CHAPTER 2

LITERATURE REVIEW

2.1 GENERAL

Air pollution and the global warming is a real threat to the mankind. Automobiles become the main culprit in polluting the atmosphere. Research is on around the globe to find suitable methods to reduce the automobile pollution. Catalytic converter is a good solution to treat the more harmful pollutants and convert to less harmful pollutants. Control of harmful emissions from automobiles during cold start has become a challenging task over the years due to the ever increasing stringent emission norms. There is tremendous improvements in the design of catalytic converters during the last two decades. Today vehicles are manufactured to meet the requirements of Euro IV/Bharath IV emission standards. However these catalytic converters will be active only after they reach the “light-off” temperature which normally takes 2 to 3 minutes when the engine is started in the ‘cold’ condition. Until the catalyst reaches light-off the harmful pollutants goes out to atmosphere un-treated. Such emission referred as cold start emission is a matter of concern considering the fleet of vehicles on roads in a city. Number of researchers have studied cold start emission in the last two decades and suggested various methods of achieving rapid light-off of the catalyst so as to reduce the cold start emission. Each method has its own merits and demerits. The salient features of the investigations carried out by various researchers have been discussed in this chapter.

2.2 MANIFOLD AND CATALYST MODIFICATION

Muraki et al. (1990) have studied the effects of palladium catalyst in a three way catalytic converter in SI engine. Increasing the palladium and rhodium
loading from 0.5 g/l and 0.1 g/l, respectively, to 1.0 g/l and 0.2 g/l, respectively, resulted in improved catalyst light-off and conversion performances. The light-off performance under the dynamic conditions improved with the increasing A/F perturbation until the optimum value, and its behavior was different from platinum/rhodium catalyst. The effect of palladium on the durability performance of the palladium/rhodium catalyst was compared with that of the platinum/palladium/rhodium catalyst. Further studies were done in the characterization of catalysts and the surface enrichment of palladium-rhodium and platinum-rhodium alloy systems heated in air and hydrogen. They reported that the light-off performance of NO\textsubscript{x} reduction efficiency has been improved with the addition of lanthanum to the palladium catalyst.

Engler et al. (1994) have studied the control of emission in SI engine with tri metal emission control catalysts with a combination of Palladium (Pd) together with Pt/Rh as precious metal components. The performance of high loaded Pd-only catalysts was demonstrated in vehicle tests according to the FTP 75, ECE and Japan-10-mode procedures. It was shown that the advantageous lean HC light-off temperature observed with high loaded Pd-only catalyst can also be reached with similar loaded Pt-only catalysts. Various alternative ways to incorporate Pd in multi-brick converters were evaluated in vehicle tests. It was shown that single brick three metal converters with high Pd-content can have advantages over conventional Pt/Rh-three way catalysts. However, the extent of the improvement depends strongly upon the particular application, and with the present trend of increasing Pd-prices these three metal converters might lead to increased precious metal costs over conventional Pt/Rh-catalysts.

Burch et al. (1995) observed vacuum insulation and phase change thermal storage could be used to enhance the heat retention of a catalytic converter. Storing heat in the converter between trips allows exhaust gases to be converted rapidly thereby reducing the cold start emission. They designed, built and tested catalytic converters with phase change material thermal storage system along with vacuum insulation. Thermal tests demonstrated the ability of vacuum insulation and 2.3 kg of PCM to maintain the converter temperature of 350°C for 17hrs compared
to 25 minutes with conventional converters. However the FTP test showed the exhaust temperature during the pre conditioning were not sufficient to melt the phase change material. However, the vacuum insulation performed well, resulting in a converter temperature of 146°C after 23 hours of cold soak at 27°C. Compared to the same converter at ambient temperature overall emissions of CO and HC were reduced by 52% and 29% respectively.

Socha et al. (1998) investigated the impact of different converter substrate cell structures on tailpipe emissions and pressure drop from a total systems perspective. They used a new technology palladium only catalyst in combination with a palladium/rhodium catalyst on a 4.0-liter, 1997 Jeep Cherokee for performing the FTP test. In the study the emissions performance was related to the converter volume for the different cell structures. The results from this study demonstrated that the 93 square cell/cm² structure has superior performance versus the 62 square cell/cm² structure and the 46 triangle cell/cm² structure when the converter volumes were relatively small. However, as converter volume increases the emissions differences diminish. For this application the results also show that the higher cell density, lower mass substrates have a slight advantage in catalyst light-off. The emphasis of this study was a comparison of different cell structures, however, other factors such as thermal management, catalyst technology and air-fuel ratio control also contributed significantly to the relative performance of these systems. The study demonstrated the advantages of higher cell density structures to help meet future emissions challenges. The authors also suggested that substrate support technology must be integrated with the catalyst technology, the converter packaging, and the engine management control to create a total system, which meets emissions and durability requirements.

Santanametal. (1998) developed FEA model of air gap manifold to predict inner and outer wall temperature and structural soundness. It was observed that dual wall manifold were durable to meet high exhaust temperature up to 900 °C while meeting performance, noise and weight reduction.
Williamson et al. (1999) have investigated the dual-brick catalyst systems containing Pd-only catalysts followed by Pt/Rh metal in three-way catalyst to achieve LEV/ULEV emissions. They reported that the dual-catalyst system allows location of precious metals and optimization of wash coat technologies in attaining ULEV emission compared to single-brick converters. Dual-brick [Pd+Pt/Rh] systems were equivalent to [Pd+Pd/Rh] systems for under floor application using the same wash coat technology, and provide an effective strategy for precious metal management while meeting 100K ULEV emissions. They reported that dual-brick [Pd+Pd/Rh or Pt/Rh] systems can reduce precious metal usage compared to Pd-only systems for ULEV applications. They have also reported that additional HC light-off and vehicle emission benefits can be achieved using thinner-wall substrates and increasing substrate cell densities, especially from 400 to 600cpsi substrates.

Gulati (1999) presents the key advances in ceramic substrates which include lower thermal expansion, lighter weight, higher surface area and improved manufacturing process all of which help meet performance requirements. In addition to above benefits, the compressive and tensile strengths of lightweight substrates, as well as their thermal shock resistance, are found to be adequate following the application of high surface area alumina wash coat. The strength properties are crucial for ensuring safe handling of the substrate during coating and canning and for its long term mechanical durability in service. This work also provides the durability data for thin wall substrates with 600/4 and 400/4 square cell structure and compare them with those of standard substrate with 400/6.5 square cell structure.

Kyu–Hyun et al. (2000) developed dual walled air gap exhaust pipe system and observed low HC emission and faster light-off of the catalyst due to low thermal capacity and high thermal insulation effect of the system. They also studied the thermal analysis of dual walled air gap exhaust pipe system using CFD and experimental methods. The results have shown excellent conformity in both methods. Also optimum gap size for dual wall exhaust system has been obtained.

Zidat and Parmentier (2000) have studied various methods of catalytic converter thermal insulation to reduce the heat transfer in the surrounding of engine
components. The converter skin temperature was reduced by giving ceramic coating on the surface of the catalytic converter. They used low thermal conductivity material as insulation to reduce the cost of the catalytic converter. The heat conduction from exhaust manifold and outlet cone, to the centre shell is not significant. This allows taking full advantage of increase in the insulation mat thickness. They reported that placing a heat shield over the catalytic converter is not significantly more beneficial than increasing the insulation mat thickness. Furthermore the heat shield had increased the insulation mat temperature to levels where the mixture ceramic fiber and vermiculite could be destroyed.

Lepperhoff et al. (2000) dealt with the plasma chemical oxidation of hydrocarbons in the exhaust gas stream during cold start conditions. The article concerns the design and development of a plasma-system in order to decrease the hydrocarbon emissions from engine start till catalyst light-off. Vehicle results in the New European Driving Cycle show a hydrocarbon conversion of more than 42% in the first 11 seconds from engine start. In this period nearly all types of hydrocarbon were reduced. The exhaust backpressure of the system is comparable to the conventional silencer. With improvement in the design of the plasma unit, the exhaust back pressure can be reduced further.

Geon Seog Son et al. (2000)suggested and studied a photo catalyst to reduce cold-start emissions. Conventional TWC can reduce more than 96% of harmful emissions after the activation, but under a cold-start condition it needs a lot of energy to activate. During the activation time (light-off time) harmful gases are exhausted without any purification and it makes the conventional TWC difficult to satisfy tightened regulation. A photo catalyst can be activated by light that has wavelengths lower than 380 nano-meters. The activation needs no time and loss of energy like a TWC. To apply the photo catalyst on a vehicle after-treatment a photo catalyst system was suggested that uses non-thermal plasma as a light source of photo catalyst. The durability of a photo catalyst was also studied with hydrothermal aging method. The properties of aged catalyst were tested with surface area, phase transformation and conversion efficiency of HC.
Nagashima et al. (2000) found that a current Pt/Rh catalyst seems to possess comparable TWC performance to the new Pd/Rh catalyst when the catalysts are aged at 900°C. However, aging at a temperature higher than 900°C significantly deactivated the activity of the Pt/Rh catalyst to a point that is much worse than the Pd/Rh catalyst. For the development of a new Pt/Rh catalyst, Alumina and Cerium materials were optimized to compensate the high mobility of Pt at the aging temperature above 900°C. The interaction between Pt and Rh needs to be redesigned to suit this kind of high temperature aging. Although the details are still not clear, an optimum degree of interaction exists for a new Pt/Rh catalyst. By combining the optimum Pt-Rh interaction concept and highly thermally durable materials, a new Pt/Rh catalyst, which performed equally under engine dynamometer and vehicle close-coupled test condition to the Pd/Rh, were developed. Surprisingly, this new Pt/Rh could reduce significant amount of Pt while maintaining the same performance level. The new Pt/Rh catalyst can be used at least for some applications where Pd/Rh catalysts are used. It is believed that the new Pt/Rh technology will help balance the PGM usage and facilitate the best utilization of PGM resource.

Kemmler et al. (2000) conducted intensive study on the cold start emission issue through various methods and described that geometric parameters of the catalyst and coating materials were the key factors in reducing emission. With a view to achieving success in terms of lowest emission levels through alternative measures, possible experimental solutions to the problems were described and commented. The authors have discussed the systems with electrically heated catalysts or combustion concepts using alternative fuels. The issue of “lean catalysts” was taken into account by reporting on the properties and some of the problem areas of NO\textsubscript{x} trap catalysts (NTC) based on diverse experience. In this context, topics such as conversion windows, thermal aging or sulphur sensitivity were commented upon based on various measurements.

Kristofor, et al. (2001) described an integrated Perforated Manifold, Muffler, and Catalyst (PMMC) for an automotive engine exhaust system. The design aims to reduce tailpipe emissions and improve engine power while maintaining low sound output levels from the exhaust. The initial design, based on
simplified acoustic and fluid dynamic considerations, is further refined through the use of a computational approach and bench tests. A prototype was fabricated and evaluated using fired engine dynamometer experiments. The results confirmed earlier analytical estimates for improved engine power and reductions of emissions and noise levels.

Marsh et al. (2001) have studied about the interactions of various physical parameters of the catalyst’s substrate such as thermal mass, hydraulic diameter and geometric surface area and has provided a guideline on how to design the optimum system for a specific application, taking into account system's back pressure and system costs based on engine test bench results. Also, the results for the optimized design regarding emission tests and maximum conversion rate at higher loads were demonstrated. The tests were performed with and without hydrogen-rich gas produced by the plasma boosted fuel converter with gasoline. A one hundred fold reduction in NO$_x$ due to very lean operation was obtained under certain conditions.

Norman et al. (2001) described the development of an integrated Perforated Manifold, Muffler, and Catalyst (PMMC) for an automotive engine exhaust system. It reduced the tailpipe emissions and improved engine power while maintaining low sound output levels from the exhaust. The initial design, based on simplified acoustic and fluid dynamic considerations, was further refined through the use of a computational approach and bench tests. A final prototype was fabricated and evaluated using fired engine dynamometer experiments. The results confirmed earlier analytical estimates for improved engine power and reductions of emissions and noise levels.

Madhusoodana et al. (2001) developed a system ceramic honey comb coated with Zeolite molecular sieves which can absorb HC during cold start period. They adopted a new method of forming the zeolite film on ceramic honey comb by in-situ crystallization. They observed that zeolite film formed on 400 and 100 cpsi cordierite honey comb showed high surface area and good thermal stability for automotive applications.
Lee et al. (2002) conducted investigation on a production N/A 1.5 liter DOHC gasoline engine during cold start to warm-up. For the effects of non-thermal plasma-photo catalyst combined reactor, 10% concentration reduction was achieved with the fuel component paraffin, and the large increase in non-fuel paraffinic components and acetylene concentrations were similar to those of base condition. However the absolute value was locally a bit higher than those of base condition since the products were made from the dissociation and decomposition of highly branched paraffin by plasma-photo catalyst reactor.

Sonet et al. (2002) suggested an innovative exhaust emission after-treatment system to cut light-off time effectively to zero. One of the key components in this system is the photo catalytic material, titanium dioxide, which is coated on a honeycomb monolith of a converter and is acting as a non-thermal catalyst in reduction of cold start THCs. In addition, non-thermal plasma is used for ultraviolet (UV) light generation source to activate the photo catalyst on the surface of honeycomb cells. Since photo catalysts are activated by UV irradiation not by thermal energy and non-thermal plasma is immediately generated with the electric power-on, catalytic reactions in this system start with the ignition of an engine; therefore unlike conventional thermal catalysts no light-off time is needed. A newly developed photo-catalyst-plasma-honeycomb system (PPH) has been tested in an ULEV vehicle (2.0 DOHC, A/T) to check the feasibility for automotive application. It is shown that the PPH system could achieve about 50% reduction of cold start THCs compared with the conventional three way catalyst for the first 40 seconds running after engine start. The electric power consumption is less than 200 watts during this running time.

Favre and Zidat (2004) have discussed the main challenges and the technical solutions to minimize light-off time and to improve steady state performance for the pollutants HC and NOx in Europe. Among them are substantial catalyst improvements needed to accommodate the progressively more severe aging related to high-speed driving conditions in Europe, and the close-coupled location of the catalyst, with the introduction of the converter welded directly to the exhaust manifold. They have also discussed the major steps that need to be taken not only to
meet European emission targets but also to minimize cost or optimize packaging. The particularly severe rapid aging procedures developed to mimic the European driving style are also discussed, as well as the trade-off between converter volume and PGM content when using ultra-thin wall substrates. Vehicles equipped with Euro IV emissions systems have shown that only a systems approach, including optimized exhaust manifold and canning designs, robust engine calibration strategies and specifically developed wash coats, can lead to a cost effective emissions solution.

Nagashima et al. (2004) observed that Pd based catalyst has been an excellent catalyst for removing THC and CO at light-off but is weak in NO\textsubscript{x}. In order to elevate the NO\textsubscript{x} activity of Pd-based catalyst, Rh has been combined into the catalyst system. The Pd-Rh, Pd-OSC and Rh-OSC interactions were found to be important for the improvement of light-off and warmed-up activities on Pd/Rh catalyst. Minimizing Pd-Rh interaction was effective for Pd/Rh catalyst performances. Selections of supporting materials for both Pd and Rh are a key for improvement of light-off and warmed-up activities. By combining the above concepts, the advanced Pd/Rh, which was significantly superior to the current Pd/Rh under engine dynamometer and vehicle close-coupled test condition, was developed.

Rohart et al. (2004) in their paper developed a new generation of mixed oxides with high OSC and high thermal stability, covering a wide range of compositions. These materials show phase stability and thermal stability at temperatures greater than 1100°C for Zr-rich as well as Ce-rich compositions. They can be used advantageously as precious metal carriers in close-coupled or under floor catalysts demonstrating improved catalytic performance. Regardless of composition (ceria-rich as well zirconia-rich mixed oxides), these materials show surface areas higher than 20 m\textsuperscript{2}/g and 5 to 7 m\textsuperscript{2}/g respectively after air aging at 1100°C and 1200°C. Aged Rh model powder catalysts based on these new materials show improved hydrocarbon and CO-light-off temperature compared to existing materials. Typically, the T20%-CO-light-off temperature is 30°C less for a Ce-Zr (50/50 at%) based catalyst than for a zirconia-rich-based catalyst. Pt-based powder catalysts show the same trend. In addition, with new ceria-rich, mixed-oxide-based
catalysts, the cross-over point (COP) conversion is less affected by a decrease of the precious metal loading than with a catalyst based on a zirconia-rich mixed oxide. Due to their high OSC, thermal stability and low light-off performance, such materials are preferred precious metal carriers for cost-effective catalysts with low precious metal loadings.

Rohart et al. (2005) in their paper focused on stability and catalytic performance of laboratory-aged PGM powder model catalysts. They showed that there is a strong relationship between catalytic activity and the nature of the PGM/support interaction. They took the example of high thermo stable rare-earth-doped zirconia containing 40\% Ceria, which promotes the light-off activity of Rh model catalysts - T20\% of NO and C₃H₆ and showed that they are respectively lower by 40°C and 50°C under rich conditions and respectively lower by 30 and 20°C under lean conditions, than current OSC Zr-rich materials containing only 20\% Ceria. On the other hand, high thermo stable Ce-rich oxides (containing more than 50\% Ceria) are preferred carriers for Pt. The same type of approach was issued to test the preferred PGM (Pt, Pd, Rh)/Support interaction. In a second part they combined the pre-screened mixed oxides in low loaded Pd/Rh and Pt/Rh technologies. These technologies were tested respectively on vehicle and synthetic gas bench (SGB). Low-loading Pd/Rh technology containing only 22 g/ft³ PGM meets euro 4 limits and showed similar efficiency as current catalysts containing 35 g/ft³ PGM. The same trend is observed for Pt/Rh technologies on SGB test.

Dou et al. (2005) in their study focused on the effect of catalyst design parameters and their performance response to different engine operating conditions. Key design parameters such as catalyst formulation (CeO₂ versus non CeO₂), precious metal loading and composition (Pd versus Pd/Rh), wash coat loading, catalyst thermal mass, substrate properties and key application parameters such as catalyst aging, exhaust A/F ratio, A/F ratio modulation, exhaust temperature, temperature rise rate and exhaust flow rate were studied on engine dynamometers in a systematic manner. Optimized Pd light-off catalysts on 400 cpsi/6.5, 600 cpsi/3 and 900 cpsi/2 mil cordierite substrates were further examined at the manifold
location for FTP-75 emission performance as a function of cold start A/F ratio to achieve the best emission results on a 1997 Nissan Altima.

2.3 CATALYST HEATING SYSTEMS

Larson (1989) in his investigation on emission control under cold ambient test conditions observed that the emission levels at 20°F were three to four times more than that at 75°F. He also observed that during cold start due to fuel enrichment and poor efficiency of the catalyst the emission values were high. It had been concluded that the vehicles equipped with port fuel injection performed better under cold ambient conditions in minimizing cold start emission.

Whittenbergerand Kubsh (1990) developed resistively heated metal substrate converters to improve the cold start emission characteristics of light duty vehicles. Electrically heated metal monoliths have been designed and tested that were able to reach catalytic light-off temperatures (350°C) in less than 30 seconds using a conventional 12 volt electrical system. A solid state controller has been developed that mates with a vehicle's 12 volt system, delivers high currents to the metal monolith, and controls the converter temperature to a given set point. Gasoline vehicle emission data were presented that show substantial improvements in cold start HC and CO emissions under both normal ambient and reduced ambient conditions by combining resistance heating and secondary air injection. In these tests Bag 1 HC and CO emissions were reduced by more than 50% versus the same metal monolith converter tested in an unheated configuration.

Kaiser et al. (1993) showed that it is possible to minimize the energy consumption of EHC system and that the required service life can be achieved. The physical characteristics such as mass, geometrical surface area, cell density and electrical resistance of the EHC construction could be optimized to save energy. This, in conjunction with the operating parameters of the engine, the controlling of the secondary air and the catalyst configuration, enabled the goals to be met. The design of the converter, the physical characteristics and the results of the tests were shown with the Porsche 944 S2 and 968 applications. To further understand thermo
mechanical durability behavior, thermo-cycling, vibration analysis and high mileage durability tests on vehicle were carried out.

Socha et al. (1994) have studied the effect of electrically heated catalyst (EHC) as an addition to the main catalytic converter. The low mass EHC quickly reaches high temperature levels, sufficient for a limited CO and HC conversion. The heat generated by the exothermic oxidations is carried down by the exhaust gas to the main converter, which consequently attains faster light-off.

Oeser et al. (1994) have studied the burner system to heat up the catalyst. They established that the energy requirement with burner system is significantly low compared to EHC system. However in real time the burner system is more complex as the system is equipped with control valves, sensors and micro processor control.

Laing (1994) observed that more than 60% of HC emission occurs during cold start period. He developed an alternator powered electrically heated catalyst system and concluded that power provided from alternator at an elevated voltage leads to reduced wire thickness and simple electrical circuit mechanism.

Langen et al. (1994) conducted test at BMW and observed that in addition to electrically heated catalyst (E-cat) and the afterburner chamber an incorporated burner system would accelerate the catalyst light-off, particularly in larger engines.

Breuer et al. (1996) conducted test with Emitech heated catalyst (EMICAT) on a gasoline engine. The influence of catalyst design, heating energy, cold start management, FTP and European test cycle were discussed. Emission results of an aged electrically heated catalyst system and mechanical service life results were demonstrated.

Takatsu et al. (1996) considered microwave dielectric technique for rapid catalyst heating to reduce the harmful pollutants in cold start emissions. A dielectric material, having a relatively large loss factor at 2.45 GHz was selected.
This was coated to the exhaust catalyst allowing microwave energy to be deposited efficiently. The developed system has been tested successfully using a single-mode cavity in conjunction with a model gas. Moreover, a concept for practical in-vehicle system using the microwave heated catalyst has been proposed.

Hayashiet al. (1997) developed an Intermittent Dual-fluid Exhaust Burner (IDEB) to reduce emissions from methanol fueled vehicles during the warm-up period after a cold start. The IDEB would not need any special fuel injector or blower, and had been built mainly through software modification of an ECU. An FTP mode test while operating an IDEB confirmed that the catalyst temperature was rapidly increased to significantly reduce the emissions to meet a level of ULEV standards.

Ahlvik et al. (1997) studied the effects on the exhaust emissions using a block heater. The car was tested according to the FTP-75 test procedure for regulated emissions at +22, +5 and -15°C ambient temperatures. At +5°C additional analysis of Polycyclic Aromatic Compounds (PAC) and 2,3,7,8-tetrachloro dibenzo-p-dioxin (TCDD) receptor affinity test was carried out. The test results showed reductions of CO and HC emissions when using a block heater. The reductions of these emissions were 60 and 65% respectively at the lowest ambient temperature investigated. NO\textsubscript{x} emissions were less affected and even increased marginally in some cases. The results also showed reductions of particulate emissions in the first phase of FTP-75, by 55% at the lowest ambient temperature. PAC emissions at +5°C are shown to decrease even more than suggested by the reduction of HC and particulate emissions, compared to the results without a block heater. The TCDD tests indicated similar results as for PAC. Real-time measurements of the emissions indicated that most of the emissions were emitted in the first two km of the test cycle. This investigation showed that the use of a block heater has a potential to reduce harmful emissions from gasoline-fueled cars at low ambient temperatures.

Lepperhoff (1999) designed, built and evaluated an improved plasma reactor. The new reactor design included a concentric inner high voltage electrode, a grounded outer electrode, a shielded high-voltage and high temperature resistant
electrical connection. A generator controller had been developed for better control of operating conditions as required during the engine cold start phase. The new reactor system was installed in the exhaust pipe of a gasoline direct injection engine. They observed that HC emission was reduced up to 30% in the first 40 seconds of cold start test.

Sendilvelan et al. (2001) dealt with the development and performance of the Low Mass Electrically Heated Catalytic (LMEHMC) converter with copper oxide as a catalyst in a spark-ignition (SI), gasoline-fueled engine. It is found that the LMEHMC reduces cold-start hydrocarbon (HC) and carbon monoxide (CO) emission, when used with existing catalytic converter. From this, the potential of catalytic systems with copper oxide as catalyst is analyzed.

Hunt et al. (2004) in their paper described a cold start emission reduction system developed for a 3.0L V6 test vehicle in order to meet SULEV emission regulations. The emphasis of their research was how the system can be used to meet SULEV emission standards without the need for a heavily loaded catalyst. A fuel-vaporizing device had been developed that generates vaporized fuel to be consumed during engine start up. The device allowed for lean A/F ratio control during engine start and idle and was called a Combustion Stabilizing Device (CSD). A vehicle with a CSD mounted to the engine was tested in an emission lab. The test vehicle resulted in approximately 50% HC emission reduction in the first 20s of engine startup and had a catalyst warm-up time to T_50 (50% converter efficiency) of less than 20s.

Bashkar et al. (2004) in their paper dealt with cold start emission control using Electrically Heated pre-Catalytic Converter (EHC) with copper oxide as catalyst in Mark IV Ambassador Spark Ignition engine. It was found that EHC with existing main catalytic converter (MC) significantly reduces cold start HC and CO emission.

Servati et al. (2005) observed that a vapor management system would control the Air-to-fuel ratio of the intake charge during “cold-starts”, idle, and drive-
away, or until catalyst lights off to a desired level. Additionally, vapor fuelling would provide solutions to the inherent problems of “cold fuel enrichment”, “wall wetting”, “lost-fuel”, and “mixture preparation”, as well as, open up beneficial opportunities for lean air-fuel ratio cold starts. They designed and developed a Vapor Management control System consisting of a Carbon Canister vapor source, supplying a traditional induction system augmented with additional subsystems in a preferred configuration and tested. The results were presented in this paper and a major reduction in HC emissions over liquid port injection (PFI) is achieved.

Presti et al. (2013) observed that for achieving fast light-off thermal management is widely used by engine manufactures although it leads to increased fuel consumption. This fuel penalty is usually higher for high power output engines that have a very low load during emission certification cycle leading to very low exhaust gas temperature and, consequently, the need of additional energy to increase the exhaust gas temperature is high. An alternative way to reach a fast light-off minimizing fuel consumption is the use of an Electrical Heated Catalyst (EHC) that uses mechanical energy from the engine to generate the electrical energy to heat up the catalyst. Following this thermal management strategy the energy input can be tailored according to the component need and the energy loss in the system can be minimized.

2.4 SECONDARY AIR INJECTION

Kollmann et al. (1994) observed that the secondary air injection at exhaust manifold aids oxidation of CO and HC and exothermic oxidation reaction increases the temperature of exhaust gas, resulting in fast light-off of catalyst.

Hernández et al. (2002) observed that Cold start emissions can be efficiently reduced by injecting secondary air (SA) in the exhaust port making compliance with the most stringent standards possible. The thermo chemical conditions (mixing rate and temperature of secondary air and exhaust gas, exhaust gas composition, etc) prevailing in the exhaust system were studied. It was observed that the exothermic reaction of exhaust gas results in faster light-off of the catalyst.
The mechanisms of this combustion were studied at different engine idle conditions and the conditions at which auto ignition takes place had been found and recommendations for exhaust system design and engine calibration were derived. It may be further used to improve system reliability and ensure reduction in cold start emissions at different start conditions. The thermo dynamical conditions in the engine and exhaust system were calculated by means of a 1-D CFD program. The simulation of the auto ignition conditions in the exhaust manifold was computed with the CHEMKIN program package.

Hummel et al. (2004) developed secondary air charger with short response time. Secondary air injection feeds fresh air into the exhaust system during cold start and achieves an oxidation of unburned HC and CO. This exothermal oxidation elevates the exhaust gas temperature and decreases light-off time of the catalyst. This requires a fast rising secondary air mass flow during the cold start of the engine. Electrically driven secondary air pumps achieve this requirement with a high cut-in current. The secondary air charger worked as a turbo charger driven by the pressure drop at the throttle valve. The first part of this paper described the performance of secondary air charger in a passenger car compared with an electrical secondary air pump. The second part of the paper compared secondary air chargers with plastic and aluminum wheels. It was established that reduction of rotating mass and decreased friction in the bearings affects short response time and increased secondary air flow with plastic wheels.

Lee and Heywood (2010) performed an experimental study to develop a more fundamental understanding of the effects of secondary air injection (SAI) on exhaust gas emissions and catalyst light-off characteristics during cold start of a modern SI engine. The effects of engine operating parameters and various secondary air injection strategies such as spark retardation, fuel enrichment, secondary air injection location and air flow rate were investigated to understand the mixing, heat loss, and thermal and catalytic oxidation processes associated with SAI. Time-resolved HC, CO and CO\textsubscript{2} concentrations were tracked from the cylinder exit to the catalytic converter outlet and converted to time-resolved mass emissions by applying an instantaneous exhaust mass flow rate model. A phenomenological
model of exhaust heat transfer combined with the gas composition analysis was also developed to define the thermal and chemical energy state of the exhaust gas with SAI.

The study found that significant emissions reduction can be achieved with SAI by the thermal oxidation process prior to the catalyst, which results in higher exhaust gas temperatures and therefore enhances the chemical process inside the catalyst by faster catalyst light-off. The engine operation, with a relative air/fuel ratio 20% rich of stoichiometric and 100% secondary air, yielded the fastest catalyst light-off time of 4.2 sec. The SAI system reduced HC emissions by 46% to 88% and CO emissions by 37% to 93% compared with the normal operating conditions. The analysis showed that the post-catalyst HC emissions levels were optimized with secondary air flow rates corresponding to an overall exhaust lambda of 1.3. The improvement in the thermal oxidation reaction with the increased mixing rates upstream of the catalyst decreased the catalytic oxidation reaction due to the increased consumption of reactants upstream of the catalyst. Therefore, the post-catalyst HC emission levels were not strongly affected by the mixing rates.

2.5 CLOSE COUPLED CATALYST

Hu and Heck (1995) have studied the positioning of catalytic converter closer to the exhaust manifold as an efficient way to increase the catalyst inlet temperature during cold start. They used palladium catalyst, which is highly stable at temperature as high as 1000°C for HC light-off behavior. They reported that the close coupled catalyst is an effective way of cold start emissions as long as the converter remains active.

Faltermeier et al. (1998) observed that in SI engines, the cold-start phase is responsible for contributing the largest proportion of total emissions. To start the chemical reaction, catalytic converters require a minimum temperature which, at present, cannot be reached quickly enough by the engine exhaust gas. They used close-coupled main catalytic converters and observed that it offered the potential necessary to achieve compliance with European emission standards. A description of
the design procedure and the installation of the series design were provided followed by a discussion of the advantages and disadvantages of such systems.

Otto et al. (1998) observed that rapid light-off can be achieved by keeping the converter closer to the exhaust manifold. They observed the conflicts such as space constraint, thermal resistance of catalytic coating and high temperature load in engine compartments in implementing the system. They also observed that greater surface area of the catalyst reduces emission with little increase in back pressure.

Bauer et al. (1999) studied the SI engine thermal management system with closed coupled catalytic converter. They measured the catalytic converter mantle temperature by three insulating methods like air gap insulation, air gap insulation with additional heat shield and air gap filled with ceramic fibers. They reported that air gap insulation with heat shield and ceramic fiber system are capable of reducing the radiation exchange between the converter mantle and the double mantle. Reducing heat loss by using a mantle with austenite phase material with low emissivity supplements insulation on the exhaust system. They concluded that the effective control of the component temperature could be achieved by reducing the emissivity of the component.

Lee et al. (2002) investigated Close-coupled catalyst temperature under various engine- operating conditions. The experiments were conducted with a 1.0L SI engine at 1500-4000 rpm. The engine was operated at no-load to full-load conditions. Exhaust gas temperature and catalyst temperature were measured as a function of lambda value (0.8-1.2), ignition timing (BTDC 30°-ATDC 30°) and misfire rates (0-28%). It was found that ignition retard and misfire can result in the deactivation of the catalytic converter, which eventually leads the drastic thermal aging of the converter. Significant reduction in light-off time can be achieved with proper control of ignition retard and misfire, which can reduce cold-start HC emissions as well. Exhaust gas temperature was also predicted according to engine speed, air/fuel ratio and ignition timing to complement the experimental results.
Grigorious and Dimitrios (2003) studied the close-coupled catalyst subjected to exhaust gas conditions typical for a modern engine warm-up phase using a time-efficient 2-dimensional modeling approach. A parametric analysis was performed to assess the significance of various design parameters affecting the cold start performance of close-coupled catalysts. It was shown that the detrimental effect of flow uniformity on light-off is associated to the non-uniform ageing.

Meda et al. (2005) developed a systematic method for analyzing the stresses produced in the close coupled system, consisting of thin walled fabricated tubular exhaust manifold and converter, due to thermo-mechanical loading utilizing both FEA and CFD. The calculation of temperature distribution in the manifold and converter is very important for accurate calculation of thermal durability. They used computational fluid dynamics (CFD) to predict transient flow and thermal conditions in the manifold and converter. The converter monolith, mat, air gap between inner and outer cones were considered in the calculations. The temperature distribution predicted in the manifold and converter was compared against the experimentally measured numbers. The temperature distribution obtained was used to calculate the thermal stresses/strains using finite element analysis. Due to the high temperatures involved in exhaust system operation, both material and geometric non-linearity were considered in the structural analysis. Material response behavior under several thermal cycles, with each cycle involving a heating and a cooling stage, that results in temperature gradients in the manifolds and converter and their overall effect on fatigue life were computed. The contraction and expansion behavior of the mat during heating and cooling were also included in the analysis. Stresses/strains, deformation, and contact forces during heating and cooling for the manifold and converter assembly were computed.

2.6 PRE-CATALYST

Konstantinidis et al. (1997) have studied the effect of pre-catalyst, which is placed in the vicinity of the exhaust manifold and the main catalyst remains at its initial position. They designed a pre-catalyst with either Pd-Rh or Pd-only with high precious metal loading and 10-30% of a main converter volume in-order to allow
installation close to the exhaust manifold, thus favoring exothermic oxidation reactions and consequently the heat utilized to heat-up the main catalyst.

Jeong and Kim (2000) used a warm-up catalyst, in addition to the main under-body catalyst, near the engine exhaust manifold for reducing start-up emissions. This study numerically considers three-dimensional, unsteady compressible reacting flow in the warm-up and main catalysts to examine the impact of a warm-up catalyst on thermal response of the main catalyst and tail pipe emission. The effects of flow distribution and loading condition on the temperature distribution and emission performance have also been investigated. The present results show that flow distribution has a great influence on the temperature distribution in the monolith at the early stage of warm-up process and optimal catalyst distribution of high loading at the entrance has no effect on conversion improvement when the space velocity is too fast for reaction to complete within high loading region.

### 2.7 HC ADSORBER SYSTEM

Burk et al. (1995) in their study formulated an effective, energy efficient strategy for dealing with cold start hydrocarbon using carbon-free hydrocarbon traps and heat exchange related TWC catalyst beds. The tests have been successfully tested on a wide variety of current model vehicles. In each case U.S. FTP 75 total hydrocarbon emissions were reduced between 45 - 75% versus the vehicle's stock exhaust system.

Hertl et al. (1996) have studied the reduction of cold start emission by inline HC adsorber system (HC trap). The HC adsorber consists of a first catalyst followed by an adsorber unit with a central hole and a downstream second catalyst. During cold start, the exhaust gas passes through the adsorber substrate channels and the central hole. The hydrocarbons are adsorbed from the exhaust gas passing through the channels and a portion of the exhaust gas passing through the hole impinges directly on and heats the second catalyst. A fluidics diverter valve is used to turn off most of the exhaust gas flowing directly through the hole to the second catalyst, thus heating it faster than the adsorber unit. As the adsorber is heated the
HCs are slowly desorbed and oxidized over the second catalyst. They reported that the adsorber system is a viable alternative to fast light-off, regarding HC emissions reduction capability. (Total hydrocarbon emissions by 45-75% compared to standard three way catalytic converter system).

Patilet al. (1996) developed an In-line hydrocarbon (HC) adsorber system to reduce cold start HC emissions. The system comprises a first catalyst, adsorber unit, and a second catalyst for oxidation of desorbed HC. During cold start, exhaust gas is directed to the hydrocarbon adsorber using a fluidic flow diverter unit without any mechanical moving parts in the exhaust system. After the first catalyst lights off, the diverter is shut off and the major portion of the exhaust gas then flows directly to the second catalyst without heating the adsorber unit. After the second catalyst reaches light-off temperature additional air was added to oxidize the desorbed HC.

Koltsakis and Stamatelos (2000) expanded an existing CAE methodology for exhaust after-treatment to include HC trap technology. The flow, heat transfer and chemical kinetics in a typical complex system, comprising a “barrel type” adsorber and two conventional catalysts are studied. A mathematical model is developed and applied for the computation of the flow and pressure distribution, as well as transient heat transfer in the barrel type adsorber. A physically relevant model is used to simulate HC adsorption desorption on the adsorbing material. The model is used in combination with an existing 2-d 3-way catalyst model to simulate different HC trap concepts. The aim is to understand and quantify the particular thermal response and HC retention behavior of hydrocarbon adsorber systems. Illustrative results with variable geometric parameters under realistic input conditions are presented.

Yamamoto et al. (2000) developed an adsorber system for reducing cold-start hydrocarbon (HC) emissions by combining existing catalyst technologies with a zeolite-based HC adsorber. The series flow in-line concept offers a passive and simplified alternative to other technologies by incorporating one additional adsorber substrate into existing converters without any additional valving, purging lines,
secondary air, or special substrates. Major technical issues to be resolved for practical use of this system are 1) the ability to adsorb a wide range of HC molecular sizes in the cold exhaust gas and 2) the temperature difference between HC desorption from the adsorber and activation of the catalyst to convert desorbed HCs. They describe the current development status of hydrocarbon adsorber after treatment technologies. They report results obtained with a variety of adsorber properties, wash coat structures of adsorber catalyst and start-up and under floor catalyst system combinations. The system was evaluated in FTP tests using a 2.4-liter L4 vehicle. The system reduced up to 60% of cold-start HC emissions beyond the three-way catalyst-only baseline system. This in-line HC adsorber system could be one of the potential technologies to meet ULEV/SULEV and future regulations, without the need for ancillary electrically heated catalyst (EHC) hardware and its associated costs.

Corbo et al. (2000) studied the results of a study on basic adsorption properties of three different zeolitic materials (HZSM5, Silicalite, HY) towards hydrocarbons present at engine exhaust during cold start. Equilibrium isotherm curves at room temperature are presented for three model hydrocarbons (ethylene, isobutene, toluene), considered as representative of the most concentrated compounds detectable at engine start-up. Breakthrough curves, obtained at different temperatures by flow adsorption tests with the selected hydrocarbons, are also discussed. Finally the results of flow adsorption tests performed on the three zeolitic materials at engine exhaust are shown. The aim is to understand how the physico-chemical characteristics of the adsorbent material can affect its trapping capability in adsorbing all the types of hydrocarbons present in the engine exhaust.

Young-Hoon Song et al. (2000) performed a lab scale test to develop a technique for reducing HC emissions from cold-starting engines using non-thermal plasma-assisted catalytic process. An A.C. power supply and a barrier discharge reactor packed with several types of catalysts have been used in the present study. The test results showed that simultaneous use of catalysts with non-thermal plasma process allows the process to be used even under room temperature conditions that is apparently too low to activate conventional catalytic process for treating HC
emissions. Parametric tests with various temperature conditions, different types of HC (C₂H₄, C₃H₆, and toluene), and several types of catalysts and adsorption materials have been performed to provide basic design criteria of after-treatment system used for automotive engines.

Yamazaki et al. (2004) describes a technology for reducing hydrocarbons (HCs) emissions during cold engine start-up. The technology consists of a new HC adsorption system and a method for detecting the deterioration of adsorption performance of the HC adsorber. This active type HC adsorption system was added to Honda's current SULEV system technologies (high performance catalysts, catalyst quick warm-up control, and high accuracy A/F control), for further reduction of cold HC emissions at start-up. In addition, a new sensor had been developed to detect humidity in the exhaust gas, which in turn was used to predict performance deterioration of the HC adsorber. During FTP (Federal Test Procedure) testing, this emission control system has achieved a reduction of more than 70% in cold HC emissions during cold start, and a reduction of about 60% in NMOG weighted mean (WM) value, as compared to without the HC adsorption system. Furthermore, using a correlation between HC and moisture adsorption performance in the HC adsorbent, a method for detection performance deterioration in the HC adsorber with a newly developed humidity sensor was developed.

Chenet al. (2013) in their paper investigated HC traps based on zeolites for cold start HC control. For cold start NOₓ control, especially in lean burn engine exhaust, NOₓ storage and release catalysts have been evaluated. They also introduced a novel catalyst which they have referred to as Cold Start Concept (CSC™) catalyst technology.

### 2.8 PHASE CHANGE MATERIAL

Korin et al. (1998) studied the exploitation of thermal capacitance to keep the catalyst temperature high during a short parking period. Under normal engine operating conditions, some of the thermal energy of the exhaust gases is stored in the PCM in which the catalyst is embedded. During parking, the PCM
undergoes partial solidification and the catalyst temperature is thus maintained inside the desired temperature range for maximal conversion efficiency. In this method no additional energy source is needed to heat the converter, since the energy of the exhaust gas from the engine is stored and used; and no control means are required. The main disadvantage of the method is that it is effective only within a specific length period after engine shut off, the time depending on the thermal specifications of the system. An experimental device was designed, built and tested. It was constructed from a commercially available catalytic converter (with a light-off temperature conversion of about 310°C), in which 3.8 kg of a PCM was embedded, composed of a eutectic mixture with additives (353°C melting point and 251.5 kJ/kg latent heat of fusion). This design included both an insulation jacket and ceramic pipe fittings to reduce heat losses to the surroundings. The results with this experimentally tested system showed that after engine shut-off, the catalyst temperature remained above the highest (for HC) light-off temperature for about 4 h. These results demonstrate that this method might be effective in reducing pollutant gases from vehicles in large cities, where the average number of restarting per vehicle per day is high.

Korin et al. (1999) have observed that the conversion efficiency of catalytic converters decline very steeply at low temperatures. At cold start and warming period the converter efficiency is very close to zero. In their work an investigation was made based on the exploitation of thermal capacitance to keep the catalyst temperature high during off-operation periods. A phase-change material (PCM) with a transition temperature of 352.7 °C, which is slightly above the light-off temperature of the metallic catalyst, was specially formulated, and a system comprising a catalytic converter embedded in the PCM was designed and tested. Under normal engine operating conditions, some of the thermal energy of the exhaust gases was stored in the PCM. During the time that the vehicle was not in use, the PCM underwent partial solidification, and the latent heat thus produced was exploited to maintain the catalyst temperature within the desired temperature range for maximum conversion efficiency.
Gumus (2009) had developed experimental setup of thermal energy storage device (TESD) with a capacity of 2000 KJ, which was used for pre heating of the catalyst to reduce the cold start emission from SI engine. The phase change material Na$_2$SO$_4$, 10H$_2$O was used as storage material. Thermal energy storage device works on the principle of absorption and rejection of heat during solid-liquid phase change of phase change material. The TESD was applied to a gasoline engine at 2°C temperature and one atmosphere pressure. The temperature of the engine was increased to 17.4°C by pre heating of the engine for a period of 500s. He reported that during the charging period the TESD was 2277 kJ and the maximum efficiency of the TESD was 57.5% after 12 hour waiting duration. Further reported that the emission of preheating engine was less than normal engine in the first 200s which is warming up period of catalytic converter. The CO and HC emission were decreased about 64% and 15% respectively with the effect of preheat of the engine. He concluded that TESD storage is a proper device to reduce cold start emission with preheating of the engine.

### 2.9 ENGINE MODIFICATION

Shayler et al. (1994) optimized engine specification to improve cold start performance. Taguchi methods were used to define a test program to assess the effect of seven build factors. Experiments were conducted to measure mixture ratio at the spark plug location after a short period of engine cranking at test conditions covering +15°C and three fuel-mass- supplied values. The analysis of the results identified build modifications which improved start quality and reduced HC and CO emissions substantially compared to a reference, base-line build. Injector design, location, and inlet valve timing were found to have most influence on robustness to uncontrolled variations in mixture preparation during starts.

Callaghan et al. (1999) at Compact Membrane Systems, Inc. have proven the benefit of using the engine's natural vacuum to drive a membrane module to supply Oxygen Enriched Air (OEA) during initial start up. The benefit of the OEA has shown to decrease emissions of carbon monoxide (CO) and hydrocarbons (HC). In addition, OEA helps to maintain the combustion flame stability when the engine
is operated in a lean mode or at a low engine speed. There is evidence that OEA may also account for to a shorter warm up time for the catalyst. A 3 inch diameter by 9 inch long module, (7.5 cm dia. × 23 cm) with a small regenerative blower, was installed to an accessory port on the intake manifold of a truck engine. A 30 second idle period was run on the engine and exhaust emissions were recorded.

Choiet al. (2000) observed the mass of THC is reduced almost 40 percent with spark timing ATDC 7.8CA during 15 seconds from engine start in phase 1 LA4 mode, comparison with TDC 2.8CA.. One of the reasons of HC reduction in vehicle test is reduction of raw THC concentration before CCC (Closed Coupled Catalyst) which is 36% lower level. The other reason is that the LOT (Light-off Time) of catalyst is shortened from 34 seconds to below 20 seconds. As the spark timing is retarded with same intake air quantity and same RPM, BMEP is reduced. Therefore in order to operate in an idle RPM in vehicle, the mass of intake air should be increased. So a catalyst is heated in shorter period. In order to find out the reason of THC reduction with spark timing, the concentration is measured at an exhaust port and manifold in single cylinder engine at the condition of AFR 15.0

Yooetal. (2000) described one of the possible approaches for reducing the cold-start hydrocarbon emissions by using a fast “light-off” planar oxygen sensor. The goal of this study was to verify the operation characteristics of Delphi’s fast “light-off” planar oxygen sensor's (INTELLEK OSP) operating characteristics and the closed-loop performance for achieving improved hydrocarbon control for stringent emission standards. Tests were conducted in open-loop and closed-loop mode under steady and transient conditions using a 1996 model year 2.4-liter DOHC in-line 4-cylinder engine with a close-coupled catalytic converter. Overall performance of the OSP showed relatively quick reaction time to reach the operating temperature. During the first 30 second cold-start period of the FTP 75 cycle, the closed-loop control and A/F ratio were adjusted as lean as possible up to the stoichiometric A/F ratio without impacting drive-ability. Engine out hydrocarbon emissions, for the first cold cycle, were reduced by 8.1% using the OSP and a shorter open-loop time. The operating characteristics of the OSP during a cold-start
made it possible to achieve closed-loop control in less than ten seconds. Early closed-loop control can contribute directly to reducing hydrocarbon emissions.

Watanabe et al. (2006) presented an efficient emission control system which was designed based on combination of advanced engine control system and catalyst technology. The system has successfully achieved the stringent US ULEV2 emission regulations and the vehicle installed with this system has been commercialized. It was observed that advanced fuel control system was able to facilitate faster light-off of the catalyst so that the cold start emission could be minimized. The engine A/F control was so precise that the catalyst can use the material which is most effective at the stoichiometric point. The catalyst material was also optimized for improved response, so that the engine control system could maximize its benefits under warmed-up condition. In addition, sulphur resistance and phosphorous poisoning issues were also addressed. As the final catalyst system, the PGM usage was reduced to a much lower level than that of the previous generation.

Sales et al. (2010) described an updated cold start system for ethanol fuelled engines using an electronic gasoline injector. The new system was a substitute to the conventional cold start system that employs a calibrated hole for gasoline introduction in the intake pipe. The new system was constituted by a gasoline reservoir, electrical fuel pump, fuel injector, fuel filter, and solenoid valve frequency controller. Experiments have been carried out in a production 1.0-liter, four-cylinder, ethanol-fuelled engine, submitted to transient emissions tests after cold start. The results showed that the updated system reduces the cold start period by 31% in comparison to the conventional system. Acceleration after cold start was also improved, with gasoline consumption reduction of 67%. Submitting a vehicle powered by the engine equipped with the new cold start system to the cold phase of the US FTP-75 emissions test cycle (first 505 s) in order to evaluate emissions before the catalytic converter, total hydrocarbons and carbon monoxide emissions were reduced by 8.6 and 17.2%, respectively.
Fan et al. (2012) investigated the effect of injection strategy (the 1st injection timing, 2nd injection timing, 1st and 2nd fuel injection proportion and ignition timing) on the cold start HC emissions in the initial 10 cycles in a two-stage direct injection (TSDI) gasoline engine. The transient HC and NO\textsubscript{x} emissions in the initial 10 cycles were analyzed. The transient misfiring HC emissions were compared between the single and two-stage injection modes. In addition, the unburned HC (UBHC) emissions in the 1st cycle are compared among the TSDI engine, Gasoline direct injection (GDI) engine, Port fuel injection (PFI) engine and Liquefied petroleum gaseous (LPG) engine at the stoichiometric ratio. Finally, the characteristics of the transient speed were presented in various boundary conditions.

2.10 FUEL MODIFICATION

Green et al. (2000) presented experimental results from a microplasmatron fuel converter which can be used for onboard generation of hydrogen-rich gas by partial oxidation of a wide range of fuels operating under variable oxygen to carbon ratios. With hydrogen supplement to the main fuel, SI engines can run very lean resulting in a large reduction in nitrogen oxides (NO\textsubscript{x}) emissions relative to stoichiometric combustion without a catalytic converter. Tests were also carried out to evaluate the effect of the addition of a micro-plasmatron fuel converter generated gas in a 1995, 2.3-L four-cylinder SI production engine with and without hydrogen-rich gas produced by the plasma boosted fuel converter with gasoline. They also observed that onboard plasma-boosted generation of hydrogen-rich gas is used only when required and can be readily turned on and off. Substantial NO\textsubscript{x} reduction should also be obtainable by heavy exhaust gas recirculation (EGR) facilitated by use of hydrogen-rich gas with stoichiometric operation.

Iodice et al. (2013) investigated the effect of ethanol-gasoline mixtures on cold emission behavior of commercial motorcycles. Ethanol is known as potential alcohol alternative fuel for spark ignition engines, which can be blended with gasoline to increase oxygen content and then to decrease emissions. They conducted a research on cold start emissions of motorcycles using ethanol-gasoline mixtures. In this specific study, a motorcycle (belonging to the Euro-3 legislative
category) was operated on a chassis dynamometer and driven according to the ECE driving cycle to analyze the exhaust cold extra emissions of CO and HC, while the ethanol was mixed with unleaded gasoline in three different percentages (10, 20 and 30 % v/v). The results of the tests indicated that CO and HC cold start extra emissions using ethanol-gasoline blended fuels decrease compared to the use of unleaded gasoline.

2.11 URBAN DRIVING CYCLE TESTING

Marsh et al. (2000) conducted test on a five cylinder engine with three fundamentally different systems, each with very high efficiency in reducing cold start hydrocarbons. Vehicle test results were presented to illustrate the potential of the respective systems towards the SULEV requirements. Durability aspects were also considered since an increased durability of 120,000 and even 150,000 miles is imposed by the legislation.

Andrews et al. (2005) in their paper studied the influence of ambient temperature on exhaust emissions for an instrumented Euro 1 SI car for urban congested traffic conditions. In-vehicle emission samples were taken directly from the exhaust, upstream and downstream of the catalyst, using the bag sampling technique. The first bag was for the cold-start emissions and approximately the first 1.1 km of travel. The following three bags were with a hotter catalyst. The cold start tests were conducted over a year, with ambient temperatures ranging from 2°C to 30°C. The results showed that CO emissions for the cold start were reduced by 70% downstream of the catalyst when the ambient temperature rose from 2°C to 30°C. The corresponding hydrocarbon emissions were reduced by 41% and NOx emissions were increased by 90%. The influence of ambient temperature was less when the catalyst was fully warmed up. The results showed that ambient temperature had a greater influence on cold-start emission under traffic jam conditions than in previous work with real-world driving closer to the ECE passenger car drive cycle.

Li et al. (2008a) in their test measured regulated and non-regulated tailpipe exhaust emissions under real world urban driving conditions using a set of
in-vehicle FTIR emission measurement system, which is able to measure 65 emission components simultaneously at a rate of 0.5 Hz. A EURO3 emission compliant SI car was used as a probe vehicle. An urban driving cycle was used for the test and four repeated journeys were conducted. The results were compared to EU emissions legislation. The results showed that the TWC needed approximately 200 seconds to reach full conversion efficiency. THC and NOx emissions exceeded the EURO 3 exhaust emission legislation. CO2 emissions were well above the type approval value of this type of the vehicle. Greenhouse gases (methane and nitrous oxide) and toxic hydrocarbons such as benzene were predominantly emitted during cold start period from 0 to 200 seconds of the engine start. The results had a reasonable repeatability for most of the emissions.

Liet al. (2008b) used Fourier transform infra red (FTIR) exhaust emission measurement system on Euro 1,2,3 and 4 SI engine passenger cars. A typical urban driving cycle was completed and emission values were calculated for the whole journey and compared with EU legislation. The cold start transient emission were also investigated and observed wide difference in emission values among these vehicles

Li et al.(2008c)developed five different driving cycles based on real world urban driving conditions including urban free flow driving, junction maneuver, congested traffic and moderate speed cruising. The test vehicle was a EURO 2 emission compliant SI car equipped with temperature measurement along the exhaust pipe across the catalyst and real time fuel consumption measurement system. Both regulated and non-regulated emissions were measured and analyzed for different driving cycles. All journeys were started from cold. The engine warm up features and emissions as a function of engine warm up for different driving conditions were investigated.

Bielaczyc et al. (2012) in their paper examines emissions at low ambient temperatures with a special focus on cold start; emissions are also compared to start-up at a higher ambient temperature (24°C). The causes of excess emissions and fuel consumption are briefly discussed. A series of tests were performed on European
passenger cars on a chassis dynamometer within an advanced climate-controlled test laboratory at BOSMAL Automotive Research and Development Institute, Poland. Emissions data obtained over the Urban Driving Cycle by testing at 24°C and at -7°C, are presented for a selection of modern Euro 5 gasoline vehicles representative of the European passenger car fleet. A full modal emissions analysis was also conducted at 24°C and at -7°C over the New European Driving Cycle. Emissions and fuel consumption were substantially higher at -7°C than at 24°C.

Woodburn et al. (2013) presents a brief literature review, and presents experimental data on ammonia emissions from seven Euro 5 passenger cars, using different gasoline fuels and a CNG fuel. All vehicles were tested on a chassis dynamometer over the New European Driving Cycle. For six of the vehicles, ammonia was quantified directly at tailpipe (using two different analyzers); emissions from one vehicle were subjected to Fourier Transform Infra-Red (FTIR) analysis. Emissions of ammonia from these vehicles were generally low in comparison to other chassis dynamometer studies, perhaps attributable to the favorable laboratory test conditions and the age of the vehicles. Transient data revealed small but significant differences in ammonia emissions, including the time of the initial ammonia surge, depending on the test fuel and the fuel injection strategy.

Bielaczyc et al. (2013) in their paper compares excess emissions of gaseous and solid pollutants following cold start at a low ambient temperature and the standard test temperature. Euro 5 passenger cars were tested on a chassis dynamometer within BOSMAL's climate-controlled test chamber, according to European Union legislation (−7°C over the urban driving cycle (UDC), and at 25°C). Two vehicles were also tested over the entire New European Driving Cycle (NEDC). Emissions of regulated compounds and carbon dioxide were analyzed; particulate emissions (both mass and number) were also measured, all using standard procedures. Over the UDC, changes in emissions of hydrocarbons (HC), carbon monoxide (CO), and Carbon di oxide(CO$_2$) were unequivocal; the situation for oxides of nitrogen (NOx) was somewhat more complex.
2.12 COMPUTATIONAL EMISSION ANALYSIS

Shen et al. (1999) describe a mathematical model that simulates transient performances of catalytic converters. The model considers the effect of heat transfer and catalyst chemical reactions as exhaust gases flow through the catalyst. The heat transfer model includes the heat loss by conduction and convection. A 13-step reaction mechanism is used to simulate the chemical kinetics, and a 9-step reaction scheme is used to simulate oxygen storage mechanism, which allows adsorption/desorption of oxygen in the catalyst during the flow of non-stoichiometric air-fuel mixtures.

McNicol et al. (2004) optimized the cold start emission by bringing a conducive trade-off between the amount of thermal energy delivered to the catalyst and the amount of exhaust emissions produced during the time before the catalyst is light-off. The authors examined whether an automated expert-knowledge based decision-making methodology can be used to find a satisfactory trade-off between these two parameters whilst reducing the iteration time and level of input required from a calibration engineer.

Shamim (2006) presented a computational investigation of the effect of engine exhaust gas modulations on the performance of an automotive catalytic converter during cold starts. The objective of investigation was to assess if the modulations could result in faster catalyst light-off conditions. The study employed a single-channel based, one-dimensional, non-adiabatic model. The modulations were generated by forcing the variations in exhaust gases air-fuel ratio and gas compositions. The results showed that the imposed modulations caused a significant departure in the catalyst behavior from its steady behavior, and modulations have both favorable and harmful effects on pollutant conversion during the cold-starts. The operating conditions and the modulating gas composition have substantial influence on catalyst behavior.

Davis and Peckham (2008) conducted a short study to measure both AFR and residual gas fraction on a cycle-by-cycle basis for a gasoline engine
during cold start and during a throttle transient. In-cylinder and exhaust port measurements were recorded using a fast response NDIR instrument to provide some insight into the dynamic processes involved during these important transient engine conditions. The CO&CO₂ results are presented showing evidence of the large cyclic variability of fuel delivery during the first few firing cycles of the start. Misfires are also identified. A description of a post-processing tool is discussed for conversion of this data to AFR. It is hoped that this measurement method will be valuable to engine researchers and calibrators as a tool for understanding and lowering cold start and throttle transient HC and CO emissions as well as validating internal EGR models.

Andrianov et al. (2012) presented a methodology that integrates appropriate physics-based models of the engine and after treatment into a numerical optimization scheme, and is proposed as a possible means of reducing this calibration effort. The methodology is demonstrated over a prescribed drive cycle by identifying the optimal spark timing trajectory that maximizes fuel economy while meeting emissions constraints. The trends in the resulting control policy are explained and the results are validated.