

Control of Combustion Generated Emissions from Spark Ignition Engines: A Review

M. Mansha^a, Ejaz M. Shahid^a A.H. Qureshi^a

^a Department of Mechanical Engineering, University of Engineering & Technology Lahore Pakistan

E-mail: engg_mansha@yahoo.com

Abstract

For the past several decades automobiles have been a major source of ground level emissions of various pollutants like CO, HC, NO_x, SO_x, CO₂, etc. Due to their dangerous effects on human health, vegetation and on climate, various pre-combustion, in-cylinder and post combustion techniques have been tried for their abatement. This paper reviews all of the workable measures taken so far to controlling the combustion generated emissions from 4-stroke Spark Ignition Vehicular Engines ever since the promulgation of emission control legislation/standards and their subsequent enforcement in the late 1960s.

Key Words: Combustion generated emissions, Spark Ignition, HC, CO, NO_x, Equivalence Ratio, and Alternative Fuels.

1. Introduction

Due to the rapid growth in the urban population world wide (more than a factor of 4), the numbers of automobiles also increased which resulted in an increase of pollution level in urban areas of the developing countries. The menace of vehicular emission was first recognized as serious threat in 1950s, when Californians encountered with photochemical smog by knowing the cause of deterioration of the automobiles tires by high concentrations of ground level ozone. Photochemical smog, a secondary pollutant from vehicle exhaust, is produced by the reaction of volatile organic compound (VOC) and nitrogen oxide in the present of sunlight. The pollutants emerging from combustion engines may include: carbon monoxide (CO), unburned hydrocarbons (UBHC), oxide of nitrogen (NO_x), oxides of sulfur (SO_x), particulate matter (PM), soot, hydrogen, oxygen, traces of aldehydes, alcohols, ketons, phenols, acid, lead aerosol etc, along with normal combustion products i.e. carbon dioxide (CO₂) and water vapors [1]. Based on their potential for oxidant formation in the photochemical smog chemistry, the hydrocarbon emissions from motor vehicles are separated into reactive and non-reactive ones. Fuels containing high proportions of aromatics and olefins produce relatively higher concentrations of reactive

hydrocarbons. The other scale divides the HC in to two classes-methane and non-methane hydrocarbons. Methane is classified as a non-reactive hydrocarbon. Presently the regulated pollutants are, CO, CO₂, HC, lead aerosol (from combustion of leaded gasoline), NO_x, SO_x and particulate matter (PM). Obert [1] categorized and quantified the key sources of pollutants within conventional S.I engine are: exhaust pipe, crank case breather, fuel tank breather and carburetor. The exhaust pipe which is considered as the primary source of emission contributes about 65~85 percent of total vehicular emission including burned and unburned hydrocarbons, various oxide of nitrogen, carbon monoxide, carbon dioxide, and traces of alcohols, aldehydes, ketones, phenols, acids, esters, ethers, epoxides, peroxides, and many others. The crankcase breather, a secondary source, discharges about 20% of burned and unburned hydrocarbons as blow by gas. The fuel tank breather contributes to 5% volatile raw hydrocarbons by evaporation during hot weather and the carburetor discharges about 5 to 10% raw fuel in to the atmosphere with evaporation and spillage losses during hot weather. The emission from any engine depends upon several factors such as engine design, operating conditions, fuel type and the exhaust gas treatment system employed. Typically in a 4-stroke S.I engine [2] the pollutants in the exhaust are found in relative amount of the order: NO_x 500 ~ 1000ppm

(20g/kg fuel); CO 1 ~2% (200g/kg of fuel) and UBHC 3000ppm (as C1) (25g/kg fuel). Apart from combustion-generated pollutants other sources of UBHC are piston blow-by gases, fuel evaporation and subsequent release to atmosphere through fuel tank vents and from carburetor after engine shut down.

Diesel engines emit particulate emission between about 0.2 to 0.5 percent of fuel mass in the form of small particles having 0.1 μ m diameter, which consists primarily of soot. The NO_x emission from diesel engine is comparable to gasoline engine; the concentration of hydrocarbons in the diesel exhaust is lower than gasoline by a factor of 5 in typical S.I engine level. Although diesel engine emits CO, but its level is quite low and diesel engines are not significant source of carbon monoxide. The production of SO_x (SO₂ & SO₃) is dependent on the amount of sulfur present in the fuel. Sulfur leaves the combustion chamber in the form of Sulfur dioxide (>95%) and Sulfur trioxide (2~5%). In the presence of water, SO₃ reacts to produce sulfuric acid. On quantitative basis [3], concentration of hydrocarbons in diesel exhaust ranges from 20 to 300ppm, carbon monoxide (CO) ranges approximately from 10~500ppm. Bosch [4] compared the regulated emissions of two engines having the same capacity and found that the emissions of CO and HC from diesel engine are significantly lower than those from gasoline engine. Diesel NO_x emissions are usually lower than those from gasoline engines. A real drawback of diesel engines is its high particulate matter emissions. Particulate matter emissions from uncontrolled diesel engines are 6 to 10 times compared to gasoline engines. Diesel smoke is also a visible public nuisance. On comparison of gasoline & diesel vehicular engines w/o any emission control systems employed [5] it was found that, light duty diesel vehicles emit 50 to 70% less NO_x than gasoline vehicles. However, heavy-duty diesel vehicles emit 50 to 100% more NO_x than their gasoline counter parts, but 90 to 95% less hydrocarbons and 98% less carbon monoxide. Generally both light and heavy-duty diesel fueled vehicles are more fuel-efficient than their gasoline counter parts (15 to 40% for light duty diesels, as much as 100% for heavy duty ones) and therefore emit less CO₂.

Two-stroke gasoline engines used in motorbikes and three-wheelers emit more pollutants than 4-stroke engines [5]. Hydrocarbon emissions from conventional two stroke engines are high (20~50%) because a significant portion of the air-fuel mixture escapes unburned in to the exhaust during scavenging period and due to the combustion of lubricating oil. In two stroke engines oil is mixed with air-fuel mixture to lubricate bearings and pistons. Some of this appears as white smoke in the exhaust, resulting in high emission of particulate matter. Particulate emissions from two stroke engines are also excessive because of burning of oil during combustion process. Hydrocarbon emissions from a single two-stroke motorbike can exceed those from three uncontrolled passenger cars and particulate matter emissions can exceed those from heavy-duty diesel truck.

The various pollutants emitted by the motor vehicles have different environmental and health implications. Most of the pollutants have adverse effect on the health of humans, animals and plants. Others may have long-term consequences on climate change. CO₂ does not harm human health directly at the concentration level present in engine operation, but being a greenhouse gas it effects global changes in climate. Carbon monoxide (CO), on the other hand, is a poison because of its stronger adherence to hemoglobin and can impair visual perception, manual dexterity and exercise capacity. Its ultimate effects include fainting and death. Un-burnt hydrocarbons contain monocyclic (benzene) and polycyclic aromatic hydrocarbons (PAH), which are carcinogenic. Hydrocarbons with nitric oxide (NO), lead to the formation of ground level ozone, which can cause lung tissue damage and respiratory illness. Nitrogen oxides also act as catalyst to initiate smog-like reactions when exposed to sunlight. Particulates penetrate the lungs, and may carry PAHs with them. Lead is a commutative poison, and can cause adverse effects in mental development in children. Multiple effects are possible with CO, VOCs and NO₂ under the action of sunlight, resulting ozone, which can cause temporary respiratory problems and aggravate asthma. With NO₂ and SO₂, ozone may promote bronchitis and other respiratory infections.

Table-1 summarizes the threshold limit values of selected emissions, typically, encountered in motor vehicle operation. The threshold limit value is the

accepted limit of concentration for repeated human exposure [6].

Table 1 Threshold Limit Value and Their Principal Effect for Selected Emissions from Automobile [6]

Emission (Pr. Effect of inh.) ^a	Threshold Value	
	PPM	mg/m ³
Acetaldehyde (Irritant)	200	360
Benzene (Toxic)	25	80
CO ₂ (Toxic)	5000	9000
CO (Toxic)	50	55
Ethanol (Narcosis)	1000	
Formaldehyde (Toxic)	5	6
Lead (Toxic)	-	0.2
Methane (No Effect)	None	None
Methanol (Toxic)	200	260
Naphta (Narcosis)	500	2000
NO ₂ (Toxic)	5	9
Octane (Narcosis)	500	2350
Ozone (Toxic)	0.1	0.2
Propane (Narcosis)	1000	1800
SO ₂ (Irritant)	5	13
Tetraethyl lead (Toxic)	-	0.075

1.1 Operating Modes and Engine Emissions

In spark ignition engines best possible efforts are made to introduce the air-fuel mixture in to the cylinder/s as homogeneous charge for combustion. Despite substantial efforts made in this regard, some non -uniformities always remain along with cycle by cycle variations in the average charge (air-fuel mixture) composition within cylinder and mal distribution of the charge in different cylinders of multi cylinder engines. Heywood [2] investigated cylinder-to-cylinder variation of equivalence ratio (ϕ) of 5% at light load, 25% at wide-open throttle (WOT) and 20~30% for some engines at some speeds from the mean value. To cope with, the leanest cylinder is adjusted to run reliably, which means that the richest cylinder is probably putting considerable unburned HC in to the exhaust.

In the carbureted engine and the engines equipped with Single Point Injection Systems (Throttle Body Injection TBI), the manifold profoundly influence the distribution of fuel to

different cylinders of multi cylinder engines. The mixture composition in the manifold consists of atomized fuel, air entrained liquid droplets and the liquid film on the manifold wall. The liquid droplets have greater inertia and tend to continue in their direction of movement whenever the direction of flow changes abruptly. Consequently variation of air-fuel ratios results between different cylinders of multi cylinder engines whereby the outer cylinders getting richer mixtures than the inner cylinders. Moreover, the throttle plate at part load position diverts the flow from nozzle towards the wall of the manifold and flow passing through the throttle plate sets up a low-pressure region on the underside of the trailing edge, which tends to deflect fuel towards the front cylinders.

The main causes of HC emissions from S.I engines are operation of engine at non- stoichiometric air-fuel ratio, incomplete combustion, and crevice volume, leakage past the exhaust valve, valve overlap, and deposits on combustion chamber walls and oil on combustion chamber walls. Fig-1 shows different emission levels as a function of equivalence ratio in S.I engines [7]. With fuel rich mixture condition the level of HC & CO are high. The most important engine parameter that affects CO emission is fuel-air equivalence ratio.

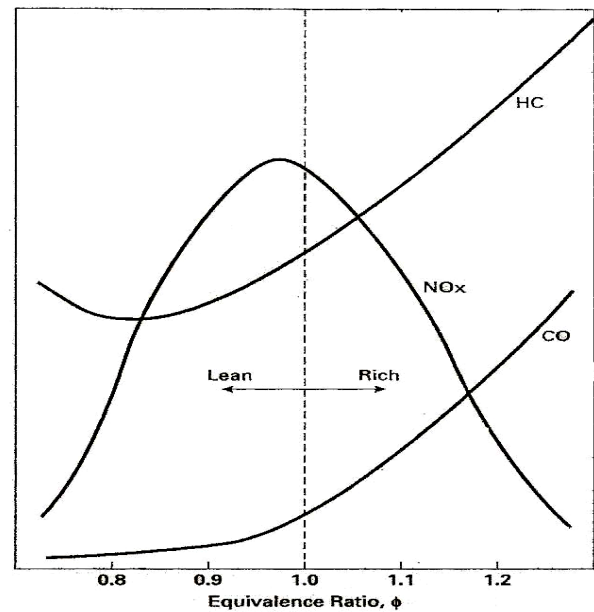


Fig. 1 Emission from an SI engine as a function of equivalence ratio.

Maximum CO is generated when engine runs richer than stoichiometric level and fuel components do not find enough oxygen to react. This condition occurs during engine transients such as start up and rapid acceleration under load. If air-fuel ratio is too lean poorer combustion occurs, resulting in large amounts of HC emissions, the extreme is total misfire at leaner air-fuel ratios. One misfire out of 1000 cycles gives exhaust emissions of 1gm/kg of fuel used [7].

Crevice are narrow regions in the combustion chamber (about 1~2% of the clearance volume) [8] in to which a flame cannot propagate and are one of the major sources of engine out HC emissions. Similarly oil layer within engine cylinder can also trap some of the fuel and later release it during expansion. Combustion chamber deposits are another source of HC emissions. These deposits absorb fuel vapors during compression & combustion when cylinder pressure is high and later on exhaust stroke expel them from the cylinder. Recent estimate suggested that about 9% of the gasoline within the cylinder remains unburned during normal combustion. The major sources of NO_x formation during combustion processes are Thermal NO_x (Zeldovich Mechanism), Fuel NO_x, and Prompt NO_x (Fennimore Mechanism). Thermal NO_x is produced when nitrogen reacts with excess oxygen at higher temperature (greater than 1800K) in the combustion process [9, 11,12] and is predominant form of NO_x (Nitric oxide) produced by Zeldovich Mechanism in internal combustion engines. The prompt NO_x is formed within the flame front and is relatively small in I.C engines. The fuel NO_x is produced when the fuel contains significant amount of nitrogen. Current levels of fuel NO_x are not significant in Gasoline & diesel engines.

In S.I engines maximum burned gas temperatures occur at $\phi \approx 1.1$, but at this equivalence ratio oxygen concentration is low [2] however at slightly lean mixture condition i.e at $\phi \approx 0.9$; NO emission level is at its peak. Under various driving modes different amounts of pollutants are generated. Typically [10] at engine warm up and idling conditions when the mixture is rich (air-fuel ratio 12:1) engine exhaust contains greater concentration of CO & HC, while the concentration of NO_x decreases to minimum due to fall in combustion temperature. At low and minimum speeds conditions

the air-fuel ratio is bit leaner (air-fuel ratio 16:1~18:1) than theoretical air-fuel ratio there by producing lower CO & HC emissions but the amount of NO_x production is high. At high speed condition the mixture is rich (air-fuel ratio 13: 1~14:1) and the concentration of CO & HC is high in the exhaust. During acceleration the concentration of CO & HC increases sharply due to very rich mixture condition (air-fuel ratio 8:1) and as the engine speed rises, the speed of combustion also increases, causing combustion temperature and NO_x to rise. During deceleration CO & HC increases due to over rich mixture and erratic combustion. The production of NO_x is low at this mode.

2. Emission Control Measures

Combination of various mechanical, electronic & chemical measures along with some add-on systems have been employed to control the engine out emissions; these include pre-combustion, in cylinder mixture treatment, and post combustion exhaust gas treatments along with some modifications in the combustion chamber geometry.

2.1 Mechanical Measures

These Include: (1) Reduction in Compression Ratio (2) Retardation of Ignition Timings (3) Increase in Idling Speed (4) Modification in Combustion Chamber geometry (5) Modification in Conventional Carburetor (6) Variable Valve Timing.

With the reduction of compression ratios of S.I gasoline engines from over 10:1 to 8.5:1, peak combustion pressure & temperature are also lowered resulting in a lower formation of NO_x. Furthermore oxidation of CO & HC is promoted in the exhaust due to the increase of exhaust gas temperature with the reduction of the compression ratio [1]

However lowering of compression ratio also results in some loss of power and fuel economy (4~5%); but there is an advantage of reduced Octane number of gasoline which makes easier to phasing out lead from gasoline [9].

Retarding the spark timing reduces NO_x emission, since a greater part of combustion occurs in expanding volume thereby lowering the peak cylinder pressure & temperature.

With the retardation of the spark timing the exhaust temperature also rises that reduces HC emissions too. The cost that has to bear is the decrease of thermal efficiency and greater cooling requirement. The ignition timing control is designed to retard the spark timing at idling, while providing normal spark advance during acceleration and cruising.

Idle speed has been increased from the past values of 450~500 rpm to around 700rpm [1] with accompanying leaner mixtures and greater spark retard; this all needs greater throttle opening with accompanying greater air flow. The result of this combination is the hotter exhaust, which reduces CO & HC emissions. It may be mentioned here that very low idle rpm demanded very rich mixtures resulting high HC and CO emissions.

Some relatively minor changes in the combustion chamber geometry like location of spark plug, positioning of piston rings, and elimination of crevices and control of turbulence resulted in emission reduction. By moving the top piston ring as close to the crown of the piston, Wentworth [2, 13] showed HC reduction of “between 47% to 74%” from base HC levels over a speed and loads. Haskell & Legate optimized piston top land clearance of 0.18 for HC emissions of zero clearance level [2, 14]. The location of ring gap with respect to spark plug also affects HC emission level; the HC emissions are highest when the top ring gap is farthest from the spark plug. Surface to volume (S/V) ratio of the combustion chamber is an important factor in the amount of unburned HC emissions from the engine. The HC emission level has been found lowest in hemispherical combustion chamber because of its lower S/V ratio. Wedge shaped combustion chamber; particularly the L-head wedge has higher S/V ratio and thus having a higher percentage of HC emissions in the exhaust [9].

The conventional carburetors in the past have been modified and/or retrofitted with some additional devices for better control of air-fuel ratios during starting, idling, acceleration and deceleration (transient modes of operation). It has been found experimentally that 90% of the HC and CO is emitted during first 120 seconds of the 23 minutes U.S certification test cycle.

For the control of engine out emissions during the transient modes of operation, the measures which have been taken, include: (1) Heating of the incoming air and provisioning of hot spots for fuel evaporation (2) Reduction of choking time to less than one minute by adapting a lighter thermostatic spring or by using hotter exhaust gases (3) Installment of fast idle cam that serves to hold the throttle partially opens during warm up (4) Installment of slow throttle returns devices for the reduction of engine out emissions during rapid deceleration (5) Incorporation of multi throat carburetors

For high speed engine operations, high volumetric efficiency can be obtained with greater valve overlap periods, which allows the inertial effect of the flow to continue filling and scavenging processes for a longer periods. However for low engine speed operations, a large valve overlap would result in excessive back flow of the residual gas in to the intake manifold which reduces volumetric efficiency, promotes erratic combustion resulting in an increased amount of HC & CO emissions (less NO_x emissions due to high exhaust gas dilution). The effect of valve overlap is more pronounced on NO_x at high engine loads and HC at low engine loads [15].

To cope with the requirements of smooth operation at low and high engine speeds and low engine out exhaust emissions, Honda Motor Company employed Variable Valve timing and Lift Control (VTEC) strategy wherein two intake valves are provided with staggered valve timing and different valve lifts. At low engine speeds the primary intake valve with a higher lift (low valve overlap) is utilized. Measures have also taken to create strong swirl at low engine speeds to improve combustion. At high speeds operation, both the intake valves are made to open using a high lift cam, thereby increasing the airflow substantially to boost engine performance. Engine manufacturers are using different methods for providing variable valve timings including mechanical, hydraulic, hydro mechanical, electromagnetic and electro-pneumatic systems.

2.2 Electronic Measures

Mechanical fuel metering through conventional carburetors proved inadequate, as carburetors cannot

maintain precise air-fuel ratio control under all driving conditions especially during transient operations thus yielding more emissions.

Following measures have been taken in this regard:

- Carburetors with electronic air-fuel ratio control.
- Electronic Fuel Injection System.
- High energy Ignition System.

Carburetors with electronic air-fuel ratio adjustment and with three-way catalyst found their use in early 80s. As such systems have its own limitations so they are no longer produced in significant numbers.

Direct control of fuel quantity through electronic fuel injection (EFI) starts during 1980s. EFI system provides a metered amount of fuel based on the measurement of airflow to the engine and ensures rapid and precise control of air-fuel ratio for all driving conditions. Typical electronic fuel controller has seven different operating modes that affect fuel control. These operating modes are: engine cranking, engine warm up, open loop control, closed loop control, hard acceleration, and deceleration and idle. There are two basic types of fuel injection systems: Central or Throttle Body Injection (TBI) System and Multi Port Fuel Injection (MPFI) system. TBI system, an electromagnetic replacement of carburetor, consisted of one or two fuel injectors mounted near the throttle plate so as to deliver fuel in to the throttle body. Requirements for the TBI were such that they only had to deliver fuel at the correct average fuel flow rate for any given air mass flow. MPFI system has one fuel injector located at the inlet to each cylinder and is better in a sense as it reduces cylinder-to-cylinder variation of air-fuel ratios when compared with TBI system in which, under transient operation, maintaining a correct air-fuel ratio is still a problem. Because of fewer parts TBI system is cheaper while MPFI is costlier but having better emission and performance characteristics.

Other classification of fuel injection systems include, timed or pulsed, continuous or steady and in

cylinder injection. In timed or pulsed injection each injector has a definite duration. Controlling the duration (pulse width) is the dominant part of the injection scheme. The injection is timed to begin and end at specific time in the cycle. Electronic MPFI either fire all injectors at once or each injector is fired sequentially with regard to engine rotation. In continuous or steady scheme the fuel is continuously flowing through the injectors all the times in engine cycle and the flow is metered by controlling the pressure upstream of the fuel injector. In another version of fuel injection scheme the fuel is sprayed directly in to the cylinder, called Gasoline Direct Injection (GDI) systems.

Microprocessor is the heart of the electronic fuel injection systems, which receives different engine operating information through various sensors located in the engine to estimate the mass air, flow and characterize the instantaneous thermodynamic state of the engine. The air mass flow is measured either directly by using mass air flow sensor (MAF) or estimated indirectly by employing speed-density method. In speed density system this estimate can be found from the measurement of intake manifold absolute pressure (MAP), engine RPM and the inlet air temperature. On the basis of the information received microprocessor determines the correct amount of fuel, which is then sprayed via fuel injectors to ensure adequate air-fuel ratios for different operating modes. Apart from fuel economy and increased power, one of the most prominent features of the EFI system is the reduction of engine out emissions during steady as well as during transient modes of operation when compared with carburetor system. During hard deceleration, the engine operates with a very lean air-fuel ratio to reduce excess emissions of HC and CO. The fuel may even be turned off completely for very heavy deceleration. During start up & Idling well atomized fuel is delivered to ease evaporation and subsequently to reduce emissions. It may be mentioned here that for quick vaporization of the fuel spray, a fuel droplet of Sauter Mean Diameter (SMD) of 10 to 20 microns is required for direct fuel injection. For indirect fuel injection, a fuel droplet of 100 micron SMD is acceptable as the fuel vaporization is still continued in the intake port and during the compression stroke [5].

The comparison of engine out emissions of vehicles having carbureted and Port Fuel Injection systems was carried out [16] which showed a reduction of HC and CO emissions by 29% to 69% with PFI system. However the NO_x emissions was increased by 47% with fuel injection.

Conventional contact breaker ignition system has been replaced with computer controlled High energy Ignition Systems (HEI) in modern vehicles. The voltage in this ignition system may reach up to 47KV. This allows the use of spark plugs with wider gap. The longer spark can ignite leaner air-fuel ratios, thus providing better fuel economy and reduced exhaust emissions. The ignition timings in HEI system is controlled by the electronic controller rather controlled by centrifugal and vacuum advance systems.

2.3 Chemical Measures

Various chemical measures have been under taken to control engine out emissions. These include pre-combustion fuel treatment, alternative fuel options, post-combustion exhaust gas treatment and the use of different add-ons systems.

Pre-Combustion Fuel Treatment and Different Fuel options (alternative Fuels) These include:

- Gasoline Reformulation.
- Alternative Fuels

a) **Gasoline Reformulation:**

Conventional gasoline in response to environmental concern has undergone substantial modification in the past decades and still modifications are under way in this regard. Gasoline reformulation has been carried out with the aim to reduce emission by reducing vapor pressure together with the contents of benzene, aromatics, olefins and sulfur plus the elimination of lead [18]. Gasoline is a mixture of 200 to 300 hydrocarbons (4 to eleven carbon atoms) that evaporates between ambient temperature and 200°C. The “front-end” volatility of a gasoline is the temperature at which 10% of the fuel evaporates (T10) and is important in cold start and vapor lock problem. The “mid-range” volatility is the temperature at which 50% of the fuel is evaporated (T50). This is important in short trip fuel economy,

warm-up and cool weather dilatibility. Back end volatility, expressed as the temperature at which 90% of fuel is evaporated (T90) and has been related to engine deposits and engine oil dilution [19]. A typical formula for Gasoline characterization is C₈H₁₅, with a molecular weight is 111 while C₇H₁₇ is used to characterize high hydrogen content gasoline [8]. Tetra ethyl lead (TEL) and Tetra methyl Lead (TML) used in the past to boost octane number of the gasoline (which allows higher compression ratios and efficient engines) has gradually been phased out from gasoline and as a first step, replaced with increased amounts of high octane hydrocarbons though retaining minimum value of lead 0.003 g/gal which is not considered to be major catalyst poison. However increased amount of high-octane hydrocarbons (benzene, toluene, xylene, olefins and other aromatic species) have their own environmental problems. Another measure taken to replace lead compounds from the gasoline was the use of oxygenated compounds.

Oxygenated compounds covering a range of lower alcohols and ethers like ethanol, methanol, tertiary butyl alcohol (TBA), methyl-tertiary butyl ether (MTBE), ethyl-tertiary butyl ether (ETBE), di-isopropyl ether (DIPE) and iso-butyl alcohol have replaced lead for octane boosting purposes. Their volume in gasoline blends varies from 3 to 22 percent. Although blending oxygenated components with gasoline reduced the volumetric energy contents of the fuel but they serve their purpose of reducing/eliminating the lead and aromatic based engine out emissions. Carbon monoxide (CO) and hydrocarbon (HC) levels are progressively reduced as quantity of oxygen increases, while NO_x emission may increase. With ethanol blends in gasoline, emission of aldehydes increases. For the same fuel oxygenate content, MTBE and ETBE exhibit similar exhaust emission characteristics [17]. The use of alcohol as blending agent may increase evaporative emissions considerably. It may be mentioned here that the blends of ethanol and methanol with gasoline have shown non-ideal behavior in solution with respect to vapor pressure. These blends have higher vapor pressure than either component alone. Similar adverse have not been reported for MTBE and other ethers. Sulfur in gasoline is undesirable because it produces sulfur dioxide, sulfate, and sulfuric acid and

hydrogen sulfide emissions. Besides their adverse effect on human health and environment, the efficiency of catalyst is also reduced by the high sulfur contents in fuel.

To remove sulfur from gasoline blending components, hydro-treatment of the blending components is required, which is indeed a cost intensive process. Table- 2 shows the comparison of the properties of the reformulated gasoline and industry average gasoline [8].

Table 2 Comparison of Reformulated and Industry Average Gasoline [8]

Sr. No	Fuel Constituents/ Parameters	Industry Average Gasoline	Reformulated Gasoline Phase-1	Reformulated Gasoline Phase-2
1	Aromatics Vol%	28.6	23.4	25.4
2	Olefins, Vol%	10.8	8.2	4.1
3	Benzene, Vol%	1.60	1.6	0.93
4	Sulfur, mass ppm	338	302	31
5	MTBE, Vol%	0	11	11.2
6	Ethanol, Vol%	0	4	0
7	Reid Vapor Pressure	60-S	50-S	46
	S=summer			
	W= winter	79-W	79-W	
8	T50, K	370	367	367
9	T90, K	440	431	418

Research indicated [5] that using reformulated gasoline with catalytic converter reduces NMHC emission by 12~27%, CO emissions by 21~28% and NOx emissions by 7 to 16%.

b) Alternative Fuels:

Following fuels have emerged as potential contenders of becoming the alternative fuels of the future.

- Liquefied Petroleum Gas (LPG)
- Compressed Natural Gas (CNG)
- Hydrogen
- Ethanol
- Methanol

Propane (C_3H_8) when blended with butane (C_4H_{10}) and with minor quantities of propene (C_3H_6), butane (C_4H_8), isobutene and small amount of ethane

(C_2H_6) is designated as LPG. A common LPG blend P92 contains 92% propane and 8% butane [8]. LPG is produced in the extraction of heavier liquids from natural gas and as by product in petroleum refining. The composition of LPG varies from country to country, in colder countries LPG has a higher percentage of propane and propene in order to provide adequate vapor pressure in winter while in warmer countries LPG consists mostly of butanes and butanes. Propane has octane rating of 112, hence permitting the use of high compression ratios in engine, generally in the range of 11-12:1 or even higher. The wide flammability limit of LPG vapor in air allows its usage in lean burns calibration. LPG is stored on board as a liquid under pressure typically 0.9 ~1.4 MPa [8] and can be delivered to the engine as bi-fuel and dedicated modes and not in common usage in dual-fuel diesel applications [5, 17]. Both lean burn and stoichiometric versions of LPG engines have been developed. Worldwide population of LPG vehicles in 2003 was 9.5 millions with annual consumption of about 16.5 million tons [15, 20]. When used in S.I engines, LPG produces near zero particles emission, very little CO and moderate HC emissions. The CO_2 emission is somewhat lower than those from gasoline whereas NOx emissions are little bit higher/similar to those of gasoline vehicle. Typical test result [8] using HD5 propane (96% propane, 4% ethane) in 3.1L engine indicated the reduction of HC and CO emission by 43% and 53% respectively when compared with gasoline emission in the same engine. However the NOx emission levels are higher by 37%. Emission levels of other toxic compounds are less than the base line gasoline toxic emissions. Major LPG users are South Korea, Poland, Italy, Mexico, Russia, Netherlands, Japan, Australia, Thailand and the United States. In Asians cities like Bangkok, New Delhi, Mumbai, Dhaka, Karachi and Lahore, LPG fuel is very common fuel for 3-wheelers auto rickshaws.

Natural gas is considered attractive alternative fuel due to its clean burning characteristics and wider flammability range ($\phi=0.4 \sim 1.6$). The composition of natural gas varies from about 90 to 95 % methane, with smaller amounts of additional compounds such as 0-4%, nitrogen, 4% ethane and 1-2% propane [8]. Other literatures [7, 5] show this variation of methane in natural gas as 60~98% and 85 to 99% respectively.

Natural gas has an energy density of about 1/1000 that of gasoline under ambient conditions of temperature and pressure so it cannot be used in its natural state as fuel on board a motor vehicle. The onboard storing techniques used include: Compressed Natural Gas (CNG), Liquefied natural Gas (LNG) and adsorbed Natural Gas (ANG). Compressed natural gas cylinder typically contains a pressure of 200bar, while LNG cylinder is kept at -160°C to get the maximum energy density. It may be mentioned here that the maximum energy density of natural gas as an automobile fuel can be obtained when the gas is at liquid state. The range (mileage) of the vehicle extends considerably when LNG is substituted as a fuel instead of CNG. The volume disadvantage of CNG with petrol is 4:1 and LNG with petrol is 1.3:1 [21, 22]. Natural gas can be stored onboard with the aid of adsorbent with out the need of high compression cylinder. An adsorbent (activated carbon, zeolite, clays and phosphorous) is typically a micro porous solid effectively condenses the gas molecules with in the pore structures by means of surface-gas interactions. The density of adsorbed natural gas lies intermediate between LNG and CNG.

CNG (molecular wt. 18.7) is rated as high-octane fuel having octane rating of 120-130. Such high octane rating enables an engine to be operated at a high compression ratio with out the on set of knocking. Methane [18] has lower flame speed (0.43 m/sec) than gasoline (0.5 m/sec) due to which advanced ignition timing is required particularly at lower engine speed. Because of the low conductivity of dry gas an increase of about 50% in ignition voltage is required than for gasoline. Natural gas engine technology can be categorized as stoichiometric, lean burn and dual fuel diesel. The engines of most of the natural gas vehicles currently in operation are converted stoichiometric engines either of bi-fuel type or dedicated to natural gas versions. Lean burn engines use an air fuel ratio with more air than is required to burn all of the fuel. However turbo charging is required to match the power out put of lean burn engine to the stoichiometric engine. In dual fuel diesel engine, the engine is operated on a mixture of natural gas and diesel fuel. Due to lower cetane rating of natural gas, it is not suited for compression ignition, but with the pilot ignition of diesel within the gas/air mixture

ignition can be initiated. Between 50% and 75% of normal diesel consumption can be replaced by natural gas when operating at dual-fuel mode. The engine can be reverted back to 100% diesel in case of non-availability of natural gas. A loss of 15-20% in engine power has been suffered when the engine is operated on CNG due to displacement of about 10% inspired air by the natural gas (whose volume is much greater than that of its related liquid) and due to the loss of evaporative cooling. Similarly a 15-20% loss in thermal efficiency has been reported [21, 22] in dual-fuel heavy-duty truck operated on CNG and diesel ratio of 60:40.

High compression dedicated natural gas engines (optimized) can give improved thermal efficiency of about 10% above that of a base case compression ratio gasoline engine, although it has been suggested that optimized engine should be up to 20% more efficient [21, 22]. Some experimental data regarding such engines showed an increase in fuel efficiency of 15% compared to the base case compression ratio gasoline powered engine. Natural gas engines emit substantially lower amounts of pollutants than their gasoline counterpart. Carbon monoxide (CO) is reduced by 70-95%, non-methane hydrocarbons by 50%, NO_x by 50-87% and CO₂ by 20-30% with almost no particulate matter in the exhaust [21, 22]. Other advantage of using natural gas is reduced engine maintenance requirement, no deposit accumulation in combustion chamber and on spark plugs; thus extending piston ring and spark plug life. Natural gas has lower adiabatic flame temperature than gasoline due to its higher product water contents. So running the engine under lean condition yields lower NO formation and produces lesser engines out NO_x. Addition of H₂ in natural gas accelerates the combustion process resulting in increased engine efficiency and more tolerance towards EGR hence reduction of engine out NO_x [23].

In Pakistan natural gas provided by Sui Northern/Sui Southern Gas Pipe Line Company contains about 9%(vol) nitrogen, so the tendency of fuel bound NO may increase. Typical molar composition of the natural gas in Pakistan is, Methane, CH₄ (75-90%), Propane (0.450-0.70%), Ethane (1.80-2.50%), i-Butane (0.105-0.20%), n-Butane (0.105-0.200%), Neo-pentane (30.00-

48.00%), I-Pentane (0.040-0.080%), N₂ (6.500-9.500%) CO₂ (1.300-1.600%) and Hexane (0.90-0.20%) [24].

There are about 2600 refueling station working in throughout Pakistan to fuel over 2.0 million vehicles plying on the roads [25]. It has been investigated [26] that high compression stoichiometric CNG engines with Pt/Pd catalyst can readily achieve ULEV emission standard and give better fuel efficiency. However, operating the engine lean at 14:1 compression ratio required more elaborate catalyst to control Non-methane Organic Gases (NMOG) emission. Some experimental results [27, 28] also showed that CNG composition had a significant influence on engine performance, fuel economy, burning rate and emission.

Hydrogen is very good alternative fuel for I.C engines due to its clean burning characteristics and its abundance through out biosphere. Hydrogen has high specific energy, 120MJ/kg, high flame speed 3.5m/s and wider flammability limits 4-75%. Hydrogen's high spontaneous ignition temperature, 574°C, provides an opportunity to operate vehicle at high compression ratios than those normally used with gasoline engines. But due to its low ignition energy, 0.019mJ, along with wider flammability limits, hydrogen operated I.C engines suffered pre-ignition and back firing problems. Hydrogen can be stored for vehicular application as in liquid form at -253C in cryogenic containers, as metal hydride (e.g FeTiH₂) or in compressed form at 20 to 70MPa [8]. Between 10 and 12 times more storage space is required for hydrogen than for gasoline to store the same energy contents. Storage and fuel weight for hydrides is 27times and for compressed hydrogen is 4 to 5 times of gasoline.

Hydrogen burns with an invisible and smokeless flame and the combustion products of hydrogen consist mainly of water and some nitrogen oxide. There are no emissions of carbon containing pollutants on hydrogen combustion such as HC, CO, and CO₂ and air toxic benzene, PAH, 1-3 butadiene and aldehydes. Trace amounts of HC, CO and CO₂ originating from burning of lubricating oil however, may be emitted. To control pre-ignition problems, water injection in the intake manifold is used and to reduce NO_x exhaust gas recirculation and leaner operation are employed.

Alcohols in the form of methanol (CH₃OH) and ethanol (C₂H₅OH) are regaining attraction as vehicular fuel both due to environmental reasons and because of depleting oil reserves. Methanol also called wood alcohol, a liquid at ambient conditions, is miscible in water and has relatively low vapor pressure. It can be used in engine in pure/neat (anhydrous) and mixture form. The mixture of methanol/ gasoline blends typically consists of 10% methanol or 85% methanol. Pure methanol is designated as M100, the mixture of 10% methanol and 90% gasoline is labeled as M10 and the mixture of 85% methanol and 15% gasoline is designated as M85. Furthermore methanol can be reacted with isobutylene to form oxygenated fuel additive methyl-tert-butyl ether (MTBE). Methanol (pure) has higher octane number (research) and higher enthalpy of vaporization than gasoline, which are 114 & 1089 KJ/kg respectively. The specific energy of air-fuel mixture of methanol is 2.67, a little bit lower than gasoline, which is 2.8. The energy density of methanol is 15.8 MJ/L, which is about half of that of gasoline, due to which about twice the mass of methanol is required to achieve the same gasoline power out put [18]. However, the higher octane number and higher enthalpy of vaporization (higher volumetric efficiency) of methanol compensated this inherent disadvantage of methanol, and dedicated methanol fuel required about 1.5 liters to give the same mileage as achieved by one liter of gasoline [5].

Cold starting the engine with methanol is difficult due to its high heat of vaporization and to start Otto cycle engines using M100 below 5°C, special pilot fuels or additional heating techniques are required. However starting problems can generally reduced by using M85 fuel; because the addition of gasoline increase the vapor pressure of the mixture making the mixture too rich to burn at cold conditions. Methanol burns with a nearly non-luminous flame that is very difficult to see in daylight. Methanol has got very similar lean burn properties as that of natural gas. Its low energy density results in a low flame temperature, which resulted in lower NO_x emissions as compared to gasoline. Methanol combustion yields reduced emission of number of toxic air contaminants especially benzene and other polycyclic aromatic hydrocarbons. Emission of formaldehyde from methanol-operated engines is investigated to be 5

times more than comparable gasoline engines and the emission of HC and CO during cold starting is on the higher side. Emission characteristics of methanol/gasoline blends, M0, M10 & M100 were investigated, and results showed M85 as most likely blend of methanol/gasoline to be used as alternative fuel [26, 29]. The results of M10 blend showed excessive evaporative and running losses of HC & NMOG when compared to M0 & M85. The usage of M85 fuel showed an average increase of 3% fuel efficiency compared to M0 (base line gasoline fuel). However M85 showed an increase of 400% formaldehyde emissions as compared to base line gasoline. Tests were also conducted [30] to compare the combustion characteristics of reformulated gasoline RFG (California Phase II) and M85. With a change in fuel from RFG to M85 the non-methane hydrocarbons and CO emissions were decreased by 30% and 17% respectively and NO_x emissions remained about the same. On comparing air toxic emissions of M85 & RFG, a reduction of 83% in 1, 3- butadiene was observed with M85 fuel. Similarly a reduction of 50% in benzene and an increase in acetaldehyde and formaldehyde was also observed. The increase in acetaldehyde was found to be 25%.

Ethanol (C₂H₅OH) also called grain alcohol, with an octane number of 111 and low Reid vapor pressure, is considered an excellent alternative to gasoline. The energy density of ethanol (21.1 MJ/L) is higher than that of methanol (which is about 15.8 MJ/L) and about two-thirds of gasoline [31]. Although the low vapor pressure of ethanol is an advantage from the point of view of its loss during the fueling of cars, it also causes some problems in cold-starting engines. Ethanol can be used in combustion engine in three ways; as anhydrous (absolute) ethanol or 100% ethanol, designated as E100, as anhydrous ethanol mixed with small percentage of gasoline, typically 5 to 15% designated as E95 to E85 respectively, as hydrous or hydrated ethanol consisting of 95% ethanol and 5% water. It may be mentioned here that when up to 22% ethanol is blended with ordinary gasoline, the resulting mixture is designated as Gasohol and because of phase separation problems with hydrous ethanol-gasoline mixture only anhydrous ethanol is used in the gasohol mixture. Ethanol is currently used as a transportation fuel typically not in pure form but blended with gasoline in different proportions. E10 is

the most common blend having nearly the same energy of combustion per unit volume of stoichiometric mixture in vapor form as that of gasoline so E10 can be used interchangeably with gasoline by vehicles without any special arrangement of the fuel/air system on the vehicle. E85 does require adjustment of the fuel/air system and is used by flexible fuel vehicles (FFVs) that are equipped to sense the alcohol content of the fuel and make the necessary adjustment. Brazil has the highest proportion of ethanol in the transportation fuel supply. It is estimated that in Sao Paulo, a metropolitan center of 17 million people, 40% of the total fuel volume is ethanol [32]. Approximately 40% of the cars in Brazil operate on 100% ethanol. The remaining cars run on a blend of 22% ethanol (78% gasoline). The U.S., by comparison, uses ethanol at a blend of 10% ethanol, and 90% gasoline, marketed under the name of gasohol. As E10 gasohol has nearly the same energy of combustion per unit volume of stoichiometric mixture in vapor form as that of gasoline so the engine using this fuel produces almost the identical power as that with gasoline with no mileage penalties. Up to a proportion of 20% anhydrous ethanol in gasoline no significant mileage penalties occur and the low energy density of ethanol is being compensated by high heat of vaporization (high vol. efficiency) & high octane number of ethanol. About 1.25 liters of pure hydrated alcohol give the same mileage as one liter of gasoline- a significant mileage penalty [5]. Although the Reid vapor pressure of ethanol is less than that of gasoline but the ethanol/gasoline blend exhibits higher vapor pressure, and can increase evaporative emissions. It may be pointed out that at about 70% concentration of ethanol in the mixture, the vapor pressure of the mixture becomes equal to the gasoline [26].

2.1 Add-on Systems for Emission Treatment

Several add-on devices have been developed & incorporated within engine to control that portion of the emission, which escapes from the engine unburned. These systems include: Positive Crankcase Ventilation (PCV), Exhaust Gas Recirculation (EGR), Air Injection, Thermal Reactors, Catalytic Converters, Selective Catalytic Reduction (SCR) and Selective Non-Catalytic Reduction (SNCR).

The gases from the combustion chamber (blow by) can leak past the piston rings and accumulates in

the crankcase. These blowby gases with high HC concentration with some CO are flammable and their buildup in the crankcase would increase crankcase pressure. Before 1963, when emission legislations were not in force these gases were vented in to the atmosphere via a draft tube. These gases were estimated to contribute about 20% of total hydrocarbon emissions from the engine. To control this emission, a PCV system was employed wherein a positive pressure is used to transfer the blow by gases from the crankcase to the intake manifold. In the intake manifold these gases are mixed with fresh charge and enter in to the combustion chamber. PCV valve is one way type which is so designed that it restricts the excessive flow of blow by to the engine during idling and low speed condition (high manifold vacuum condition) while at wide open throttle condition (WOT) the flow from the crankcase is unrestricted. Between Idling & WOT conditions the PCV valve is calibrated to open in proportion to the intake manifold vacuum.

To reduce the combustion temperature and subsequent reduction of thermal NO_x, exhaust gases may be utilized. Exhaust Gas Recirculation (EGR) system refers to the introduction of exhaust gases in to the engine to reduce the peak combustion temperature and to reduce the flame speed. Use of EGR also reduces mass fraction of O₂ in the cylinder as the exhaust gases replaces part of the air. It may be mentioned here that CO₂ and H₂O (the major constituents of the exhaust) has greater heat capacity than air.

EGR percentages in the 15 to 30 ranges are maximum amounts that an S.I engine can tolerate [2]. EGR systems are required to be functional in the part-load range and closed at idling. Most EGR valves are of proportional type (spring loaded & vacuum controlled), which adjusts gas recirculation rates to engine at different operating conditions. Other types of valves utilized backpressure in the exhaust manifold to control exhaust gas recirculation. Modern vehicles employed Electronically Controlled EGR valves actuated by a high response stepper motor. The electrically controlled valve can reduce engine-out NO_x emission by 35% compared to mechanical system at the same HC level. When EGR rate was reduced within the allowable margin, 5%

reduction was obtained along with 10% reduction in NO_x when compared to the mechanical control system [33]. Exhaust gas temperature may vary from 300 to 400°C from idling to around 900°C at full load condition in conventional spark ignition engines. However the most common range of exhaust temperatures is 400 to 600°C. A lower temperature is required to oxidize HC than CO at a specified residence time. If excess air is present or injected in the exhaust gas, the HC, CO & aldehydes in the exhaust may be oxidized and their emission is greatly reduced. With out using catalyst temperatures in excess of 600°C (with a residence time of greater than 50 ms) are required to oxidize HC and temperatures in excess of 700°C are required to oxidize CO [2, 9].

In older engines air injection system had been employed wherein air via a vane pump had been injected in the hot exhaust gases to reduce greatly the concentration of CO, HC and aldehydes emissions. This system was most effective with rich mixtures, retarded spark and with shielded and larger exhaust manifolds. Air injection system can also be used at lean mixtures because exhaust temperatures in either case are relatively high. Thermal reactor was designed to increase the residence time of the exhaust gases by increasing the exhaust manifold volume. It was generally in the form of an enlarged exhaust manifold directly bolted to the engine cylinder head. Thermal reactors can be effective both rich and lean mixture conditions but more with fuel rich operations. With rich mixtures, supplementary air causes a noticeable temperature rise from oxidation of CO and HC hence greater reduction in HC & CO in the exhaust can be achieved. With thermal reactors NO_x emission cannot be controlled. Due to their complexity, space requirements and unable to reduce NO_x, thermal reactors were not proved successful as long-term emission control technology.

In the presence of a catalyst, temperatures in the range of 250-300°C [7] are required for oxidation of HC & CO. A catalyst is a substance that accelerates a chemical reaction by lowering the energy needed it to proceed. Catalytic converters are chambers mounted in the exhaust flow system and contain active catalytic materials, which promote oxidation of CO & HC and reduction of NO_x. The catalytic converter has advantage over thermal reactor as the high

conversion rates of pollutants are obtained at moderately low exhaust gas temperatures with out modifying engine parameters like compression ratio, spark timing, air-fuel ratio etc from the optimum engine performance level.

For vehicular applications different catalytic materials like copper, chromium, nickel, cobalt etc were tried but noble metals Platinum (Pt), Palladium (Pd) and Rhodium (Rh) gave best results in controlling CO, HC & NO_x simultaneously. These metals have excellent properties e.g. high specific activity, high resistance to thermal degradation, superior cold start performance and low deactivation caused by fuel sulfur.

Pd and Pt are used, as oxidation catalyst to oxidize CO & HC while Rh is primarily a NO reduction catalyst. In three- way catalytic converter efficient reduction of all the three pollutants CO, HC and NO_x are simultaneously done on the same catalyst bed. This is achieved by operating the engine near stoichiometric condition and by employing oxygen sensor in the exhaust along with electronic fuel injection for precise control of air-fuel ratio in a close loop engine operation. Heywood [2] quoted the air-fuel ratio variation window of 0.1 (or .007ø) for such systems and Richard Stone [34] quoted air-fuel ratio perturbation of ± 0.25 (or $\pm 0.02 \text{ ø}$). More than 80% conversion efficiency of these three pollutants is obtained through this control system. Experimental data showed that cyclic variation may lower the peak efficiency of the catalytic converter but it broadens the width of the air-fuel ratio envelope to 1. A properly working fully warm up three-way catalyst reduces the emissions of HC, CO & NO_x by a factor of 10 [35]. During cold starting, catalytic converter is very inefficient. The temperature at which a converter becomes 50% efficient is called light off temperature. Different measures have been taken to decrease the converter warm up time. The measures include the use of an after burner, location of the converter closer to the exhaust manifold and electric heating [36]. Prior to the introduction of the catalytic converters, oxidation catalysts (Two ways) were used along with EGR in the automotive engine. The oxidation catalyst controls HC and CO emissions while EGR system controls the NO_x emission from the exhaust stream. To ensure that the catalyst could

always oxidize CO & HC, excess air was added to the exhaust by the air pump. Table - 3 shows the U.S Federal emission limits & summarizes the technological measures taken to reduce CO, HC and NO_x [35].

Table 3 U.S Federal Emission Limits (grams of pollutants per mile) [35]

Model year	CO	HC	NO _x	Control measures
1966	87	8.8	3.6	Pre control
1970	34	4.1	4.0	Retarded Ignition, Thermal reactors, EGR
1974	28	3.0	3.1	Retarded Ignition, Thermal reactors, EGR
1975	15	1.5	3.1	Oxidation Catalyst
1977	15	1.5	2.0	Oxidation Catalyst & Improved EGR
1980	7	0.41	2.0	Improved Oxidation Catalysts and 3-Way Catalytic Converter
1981	7	0.41	1.0	Improved 3-Way Catalytic Converter and Support material

With the rising emphasis on controlling CO₂ emissions (a green house gas) and on fuel economy, it is imperative to operate the engines on fuel lean mixtures. Gasoline Direct Injection (GDI) engines have been developed by different manufactures which work on the principle of charge stratification. In these engines, the fuel burns more efficiently yielding less pollutant emission of CO, HC and CO₂ and fuel consumption is lowered up to 30% compared to the stoichiometric combustion [37]. These engines can operate very lean overall mixture strength; the air-fuel ratio near the spark plug is nearly stoichiometric or slightly fuel rich while the other parts of the combustion chamber are provided with very lean air-fuel ratios. Mitsubishi GDI engine operates on up to 40:1 air fuel ratio and uses EGR (up to 30%) & de-NO_x catalyst for exhaust emission control. Toyota GDI engine operates on up to 55:1 air fuel ratio and uses electronically controlled EGR (up to 40%) to control exhaust emissions [38]. GDI engines give 20-30% higher fuel efficiency compared to conventional stoichiometric engines [39].

In lean burn engines conventional 3-way catalytic catalysts cannot be used to control NO_x emissions. To control NO_x from these engines, generally, EGR, Selective Catalytic Converters (SCR) by hydrocarbon & urea (ammonia), Passive & Active DeNO_x and NO_x traps can be used along with Pt/Pd catalyst for controlling CO & HC emissions [34, 37, 39]. SCR & DeNO_x techniques are more suitable to stationary engines specifically to diesel engines [41].

In selective catalytic reduction (SCR) ammonia (NH_3) or urea ($\text{NH}_2\text{CO NH}_2$) is added to exhaust gases to effect chemical reduction of NO to N_2 . Conversion efficiencies up to 80% have been reported [34] with this technique. In passive DeNO_x, hydrocarbon present in the exhaust gases has been used to reduce NO chemically. A narrow temperature window of 160°C to 220°C is required for platinum catalyst for NO_x reduction [42]. A peak NO_x conversion efficiency of 40% has been reported [34] at 400°C and 62.32% at 450°C [43] with copper-exchanged zeolite catalyst with passive DeNO_x technique. In active DeNO_x technique hydrocarbon fuel is injected in to the exhaust stream for NO_x reduction. Up to 20% NO_x reduction in diesel engines have been reported [34] with 1.5% increase in fuel consumption. In NO_x trap Technology; a 3-way catalyst in conjunction with NO_x absorbing material is utilized. Under lean conditions NO is oxidized to NO_2 over Pt catalyst and then is stored in the form of nitrate at the surface of NO_x absorbing material (Ba-containing material). Under fuel-rich condition the stored NO_x is released which is then reduced to N_2 by HC, CO and H_2 over noble metal catalyst (3-way catalyst) [34, 39].

3. Conclusions

The process of fuel metering, mixture preparation and subsequent distribution to engine cylinders play a vital role in determining the completeness of combustion process. Incomplete combustion not only yields harmful pollutants but also decreases power and efficiency of the engine. The three pollutants of concern emitted from the spark ignition engines are HC, CO and NO_x (currently regulated).

Different emission control strategies evolved gradually ever since the introduction of the emission control standards in late 1960's have been tried by

developed countries to control the vehicular emission and a considerable reduction in emission limit of HC, CO and NO_x has been achieved.

4 References

- [1] Obert Edward E. Internal Combustion Engines and Air Pollution, 3rd ed., 1968.
- [2] Heywood, John B. Internal Combustion Engines Fundamentals, McGraw-Hill, 1998.
- [3] WWW.dieselnet.com "Diesel Net Technology Guide", 1998. Last Accessed on 5th November 2010.
- [4] Robert Bosch G H; Diesel Fuel Injection, 1994.
- [5] Asif F, Christopher S. W., Michael P. Walsh, Air Pollution from Motor Vehicles, Standards and Technologies for Controlling Emissions, 1996.
- [6] R.E. Bolz and G.L. tuve (eds), CRC handbook of Tables for applied engineering Sciences, 2nd ed. Chemical hazard Information, 766-770, CRC press Inc., Boca Raton, FL, 1979.
- [7] Pulkrabek, Willard W. Engineering Fundamentals of the Internal Combustion Engine, First Indian reprint, 2003.
- [8] Ferguson Colin R., Kirkpatrick Allan T. Internal Combustion Engines Applied Thermo sciences, 2nd ed. 2004.
- [9] Mansha M, Control of Exhaust Pollution in Spark Ignition Engines, MSc Thesis University of Engineering & Technology Lahore, 1998.
- [10] Training Manual, Electronic Fuel Injection System, Step-II Vol. 14, Toyota Motor Corporation Japan, 1990.
- [11] Chon-Lin S, Feng B, Ze-Min T, Fang-Cheng Li, Qi-Fei Huang, Simultaneous Removal of NO_x , HC and PM from diesel exhaust emissions by dielectric barrier discharges, J. of Hazardous Mat. 2009; 166 : 523-30.
- [12] Mansha M, Qureshi A H, Shahid E M, , Pak Journal of Engineering and Applied Science. 1 (2007) 67-72.
- [13] Went worth J T.. Combustion Science & Technology, 4(1971) 97-100.
- [14] Haskell N.W, Legate C.E. Surface Phenomenon SAE paper 720255, 1972.
- [15] Pundir B.P., Pollutant Formation and advances in Control Technology, India, 2007.

- [16] Jemma, C.A, Lance, D.L., and Shore, P.R., Specification of Hydrocarbon Emissions from European Vehicles SAE Paper 922376 (1992).
- [17] Hutcheson, R.C. Alternative Fuels in the Automotive Market, CONCAWE Report No.2/95 Brussels 1995.
- [18] Goodger Eric M, Transport Fuel Techn. Landfall Press Norwich, 2000.
- [19] Aguila, J, Chan N, Curtis j. Proposed Regulations for California Phase -2 Reformulated gasoline, Technical Support document, California Air Resources Board, Sacramento, California 1991.
- [20] Bernard Bensaid, Alternative Fuels: Today and tomorrow, Panorama 2005, Institut Francais du Petrole (IFP) France, 2005.
- [21] Poulton, M.L Alternative Fuels for Road Vehicles, Computational Mechanics Publications, U.K 1994.
- [22] Semin, Rosli Abu B., American Journal. of Engineering. and Applied Science, 194 (2008) 302-311.
- [23] P. Dimopoulos, C. Bach, P. soltic, K. Boulouchos, International Journal of Hydrogen Energy, 33(2008) 7224-7236.
- [24] ECTECH- Environment Consultants Pak., Sui Southern Gas Composition, 2007.
- [25] www.iangv.org , Las Accessed on 5th October 2010.
- [26] Ingersoll John G. Natural Gas Vehicles, The Fairmont Press Inc. 1995.
- [27] Kubesh J., king S.R. Liss W.E., Effect of Gas Composition on Octane Number of Natural Gas Fuels, SAE paper 922359, 1992.
- [28] K.Kim, H.Kim, B.Kim, K.Lee and K.Lee, Oil and Gas Service Technology-Review, 64(2009) 199-206.
- [29] R.A.Gosse, J.D. Benson et al. Automotive Engineering, 100(1992) 170-79.
- [30] Cadle.S.,P. Groblicki, R.Gosse, et al. Dynamometer Study of Off Cycle Exhaust Emissions- The Auto/Oil Air Quality Improvement Research Program, SAE Paper 971655.
- [31] Goodger Eric M. Transport Fuelling- Update on Alternatives, Landfall Press 2006.
- [32] Colon, M.; Pleil, J.D. Hartlage, T.A. Lucia Guardani, M. Martins, M.H. Atmospheric Environment, 35(2001) 4017-31.
- [33] Takahashi, H., Ishizuka, Y., Tomita, M., and Nishizawa, K, Engine Out and Tail Pipe Emission Reduction Technologies of V-6 LEVs, SAE paper 980674 1998.
- [34] Stone Richard, Introduction to Internal Combustion engines” 3rd ed. Macmillan Press Ltd. London, 1999.
- [35] Heywood John. B “Motor vehicle emission Control: Past Achievements, Future Prospects” George Stephenson Lecture- Institution of Mechanical Engineers 1997.
- [36] Becker. E and R. Watson, “Future Trends in Automobile Emission Control” SAE Paper 980413, (1998).
- [37] Zhiming Liu., Seong Ihl Woo, Catalytic Reviews, 48(2006) 43-89.
- [38] John L. Lumley, Engines- An Introduction, Cambridge University Press 1999.
- [39] Kume, T., Iwamoto, Y., Iida, K., Murakami, M., Akishino, K. and Ando, H., Combustion Control Technologies for Direct Injection S.I Engines, SAE paper 960600.
- [40] Freeley J., M. Deebe and R.J. Farrautao,. Studies in Surface Science and Catalysis, 122(1999) 157-164.
- [41] Koebel M., M.Elsener and M. Kleemann, Catalysis Today 59(2000) 335-45, 2000.
- [42] Jochheim J., Hesse D., Duesterdick T., Engeler W., Neyer D., Warren J.P., Wilkins A.J.J and Twigg M.V., A Study of the catalytic Reduction of NO_x in Diesel exhaust” SAE paper 962042 (1996)
- [43] Abdallah M. Hasna. Reduction of NO_x Gases Using Copper Zeolite Catalyst, Proceedings of the World Congress on Engineering WCE (1): 657-61 London 2009.