, and FIP and ECU programmers to optimize various parameters related to the Phenomena of particle formation.

Chapter 5: Results and Discussions

This chapter is divided into three parts, in Part-1, gaseous pollutants, CO, HC, NOx, emissions test results are analyzed and discussed. In the Part-2 characterization of particles in terms of their number, size, surface area and volume are analyzed and discussed. In this part physical characterization of ultrafine and nanoparticles emitted from diesel, gasoline and CNG vehicles are investigated as these particles are more vulnerable. To identify the
contributions by all the phases and gears a detailed analysis is carried out on urban as well as on extra urban part of the MID cycle and this has also helped in identifying the most significant driving phases and operating gears contributing to ultrafine and nanoparticle emissions is reported here. Transient behavior of the particles over MID cycle is also explained in detail for all diesel, gasoline and CNG vehicles tested as per test matrix to understand the Phenomena. In the Part-3 of this chapter PM$_{2.5}$ speciation carried out by chemical analysis results are analyzed and discussed understanding their significance to human health.

Chapter 6: Development of Statistical Model

This chapter covers the specific literature survey carried out to finalize the strategy to develop theoretical model. The information collected was useful to understand the data type, steps to be followed for good regression modeling, how to find out good subset and the variables which are having good relationships to be used to develop good and simplified model. Chapter covers the steps followed like specifying the model, determine predictor and deterministic variables and statistical method applied to formulate the theoretical model based on the experimental data on the tested vehicles for particle number. Regression models established for diesel, gasoline and CNG vehicles using statistical technique to the best subset and their validation is also covered in this chapter.

Chapter 7: Conclusions

In this chapter summary of the result analysis and the inferences are reported specifically in line with the objectives on physical characterization of ultrafine and nano particles. Similarly, conclusions on the chemical characterization of ultrafine and nano particles from gasoline, diesel and CNG vehicles are reported here. The statistical models developed based on the limited data are also reported. Finally, some recommendations for the future scope of the present research work are given.