Thermal Management of Catalytic Converter to Reduce Cold Start Emissions from I.C Engine

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"I dedicate my dissertation work to my family and teachers. A special feeling of gratitude to my loving parents whose words of encouragement and push for tenacity ring in my ears"

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TABLE OF CONTENTS

ACKNOWLEDGEMENTS iv
TABLE OF CONTENTS v
LIST OF FIGURES vii
LIST OF TABLES viii
LIST OF ABRIVATIONS ix
ABSTRACT 1
1 Chapter 1 2
INTRODUCTION 2
  1.1 General 2
  1.2 Problems Identification 5
    1.2.1 Cold start Emissions (CSEs) 5
    1.2.2 Global warming and Climate Change due to Transportation 5
  1.3 Objectives of the Study 6
  1.4 Exhaust pollutants 6
  1.5 History of Air Pollution 7
  1.6 Introduction to Catalytic Converters 9
2 Chapter 2 11
LITERATURE REVIEW 11
  2.1 Three-way catalyst 11
    2.1.1 Components of Catalytic Converter 12
  2.2 Characteristics of Catalytic Converters 13
    2.2.1 Conversion 13
    2.2.2 Light-off temperature 13
    2.2.3 Oxygen Storage Capacity 14
  2.3 Material Concerns in Catalytic Converters 15
    2.3.1 Catalyst Bed Deactivation 15
    2.3.2 Thermal Deactivation 16
    2.3.3 Fouling 16
    2.3.1 Crushing 17
    2.3.2 Poisoning 17
  2.4 Limitations and Disadvantages of Catalytic Converters 19

    - 2.4.1 Light-Off Period and Cold-Start Emissions 19
    - 2.4.2 High Costs and Environmental Impacts of Catalysts 21
  - 2.5 Solution of Cold Start Emissions 23
    - 2.5.1 Shortening the Light-Off Period 23
    - 2.5.2 Variable Conductance Insulation 24
    - 2.5.3 Phase Change Material 27
    - 2.5.4 Electrical Heating of Catalyst 28
- 3 Chapter 3 30

MATERIALS AND METHODS 30
  - 3.1 Catalyst-PCM Configuration 30
  - 3.2 Phase change material and Insulation 31
  - 3.3 Preparation of Wire meshes 32
  - 3.4 PCM case and Thermocouples 33
  - 3.5 Experimental Setup for Thermal Management System 33
- 4 Chapter 4 36

RESULTS AND DISCUSSION 36
  - 4.1 Testing of thermal management system 36
    - 4.1.1 Engine operation without insulation and PCM 36
    - 4.1.2 Engine operation with only insulation (only insulation) 38
    - 4.1.3 Engine operation with PCM and insulation (PCM +Insulation) 39
  - 4.2 Comparison of Heat Retention after 2.5 Hour 41
  - 4.3 Electrical Heating by glow plugs 41
- 5 Chapter 5 43

CONCLUSIONS AND RECOMMENDATIONS 43
  - 5.1 Conclusions 43
  - 5.2 Recommendations 43

REFERENCES 45

LIST OF FIGURES

Figure 1: Conversion of HC, CO, NO with A/F (A. Fathali, 2014) 12
Figure 2: Fouling of a CC (Eastern Catalytic, 2013)...17
Figure 3: A Corroded CC (Eastern Catalytic, 2013) 18
Figure 4: CSEs during an FTP-75 cycle (Kašpar et al., 2003) 21
Figure 5: VCI in a TWC (IneffableIsland, 2013) 26
Figure 6: PCM location in a TWC (Korin et al., 1999)..28
Figure 7: Possible Catalyst and PCM configurations 30
Figure 8: Wire mesh cutting stage by stage...32
Figure 9: Phase Change Materiel case (SS302)..33
Figure 10: Schematic diagram of experimental setup 34
Figure 11: Catalytic converter assembly with PCM..35
Figure 12: Catalytic converter assembly with glow plugs..35
Figure 13: Heating of catalyst in case 1..37
Figure 14: Cooling of catalyst in case 1 37
Figure 15: Cooling curve for case 2 where only insulation is used. 38
Figure 16: Cooling curve when PCM and Insulation both were used.............................39
Figure 17: Temerature vs removal effeciency 40
Figure 18: Heat retain profile by all variation after an hour..41
Figure 19: Profiles for electrical heating of catlyst..42

LIST OF TABLES

Table 1: Current Prices of Precious Metals on a 1 lb. (0.45 kg) basis 21
Table 2: Cost Breakdown of a Typical TWC..22
Table 3: Thermal Conductivities of some Gases 25
Table 4: Reduced Emissions by TWC with and without VCI 26
Table 5: Phase Change Materials and their thermal characteristics.................................31

LIST OF ABRIVATIONS

PCM	**Phase Change Material**
CSEs	**Cold start emissions**
NMHC	**Non methane Hydrocarbons**
EFI	**Electronic fuel injection**
LPG	**Liquefied petroleum gas**
NaOH	**Sodium hydroxide**
$NaNO_2$	**Sodium Nitrite**
ICE	**Internal combustion engine**
A/F	**Air to fuel ratio**
CC	**Catalytic converter**
TWC	**Three way catalytic converter**
CO	**Carbon monoxide**
HCs	**Hydrocarbons**
NO_x	**Oxides of nitrogen**
SO_x	**Oxides of sulfur**
CO_2	**Carbon dioxide**
CH_4	**Methane**
CNG	**Compressed natural gas**
GHG	**Greenhouse gases**
O_3	**Ozone**
EPA	**Environmental Protection Agency**

ABSTRACT

In optimum working conditions catalytic converters are the most effective and reliable source for reducing pollution caused by vehicles. But unfortunately their conversion efficiency decreases rapidly below certain temperature and is almost zero during the startup and warming periods. In cities where the soak time for different vehicles is low, there is need to improve the conversion efficiency of the catalyst to minimize the cold start emissions from engine. For this purpose, different methods have been used such as installation of adsorbing unit between two working catalysts, use of electrically heated catalyst and heating of the catalyst in the additionally mounted combustion chamber. These methods are quite effective to reduce cold start up emissions but have some disadvantages like extra energy is required to operate these techniques and as additionally system for these methods are used so they become very bulky. In present study heat storage capacity of the phase change material is used to keep the catalyst heated during the soak period. A phase change material (PCM), having melting point of 237ºC nearly close to light off temperature of catalyst along with insulation, is used and catalyst embedded in this PCM is tested. During operation PCM is melted and energy of gases is stowed in melted PCM. When engine was switched off PCM solidified and latent heat stored in PCM released keeping catalyst at optimal temperature to get maximum conversion efficiency for next trip.

Chapter 1

INTRODUCTION

1.1 General

Air pollution control is getting the worldwide interest as it is strongly related to environment and human life as well. Anything present in the air that has detrimental consequences on the living specie as well as on environment and is responsible of air pollution is termed as air pollutant. The sources of atmospheric pollution include, on and off-road automobiles, power generating plants, and other anthropogenic activities that include the usage of fossil, gasses emitted from air conditioners and from other cooling and heating activities on work place. The pollutants generated from a single automobile are relatively less as compared to lot of other natural and anthropogenic sources however pollutants generated by millions of automobiles sum up making automobiles sector a major contributor of air pollution (EPA).

Emissions from the automotive industry have a direct negative impact on both the environment and our health. These emissions mainly consist of nitrous oxides (NOx), which contributes to acidification of lakes, carbon monoxide (CO) and hydrocarbons (HC), which can be extremely poisonous, and carbon dioxide (CO2) which is a greenhouse gas. It is therefore of great importance to reduce the amount of these substances in the exhaust gases. The emissions of the nitrous oxides, carbon monoxides and hydrocarbons are today reduced by the help of different catalytic systems, but it is unfortunately not possible to decrease the emissions of carbon dioxide. However, if alternative fuels are used it would result in a decrease of the net CO2 formed. The most commonly used system for petrol engines is a so called three-way catalyst (TWC), while a lean NOx trap (LNT) is more common for diesel engines. Both of these techniques are very effective at decreasing the emissions of hazardous gases.

Automobiles are prevailed thorough out the world and are considered main source of pollutants like hydrocarbons (HC), carbon monoxide (CO) and different oxides of nitrogen (NOx) (Kaspar *et al., 2009)*. The production of oxides of nitrogen and carbon monoxide by automobiles in 2008 was 10,037,168 short tons and 59,383,083 short tons respectively (EPA 2009). About 60% to 80% of all CO and HCs (NMHC) emissions take place in first few minutes of operation when converter is warming up (Laing, 1998).

These pollutants have adverse effects on humans, animals and environment. NOx are responsible for respiratory diseases, acid rain, global warming and visibility impairment. Photochemical smog species such as Ozone is caused by HC and CO is poisonous to breathing humans and animals (William *et al., 2000)*

As safety of environment is imperative therefore reduction of these pollutants from the exhaust gases is vital and biggest challenge throughout the world especially in cities where number of automobiles and as well as engine startups per day is very high. Catalytic converter has become most effective source of reducing pollutants originated from automobiles exhaust (Korin *et al.*, 1999).

First catalytic converters were made to purify the emissions from factory machines and were not applied to the automobiles due to the presence of lead in the gasoline/fuel because lead can damage the catalyst and reduced its effectiveness. After lead was reclaimed illegal in gasoline/fuel, the Engelhard Corporation made first catalytic converter.

Latest converters are able to reduce more than 97% HC and CO emissions but unfortunately their efficiency decreases below 250ºC for CO and 250ºC -340 ºC for HC emissions. Automobiles manufacturers specify that more than 60% HC emissions occurs when catalyst is at temperature below its "light off temperature". Emissions that occurs when catalyst is not active are called cold start emissions (Burch *et al.*, 1997).

Different methods were used to eliminate/reduce cold startup emissions from automobiles such as electrical heating of catalyst (Laing, 1998), use of external combustion chamber (Kollman *et al.*, 1998) placement of the absorber between two catalysts (Noda *et al.*, 1998) and onboard fuel reformer (Isherwood *et al.*, 1998) These methods were bulky and costly because the required external energy source to operate.

Alternate panacea to this Specific menace is application of PCM and proper insulation into three-way catalytic converter (TWC). PCM uses heat of fusion to store large amount energy depending upon amount of PCM used. PCM utilizes extra heat of exhaust gases and does not require an extra energy source to work. Energy storage density of the phase change material (PCM) is high and heat can be back to the system at almost constant temperature (Korin *et al.*, 1999).

In present work about 1 kg eutectic mixture of sodium hydroxide and sodium nitrite (73%NaOH + 27%$NaNO_2$), having phase transition temperature of 237ºC along with thermal insulation jacket of glass wool, is used as a phase change material. The heat of exhaust gases of engine is used to melt the PCM and energy of gases is stowed in PCM. When engine is switched off and as temperature of surroundings is decreased PCM solidified and energy was released from PCM that maintained temperature of catalyst for sock period. When engine started again after that sock time catalyst did not require any time to become active and cold start emissions were relatively reduced.

Electrical heating of catalyst is also carried out to get the catalyst light off temperature as soon as possible. Glow plugs were used as small electric heater that were operated by 12 volt battery.

1.2 Problems Identification

1.2.1 Cold start Emissions (CSEs)

At low temperatures, a catalytic converter is unable to treat pollutant-laden emissions stream passing through it. The conventional noble based catalyst bed requires a temperature of 300^{o}C to be effective (Degobert, 1995). When a vehicular engine is started, the engine walls manifold as well as the catalyst are at atmospheric temperatures. As the engine operates further, hot gases heat up and exhaust gases emitted from the engine start warming up catalyst gradually. The time required by a catalyst to get optimal conversion for specific pollutant is known as “Light-Off” period of that catalyst for that specific pollutant. Due to incapability of the catalyst to treat the CSEs during light-off period, the emissions that occur in this period are relatively higher (Amin et al., 2011). About 70% of the total unburned hydrocarbons (UHC) and CO emissions occur during the light-off period of the FTP-75* cycle (Burch et al., 1996). These emissions are known as Cold-Start Emissions.

1.2.2 Global warming and Climate Change due to Transportation

The disastrous storms, floods, dearth, frozen and snow are out of control today. The occurrence of these weather conditions are not simple response to the reality that the influence of universal warming is the reason. Ozone depletion layer which prevents ultra violet heat from the sun to earth. Information showed that the greenhouse gasses, (GHG) which is identified to reduce the ozone layer are contributed by the road pollution which has not better post combustion technology (Peter et al., 2010). Hence a knowledge of new fuel energy resources, catalysis and post combustion technology for automobiles are necessary to understand.

1.3 Objectives of the Study

- To explore usability potential of PCM for cold start emission reduction for non-noble metal catalyst
- To use Heating elements to achieve light off temperature after cold engine startup as soon as possible

1.4 Exhaust pollutants

Gases produced in gasoline engine comprises of harmful pollutants that are responsible for air pollution. These pollutants are generated from the combustion chamber where incomplete burning of fuel. The main pollutants in the tail emissions are carbon monoxide, nitrogen oxides (NOx), and unburned or partially burned hydrocarbons (HCs) especially nitric oxide. Other than these pollutants, it comprises of nitrogen, oxygen, hydrogen, water gas and CO_2 as end products and SO_2 is produced from the Sulphur (S) in the fuel (Kaspar et al., 2003a; Ulla, 2003). As the air pollution has got worldwide attention, limits of these fatal pollutants has become more stringent by environmental legislations (Fornasiero et al., 2008). Nowadays Three-way catalytic converter (TWC) are provided in the automobiles exhaust stream to convert the harmful pollutants into benign gases. TWC are capable off converting deleterious NOx, HCs and CO efficiently and simultaneously into less harmful CO2, H_2O and N2 (Ulla, 2003).

1.5 History of Air Pollution

It could be said that environmental pollution and industrial development are mutually inclusive events. Every element of a developing city or nation contributes to environmental pollution in one way or the other. The broadest classification of environmental pollution could be on the basis of the three basic elements that support life on Earth: air, water and land.

The history of air pollution, its awareness among people and methods of controlling it could be traced back hundreds of years ago. Roman philosopher Seneca first made an observation about the highly polluted air of Rome, when he said, “As soon as I had gotten out of the heavy air of Rome, I felt an alteration to my disposition” (Miller et al., 1989). King Edward I of England took a strong stand against the coal, by announcing a beheading punishment for all those who burned coal (Franek et al., 2003).

However, as the world reached the cusp of industrial revolution in the 18th Century, the fouling of the environment with pollutants became a very common unwanted yet inevitable side effect. Large quantities of smoke emitted from the many industries where coal was being burnt to produce energy. Air pollution had already reached quite a high level and this was still the time when automobile industry had not emerged yet. In the 20th century, the use of automobiles increased and along with it, there occurred a rise in air pollution (Franek et al., 2003). Moreover, the constantly increasing population of the world created larger demand for energy, larger demand for resources and larger demand for facilities. In order to meet this demand, more fossil fuel was burnt and obviously, air quality worsened drastically (Franek et al., 2003).

Fortunately, the public awareness about air pollution, its sources and its effects also started increasing. This popular opinion, in conjunction with the obviously high levels of air pollution, finally forced the United States Government to start taking measures to improve air quality. The very first air pollution regulations were enacted by California State in 1947 (Franek et al., 2003). This first step towards air quality improvement was followed by a series of steps taken all over the country for achieving the common goal.

Several regulatory acts were passed over the following years (Wark et al., 1998):

- Air Pollution Control Act, 1955
- Clean Air Act (CAA), 1963
- Motor Vehicle Air Pollution Control Act, 1965
- Air Quality Act, 1967
- Clean Air Act Amendments, 1970, 1977, 1990.

Under the Clean Air Act Amendments of 1970, the newly formed United States Environmental Protection Agency (USEPA) was assigned authority for establishing National Ambient Air Quality Standards (NAAQS). Consequently, each state was required to submit a State Implementation Plan (SIPs), declaring the measures that would be taken by the State to meet air quality standards set by the NAAQS. Moreover, under the amendments made to CAA, National Emission Standards for Hazardous Air Pollutants (NESHAPs) were enacted in order to control hazardous air pollutants emissions. A third major development was the establishment of New Source Performance Standards (NSPS), which were focused on specific categories of industries and the pollutants emitted by them.

There were amendments made to the CAA again in 1977 and in 1990. In the latter, the Act was made much more stringent owing to the fact that the improvement to air quality after the 1977 amendments was very small *(Wark et al., 1998).* The amendments considered acid rain, ozone depletion, carbon monoxide and particulate matter. 189 hazardous air pollutants were defined. *(Wark et al., 1998).*

1.6 Introduction to Catalytic Converters

Gasoline combustion in the internal combustion engines of automobiles mainly contributes to the presence of NO_2, CO and UHCs, as can be inferred from previous sections. As mentioned in Section 2.1, O_3 emission is also an indirect result of gasoline combustion, since O_3 is formed due to the photochemical reactions occurring between NO_x and UHCs. Several methods have been devised till date to control these harmful emissions from vehicles. One such technique is the use of Exhaust Gas Recirculation; as the name of the process suggests, the exhaust gases are recirculated back into the intake system of the engine. This stream of recirculated exhaust acts as a “diluent” with the combustion mixture in the engine, thereby making it a lean mixture (and from previous section, we know that when the air-fuel mixture is lean, NO_x formation is marginally reduced). The exhaust stream being relatively cooler and of higher specific heat capacity, absorbs some of the heat generated and thus the formation of NO at high temperature is averted (Agrawal et al., 2003). Some other techniques that were developed over time to control gasoline emissions were better design of engine cylinder, control of spark and valve timing, improved carburetion (optimized airto-fuel ratio), fuel injection timing and metering, Positive Crankcase Ventilation (PCV) valve for controlling crankcase emissions and evaporative emissions control. However, these changes could only reduce emissions by a small margin

(Wark et al. 1998). Stringent air emissions standards set by the USEPA had to be met. Thus, the concept of post-combustion treatment of exhaust gases was developed. “The goal of after-treatment technologies is to adjust the chemicals in the exhaust system to a composition as close as possible to a mixture of water vapor and carbon dioxide, sinceCO_2 was considered to be a non-pollutant before the emergence of the greenhouse effect” (Degobert, 1995). The use of catalytic mechanisms is done for treating the exhaust gases before emitting them into the atmosphere.

Chapter 2

LITERATURE REVIEW

2.1 Three-way catalyst

The most common way to decrease the emissions from petrol cars today is to use a so called three-way catalyst, TWC. These catalysts are often in the form of monoliths with around 300-900 cpsi (channels per square inch). The monolith structure often consists of the ceramic material cordierite (2 Al2O3 · 5 SiO2 · 2 MgO) but can also be made up of corrugated metal (A. Holmgren, 1998). The active sites, often consisting of highly dispersed precious metals such as Pt, Pd and Rh (H. Gandhi, 2003; H. Muraki., et al 2000), are distributed on the channel walls in the wash coat. The wash coat also contains Ce for oxygen storage capacities and other substances such as Zr, Al and Ba to increase the activity as well as the resistance to ageing (A. Fathali, 2010). The three-way catalyst is able to simultaneously reduce the emissions of CO, HC (collective name for all hydrocarbons) and NOx, which is from where it got its name. The overall reactions happening in the catalyst are shown in table 1 (I. Chorkendorff., et al 2007). This is done most effectively at a stoichiometric air-fuel ratio of 14.7:1, also referred to as $\lambda = 1$, which is when the exact amount of air needed to completely oxidize the fuel, is supplied. The dependence of conversion of CO, HC and NOx with respect to air feul ratio is shown in figure 1, together with operating region of where the catalyst has high conversion of all three species, called lambda or TWC-window.

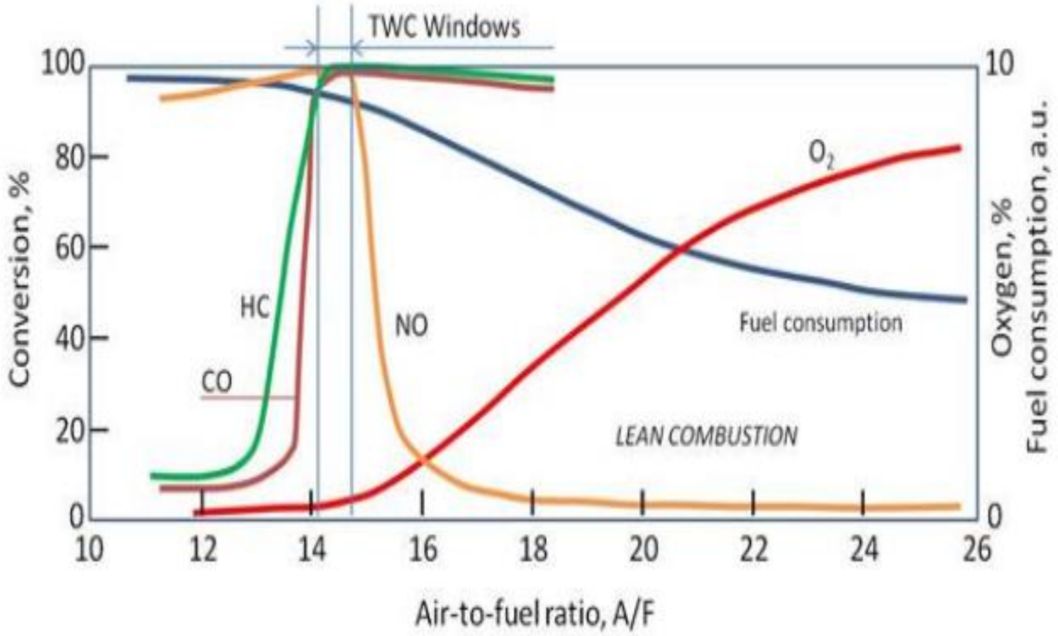

Figure 1: Conversion of HC, CO, NO with A/F (A. Fathali, 2014)

A mixture with an air-fuel ratio smaller than 14.7:1 is called rich, which means that there is a deficit of oxygen in the exhaust gases. The lower oxygen concentration results in a lower conversion of CO and HC, but the reductive environment is advantageous for the conversion of NOx. Conversely, a mixture with an air-fuel ratio above 14.7:1, called lean, results in an oxygen access which increases the conversion of CO and HC but decreases the conversion of NOx.

2.1.1 Components of Catalytic Converter

The main components of TWC include substrate that is made of ceramic or metal, wash coat that is use to increase the surface area for catalyst impregnation and the catalyst that is responsible for reactions. Substrate either ceramic honeycomb or metal has usually less surface area, to increase surface area washcoat is used over substrate over witch catalyst is deposited. Alumina is used as washcoat to increase surface area for catalyst dispersion. Among the alumina alpha alumina has high thermal stability. Stabilizers are used to enhance the surface area stability of washcoat. Oxides of Ce and Zr, barium and lanthanum are used as stabilizers (Kaspar et al., 2003a). Ce and Zr oxides act like promoters. CeO_2 stabilize dispersion of catalyst, enhance thermal characteristic of alumina especial stability against temperature, increase water-gas shift at relatively low temperatures and help in oxygen transfer under different air to fuel ratios (Kaspar et al., 2003a; Yao et al., 1997). To enhance the thermal stability, oxygen storage capacity and to lower the light off temperature of catalyst zirconium oxide is used along with cerium oxide (Yingying et al., 2007)

2.2 Characteristics of Catalytic Converters

Automotive catalysts are characterized through many different measurable characteristics and the most frequently used are presented in brief below.

2.2.1 Conversion

One of the most important variable to measure is the conversion of CO, HC and NOx over the catalyst. Since it is the catalysts main purpose to decrease the emissions, it is crucial to measure and verify that the conversion is high enough to be able to decrease the emissions below the threshold. This can for example be measured from a real car, in a motor-rig or in a flow reactor.

2.2.2 Light-off temperature

A drawback with today’s catalysts is that they require a high temperature to function properly. This is not a problem at normal driving conditions but becomes problematic when the car starts with a cold catalyst. This results in a so called cold start, meaning that the temperature of the catalyst is much lower than what is needed for the reactions to take place, resulting in increased emissions. One way to measure how well the catalyst will be able to handle cold starts is to perform light-off experiments. The light-off curves describes how the conversion depends on the temperature of the catalyst, and can therefore be used to evaluate how well the catalyst performs at lower temperatures. The temperature at which 50 % conversion of specific pollutants is achieved is termed as light off temperature of that pollutant (A. Fathali, 2010). A lower light-off temperature means that the reactions will start earlier after a cold start and lower emissions will be released.

Light-off experiments can also be used to evaluate the kinetics of the catalyst in some extent (F. Duprat, 2002). There have been several proposed solutions to this problem which have included electrical heaters around the catalyst, or re-routing of the exhaust gases to accelerate the heating. Another proposed solution is to use secondary air injections (SAI) which increases the amount of oxygen in gases into the catalyst. This results in an exothermic oxidation of the unburned HC and CO heating the catalyst.

2.2.3 Oxygen Storage Capacity

The oxygen storage capacity (OSC) is a key parameter of TWC that is a measurement of how much oxygen that can be stored in the catalyst material. A TWC system is normally run at an air-fuel ratio of $\lambda \approx 1$, as described above, which means approximately stoichiometric conditions. But because of varying engine loads and vehicle speeds, this ratio can differ from $\lambda = 1$, resulting in increased emissions. A high oxygen storage capacity can help reduce this effect by storing oxygen in lean conditions and releasing oxygen at rich conditions. This helps to oxidizer CO and HC even when there is a deficit of oxygen in the exhaust gases. The OSC of a catalyst can be measured in several ways, where one way is to use CO or H2 pulses (P. Lambrou., et al 2004). This technique will measure the "standard" OSC, that is, it will measure the most loosely bound oxygen. Another kind of oxygen storage capacity, called the oxygen storage capacity complete (OSCC), is a measurement of both the more loosely and strongly bound oxygen (H. Yao., et al 1984). These two differ because of how the oxygen is bound to the catalyst wash coat. The most common materials used in the catalysts to promote the OSC is CeO_2 together with ZrO_2 for thermal stability (M. Ozawa, 1998).

2.3 Material Concerns in Catalytic Converters

The emission of NO_x, UHCs and CO from gasoline combustion engines is catalyzed chemically within the catalytic converter resulting in the formation of harmless N_2, CO_2, O_2 and water vapor. Three simultaneous catalytic reactions occur within the catalytic converter, as described in the previous section. The product gases are safe to inhale and are able to exist neutrally in the environment. Today, the use of catalytic converters is done extensively in vehicles and thus it is important to study the impacts of various automobile engine performance parameters on the efficiency and durability of a catalytic converter.

2.3.1 Catalyst Bed Deactivation

Deactivation is the loss of catalytic efficiency over time. The five major mechanisms which result in de-activation of a catalytic converter bed are:

- Thermal Deactivation
- Fouling
- Crushing
- Poisoning

2.3.2 Thermal Deactivation

The thermal deactivation occurs due to the ‘sintering’ process. Sintering is the loss of active surface area of the adsorbent, i.e. the catalyst. Sintering occurs due to agglomeration of small metal crystallites into larger ones. At high temperatures, extreme sintering leads to the transformation of the catalytic crystalline phase of the metal into a non-catalytic one. This phenomenon is called solidstate transformation (Forzatti et al., 1999).

2.3.3 Fouling

Fouling is the physical deposition of substances from gaseous phase onto the catalytic surface and in catalyst pores. Fouling occurs due to production of unburnt fuel components resulting due to incomplete combustion. Large pressure drop across the catalyst bed is a result of fouling (Bartholomew, 2001). As discussed in an earlier section, the use of TEL was done as a fuel additive in the 1970s. TEL in the gasoline decomposed in the cylinders and formed a mixture of halides and oxides. A part of this mixture was emitted as gases and remaining left as particulate matter ranging in diameter from 0.3 to 10 µm (Wei, 1975). This blocked the pores of the honeycomb structure in the catalytic converter and thus resulted in reduced efficiency (Wei, 1975). As mentioned earlier, the use of TEL as a gasoline additive was significantly reduced by the USEPA in 1976.

An example of fouling in a catalytic converter is shown in Figure 2.

Figure 2: Fouling of a CC (Eastern Catalytic, 2013)

2.3.1 Crushing

Crushing of the catalyst is a mechanical attrition process involving the loss of catalytic material and subsequent loss of internal surface area of a catalyst due to mechanical forces acting upon the catalyst bed. Very high velocity of exhaust gas can also result in erosion of the catalyst bed. (Bartholomew, 2001).

2.3.2 Poisoning

Poisoning of the catalyst if a chemical deactivation mechanism occurring due to strong chemical adsorption of species on catalytic pores. An example of poisoning in a catalyst bed is shown in Figure 3.

Figure 3: A Corroded CC (Eastern Catalytic, 2013)

Phosphorus (P): P could be present in the form of impurities in the fuel and also in engine lubricants. A layer forms on the wash-coat surface, comprising of Zn, Ca and Mg phosphates. Phosphate compounds such as $CePO_4$, $Ce(PO_3)_3$ and $AlPO_4$ may also be formed directly as a product of reaction between phosphorus and the wash-coat material (Christou et al., 2007). An analysis of aged and exhausted TWCs revealed the presence of Fe, Cu, Ni and Cr metal contaminants in the catalyst bed (Christou et al., 2007).

Sulfur (S): SO_2 in the exhaust gas affects the activity of a TWC by causing a reduction in the rate of reduction of NO_x and also the oxidation of UHCs and CO. This occurs due to the dissociation of SO_2 into oxygen and free sulfur; the latter gets strongly adsorbed onto the precious metal sorption site, thus blocking the site from interacting with NO_x, CO and UHCs (Degobert, 1995).

Silicon (Si): While the presence of Si in the fuel is very low, fugitive presences of soluble forms of Si in the fuel could occur, resulting in the formation of Si deposits on the catalyst bed. Moreover, deposits of Si on the exhaust electrode surface of the λ-O_2 sensor results in reduced mass transfer of O_2 to the electrode surface and thus affects the performance of the sensor (Degobert, 1995)

2.4 Limitations and Disadvantages of Catalytic Converters

Catalytic converters are a major means in controlling the emissions of NO_x, UHCs and CO, three harmful products emitted by gasoline combustion engines. Up to 97% reduction in CO and UHC emissions are caused by catalytic converters (Burch *et al*., 1995). However, the use of catalytic converters is not the very ultimate solution to the control of these harmful emissions. There are several limitations and disadvantages of proliferating the use of catalytic converters in automobiles. This section deals with the negative aspects of using catalytic converters.

2.4.1 Light-Off Period and Cold-Start Emissions

During cold engine start up, in order to help proper ignition of fuel and to enhance cold engine operations, air-fuel mixture is deliberately kept multiple times richer than that in warmed-up engine operation, resulting in excessive release of pollutants, also known as cold start emissions (CSEs) (Purtolas et al., 2014). In automobiles a number of sources of unburned HCs have been spotted during cold start and warming up process of cold engines (Boam et al., 1994). On one side, lower engine temperatures and enriched A/F ratio during cold start up, increase formation of HC and CO while on the other side due to low operating temperatures at this particular time, the activity of catalytic converter to oxidize these pollutants is also extremely low (Singer, Kirchstetter, Harley, Kendall, & Hesson, 1999). About 70 to 80% of total HCs emissions take place in first few minutes of engine operation when converter is warming up (Sarshar, Zahedi-Niaki, Huang, Eić, & Kaliaguine, 2009).

Temperature above 150^{o}C is required to start catalytic activity in case of commercially available catalytic converters (Iliyas, Zahedi-Niaki, Eić, & Kaliaguine, 2007). HC and CO are major contributors in CSEs for gasoline engine (Hao et al., 2016).

At low temperatures, a catalytic converter is unable to treat pollutant-laden emissions stream passing through it. The conventional noble based catalyst bed requires a temperature of 300^{o}C to be effective (Degobert, 1995). When a vehicular engine is started, the engine walls manifold as well as the catalyst are at atmospheric temperatures. As the engine operates further, hot gases heat up and exhaust gases emitted from the engine start warming up catalyst gradually. The time required by a catalyst to get optimal conversion for specific pollutant is known as “Light-Off” period of that catalyst for that specific pollutant. Due to incapability of the catalyst to treat the CSEs during light-off period, the emissions that occur in this period are relatively higher (Amin et al., 2011). About 70% of the total unburned hydrocarbons (UHC) and CO emissions occur during the light-off period of the FTP-75 cycle (Burch et al., 1996). These emissions are known as Cold-Start Emissions. Figure 4 below shows the UHC emissions from a gasoline engine during an FTP-75 cycle testing carried out for determining cold-start emissions. The UHC emissions on the vertical axis are in cumulative form. It is evident from the graph that the highest proportion of the emissions occur during the first 500 seconds of the cycle, which is the light-off period.

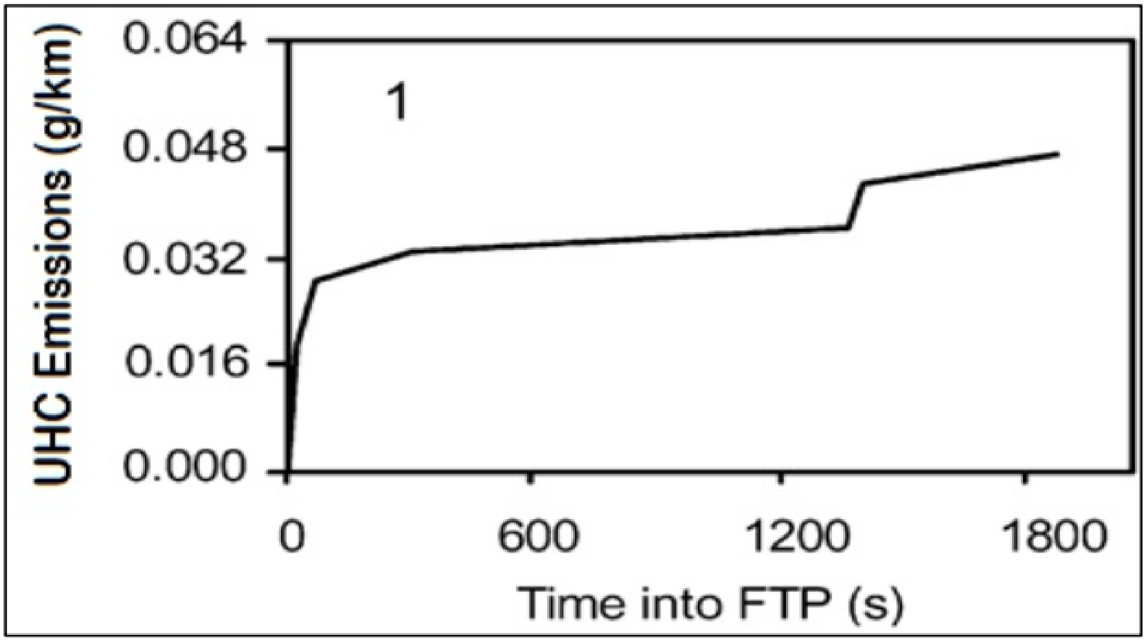

Figure 4: CSEs during an FTP-75 cycle (Kašpar et al., 2003)

2.4.2 High Costs and Environmental Impacts of Catalysts

As described earlier, the use of platinum, rhodium and palladium is done as catalysts in catalytic converters. These are precious metals and are thus expensive. As of November 2013, the prices of the precious metals used as catalysts are given in Table 1,

Table 1: Current Prices of Precious Metals on a 1 lb. (0.45 kg) basis

Noble Metals	Price per lb.
Platinum	$22928
Rhodium	$15584
Palladium	$11694

(Platinum Today, 2013)

In a typical TWC, the oxidation catalyst has a Pt/Pd mass ratio of 2:1 and the reduction catalyst has a Pt/Rh mass ratio of 5:1; this brings the overall Pt:Pd:Rh mass ratio of the three noble metals to 10:4:1 (Degobert, 1995). As can be seen in the table above, the cost of Pt is higher than both Rh and Pd. Because of the high cost of these noble metals, the overall price of a catalytic converter increases. Apart from noble metals, a TWC also requires the use of electronic fuel injection which can control the air-fuel ratio in accordance with the signal from the λ-O_2 sensor. The cost of electronic fuel injection combined with the catalytic converter increases the overall cost of a typical car by 10%, of which the cost contribution by the noble metals is 28% (Degobert, 1995). The cost breakdown of the catalyst bed of a typical TWC is shown in table 2.

Table 2: Cost Breakdown of a Typical TWC

Components of TWC	Cost Contribution (%)
Catalyst support	13.3
Cost of impregnation	36.7
Noble Metal	23.3
Casing	26.7
Total	**100**

(Lee et al., 2010)

Moreover, the mining and extraction of these noble metals from their ores has a significant impact on the environmental quality in the vicinity of the mining area. Platinum mining, for instance, has been proven to have negative effects on the aquatic ecosystems, water quality and sediment quality of the water bodies around the mining operation site (Gumede, 2012). Platinum occurs in deposits with 5 other elements: palladium, rhodium, iridium, ruthenium and osmium, referred to together as the platinum-group metals or PGMs. Tailings are the non-metallic materials and often contain undesired toxic metals (such as cadmium, lead, and arsenic) present in the ores of PGMs. The mining and extraction process generates large amount of tailings (ELAW, 2010).

2.5 Solution of Cold Start Emissions

It has been established in the previous Section that though catalytic converters are effective in controlling the harmful emissions from automobiles, they have certain limitations such as light off and high capital costs. There have been several recent developments in the field of catalytic converters in order to mitigate these limitations. Some of these developments have been discussed in this section.

As this thesis is mainly concerned with the cold start emissions so following are the solution techniques for the reduction of CSEs by using PCM.

2.5.1 Shortening the Light-Off Period

As described in previous Section, a TWC has no effect on the pollutant-laden gas stream until it reaches at least 300^{o}C. The duration of this ‘light-off’ period is in a direct variation with cold-start emissions from automobiles. A clear solution to this limitation would be to employ a heat source that can heat up the catalyst bed rapidly after cold start and thus effectively eliminate light-off period. However, a large amount of energy is needed for heating the catalyst bed to such a high temperature. The TWC could be moved closer to the engine itself, so as to attain rapid heating of the bed due by convection from the engine. But this could result in overheating of the catalyst bed and cause thermal degradation of the precious catalysts used Variable-Conductance Insulation

2.5.2 Variable Conductance Insulation

The National Renewable Energy Laboratory (NREL) has done extensive research and progress in designing several variations of vacuum insulation for a variety of energy conservation purposes since the early 1990’s. One effective solution to shortening light-off is employing the use of Variable-Conduction Insulation (VCI). The technology is based on the principle that hydrogen gas has a very high thermal conductivity even at low pressures. The high thermal conductivity of hydrogen gas is evident from the data in Table 3 in comparison with some other gases. An insulation jacket is placed around the TWC with metal hydride (typically zirconium hydride) coated on the cooler side, as shown in Figure 5. The metal hydride is electrically heated. As the temperature is increased, the metal hydride undergoes thermal oxidation and releases hydrogen gas. H_2 absorbs the heat, expands and settles exothermally on the other end of the jacket, which is adjacent to the TWC. Thus, the TWC is heated and light-off period is shortened. Once the light off period is over, the electrical heating is stopped and H_2 gas is reduced back to hydride form, thereby reducing the conductance (Benson et al., 1994). By using VCI, energy saving is also achieved: when the engine is turned off, heat is stored by the H_2 gas. As the engine is started again, the stored heat is utilized to heat up the TWC (Adams et al., 2013).

Variable-Conduction Insulation (VCI). The technology is based on the principle that hydrogen gas has a very high thermal conductivity even at low pressures. The high thermal conductivity of hydrogen gas is evident from the data in table 3 below in comparison with some other gases.

Table 3: Thermal Conductivities of some Gases

Gas	**Thermal conductivity (w/m-k)**	**Normalized to air**
N_2	0.0259	1.079
O_2	.2662	1.109
CO_2	.0166	.691
CH_4	.03423	1.42
Air	.024	1
H_2	**.1816**	**7.57**

(Sluder et al., 2004)

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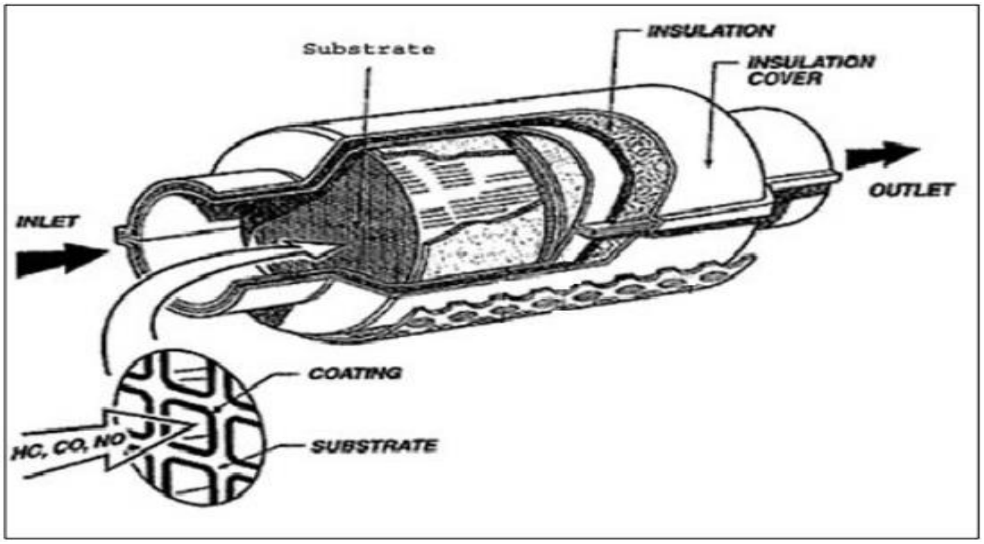


Figure 5: VCI in a TWC (IneffableIsland, 2013)

The reduced emissions obtained as a result of employing VCI in a TWC are shown in the Table 4.

Table 4: Reduced Emissions by TWC with and without VCI

Pollutants	Conventional TWC (g/mi)	TWC with VCI(g/mi)	Decrease in emission
UHC	0.194	.031	84%
CO	1.463	.131	91%
NO_x	.135	.066	51%

(NREL, 2013)

2.5.3 Phase Change Material

Noble metal based catalyst can only operate optimally above 300oC. VCI can maintain this temperature for up to 10 hr (Adams et al., 2013). However, when engines are started after longer periods of rest, the heat stored by the VCI is lost. This issue is resolved by introducing Phase Change Material (PCM) to the cold-start emissions technology. PCMs are organic and/or inorganic salts as well as their eutectic mixtures which have been used for thermal storage because of their capacity of storing and releasing energy during their phase change (Kumar & Shukla, 2015). Initially used for lower temperature application, PCMs today are being used in applications ranging 120^{o}C to 1000^{o}C (Kenisarin, 2010). Inorganic PCMs such as hydroxides, chlorides, fluorides, nitrites, nitrates and eutectic mixtures of these compounds are suitable in thermal energy storage system at relatively higher temperature (Cárdenas & León, 2013). PCM is selected on bases of thermal, chemical and physical characteristics as well as cost factor (Socaciu, Giurgiu, Banyai, & Simion, 2016) .

It is also to be noted that higher the amount of PCM used higher the energy storing capacity of the PCM. Heat storing and releasing is spontaneous and any external energy is not required for this purpose (Jankowski & McCluskey, 2014). In past, different PCMs (depending on their melting points) have been used for different services e.g. solar applications (Elarga, Goia, Zarrella, Dal Monte, & Benini, 2016; Hoshi, Mills, Bittar, & Saitoh, 2005; Iverson, Broome, Kruizenga, & Cordaro, 2012), Environmental friendly energy storage applications (Anisur et al., 2013; Kenisarin, 2010; Zalba, Marín, Cabeza, & Mehling, 2003), cooling of buildings (Cerón, Neila, & Khayet, 2011; Ravikumar & Srinivasan, 2008) and in automobile for different purpose (BOKDE & WAGHMARE, 2013; Jankowski & McCluskey, 2014; Oró, de Jong, & Cabeza, 2016) etc. (BOKDE & WAGHMARE, 2013). In converter PCM utilizes the heat of melting/solidification and has higher heat storage capacity than VCI. Moreover, no additional energy input is required to heat the converter because the energy of the exhaust gases from previous run of the engine is stored for subsequent uses. PCMs typically used in TWCs are metal alloys and eutectic salt mixtures because of their high heat of solidification and melting (Korin et al., 1999). When engine is turned off, PCM starts undergoing partial solidification and the latent heat released keeps the TWC hot for a long duration (Bokde et al., 2013). Figure 6 shows the cross-sectional view of a catalytic converter with PCM.

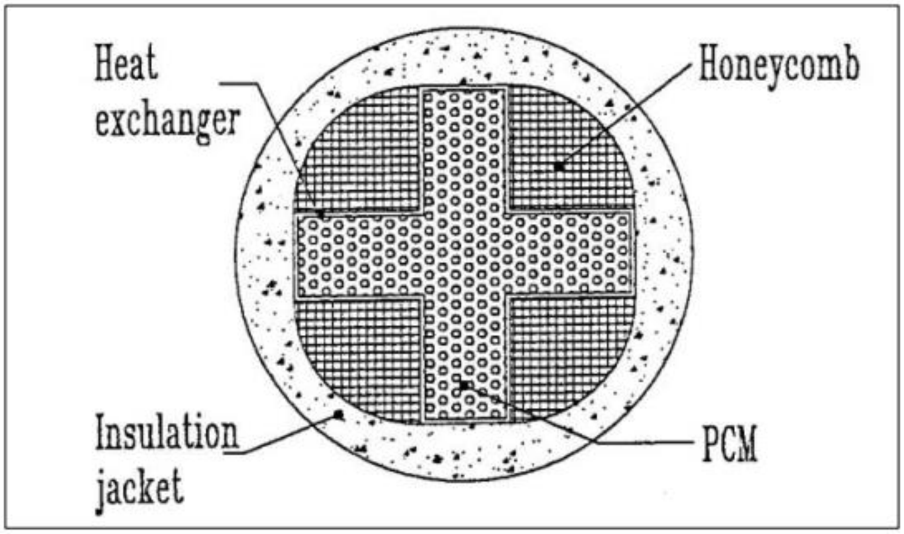


Figure 6: PCM location in a TWC (Korin et al., 1999)

2.5.4 Electrical Heating of Catalyst

Past approaches to solving the issue of cold-start emissions have included electric heating of the catalyst. This approach requires a large energy input of 2kW and reduces the light-off period to 30 seconds. But by this approach, cold start emissions are only reduced, not eliminated. Moreover, electrically heating the catalyst causes physical stress that causes distortion of shape and deactivation of the catalyst bed (Adams et al., 2013)

Electrical heating of catalyst involves the heating with small electric heaters to get the light off temperature of catalyst as soon as possible. For this purpose different studies have been carried out by researchers. Electrically heating along with CO setting level is also used to achieve the required temperature by electrically and chemically heating (Horng et al., 2004). To make the electrical heating more and more reliable and effective automation of electrical heating system has been also carried out.

Chapter 3

MATERIALS AND METHODS

3.1 Catalyst-PCM Configuration

The configuration of catalyst/ PCM is important in heat retention as well as its transfer within system. PCM and catalyst coated substrate (wire mesh) are arranged in such a manner that area of contact between catalyst and PCM should be maximum to maximize heat transfer between the two during charging (engine in operation) and discharging (engine shutoff) phase and outer surface of converter which is to be insulated should be minimum to minimize heat losses. Briefly, the ratio of PCM/catalyst contact surface area to the converter outer surface area, here on ward called as contact area ratio, should be maximum. Some possible configurations are given in Figure 7.

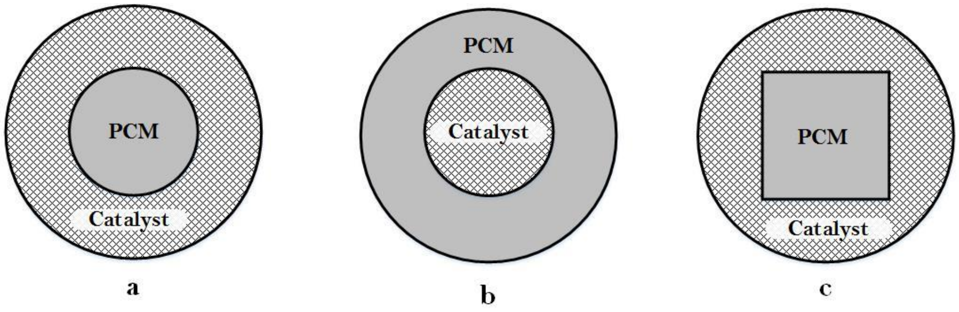


Figure 7: Possible Catalyst and PCM configurations

Length of the converter case was fixed in order to calculate dimensions of converter suitable to be installed on a motor bike exhaust. Besides, the volume of PCM was also kept equal to volume of the catalyst (Korin et al., 2005). With these assumptions, the contact area ratios in the Figure 7a, b and c configurations were calculated to be 0.70, 0.70 and 0.80 respectively. Configuration b was found to be better than a as in b, converter is to lose more heat during soak time as PCM is packed in the outer annulus of the converter and is more exposed to ambient atmosphere. Configuration c, on the other hand, not only offers more contact area ratio but also helps in retaining heat during soak time as PCM is covered with catalyst, in turn, covered with the insulation. Hence configuration c was selected and consequently, the catalyst coated substrate was cut accordingly.

3.2 Phase change material and Insulation

Some phase change materials and their thermal characteristics are given in table 5

Table 5: Phase Change Materials and their thermal characteristics

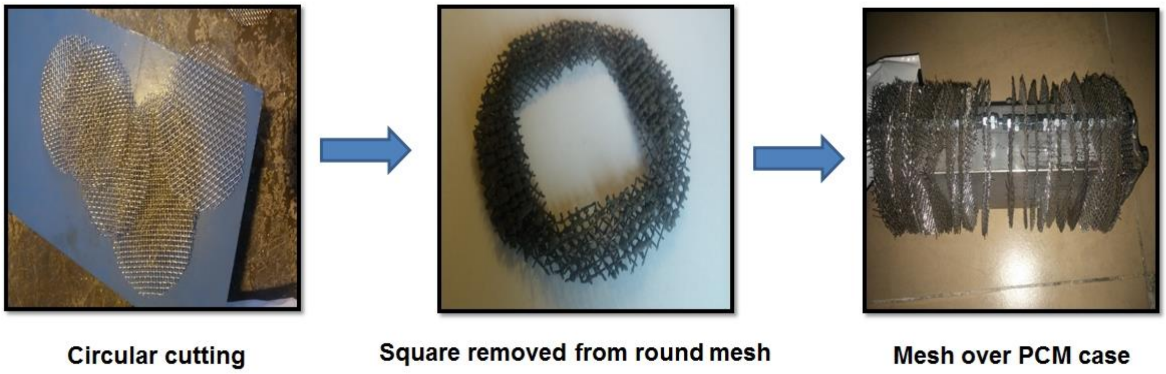
Material	Melting point (°C)	Latent heat (kJ/kg)
$LiNO_3$	253	389
$NaNO_3$	307	176
50NaOH + 50 KOH	169-171	202-213
$73NaOH + 27NaNO_2$	**237**	**249-295**
$54NaNO_3 + 46KNO_3$	222	117

A eutectic mixture of $73NaOH + 27NaNO_2$ was selected in present study because its transition temperature is close to light off temperature of the non-noble metal catalyst used. The $NaNO_2$ was in powder form already but NaOH was available in pellets so the pellets were crushed into powder and homogenous mixture of NaOH and $NaNO_2$ was formed.

Stone wool insulation was used over final case of catalytic chamber. The thermal range of glass wool insulation is 600°C. Mica sheet was used to avoid the direct contact between insulation and chamber. Thermal cloth bandage was wrapped over final insulation to hold the insulation and to minimize the minor losses as well

3.3 Preparation of Wire meshes

The substrate Stainless steel Wire mesh with opening size of 0.097 inches was cut in circular shape first and then from the cut pieces of wire mesh a square was further cut to create space for the PCM case as shown in Figure 8. The final prepared meshes were coated with catalyst slurry prepared in laboratory. After that these coated wire meshes were put on PCM case one by one and PCM case along with the coated meshes with catalyst was finally put into the final catalytic case over which stone wool insulation jacket was rapped. The ends of catalytic case were also insulated to reduce minor heat losses from ends.


Circular cutting

Square removed from round mesh

Mesh over PCM case

Figure 8: Wire mesh cutting stage by stage

3.4 PCM case and Thermocouples

PCM case was made of stainless steel 302 with dimensions of 2.2″ * 2.2″ * 10″. Thermal conductivity of SS302 is 16.2 W/m-K. A whole was provided at the center of the PCM case for temperature measure of PCM in the case as shown in Figure 9.

Three K-type thermocouples were used at different location in the system. Two thermocouples 1 and 3 were used on front and back of catalyst respectively to measure the catalyst temperature at front and back side of catalyst and one thermocouple (3) was inserted at the middle of PCM case for temperature measurement of PCM inside the case.

Figure 9: Phase Change Materiel case (SS302)

3.5 Experimental Setup for Thermal Management System

2.1 Experimental setup

The schematic description of experimental setup is presented in Figure 10. The study can be divided into two parts. First part focuses on the use of PCM and explores its potential to retain heat in converter during brief to medium lengths of soak times. Second part focuses on use of glow plugs and investigates their usability potential to warm up the converter at least up to the light off temperature of the catalytic converter after a cold engine startup. Hence, it is to be noted here that either of PCM or glow plugs were inserted in the catalyst at a time in Figure 10.

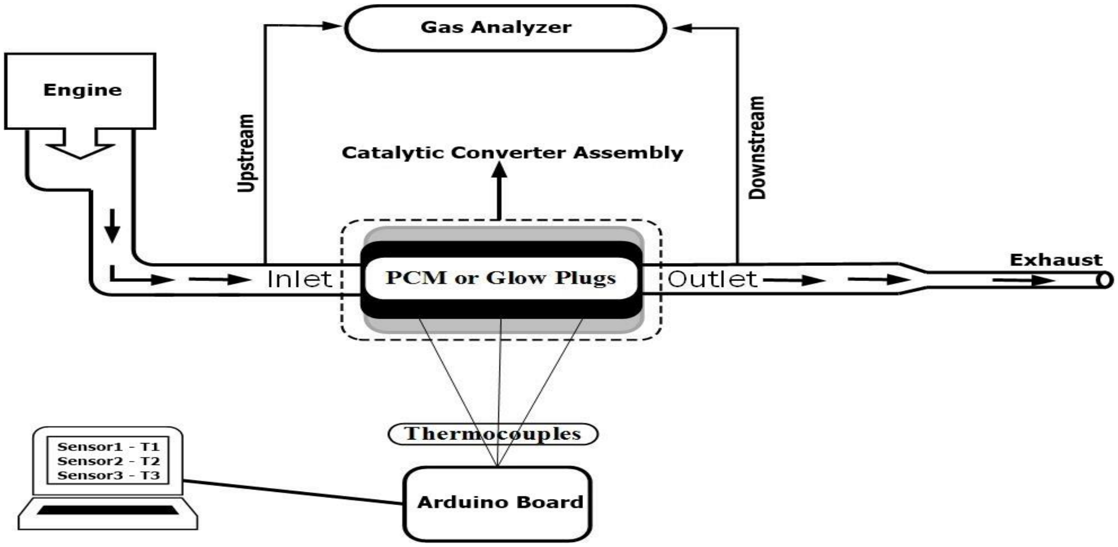


Figure 10: Schematic diagram of experimental setup

The setup comprised of a gasoline powered Internal Combustion (IC) engine, gas analyzer, thermocouples attached with Arduino board and insulated catalytic converter assembly. A 70 cc gasoline powered motor bike engine (Honda CD70) was used in the study, operated on idle at varying RPM. The RPM of the engine were monitored by tachometer (RS Pro 445-9557). Two K-type thermocouples were used to monitor the temperature of catalyst, one each at flue gas inlet and outlet Figure 11. Whereas a third thermocouple was inserted at the middle of PCM case for PCM temperature measurement. Thermocouples were connected with PC for data display and logging through an Arduino board. Concentrations of HCs and CO were measured at inlet and outlet of catalytic converter by using a gas analyzer (Crypton 295). Converter was heated by using electrically powered glow plugs (TOYOTA 19850-64010). Glow plugs were powered up by 12 volt battery (Volta N260) and current supplied was monitored with a multi-meter (Digit Bench 5492B).

2.2 Catalytic Converter Assembly

Detailed diagram of insulated catalytic converter assembly with PCM and glow plugs arrangement are given in Figure 11 and Figure 12 respectively.

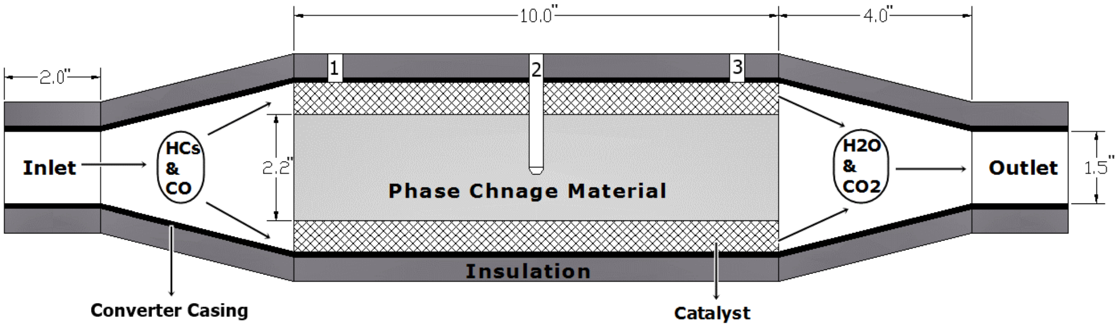


Figure 11: Catalytic converter assembly with PCM

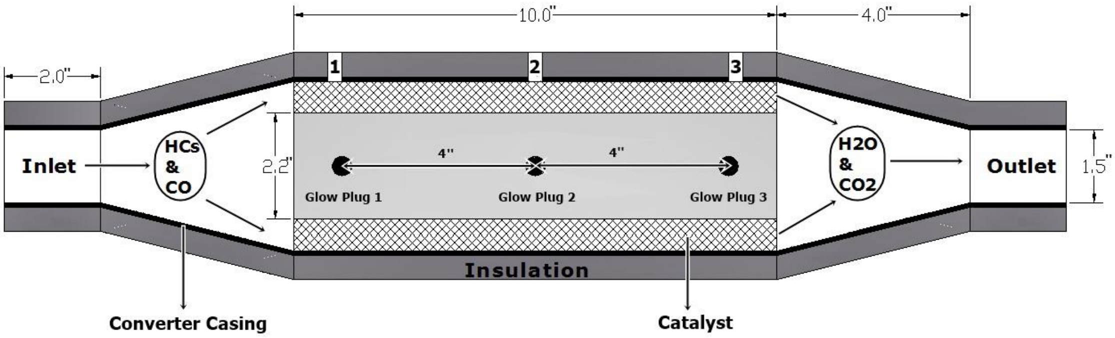


Figure 12: Catalytic converter assembly with glow plugs

Chapter 4

RESULTS AND DISCUSSION

4.1 Testing of thermal management system

Original bike silencer was replaced by specially made silencer, connected with catalytic converter.

Experiment was performed for three variations as given below

- Engine operation without insulation and PCM
- Engine operation with only insulation
- Engine operation with PCM and insulation

4.1.1 Engine operation without insulation and PCM

In first case there was neither PCM embedded in system nor any insulation. To assess the effeteness of the catalyst heating system, catalyst mounted on bike was heated up to 240°C in idol condition. When the engine was shut off the temperature of catalyst dropped rapidly from the peak (240°C) and reached to room temperature in one hour. It was noted that the temperature of the catalyst increased easily up to 230°C and after that it was not increasing easily as there was direct contact between catalyst and atmospheric air due to witch heat was dissipating into the atmosphere. The atmospheric temperature during the testing was atmospheric temperature (36^{o}C).

The negative slope in the first case is much steeper. Its reason is that when catalyst was heated up to maximum temperature that can be achieved without insulation and PCM then the difference in temperature between the achieved temperature during heating and atmosphere was high due to which temperature decreases very fast. Heating and cooling patterns of the catalyst are given below in Figure 13 and Figure 14 respectively.

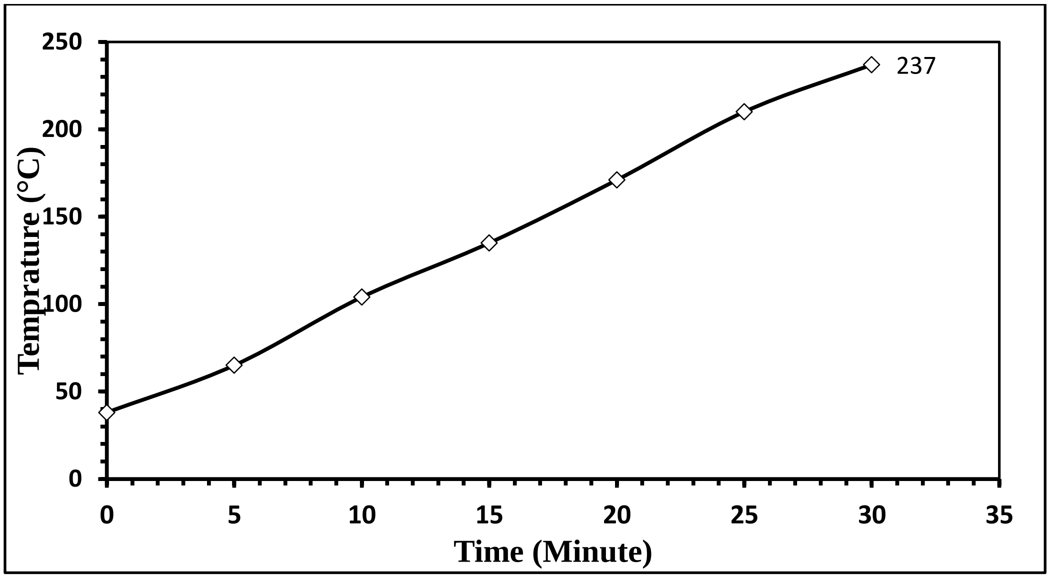


Figure 13: Heating of catalyst in case 1

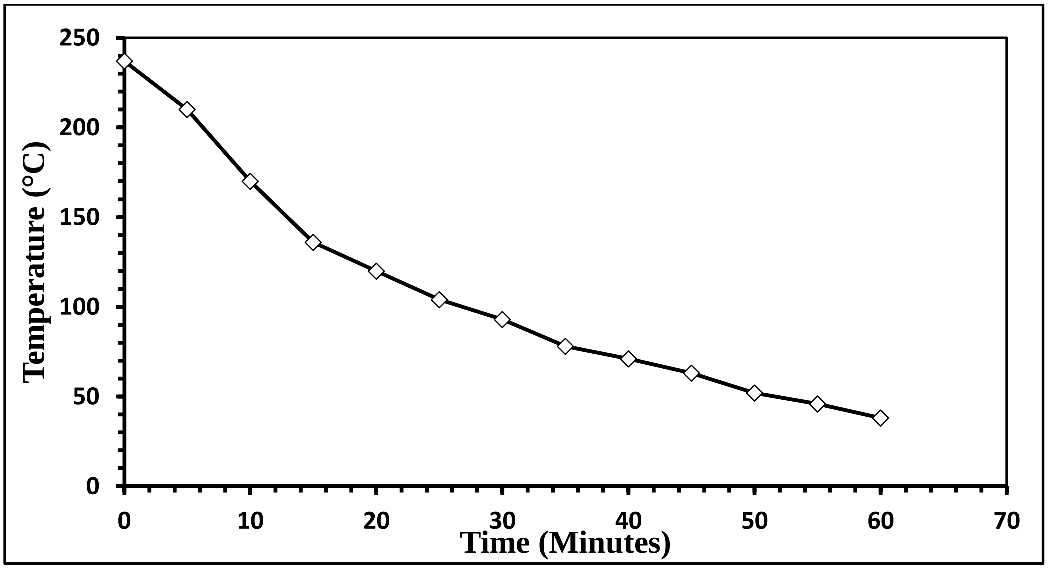


Figure 14: Cooling of catalyst in case 1

4.1.2 Engine operation with only insulation (only insulation)

In this case only stone wool insulation was used and the temperature withstand range of the stone wool is 450°C. Due to insulation there was no direct contact between catalyst case and atmosphere the temperature inside the case was increased up to 354°C because there was no heat loss in this case. The cooling curve for this case is shown in Figure 15

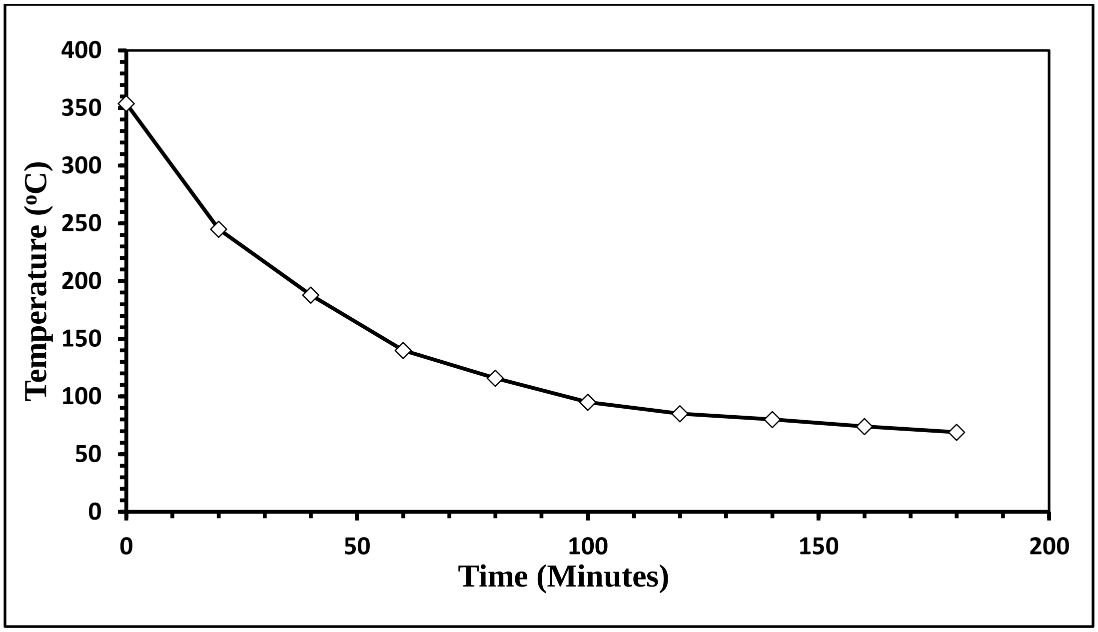


Figure 15: Cooling curve for case 2 where only insulation is used.

At the start the temperature was high so temperature dropped rapidly due to high temperature deference due to witch curve at the start is steeper.

It is shown that due to stone wool insulation catalyst heated up easily up to 354°C as compared to case one where no insulation was used. The heat retention took place due insulation and catalyst remained heated up to 80°C after almost two and half hour.

4.1.3 Engine operation with PCM and insulation (PCM +Insulation)

In this test PCM along with the stone wool insulation was used. Mica sheet was also used on catalytic converter case and then insulation was wrapped around the case. The purpose of mica sheet was to avoid the direct contact of case surface with insulation and to trap more heat with in system. Thermal bandage was wrapped over the stone wool insulation to retain the heat and to hold insulation properly. The profile for this case is given in Figure 16.

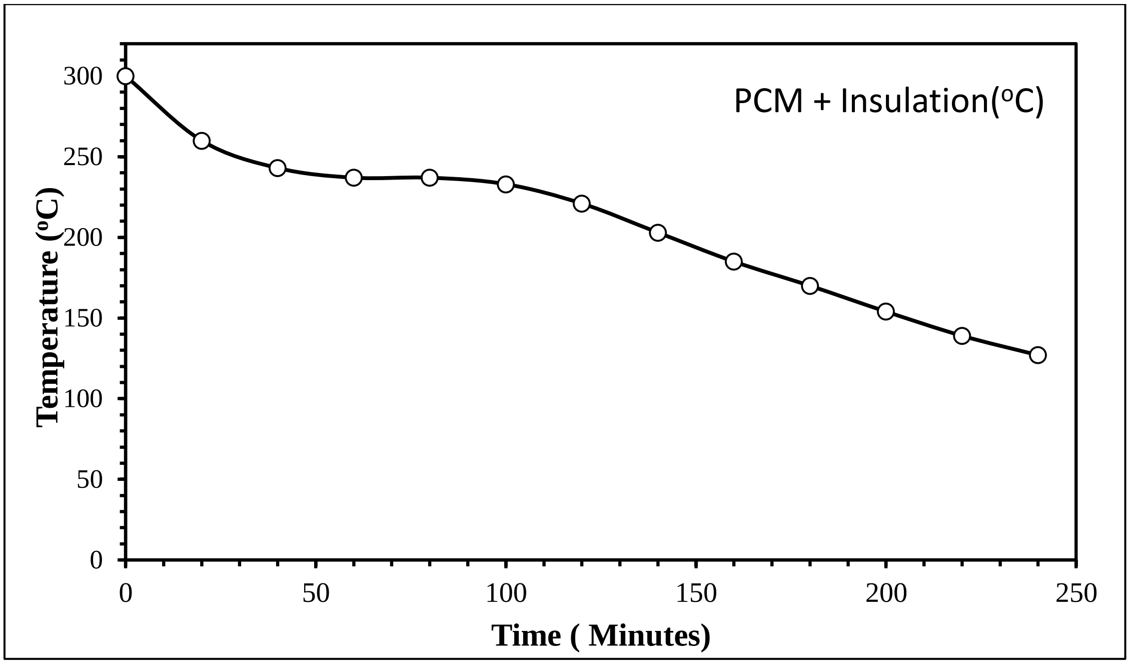


Figure 16: Cooling curve when PCM and Insulation both were used

From above figure three phase can be noticed in cooling phase. In first period that was about almost 41 minutes the temperature of PCM, when PCM was in liquid state, was declined until it reached at its solidifying temperature that is 237°C. In second period (about 60 minutes) temperature remained constant until entire PCM was solidified. In the third phase PCM is solid and the temperature of PCM declined gradually. It is noted that the temperature of the catalyst after three and half an hour was 125°C. The conversion for the CO and hydrocarbons started when catalyst was at 98 °C and 110 °C respectively as given in Figure 17.

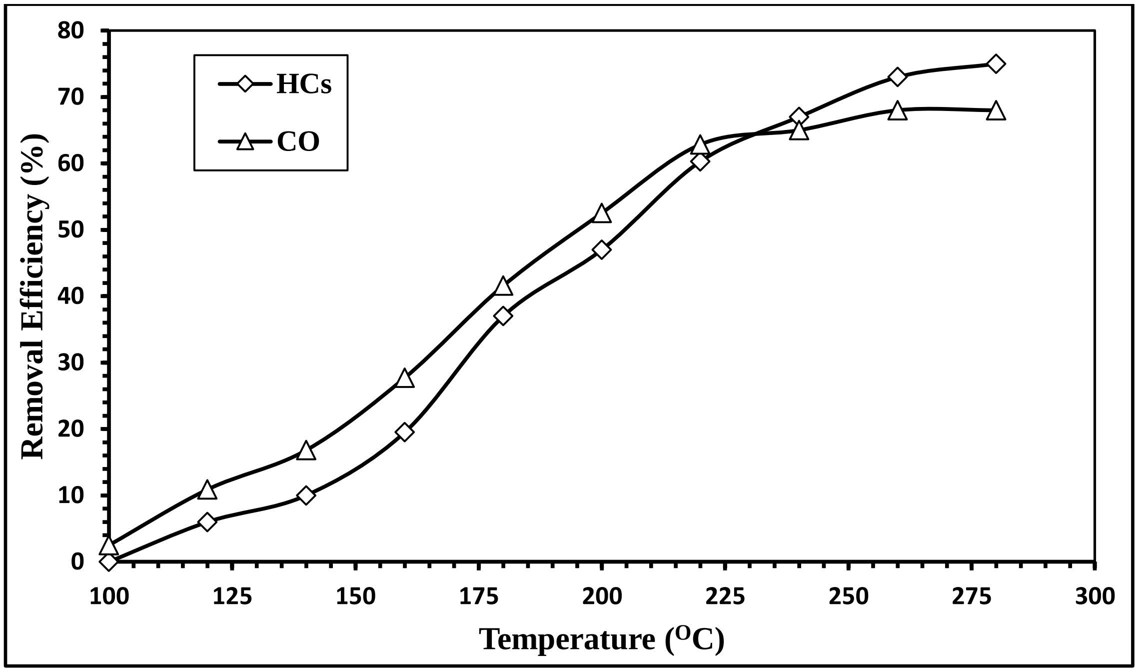


Figure 17: Temerature vs removal effeciency

From above curves light off temparute of the catalyst for CO apeared to be 195 °C and for the HCs 206°C.

4.2 Comparison of Heat Retention after 2.5 Hour

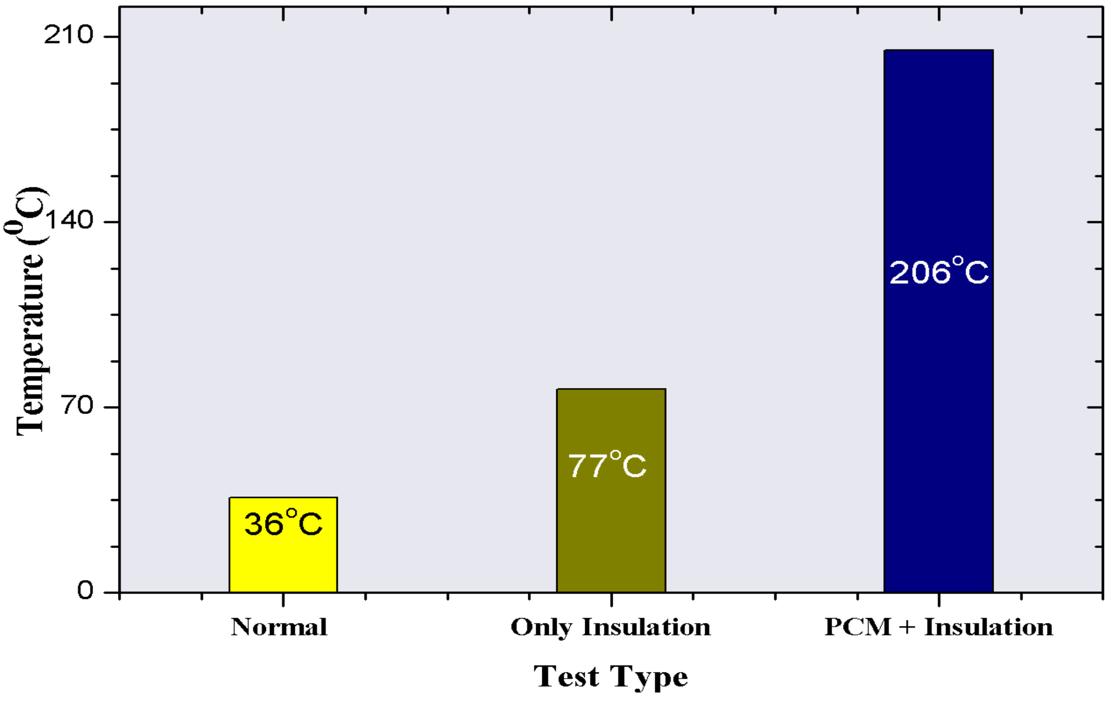


Figure 18: Heat retain profile by all variation after an hour

4.3 Electrical Heating by glow plugs

This part of study focuses on exploring option of heating the converter electrically to achieve light off temperature after cold startup as soon as possible. For this purpose converter (Figure 2b) heating profiles were monitored under 4 different conditions; a) glow plugs off and engine operated at 5000 RPM, b) glow plugs on and engine shut off, c) glow plugs on and engine operated at 2500 RPM and d) glow plugs on and engine operated at 5000 RPM The profiles for electrically heating of converter are given in figure 19.

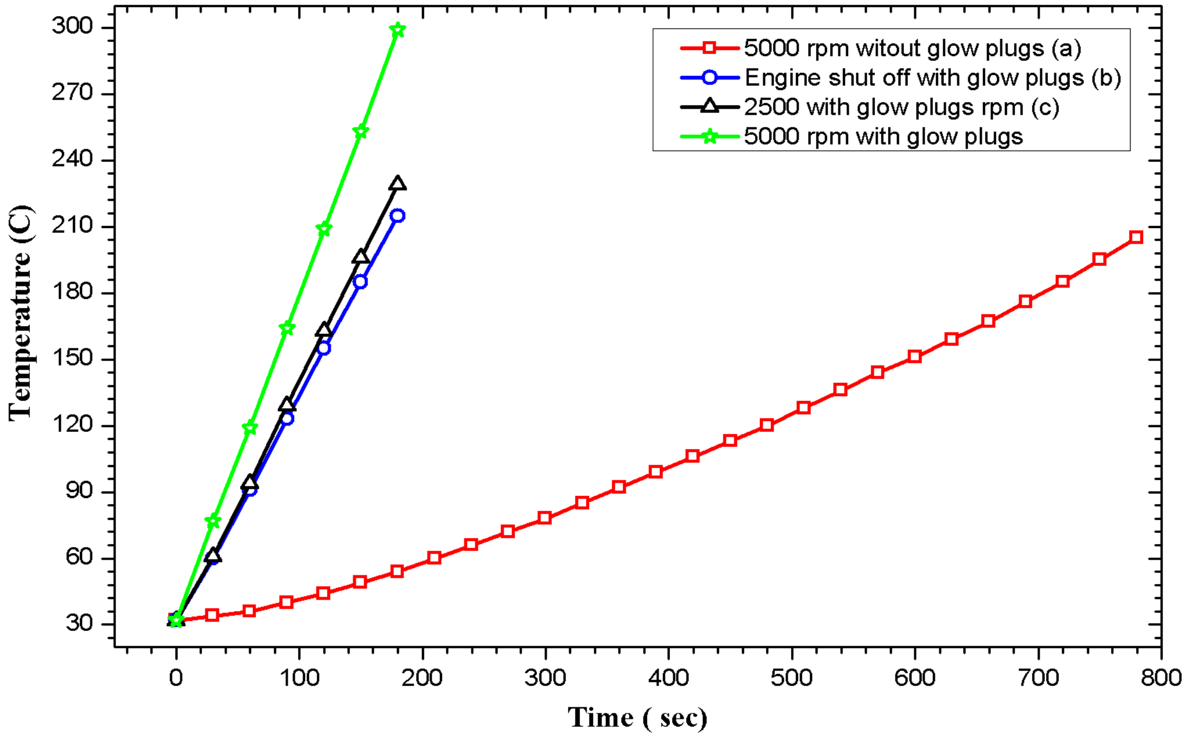


Figure 19: Profiles for electrical heating of catlyst

Converter heating profile Figure 19(a) shows that converter takes around 13 minutes to achieve light off temperature for CO and HCs without electrical heating while engine being driven at 5000 RPM on idle. However, electrical heating speeds up the heating. Only glow plugs, being single source of heating, while engine is off, (heating profile b) reduces the light off time to less than 3 minutes for both pollutants. Similarly, use of glow plugs while engine operates at 2500 (profile c) and 5000 RPM (profile d) further decreases the light off time to 146 and 110 seconds for CO and 156 and 118 seconds for HCs respectively.

Chapter 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

From this whole study is concluded that,

- If Catalytic converter is intended to be applied for small engine then thermal management system Catalytic converter is necessary because temperature required for catalyst activation is not achieved easily in small engines.
- Only insulation was less effective but both insulation and PCM enhanced heat retention with in system.
- After a soak time of 2.5 hour the catalyst temperature was noted 206°C.This temperature is above the light of temperature of Catalyst for CO and HCs(195°C)
- Electrical heating reduces light off time from 13 to less than 3 minutes, further reduce able to less than 2 minutes if engine operating at 5000 rpm.

5.2 Recommendations

This study can be pursued and improved in the future, here are some recommendations for the future work.

- Heat retention can be increased by using PCM with relatively high latent heat ultimately giving longer safe soak time.
- If phase change material is used with other oxides nano-additives, its thermal characteristics can be improved for high temperature applications like this PCM

can be used to stow solar energy that further can be used in cocking by incorporating PCM in stoves as energy storage device for a reasonable time. This can be good alternative energy storage technique where ample amount of sunshine is available.

- In the future better results can be achieved by the same set up if better insulation material is employed.
- If a catalyst having low light off temperature is used results can be improved.

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