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AUTOMOBILE POLLUTION CONTROL USING CATALYSIS

Shamuratov Jamshidbek Ulugbek ugli

PhD student of Tashkent state technical university named after I. Karimov

e-mail: jamshid.shamuratov.phd2022@gmail.com

Masharipov Bakhtiyor Raximboy ugli

Teacher of vocational school, Khiva district,

e-mail: bakhtiyor.masharipov1994@mail.com

Kadirov Islom Rayimbergan ugli

Teacher of Urgench State University

islomqadirov1415@gmail.com

ABSTRACT

The emissions of pollutants from vehicles are generally low but the number of vehicles increasing on the road, therefore, the environmental pollution are also increasing. About 35% of CO, 30% of HC and 25% percent of NO_x are produced into the atmosphereares from the transportation sector. These pollutants have adverse effects on the environment and human health. The emissions from vehicles generally depend upon the air-fuel ratio. The control techniques for exhaust gas emissions are engine modifications, fuel retreatment, fuel additives, exhaust gas recirculation (EGR), positive crankcase

ventilation (PCV) and anthem, application of catalytic converters. A catalytic converter is a device that converts more toxic exhaust gas pollutants into less toxic pollutants. There are different types of catalysts used in the automobile exhaust gas treatment like noble metal and base metals catalysts etc. The catalytic converter was effective and consistent for reducing the noxious tailpipe emissions so that it was developed for use in the trucks, buses, cars, motorcycles and other construction equipped. This paper will discuss the different types of recent developments in catalysis for automobile exhaust pollution control.

Keywords: Automotive emissions, Catalytic converter, air-fuel ratio, Engine, and fuel modification.

Introduction

The emissions from vehicles are increases with the increasing of population. This world is more concerned about the environmental pollution due to automobile pollution exhaust. In 1951 the total number of vehicles present in India is 310,000 and it increases up to 8,900,000 at the end of year 2005-06. The major source of pollution produces from the internal combustion engine which are carbon monoxide (CO), hydrocarbons (HC), nitric oxide (NO_x) and small amounts of sulfur oxide (SO_x), lead (Pb) and particulate matter. The internal combustion engine is operated by the burning of fossil fuels. The emissions from vehicles are responsible for the two-third of air pollution in the urban area. Automobile pollution is one of the major problems of most country around the world. This is responsible for causing respiratory diseases, asthma, cancers, chronic disease and other serious health effects. Automobile pollution is responsible for such a serious problem like acid rain and global warming. For running a vehicle, the internal combustion engine required the mixture of fuels and air. It depends upon the air-fuel ratio. In the lean mixture conditions, the vehicle produce less CO, less HC and more NO_x gases but in the rich mixture conditions the vehicle produce more CO, more HC and less NO_x gases. In comparison between petrol engine and diesel engine, the petrol engine produces more CO, HC but less produce NO_x and particulate matter. The

evaporation from gasoline engine vehicle increases as the increase's temperature of the day and heating of fuel tank, venting of gasoline vapors. The controlling techniques of exhaust gas emissions are engine modification, fuel pretreatment, fuel additives, exhaust gas recirculation (EGR) and catalytic converters. A catalytic converter is an emissions control device that converts more toxic exhaust gas pollutants into less toxic pollutants. There are different types of catalysts used in the automobile vehicles exhaust gas emissions controls like noble metal, base metal and transition metal catalysts etc. The surface area, pore volume and pore size of catalysts are highly effective on the catalyst activity. The catalytic converters are highly active and consistent for reducing the poisonous tailpipe emissions so that it was developed for the use in trucks, buses, cars, motorcycles and other construction equipped. The emissions from automobile vehicles engines are more when the engine is in cold conditions. On a cold start conditions the petrol may take up 10 km to warm up and in diesel engine may take up at 5 km. In cold start conditions the diesel engine vehicle produces less unburned fuel as compare to petrol engine vehicle [1].

In the lean burning conditions the combustion of fuel in the internal combustion engine with an excess of air. The air: fuel ratio may be as lean as 14.64:1 (by mass). To control the air pollution from automobile vehicle exhaust the Bharat stage emissions standards sets the emissions standards instituted by the Government of India that regulate the formation of certain major automobile exhaust pollutants such as CO, SO_x, NO_x, HC and particulate matter (PM) by the vehicles from internal combustion engines. There are various factors which can affects on the automobile pollution control are fuel injection, engine design and engine life and engine maintenance. The main objects of catalysts in the catalytic converter to convert CO, HC and NO_x gasses into less poisonous CO₂, H₂O, N₂ and O₂ gasses. The oxidation and reduction mechanism has been applied for the emissions control system. The platinum group metal is very active materials to control the pollutants emissions from the automobiles vehicles exhaust but its price is so high. The catalyst is very insensitive to air/fuel ratio. Catalysts operating efficiently at the ambient conditions are a challenging class of materials, covering application as different

as the cold start of engines to indoor air quality. In the cold start period, the catalytic converter is totally inactive, because it has not warmed up. The cold start phase is also depending upon the types of vehicles. The total amount of fuel required for a cold start of the engine is a function of ambient air, engine design and coolant temperatures. The cold start emission was more at the starting of engine and over emissions during the warm-up process of engine and catalyst. The higher tailpipe emissions (60%-80% of CO and HC) occur from a motor vehicle even equipped with threeway catalyst (TWC) converter within first few minutes or approximately first few kilometers after the vehicle starts. Low temperature and high pressure in the engine cylinder make it difficult for fuel to vaporize. Hence, engines require an enriched mixture to ensure that an adequate amount of fuel is vaporized to achieve a combustible mixture. The fuel-rich mixture leads to incomplete combustion, resulting in partially burned fuel (CO emissions) and unburned fuel (HC emissions).

The emission of pollutants from automobile vehicles decreases with the increase of temperature in engine and catalyst followed by the stable operation conditions. Two and three-wheelers remain important modes of transport in many Asian countries and cities now and in the future, and contribute to a large share of air pollution and traffic congestion. Most of the cities and towns in India are highly polluted, especially due to petrol and diesel-powered two and three-wheelers as they constitute about 80% of the total number of vehicles. The national effort to control this automobile pollution can be traced to the 1970 Clean Air Act, which required a 90 percent reduction in CO, HC and NO_x emissions from automobiles. The emission standards were first adopted in 1991 and have been constantly upgraded since then. The first major revision occurred in 1996, the second in 2000, the third in 2005 and the next in 2010. With effect from 1st April, 1996, the test as per Indian driving cycle with cold start on a chassis dynamometer, mass emission standards for diesel vehicles (including two and three-wheelers). With the effect from 1st April, 1998, the test run as per Indian driving cycle with cold start on a chassis dynamometer, the standard for CO emission was 4.5 g/km for all categories of petrol-driven two and three-wheelers. The growth of environmental concerns over the

past three decades has resulted in regulatory action around the globe to begin more rigorous emission standards successively. Partial oxidation (POx) catalysts convert HCs to CO and H₂ under rich exhaust conditions. A partial oxidation catalyst is interposed between an exhaust manifold and a catalytic converter in the exhaust system of an engine. The hydrogen produced is used to promote faster light-off of the catalytic converter in the exhaust system. The efficiency of catalysts for reactions with stable CO, HC, NO_x and Soot particles is also depending upon the chemisorptions processes. The chemisorption of reacting gasses is an important step, which increases the concentration of reactant on the catalyst surfaces which inducing the adsorbed molecules processing on high energy to be get easy the chemical reactions. A better tool for measuring the performance of catalyst for CO and HC oxidation and NOX reduction is reported by the activation energy of the process. The amount of reactant consumed and product formed can be monitored as a function of the surface composition of the catalyst. Emission standards are set specific limits of CO, HC and other pollutants that can be produced in the air that people breathe. Many emission standards focus on the regulating pollutants produced by the motor vehicles and from industry, power plants, small equipment such as forklifts, lawnmowers and generators, etc.

Catalytic converter

The catalytic converter was first invented by a French mechanical engineer Eugene Houdry in the year 1930. A catalytic converter is an automobile pollution control device. It converts more toxic pollutants produced from the automobile vehicles exhaust into the less toxic pollutants. The broad application of catalytic converters did not occur until more stringent emission control regulations forced the removal of antiknock agent tetraethyl lead from most types of gasoline. The catalytic converters were initially introduced in American production cars in 1975 due to the Environmental Protection Agency regulations on the poisonous gasses emissions reductions. The United States Clean Air Act required a 75% decrease in emissions of all the new model vehicles after 1975, a decrease to be carried out with the use of catalytic converters without catalytic converters, vehicles release HC, CO and NO_x. A catalytic converter is placed in the

internal combustion engine of vehicles. The catalytic converter is divided into three parts:

1. Two-way catalytic converter
2. Three-way catalytic converter
3. Four-way catalytic converter

The two-way catalytic converter is converting CO and HC into CO₂ and H₂O. The three-way catalytic converter is shown in Fig. 1. It also uses for the reduction of NO_x. The four-way catalytic converter has ability to converts CO, HC, NO_x and particulate matter on a single support.

Catalytic converters are used in the internal combustion engines fueled by either gasoline or diesel includes lean-burn engines as well as kerosene heaters and stoves. A catalytic converter is a simple device that uses basic redox reactions to reduce the pollutants emitted from vehicles. It converts the harmful pollutants produced from the car engine into less harmful gases. It is composed of a metal housing with a ceramic honeycomb-like interior with insulating layers. This honeycomb interior has thin wall channels that are coated with a wash coat of aluminum oxide. This coating is porous and increases the surface area, allowing more reactions to take place and containing precious metals such as platinum, rhodium, and palladium. The converter uses simple oxidation and reduction reactions to convert the unwanted pollutants. The oxidation is the loss of electrons and that reduction is the gaining of electrons. The catalytic converter controls the fuel-injection system. This control system is aided by an oxygen sensor that monitors how much oxygen is in the exhaust stream and engine adjust the air-to-fuel ratio, keeping the catalytic converter running at the stoichiometric point and near 100% efficiency.

Construction of catalytic converter

The construction of catalytic converter is monolith structure, which is coated with wash coat that support the catalytic material. The construction of catalytic converter is a complex process.

The Catalyst Support: - The catalyst support is made up of ceramic monolith with high heat resistance at a honeycomb structure. The catalyst support provides a large surface

area. The catalyst material as shown in Fig. 2 was deposited on a packed bed of alumina pellets in the applications. Metallic foil monoliths made of Kanthal (FeCrAl) are used in applications where particularly high heat resistance is required. The substrate is structured to produce a large surface area.

The ash Coat: - A washcoat is a carrier for the catalytic materials and used to disperse the materials over a large surface area. The wash coat of a catalytic converter is generally made of largest surface area Al_2O_3 , TiO_2 , SiO_2 , or a mixture can be used in the wash coat. The catalytic materials are suspended in the wash coat prior to applying in the core. ashcoat materials are selected to form a rough, irregular surface, which more increases the surface area as compared to the smooth surface of the bare substrate. This in turn maximizes the catalytically active surface available to react with the engine exhaust [2]. The coat must retain its surface area and prevent sintering of the catalytic metal particles even at high temperatures. The wash coat and catalyst present in the catalytic converter is showed in Fig. 3.

III. The Catalyst: - The catalyst is generally selected for oxidation of pollutants to converts high toxic gases into less toxic gases. The catalyst itself is most often a mix of precious metals, mostly from the platinum group. Platinum is the most active catalyst and is broadly used, but is not suitable for all the applications due to the unwanted more additional reactions and high cost. Palladium and rhodium are two other precious metals used in the catalytic converter. Rhodium is used as a reduction catalyst, palladium is used as an oxidation catalyst, and platinum is used for both the reduction and oxidation. Cerium, iron, manganese and nickel are also used, although each has certain limitations.

Types of catalysts

Catalyst can be selected homogeneous or heterogeneous is generally depends upon whether a catalyst and a reactant as a same phase or not. At the time both are in same phase the catalyst is called a homogeneous catalyst and in the different phase the catalyst is called heterogeneous catalyst. Diesel engines can and do use catalytic converters, but there are major differences from how they work in the gasoline engines. Instead of three-

way catalysts, diesels use two-way oxidation catalysts (CO and HC) and ones specifically designed to work with the diesel exhausts, which are cooler than the gasoline exhausts. The diesel engines produce much higher tailpipe emissions of nitrogen oxides than the gasoline engines [3].

Different types of catalysts used in the catalytic converter

I. Noble Metal Catalysts: - The noble metals (Pt, Pd, Rh, Ir, Au and Ag) are most commonly considered for primary use in the automobiles as a catalytic converter, which converts harmful toxic HC, CO and NO_x gasses emitted from the automobile engine into less toxic H₂O and CO₂ gasses. The Pt/SnO₂ and Pd/SnO₂ catalysts are more commonly used as the low-temperature CO oxidation catalysts. The disadvantages of a noble metal catalysts are a high-cost materials. In the noble metals catalysts rhodium is used as a reduction catalyst, palladium is used as an oxidation catalyst, and platinum is used for both the reduction and oxidation. Gold is very active for the low-temperature oxidations of CO, if dispersed on suitable metal oxides and composite oxides. Gold supported on reducible oxides is known to catalyze CO oxidations efficiently at very low temperatures (even below 0°C). The gold catalytic system could be very important for CO safety gas masks, purification of air in CO₂ lasers and CO sensors [4].

Base Metal Catalyst: - In the base metal catalysts include the Co, Ni, Cr, Fe, Mn and Cu are most active catalyst. The base metal oxides like Co₃O₄, CuO and MnO₂ have been found to be high catalytic activity per unit surface area for CO oxidation reactions. The low-cost and high-performance supported base metal catalysts may have high potential to find its application to the catalytic activity. The different supported base metal oxide catalysts can be arranged in terms of their catalytic activity for CO oxidations is as follows CuCr₂O₄ > Co₃O₄ > Cu₂O > Fe₂O₃ > MnO > NiO > Cr₂O₃ > V₂O₅. The supported Cu oxide catalysts have been not only used for CO oxidations but also for the oxidations of VOCs and NH₃. Copper catalyst supported on CrO₂ or Al₂O₃ are highly effective for oxidation of CO and CH₄ in comparison to other base metal catalyst. The base metals contain a large amount of surface structures which involve the surface energy of compounds and affect their chemical properties. It is contained oxygen atoms bound to

the transition metals. This bimodal pore structure present in base metal catalysts will provide as more favorable pore size for the chemisorptions of reactants [5].

Perovskite: - The Perovskite metal oxide structure is generally (ABO₃), where A is a rare earth elements and B is a transitions metals, this metal oxide is used alternatively of noble metal catalyst for automotive exhaust emissions control. The very few number of perovskite is until reported, which are very active at the ambient conditions CO oxidations. Example Au/LaMnO₃ is

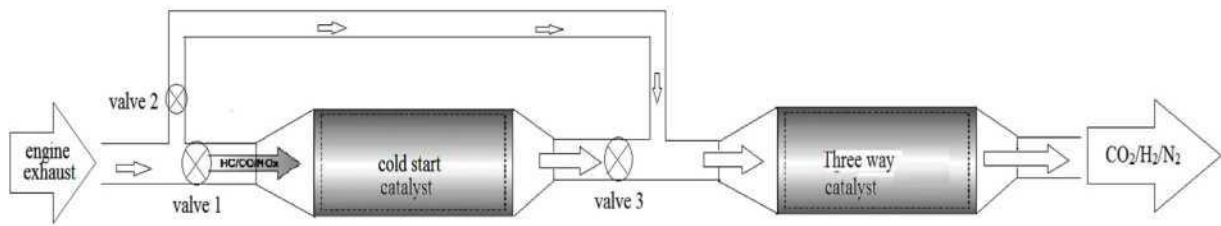


Fig. 1. Schematic diagram of a catalytic converter.

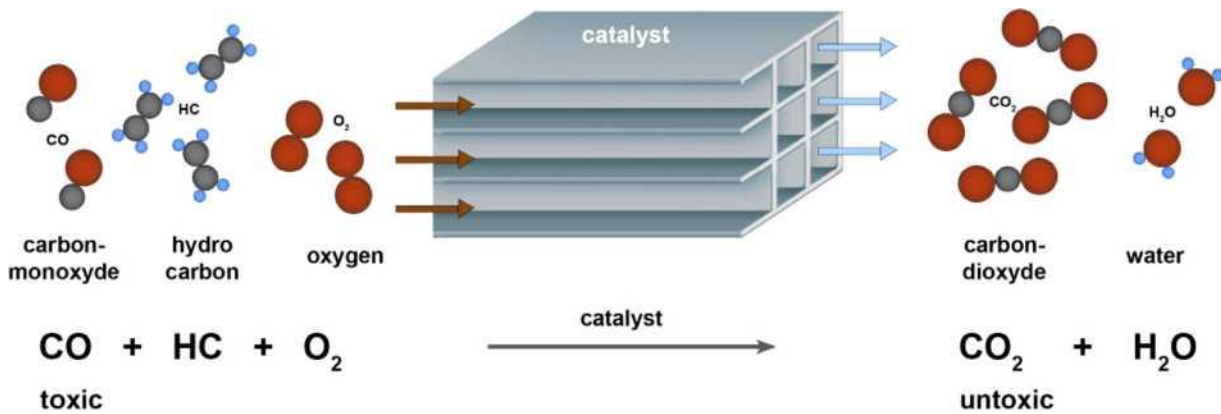


Fig. 2. Catalytic conversion of CO and HC over catalysts.

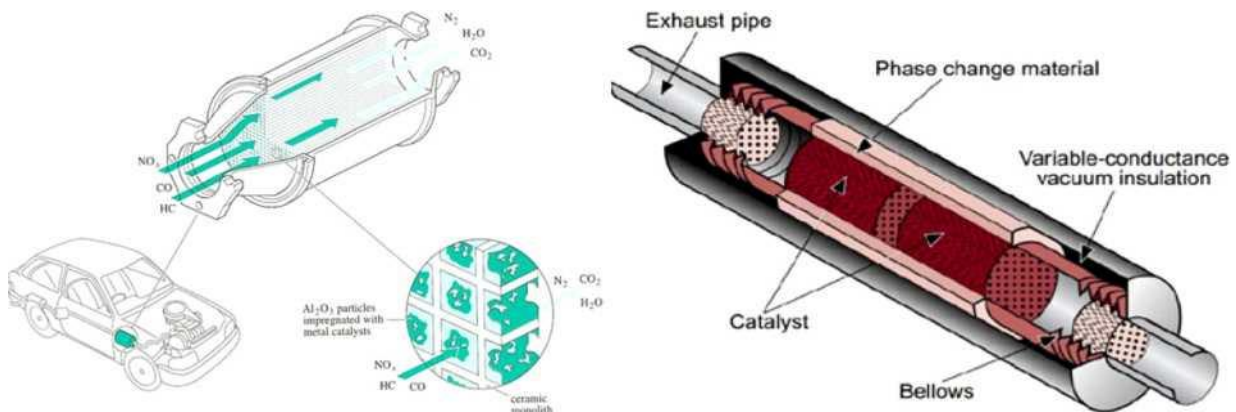


Fig. 3. Catalyst used in a catalytic converter.

converted 60% CO at 50°C. Rare earth oxides crystallizing in perovskite-structure have been found suitable to make low-cost oxidation catalysts for automobile exhaust pollution control.

Spinel: - The spinels are any class of minerals of formulation $A_2+B_2+O_2$ which crystallize in the cubic (isometric) crystal system, with the oxide anions arranged in a cubic close-packed lattice and the cations. The A and B are occupying the octahedral and tetrahedral sites in the lattice. It is divalent, trivalent or quadrivalent cations including Mn, Zn, Fe, Al, Cr, Ti and Si. Members of the spinel group include Aluminum spinels (Ex. $MgAl_2O_4$), Iron spinels (Ex. $CuFe_2O_4$) and Chromium spinels (Ex. $FeCr_2O_4$). There are many more compounds with a spinel structure, e.g., the thiospinels and selenospinel, that can be synthesized in the lab or in some cases occur as minerals. The heterogeneity of spinel group members based on the composition with Fe and Mg members varying in solid solution, which requires same sized cations. However, Fe and Al-based spinels are almost homogeneous due to their large size difference.

Monel: - The monel catalyst is generally mixture of Ni and Cu. The composition of monel catalyst which typically contains about 66.5% by weight of Ni, 31.5% by weight of Cu and 2% by weight of impurities. This catalyst used for controlling the emissions of CO, HC and NO_x from the automobile exhaust. Monel is a lower cost catalyst but its life is shorter and durability is also lower.

VI. Hopcalite: - Lamb, Bray and Frazer (1920) discovered that the mixture of various oxides Cu, Mn, Ag and Co. This catalyst is very effective for CO oxidation in room temperature. This group consists of the equal parts of MnO_2 and Ag_2O and a four-component mixture of 50% MnO_2 , 30% CuO , 15% Co_2O_3 and 5% Ag_2O , which was known as the standard hopcalite. Hopcalites have high durability for oxidation of CO in the dry conditions. The addition of Au, Ag, Ce, Co, Fe and Ni improves the catalytic performances of catalysts. The $CuMnO_x$ prepared by the sol-gel method were shows better catalytic activity than the commercial hopcalite. The crystalline Cu_2MnO_4 has also been reported to be active in the low-temperature CO oxidations [6].

Formation of pollutants in the automobile vehicles exhaust

The formation of toxic gasses from automobile vehicles exhaust is depending upon the combustion process, air/fuel ratio, engine performance, compression ratio, temperature of flame and function of carburetor etc. The stoichiometric amount of air is needed to completely burn the fuels. The types of pollutants are also depending upon the quality of fuels, volatility and types of minerals and impurity is present in the fuels. The major factors affect the automobile vehicles exhaust highly toxic to human health and living things. It also depending upon the physical and chemical property of pollutants, concentration of pollutants and proportion of population exposed. To controlling the formation of pollutants it is necessary to properly maintain the vehicles and use a durable, economical, long time stable and easily available catalyst in the automobile catalytic converter system. The catalytic converter is a device it placed in the vehicle exhaust pipe for converting HC, CO and NO_x into less harmful gasses. In comparison between urban area and rural area we have to find out that urban area is highly affected by automobile vehicles exhaust pollution. In the vehicle source of automobile exhaust pollutants control the certain emissions standard of tailpipe, evaporative emissions controlling, increased durability and application of computerized diagnostic system. The older and heavy vehicles emit more pollutants like HC, CO, NO_x and particulate matter per mile as comparison to new and small-sized vehicles [7].

Human health effects on automobile pollution

The automobile pollutants like CO, HC, NO_x, SO_x and PM have bad effects on the human health and environments. These pollutants are directly affects on the respiratory tract and cardiovascular systems of humans.

Carbon Monoxide (CO) It effects on the cardiovascular system, central nervous system, headache, creating nausea and judgment problem. The CO combines with hemoglobin present in the blood cells and converted into carboxy-hemoglobin which reduces the oxygen carrying capacity of the human beings. The effect of CO on human health is shown in Fig. 4.

Hydrocarbon Compounds (HC) HC caused respiratory tract illness and lung cancer. The exposure of HC on the human body to significant amounts of these chemical compounds

causes eye irritation, nausea and dizziness. The long-term exposure, in addition to the carcinogenic effect, can cause skin, liver, kidney and cataract damage.

Carbon Dioxide (CO₂) CO₂ caused suffocation, dizziness; destroy central nervous system and death also. Breathing becomes more difficult as carbon dioxide levels rise. In closed areas, high levels of carbon dioxide can lead to health complaints such as headaches. If CO levels are high enough therefore human or animals become unconscious or die. Exposure to moderate and high levels of CO over long periods of time has also been linked with the more risk of heart disease. It is also known as the greenhouse gas was associated with global warming and increased from the combustion of fossil fuels including motor vehicle fuels. A high concentration of CO₂ can displace oxygen in the air. If the less oxygen is available to breathe, symptoms such as rapid breathing, rapid heart rate, clumsiness, emotional upsets and fatigue can result.

Sulfur Oxide (SOX) The SO₂ can affect the lung function and irritate the mucous membranes of the respiratory tract and foster the development of chronic respiratory diseases and particularly bronchitis. When it is breathed in irritates the nose, throat and airways to cause coughing, wheezing, shortness of breath, or a tight feeling around the chest. The most risk of developing problems if they are exposed to sulfur dioxide at people with asthma or similar conditions.

Nitrogen Oxides (NOX) Nitrogen oxide can effect on the respiratory system. It caused irritations on lungs, nose, eyes, and throat sections. NO_x has direct and indirect effects on the human health. It causes breathing problems, headaches, chronically reduced lung function, eye irritation, loss of appetite and corroded teeth. Indirectly, it can affect humans by damaging the ecosystems they rely on water and on land harming animals and plants. The NO and NO₂ play a major role in the formation of photochemical smog [8].

Various types of emissions from the vehicles

The heavy-duty vehicles comprise only 5% of all vehicles on the road, yet they generate more than 25% of global warming emissions that come from the transportation sector and significant amounts of air pollution. The automobile pollution is the source of two-

third air pollution in the urban area. Emissions come principally from three automotive sources: the exhaust system, fuel system (evaporative) and crankcase ventilation gases [9].

Crankcase Emissions

In the crankcase emissions the unburnt or partially burnt fuel products enter into the crankcase from the combustion chamber pass it through the piston. The crankcase vapors contain light HC, crankcase oil vapors and combustion chamber gases. Crankcase oil vapors compose the light volatile portions of the motor oil, evaporated at engine operating temperature. To controls the crankcase emissions a crankcase ventilation system is adopted. For reduction of crankcase emissions introduced positive crankcase ventilation systems, which work on intake manifold vacuum to draw vapors from the crankcase into the manifold. The combustion chamber gases, which have entered into the crankcase mainly, come from the quench area within 0.05 mm to 0.5 mm of the combustion chamber surface.

Evaporative Emissions

The Evaporative Emission Control System (EECS) is shown in Fig. 5 used to prevent the gasoline vapors escaping into atmosphere from the fuel tank and fuel system. The ECS usually require no maintenance, but faults can turn on the check engine light and prevent a vehicle from passing an OBD II plug-in emissions test. The fuel tank must have some type of venting so air can enter to replace fuel as the fuel was sucked up the fuel pump and sent to the engine. If the tank were sealed tight, the fuel pump would soon create enough negative suction pressure inside

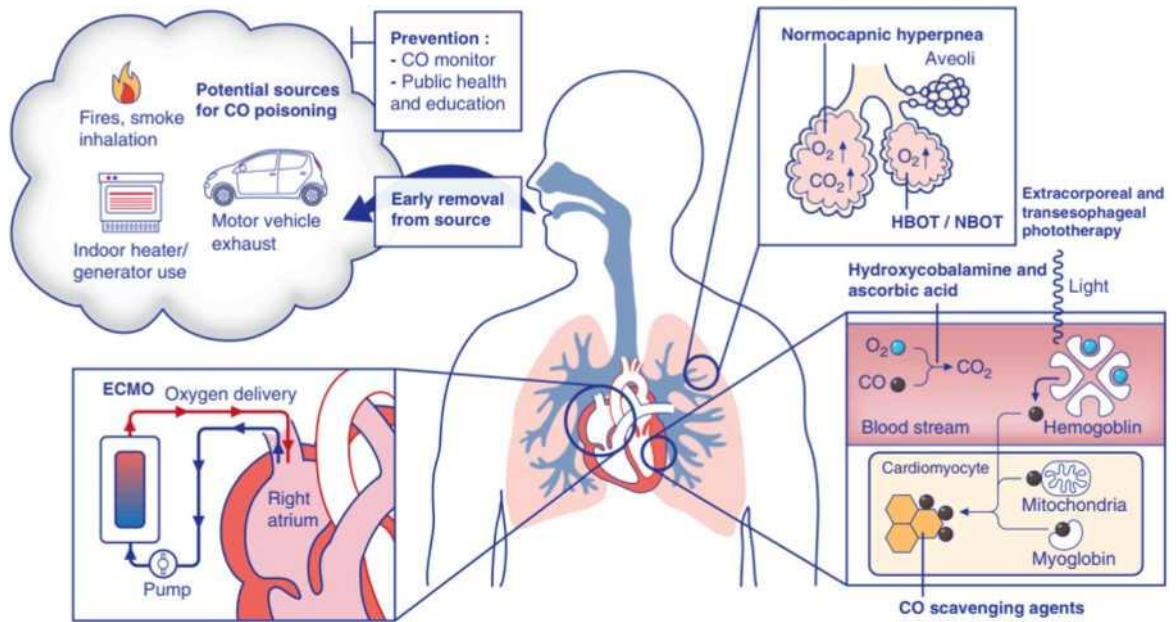


Fig. 4. Exposure of CO, HC, NO_x and PM effects on the human health.

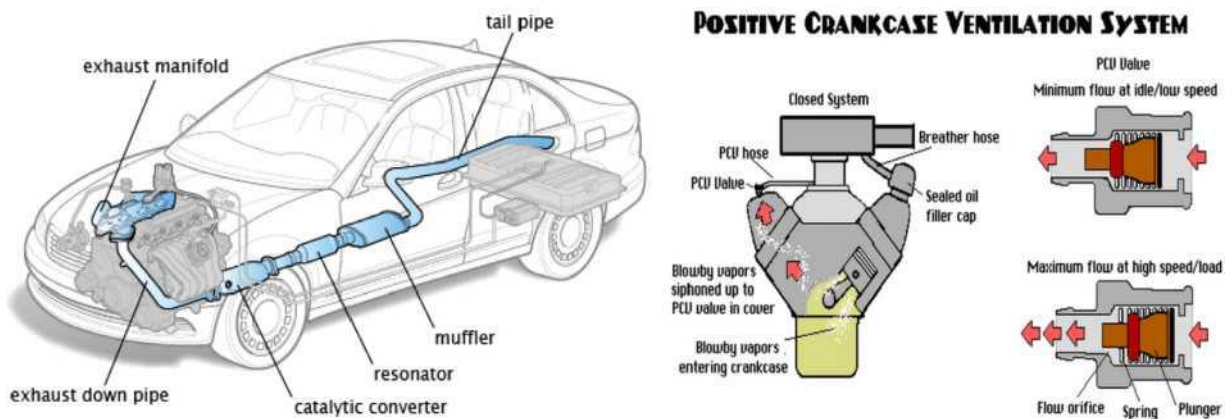


Fig. 5. Crankcase emissions and evaporative emission from the vehicles.

the tank to collapse the tank. The petrol is volatile in nature. It contains HCs vapors, is evaporated constantly in the atmosphere from the fuels tank, tailpipe and carburetor. The evaporative emissions are depending upon the composition of fuel, engine and carburetor conditions. The evaporative emissions from petrol engine are higher as compared to diesel engine. The evaporative emission is controlled by the adsorption regeneration carbon canister technology [10].

Exhaust Emissions

The exhaust gas is emitted as a result of the combustion of fuels such as natural gas, gasoline, petrol, biodiesel blends, diesel fuel, fuel oil or coal. According to the type of engine, it is discharged into the atmosphere through an exhaust pipe, flue gas stack, or

propelling nozzle. It often disperses downward in a pattern called an exhaust plume. Exhaust gas temperature (EGT) is important to the functioning of catalytic converter of an internal combustion engine. Recent trends in diesel fuel properties have an adverse effect on the particulate emissions. The automobile exhaust is consisting of CO, HC, Pb, NO_x, SO_x and particulate matter. Nowadays, the exhaust gases from automobile engines are treated by catalytic converters. The catalytic cleaning process is controlled by the engine control unit. The efficient particulate control method has better understand emission characteristics by the various types of measurement instruments [11].

Regulations of CO, HC, NO_x and PM emissions and recommended limits

The emission standards are requirements that the set of specific limits to the amount of CO, HC, NO_x and PM pollutants that can be released in the air that people breathe. Many emission standards focus on regulating pollutants produced by motor vehicles and from industry, power plants, small equipment such as forklifts, lawnmowers, generators etc. The emission standards are governing air pollutants released into the atmosphere. Recommended standards are being developed within the framework of world set of limits on the emissions of pollutants by the road vehicles [12].

Comparison between Bharat Stage and Euro norms

Due to increasing the number of automobiles vehicles on roads, the CO, HC, NO_x and PM concentrations have reached an alarming level in the urban areas. Due to increase the public awareness and concern for the danger to human health and the environment, regulatory measures have been adopted to curb the menace of vehicular pollution. There had been a much perceptible concern in the early 1980s on the adverse environmental impact of increased automobile traffic in developing

Table 1

Emission norms in India parallel to EU emission standards.

Norms	European Year	CO (g/Km)	HC + NO _x (g/Km)
1991 Norms	--	14.3-27.1	2.0(Only HC)
1996 Norms	--	5.6S-12.40	3.00-4.36

1998 Norms	--	4.34-6.20	1.50-2.1S
India Stage 2000 Norms	Euro 1 2000	2.72	0.97
Bharat Stage-II	Euro 2 2001	2.2	0.50
Bharat Stage-III	Euro 3 2005	2.3	0.35
Bharat Stage-IV	Euro 4 2010	1.0	0.1S
Bharat Stage-V	Euro 5 2017	0.63	0.10
Bharat Stage-VI	Euro 6 2020	0.50	0.07

Table 2

The pollution load estimated in different city of India, CPCB (2007-2010).

City	Pollution load in metric tons per day			
	CO	NOx	HC	PM
Delhi	412.S4	123.45	164.37	11.77
Mumbai	179.55	45.37	SS.93	10.2S
Kolkata	129.50	52.09	45.63	10.20
Chennai	167.00	26.30	94.64	7.49
Bangalore	209.04	2S.72	116.37	S.21
Hyderabad	153.95	34.S9	91.09	7.70
Kanpur	27.73	7.45	10.70	1.71
Agra	16.93	3.40	10.7S	0.S1

countries like India. The first Indian emission regulations were idle emission limits which became effective in 1989. Since the year 2000, India has started adopting European emission norms as discussed in Table 1 and fuel regulations for four-wheeled light-duty and heavy-duty vehicles. All new vehicles manufactured after the proceeding of norms have to be compliant with the regulations. At present, Bharat Stage IV (BS-IV) parallel to Euro IV regulations since April 1st, 2010 was applicable for various types of vehicles; this is given in Table 5 for CO emissions [13].

India has established limits on CO, HC and NOx emissions from motorcycles, gasoline-fueled cars and new emission standards for gasoline-fueled cars took effective in 1991. The automobile emissions are affected by driving pattern; overcrowding, temperature, traffic speed, vehicle's engine conditions and emissions control equipment and its maintenance.

Motor vehicle emission standards

The differences are essentially in environmental and geographical needs, even though the emission standards are near to the same. For instance, Euro-III is tested at sub-zero temperatures in European countries. In India, where the average annual temperature ranges between 24 and 28 degrees Celsius, the test is done away with. Another major difference is in the maximum speed at which the vehicle is tested. A speed of 90 km/h is predetermined for BS-III, whereas it is 120 km/h for Euro-III, keeping emission limits similar in both cases. In addition to limits, the test process has certain advanced points too. For instance, the mass emission test measurements done in g/km on a chassis dynamometer requires loading of 100 kg weight in addition to unloaded car weight in Europe. In India, BS-III norms require an extra loading of 150 kg weight to achieve the desired inertia weight mainly due to road conditions here [14].

Due to increasing the number of automobile vehicles on roads CO, HC, NO_x and PM concentrations have reached an alarming level in the urban areas and it also discussed in Table 2. Due to increased public awareness and concern for the danger to human health and environment, regulatory measures have been adopted to curb the menace of vehicular pollution. There had been much perceptible concern in the early 1980s on the adverse environmental impact of increased automobile traffic in developing countries like India. The first Indian emission regulations were idle emission limits which became effective in 1989. Since the year 2000, India started adopting European emission norms and fuel regulations for four-wheeled light-duty and for heavy-duty vehicles. All new vehicles manufactured after the implementation of the norms have to be compliant with the regulations. India's own emission regulation applies to two- and three-wheeled vehicles, as large numbers of such vehicles are employed in the country. At present, Bharat Stage IV (BS-IV) parallel to Euro IV regulations since April 1st, 2010 is applicable for various types of vehicles; this is given in Table 1 for CO, HC, NO_x and PM emissions. The emission standards are legal requirements governing the air pollutants released into the Bharat Motor Vehicle Safety Act [15].

Automobiles exhaust pollutants emissions regulations

The automobiles vehicles exhaust gas or flue gas is emitted as a result of the combustion of fuels such as natural gas, gasoline, petrol, diesel fuel, fuel oil, or coal. According to the type of engine, it is discharged into the atmosphere through an exhaust pipe, flue gas stack, or propelling nozzle. The largest part of most combustion gas is N_2 , water vapor (H_2O) and CO_2 these are not toxic or noxious although water vapor and carbon dioxide are greenhouse gases that contribute to global warming. A small part of combustion gas is undesirable, noxious or toxic substances, such as CO from incomplete combustion of HC from unburnt fuel, NO_x from excessive combustion temperatures and particulate matter (mostly soot). In spark-ignition engines the gases resulting from combustion of fuel and air mix are called exhaust gases [16].

Permissible limit of CO produced from the automobile's vehicle emission regulations Carbon monoxide is one of the most poisoning gasses present in the atmosphere. The main contribution of CO in the air is transportation section therefore catalytic converter has been invented. Catalytic oxidation has been widely studied for two main reasons first CO is a toxic molecule which should be eliminated from exhaust gases present in mobile and stationary sources second the CO oxidation is a simple reaction broadly used for evaluating the catalytic activity of new materials. The activity of catalyst is highly dependent on the reaction conditions (CO/O_2 ratio, presence of steam or other impurities in the gas). The oxide catalysts appear much more versatile than metal catalysts for CO oxidation reaction. Cold-start emission of pollutant gases from automobile vehicles is one of the major problems in large cities, where the number of vehicles and daily engine starting per populated area is high. Various techniques have been applied to solved the cold start emissions problem of the vehicles and added significant complexity cost to the emission control system [17].

The CO poisoning is responsible for up to 40,000 emergency department visits and 5000 to 6000 deaths per year, making it one of the leading causes of poisoning death in the India. In Table 3 observed that the permissible limit of CO produced from the two-wheelers, four-wheelers and six wheelers' vehicles. The EPA and HO has recommended exposure of ambient air quality guideline values for CO of 9 ppm and 25 ppm as an 8 h

and 1 h time-weighted average concentration respectively. The CO concentrations inside motor vehicles are generally around 9-25 ppm and occasionally over 35 ppm. Workers exposed to vehicle exhaust may have peak exposures over 200 ppm [17].

Table 3

Permissible limit of CO produced from the automobile's vehicle exhaust.

Vehicle type	India (gm/Km)	U.S. (gm/Km)	Canada (gm/Km)	China (gm/Km)	Europe (gm/Km)	Japan (gm/Km)
Two wheelers	1.5	0.80	1.42	0.75	0.80	1.36
Four wheelers (Petrol engine)	2.25	1.70	2.11	2.1	1.22	2.04
Four wheelers (Diesel 1.00 engine)	3.20	0.50	1.50	1.5	0.70	1.60
Up to six wheelers (Petrol engine)	3.20	2.60	4.20	4.0	2.20	4.20
Up to six wheelers (Diesel engine)	2.20	2.00	2.20	4.0	1.02	4.05

Permissible limit of HC produced from the automobile's vehicle emission regulations

The union government produced a revised Motor Vehicle Act in 1990, making emission regulations a federal government responsibility. India has established limits on HC emissions (at idle) for gasoline- fueled cars, motorcycles and three-wheelers; diesel smoke emissions are limited to 75 Hartridge units at full load. New emission standards for gasoline-fueled cars took effect in 1991. Emissions from diesel vehicles came under control in 1992 based on ECE R49 regulations. These limits are similar to the ECE 15-04 limits but with test procedures tailored to Indian driving conditions. Japan revised its emissions test procedures for light-duty vehicles in 1991. Since 1982, all in-use vehicles have been required to undergo a periodic, compulsory mechanical inspection [18].

The standards apply to light and heavy-duty vehicles, as well as two and three-wheeled vehicles. As proposed, the BS-VI standards for all vehicles in these categories manufactured on or after April 1, 2020. The draft BS-VI proposal specifies mass

emission standards, type approval requirements, and on-board diagnostic (OBD) system and durability levels for each vehicle category and sub-classes therein. In addition, reference and commercial fuel specifications are included in the BS- VI proposal. The adoption of proposed BS-VI emission standards will essentially bring Indian motor vehicle regulations into alignment with European Union regulations for light-duty passenger cars and commercial vehicles, heavy-duty trucks and buses, and two-wheeled vehicles. As proposed, the BS-VI regulations largely align emission limits for two-wheeled vehicles with the most stringent standards adopted for similar vehicle types in the EU, and ensure that these vehicles will generally no more polluting than BS-VI four-wheel passenger vehicles. The permissible limit of HC produced from the vehicles is discussed in Table 4. In the BS-VI standards, an independent tailpipe HC emission limit of 0.10 g/km is also introduced. In previous regulatory stages, HC emissions from two-wheelers were regulated under a combined NOX + HC standard. By setting the independent emission standards for both HC and NOX, BS-VI emission standards will help to ensure that the emission control strategies do not reduce emissions of one pollutant at the expense of other [19].

Permissible limit of NO_x produced from the automobile's vehicle emission regulations Regulations strict control of NO_x emissions from automobiles come into force at 1981 in the US. The NO_x is very poisonous and highly reactive gases. These gases form when the fuel is burned at high temperatures. NO_x pollution is emitted by automobiles, trucks and various non-road vehicles. The NO_x often appears as a brownish gas and strong oxidizing agent and plays a major role in the atmospheric reactions. The Clean Air Act Amendments of 1990 required major stationary sources of NO_x to install and operate reasonably available control technology (RACT) by May 31, 1995. All of the New England States

have developed and implemented NO_x RACT regulations. Region-wide, these regulations have reduced NO_x from stationary sources by more than 50% from 1990 levels. The lowest level of NO_x emissions that can be achieved taking into account technical and economic considerations. The permissible limit of NO_x produced from the

automobile vehicles exhaust is discussed in Table 5. The N_2O , NO and NO_2 are most abundant nitrogen oxides in the air. The NO_2 is present in the atmosphere and in acid rain [20].

The N_2O_3 and N_2O_4 present in very small concentrations in the flue gas. However, they present in such low concentrations in the atmosphere that both their presence and their effect are often ignored. The N_2O_4 is two NO_2 molecules joined together and react NO_2 so that the presence of N_2O_4 may be masked by the more abundant NO_2 . The automobiles and other mobile sources contribute about half of the NO_x that is emitted. Comparing estimated the actual NO_x emissions from a new, well-designed system to NO_x emitted by a similar well- controlled and operated older system may be the best way of evaluating how effectively a new combustion system minimizes the NO_x emissions [21].

Permissible limit of SO_2 produced from the automobile's vehicle emission regulations Sulfur dioxide (SO_2) belongs to the family of sulfur oxide gases. These gases are produced when fuel containing sulfur and oil is burned. The large concentrations of SO_2 are associated with multiple health and environmental effects. The SO_2 emissions data are tracked by the National Emissions Inventory (NEI). The NEI is a composite of data from many different sources, including various automobiles vehicles. In 1999, the average sulfur content of diesel was 1300 parts per million (ppm). In December 2002, a new standard was introduced, reducing the maximum sulfur content of diesel to 500 ppm. Sulfur emissions attributed to the transport sector will be further reduced in the future. By 2008, the sulfur level in premium unleaded petrol will be 50 parts per million and, by 2009, sulfur levels in diesel will be 10 parts per million. The sulfur poisoning and thermal degradation of catalyst is one of the main reasons for catalysts deactivation. The poisoning is highly affected of reactants, impurities present on the sites for catalysis. The permissible limit of SO_2 produced from the automobiles vehicles is discussed in Table 6. Recent time-series studies on hospital admissions for cardiac disease in U.S. and Europe, produced no evidence of a threshold for health effects at 24-h SO_2 concentrations in the range of 5-40 ig/m^3 . The 24 h SO_2 concentration are associated

with daily mortality rates in 12 Canadian cities, which had an average concentration of 5 $\mu\text{g}/\text{m}^3$ [22].

Table 4

Permissible limit of HC produced from the automobile's vehicle exhaust.

Vehicle type	India	U.S.	Canada	China	Europe	Japan
	(gm/Km)	(gm/Km)	(gm/Km)	(gm/Km)	(gm/Km)	(gm/Km)
Two wheelers	0.12	0.06	0.10	0.20	0.14	0.20
Four wheelers (Petrol engine)	0.28	0.10	0.25	0.42	0.24	0.32
Four wheelers (Diesel engine)	0.28	0.22	0.40	0.42	0.40	0.40
Up to six wheelers (Petrol engine)	0.40	0.34	0.50	0.80	0.50	0.45
Up to six wheelers (Diesel engine)	0.40	0.34	0.79	0.80	0.70	0.60

Table 5

Permissible limit of NOx produced from the automobile's vehicle exhaust.

Vehicle type	India	U.S.	Canada	China	Europe	Japan
	(gm/Km)	(gm/Km)	(gm/Km)	(gm/Km)	(gm/Km)	(gm/Km)
Two wheelers	0.25	0.15	0.20	0.15	0.25	0.30
Four wheelers (Petrol engine)	0.40	0.25	0.62	0.40	0.30	0.60
Four wheelers (Diesel engine)	0.85	0.50	0.80	0.46	0.65	0.78
Up to six wheelers (Petrol engine)	0.60	0.75	1.10	0.70	1.10	1.10
Up to six wheelers (Diesel engine)	1.20	1.10	1.40	1.10	1.60	1.32

Table 6
 Permissible limit of SO₂ produced from the automobile's vehicle exhaust.

Vehicle type	India (gm/Km)	U.S. (gm/Km)	Canada (gm/Km)	China (gm/Km)	Europe (gm/Km)	Japan (gm/Km)
Two wheelers	0.02	0.03	0.01	0.04	0.02	0.02
Four wheelers (Petrol engine)	0.04	0.06	0.03	0.08	0.06	0.05
Four wheelers (Diesel engine)	0.04	0.06	0.03	0.08	0.06	0.06
Up to six wheelers (Petrol engine)	0.10	0.09	0.07	0.12	0.10	0.12
Up to six wheelers (Diesel engine)	0.10	0.09	0.07	0.12	0.12	0.12

Permissible limit of PM produced from the automobile's vehicle emission regulations

There has been a major research effort during the past seven years to develop after-treatment devices for diesel passenger cars to meet the federal 0.2 g/mi standard first proposed for 1985 and later put off until 1987. California has a 0.2-g/mi standard that was initiated in 1986, and will be lowered 0.08 g/mi in 1989. A number of prototype systems have been built and field-tested to meet the 0.2 g/mi standard. Diesel-powered heavy-duty vehicles use direct-injection turbocharged engines of two-cycle as well as four-cycle design. The applications of various additives, substrate materials, regeneration systems and controls to develop optimum systems that are able to decrease the diesel particulate emissions to the levels of 0.1 g/bhp-hr for heavy-duty diesels and 0.08 g/mi for light-duty vehicles required in California. Recent trends in diesel fuel properties have an adverse effect on particulate emissions. They make it harder to meet stringent particulate emission standards for cars and trucks (0.2 g/mi in 1987 for cars and 0.6 g/bhp-hr in 1988, 0.25 g/bhp-hr in 1991 for trucks) [23].

The diesel exhaust particulate material has been the subject of more study in the past five years. The 25% produced into organic solvents, although different vehicles may

have extractable fractions of 5%-90%, depending to some extent on operating conditions. The particulate emission standards should be based on amount of total particulate matter, on which current standards are based, or amount of soluble organic component extracted from the particulates [24].

The confirmatory tests are targeted and random tests performed by Environmental Protection Agency to validate the emission and fuel economy results reported for certification. The reduction in fuel consumptions and reduces the PM emissions highly depending upon the engine performances as shown in Fig. 6. In recent years, EPA selected about 15% of all test groups for confirmatory testing; two-thirds of the selected test groups 10% are randomly selected and remaining one- third 5% are targeted test groups. Currently, the emission standards for motor vehicles in India are at BS III or BS-IV levels. Nationwide implementation of BS-IV standards for new vehicles is expected beginning in the April 2017. In addition to emission standards for new vehicles, the BS-VI regulation also includes specifications for reference and commercial fuels. Diesel exhaust contains relatively high levels of particulate matter (PM) [25]. Catalytic converters do not remove PM so particulates are cleaned up by a soot trap or diesel particulate filter. In some high exposure areas, there might be the need to set up policy measures aimed at replacing vehicles equipped with older engine technologies with new vehicles complying with the new regulations or to retrofit the engines with appropriate emission control devices. In this respect, countries like Canada and USA are looking at initiatives aimed

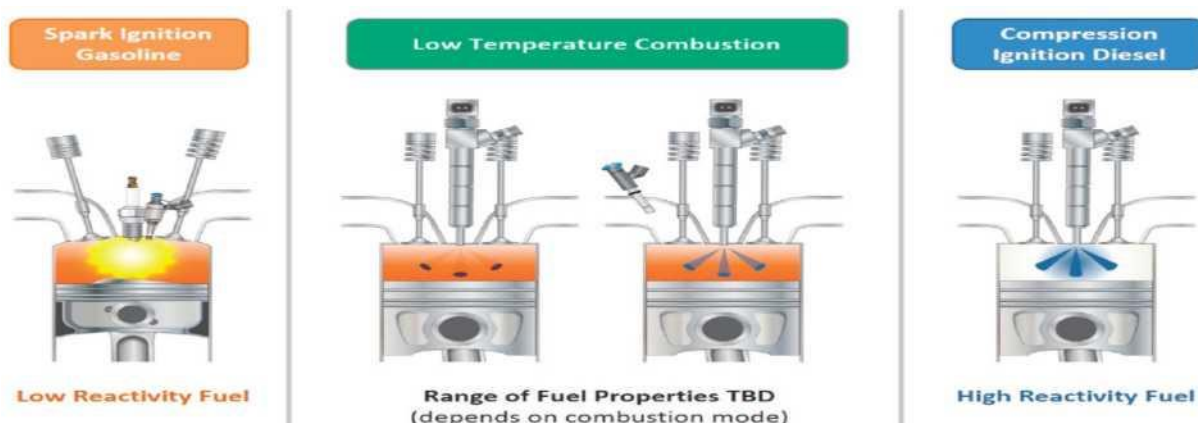


Fig. 6. Reduction in fuel consumptions and reduces the PM emissions.

at exploring the financing options that can help support heavy-duty fleets to further reduce air pollutant emissions by making the purchase of emission reduction technologies for their in-use fleets more feasible and affordable. In road transport, accelerating the worldwide rate of introduction of cleaner and more efficient vehicle technology remains more important. Equally important is the parallel introduction of low sulfur diesel fuels [26].

Applications of alternative source of fuels for reducing the automobiles exhaust pollutions

The alternative fuels, known as non-conventional and advanced fuels are any materials or substances that can be used as fuels, other than conventional fuels. The automobile vehicles exhaust pollution control use by alternative fuels like LPG, CNG, Battery operated, Hydrogen fuels and Bio-Diesel blends. In the developing country rapidly increase in population, economics and increasing standard of living so that the number of vehicles is generally increases their air pollution is also increases. Bio-fuels are also considered as a renewable source [27]. The renewable energy is used to generate electricity; it is often assumed that some form of renewable energy or a percentage is used to create alternative fuels. Research is ongoing into finding more suitable biofuel crops and improving the oil yields of these crops. Bio-diesel is made from animal fats or vegetable oils, renewable resources that come from plants such as atrophy, soybean, sunflowers, corn, olive, peanut, palm, coconut, save- flower, canola, sesame, cottonseed, etc [28]. Once these fats or oils are filtered from their hydrocarbons and then combined with alcohol like methanol, diesel is brought to life from this chemical reaction. Methanol and ethanol fuel are primary sources of energy; they are convenient fuels for storing and transporting energy. These alcohols can be used in internal combustion engines as alternative fuels. Butane has another advantage: it is the only alcohol-based motor fuel that can be transported readily by existing petroleum-product pipeline networks, instead of only by tanker trucks and railroad car. Hydrogen is an emission less fuel. The byproduct of hydrogen burning is water, although some mono-nitrogen

oxides (NO_x) are produced when hydrogen is burned with air. Hydrogen compresses natural gas mixtures is a mixture of compressed natural gas and 4-9 percent hydrogen by energy. Hydrogen could also be used as Hydroxyl gas for better combustion characteristics of C.I. engine. Hydroxy gas is obtained through electrolysis of water [29].

Conclusion

This paper represents various types of pollutants are emitted from vehicles and their effect on human health. The automobile exhaust pollution control is one of the serious environmental concerns in the worldwide. The use of alternative fuels, catalytic converter and emission reduction is controlling the automobile exhaust pollution. Cold-start emission of pollutant gases from automobile vehicles is one of the most severe problems in the large cities, where the number of vehicles running per populated area is very high. A catalytic converter is an emission control device that converts more toxic gases produced from the exhaust of an internal combustion engine and converted into less-toxic pollutants. The performances of catalytic converter are highly depending upon the types of catalysts was used. As compared to petrol engine the diesel engine vehicles produce more particulate matter into the environment. The emission control system in automobiles applied to limit the discharge of noxious gases from the internal-combustion engine and other components. In India the Air Pollution Control Act 1981, established right of the government to set vehicular emission standards. To regulate the pollution emitted from the two-wheelers and four-wheelers vehicles by the Bharat Stage Emission Standard. This paper reviews our current knowledge of automotive emissions, including standards, control technology; fuels additives, in use emissions, measurement methods for unregulated pollutants, and models for predicting future automotive emissions.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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