Influence of Prototype Three Way Catalytic Converter on Regulated and Unregulated Emissions from Gasoline HCCI/SI Engine

by

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ABSTRACT

Designing automotive catalysts for the effective control of NOx, HC (Hydrocarbon) and CO (Carbon Monoxide) emissions under both lean and stoichiometric engine operation is a challenging task. The research presented in this thesis assesses the performance efficiency of a three-zone prototype catalytic converter in reducing exhaust emissions from a gasoline engine, operating in HCCI (Homogeneous Charge Compression Ignition) and SI (Spark Ignition) mode under lean and stoichiometric conditions. The research was carried out using Jaguar V6 engine operating in SI and HCCI mode using commercial unleaded gasoline fuel. The catalyst efficiency in reducing the three pollutant emissions is closely related to the exhaust gas conditions (e.g. temperature and space velocity), oxygen content and composition i.e. NO_x, CO and HC concentrations.

As part of this study a quantitative and qualitative analysis of C1-C11 hydrocarbon compounds achieved before and after the catalytic converter. The results show that hydrocarbon species formation in the combustion process and destruction over the catalyst is primarily dependent on the engine operation and combustion mode (i.e. HCCI or SI). Alkane concentrations were found to be higher in the HCCI mode, while alkene species were mainly found in the engine exhaust under SI mode. The analysis showed that the HCCI exhaust contained heavier hydrocarbon species (e.g. toluene, p-exylene, naphthalene and methylnaphthalene) compared to the exhaust from the SI engine operation. Methane, Naphthalene and methylnaphthalene were the most resistant compounds while toluene was the most degradable compound over the catalyst.

Carbonyl species which are more likely to be formed as a result of partial oxidation of the fuel components were also investigated. It was found that, during HCCI engine operation the percentage contribution of carbonyl compounds to the total hydrocarbon emissions was higher under stoichiometric operation. The prototype catalytic converter eliminates most of the carbonyls species in the exhaust in all combustion modes and engine operating conditions except for acetaldehyde species. Conversion efficiencies for the different hydrocarbon species over the catalyst were in the order of alkenes > alkanes > aldehydes> aromatics. Hydrogen was added upstream of the catalyst primarily to assess its ability to promote NOx reduction, however it was also found to influence the oxidation characteristics of the catalyst.

DEDICATION

To the souls of my father
And mother,
To my beloved wife and beautiful daughters,
To my son, brothers and sisters,
I dedicate this thesis…
With
Love and Respect

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LIST OF ABBREVIATIONS

A/F	Air to fuel ratio
A-Cat	After catalyst
B-Cat	Before catalyst
CIDI	Compression ignition direct injection
CI	Compression ignition
CPS	Cam profile switching
CR	Compression ratio
DNPH	Dinitrophenylhydrazine
DI	Direct injection
EGR	Exhaust gas recirculation
FID	Flame ionization detector
GC	Gas chromatography
GHSV	Gas hourly space velocity
H2	Hydrogen
HC	Hydrocarbons
HCCI	Homogeneous charge compression ignition
HPLC	High-performance liquid chromatography
IARC	International Agency for Research on Cancer
IC	Internal combustion
IMEP	Indicated mean effective pressure
MAH	Mono aromatic hydrocarbon
MF	Methane formation
MS	Mass spectrometer
MSDS	Material Safety Data Sheet
N2	Nitrogen
NMEP	Net mean effective pressure
NO	Nitrogen oxides
NS	Nett specific
O/C	Oxygen to carbon atomic ratio

OSHA	Occupational Safety and Health Administration
OHC	Oxygenated hydrocarbons
PAH	Poly aromatic hydrocarbons
PELS	permissible exposure limits
PLOT	Porous layer open tube
PM	Particulate matter
ppm	Parts per million
REGR	Reformed exhaust gas recirculation
Rh	Rhodium
RON	Research octane number
SI	Spark ignition
TCD	Thermal conductivity detector
TDC	Top dead centre
THC	Total hydrocarbon
TWA	Time Weight Average
TWC	Three way catalysts
UHC	Unburned hydrocarbon

CHAPTER 1:

INTRODUCTION

1.1 Introduction

In recent years, much attention has been focused on the engine emissions due to the stricter emission regulations worldwide and the global air pollution problems, the seek to develop more efficient but cleaner, engines is of increasing importance for automotive industries. The contribution of exhaust emissions reduction via sophisticated engine system is relatively limited; however, increased environmental awareness has led to the demand for products and processes which are more compatible with the environment. The call for reduced emission is continuing to gain strength. Homogenous charge compression ignition (HCCI) engines offer high efficiency and low emissions [1]. It has been found in the automotive industry that the HCCI engine is a promising concept for future automobile engines and stationary power plants. HCCI engines have numerous advantages over SI and CI engines. Relative to SI gasoline engines, HCCI engines are more efficient, approaching the efficiency of compression ignition direct injection (CIDI) engines. Relative to CIDI engines HCCI engines have substantially lower emissions of particulate matter (PM), and NOx which is attributed to the dilute homogenous air and fuel mixture in addition to low combustion temperature. HCCI engines can operate using a variety of fuels such as gasoline, diesel, natural gas, bio-fuels and hydrogen. In HCCI engine the air and fuel are mixed together either in the cylinder with direct injection or in the intake system. The premixed homogenous mixture of air and fuel vapour is then compressed to the point of auto-ignition. The temperature of the charge before starting the compression stroke has to be increased to reach auto-ignition conditions at the end of the compression stroke, this could be done by keeping part of the hot combustion products in the cylinder which in turn speed up the chemical reaction which lead to the start of combustion mixture. The reaction is initiated at multiple sites through the cylinder, so ignition in the HCCI engine occurs nearly simultaneously throughout the combustion chamber, though there is no direct initiator of combustion and no discernable flame propagation, which makes the control of the start of auto ignition challenging [1-2]. However, regardless of all the advantages mentioned above there are several technical difficulties which need to be resolved before HCCI can be implemented in production engine. Expanding the load range of the engine operation and controlling the phasing of HCCI combustion are current problem areas [1].

HCCI engines can operate at narrow load window low to medium loads, however difficulties start when changing to high load condition, the combustion process can become very rapid and intense causing unacceptable noise, potential engine damage, and higher NOx exhaust emissions [3]. HCCI engines have inherently low emissions of NOx and PM but relatively high emissions of HC and CO, some potential exists for reducing these emissions at light load by using direct in-cylinder fuel injection. However, regardless of the ability to minimize engine-out HC and CO emissions by altering engine operations or changing engine design, HCCI engines will likely require advanced exhaust emission control device, thus, engine exhaust after treatment systems are widely considered. Catalyst technology for HC and CO removal is well understood and used in gasoline-fuelled automobiles for twenty five years. Although some oxidation catalysts were introduced much earlier, it was not until the 1980s that the Three-Way-Catalyst (TWC) was developed by which NOx, CO and HC can be converted simultaneously [3]. Reducing HC and CO emissions from HCCI engines requires advanced exhaust after treatment due to the low combustion temperature [1]. Although, TWC technology has been perfected over the years for use in SI stoichiometric combustion engines, under HCCI stoichiometric or lean operation those catalysts are ineffective in reducing NOx emissions, because the only efficient methods known for the removal of NO from exhaust gas either at stoichiometric or lean A/F conditions, which involve catalytic processes, consumption of NO by the reducing species present in the exhaust such as CO, hydrocarbon or H_2 is the preferred catalytic process. In addition switching engine operation to lean, stoichiometric or even rich may generate more HC and CO emissions, making the application of conventional catalysts challenging especially at the low exhaust temperatures associated with HCCI engines .

Hydrogen has been long believed to be one of the most promising energy carriers for internal combustion engines from the point of emission control and engine performance. The use of hydrogen as pure or an addition to the main hydrocarbon fuel has been reported to be beneficial in terms of emissions (NO_x, HC, CO, Particulate Matter) and engine performance [4]. Furthermore, hydrogen has also been used to improve the performance of the engine exhaust gas after treatment devises such as Selective Catalytic Reduction (SCR) of NO_x (specially at low temperatures), NO_x traps and diesel particulate filters (DPF) [5-6].

The compounds emitted in the exhaust can be divided into two categories; those that are regulated , i.e., CO, NOx, HC, soot and particulate matter (PM), and u regulated constituents such as benzene, toluene and 1,3 butadiene [7]. The unregulated constituents can contribute to smog formation in urban areas and have potential health effects on humans [8]. Due to these issues the legal demands concerning vehicle exhaust have been strengthened during the last two decades. Vehicle emissions comprise of total hydrocarbons (THC) which consist of unburned fuel, components of cracked fuel, and combustion products such as oxygenated hydrocarbons (OHC) consist mainly from Carbonyl (Aldehydes and Ketones), alcohols, and organic acids. These unregulated emissions need to be eliminated from the tail pipe in order to reduce risk to human health. Emissions standards have only addressed the mass of total hydrocarbons (THC), but there has been growing awareness that individual HC, can have vastly different inherent toxicities and photochemical reactivates (or ozone-forming potentials) [9] and this is raising the possibility that new regulatory requirements might be considered for selected compounds. It is therefore important that the concentrations of individual HC species in the exhaust are measured accurately. The Clean Air Act in the USA (1990) has resulted in tightened controls on total organic emissions and species, five individual species (formaldehyde, acetaldehyde, benzene, 1,3 butadiene and polycyclic organic material) present in motor vehicle exhaust as toxic air pollutants which may be subjected to future control. Benzene and 1,3-butadiene are classified by the US Environmental Protection Agency (EPA) as group B2 probable human carcinogen of medium carcinogenic hazards [10].

1.2 Research outline

The research work presented in this thesis has been carried out at the University of Birmingham involving a Jaguar V6 HCCI/SI research engine and a prototype 3-zone monolith catalyst supplied by Johnson Matthey. Organic analytical chemistry equipments such as Gas Chromatography-Mass Spectrometry (GC-MS), Gas Chromatography-Flame Ionization Detector (GC-FID), and High-Performance Liquid Chromatography (HPLC) were used to separate individual hydrocarbons compounds in to their various components. The aim of this work was to study an after treatment system suitable to function as two-modes, stoichiometric and lean HCCI/SI engine operation. This study is expected to bridge the gap between the catalytic technologies for lean and stoichiometric engine operation in both HCCI and SI modes. In this work several parameters including engine loads, speeds, air fuel ratio, boost pressure and hydrogen addition upstream the catalyst, were examined.

1.3 Objectives

The main objective of this work was to study the engine – prototype catalytic converter system under HCCI/SI operation and range of engine conditions. Developing hydrocarbon speciation methodology was another task of this work to provide information of used fuel components and HC species in the engine out emissions from both engine modes.

This research includes:

1) Designing TWC converter capable of performing under Stoichiometric and lean engine operation to suit HCCI and SI combustion modes. Investigating

the performance of proto type TWC converter based on its function of eliminating NOx, CO, THC, and individual HC (C1-C11) from HCCI/SI stoichiometric and HCCI lean operation.

2) Detecting the individual hydrocarbons (C_1-C_7) of alkanes, alkenes, and aromatic compounds from HCCI/SI engine operations by using HC speciation technique with GC-FID instrumentation.
3) Investigating heavy HC species (C_5-C_{11}) from HCCI/SI engine operation by using HC speciation technique with (GC-MS) instrumentation.
4) Identifying the carbonyl compounds generated from both HCCI/SI modes and HCCI lean operation by using HPLC Technique.
5) Investigating the influence of H_2 addition on the catalyst performance in reducing emissions under HCCI lean engine operation..
6) Providing data base with individual HCs information to help improving the HCCI fuel components.

1.4 Thesis outline

In this thesis, a concept of integrated after treatment system of prototype Three Way Catalytic Converter in reducing engine-out emissions from HCCI/SI operation is implemented. Information of regulated and unregulated hydrocarbon species upstream and downstream of the catalyst is also presented. This thesis will be organized as follows:

Chapter 2: Literature review

This chapter reviews literature relevant to this work on regulated (HC, CO, and NO_x) and unregulated C1-C11 emissions in HCCI/SI gasoline engines. This includes work on catalytic converters, HCCI engines characteristics, legislative features, hydrocarbon speciation, and sampling methods will be reviewed.

Chapter 3: Experimental set up and procedure

This chapter presents an overview of the research engine, prototype catalyst and detailed description of the equipments that has been used. Procedures used for data processing are also explained.

Chapter 4: Catalyst design for HC, CO and NO_x emissions reduction in gasoline bi-mode SI/HCCI engine

This chapter presents research on a new catalytic converter design, which aims to control HC, CO and NOx emissions under lean (excess oxygen) and stoichiometric, HCCI/SI engine operation. The experiments were conducted on a Jaguar V6 gasoline engine equipped with the prototype catalyst at the one bank from engine side. The effects of engine load speed (i.e. space velocity), air/fuel ratio, and boost pressure on exhaust emissions were studied. The influence of H2 addition upstream the catalyst on engine-out emissions produced from HCCI lean operation at 1500rpm was analysed.

Chapter 5: Effect of composite after treatment catalyst on alkane, alkenes and monocyclic aromatic emissions from an HCCI/SI gasoline engine

This chapter covers an important aim of this study, namely the investigation into whether a prototype catalyst has the potential to reduce specifically 1, 3 butadiene and benzene emissions together with the other unregulated hydrocarbons from HCCI/SI working in both modes under lean and stoichiometric engine operation. Emission measurements and C1-C7 hydrocarbon speciation of the exhaust gases from HCCI/SI engine operation have been carried out under five engine conditions upstream and downstream the catalyst. The variables studied a) engine load effect under HCCI stoichiometric operation, b) air to fuel ratio, c) HCCI and SI combustion modes under the same load, and d) hydrogen addition upstream of the catalyst.

Chapter 6: Determination of hydrocarbons species (C_5-C_{11}) from HCCI/SI gasoline engine, equipped with prototype catalyst

In this chapter heavy hydrocarbons species (e.g. p-xylene, ethyl benzene, naphthalene, and methylnaphthalene) were analysed along with the other chemical compounds from HCCI and SI combustion.

Hydrocarbon speciation (C5 to C11) of the exhaust gases from HCCI/SI engine operation before and after the catalyst was carried out. The conditions studied here are a) engine load effect under HCCI stoichiometric conditions; b) air to fuel ratio (stoichiometric and lean), c) HCCI and SI combustion modes under the same load and d) hydrogen addition upstream of the catalyst.

Chapter 7: Determination of carbonyl species with 2,4-Dinitrophenyl-hydrzine method from HCCI/SI gasoline engine, equipped with prototype catalyst

This chapter describes whether a prototype catalyst has the potential to reduce specifically formaldehyde, acetaldehyde, acroline and benzaldehyde emissions together with the other aldehydes compounds in HCCI/SI modes under lean and stoichiometric engine operation. Emission measurements and aldehydes speciation of the exhaust gases from HCCI/SI engine operation have been carried out under five engine conditions before and after the catalyst. The variables studied here have been a) engine load effect under HCCI stoichiometric operation, b) air to fuel ratio, c) HCCI and SI combustion modes under the same load, and d) hydrogen addition upstream of the catalyst.

Chapter 8: Conclusions and recommendations

Conclusions resulting from the work presented this thesis are discussed and the most important findings summarised in this chapter. Suggestions for future work are also discussed.

CHAPTER 2:

LITERATURE REVIEW

2.1 Introduction to gasoline emissions

Early in 1952 Haagen-smit was the first researcher in USA who linked the air pollution to the automotive industry [11]. The spark-ignition engine exhaust gases contain oxides of nitrogen (nitric oxide, NO, and small amounts of nitrogen dioxide, NO_2- collectively known as NOx), carbon monoxide (CO), and organic compounds which are unburned or partially burned hydrocarbons (HC). The relative amounts depend on engine design and operating conditions. The formation of nitric oxide occurred throughout the high-temperature burned gases. During the combustion NOx forms behind the flame through chemical reactions involving nitrogen and oxygen atoms and molecules, which do not attain chemical equilibrium. The higher the burned gases temperature, the higher is the rate of NO formation. As the burned gases cool down during the expansion stroke the reactions involving NO freeze, and leave NO concentrations far in excess of levels corresponding to equilibrium at exhaust conditions [12]. Carbon monoxide also forms during the combustion process. With rich fuel-air mixtures there is insufficient oxygen to burn fully all the carbon in the fuel to form CO_2, also in the high-temperature products, even with lean mixtures, dissociations ensure there are significant CO levels. Later in the expansion stroke, the CO oxidation process also freeze as the burned gas temperature falls. The unburned hydrocarbon emissions have several different sources, for example, during compression and combustion the increasing cylinder pressure forces some of the gas in the cylinder in to the crevices, or narrow volumes connected to the combustion chamber, the volumes between the piston rings and cylinder wall are the largest. Most of this gas is unburned fuel-air mixture, much of it escape the primary combustion process because the entrance to these crevices is too narrow for the flame to enter. This gas, which leaves these crevices later in the expansion and exhaust processes, is one source of unburned hydrocarbon emissions. Another possible source is the combustion chamber walls. A quench layer containing unburned and partially burned fuel-air mixture is left at the wall when the flame is extinguished as it approaches the wall. There are also some sources of unburned hydrocarbons which are believed to be, any engine oil left in a thin film on the cylinder wall, piston and perhaps on the cylinder head. These oil layers can absorb and desorb fuel hydrocarbon components, before and after combustion, respectively, thus permitting a fraction of the fuel to escape the primary combustion process unburned.

Homogeneous Charge Compression Ignition (HCCI) engines are being investigated widely because they can provide both high diesel-like efficiencies and ultra-low NOx and particulate emissions. However, there are several technical challenges that must be overcome before this promising technology is commercially viable. One significant challenge is that HCCI engines produce emissions of unburned hydrocarbon (HC), oxygenated hydrocarbons (OHC), and carbon-monoxide (CO) [1].

Several works have concentrated on different methods to eliminate or reduce the internal combustion engines emissions. The focus in this research will primarily be on the hydrocarbons (their formation, effects, and removal).

2.2 Emissions in gasoline engines

2.2.1 Nitrogen Oxides Emissions (NO_x)

The formation of Nitric oxide (thermal) is fully explained by the mechanism proposed by Zeldovich ,Heywood 1988 [12].

$$O + N_2 \Leftrightarrow NO + N \quad \text{(2-1)}$$

$$N + O_2 \Leftrightarrow NO + O \quad \text{(2-2)}$$

$$N + OH \Leftrightarrow NO + H \quad \text{(2-3)}$$

Oxygen atoms are produced by the unimolecular thermal decomposition of molecular oxygen, chemical kinetics shows that NO_x increase sharply with increasing flame temperature. However, the most important engine variables that affect NO emissions are the fuel/air ratio, the burned gas fraction of the in-cylinder, unburned mixture, and spark timing. The burned gas fraction depends on the amount of diluents such as recycled exhaust gas (EGR) used for NOx emissions control, as well as the residual gas fraction. Reducing the burned gas temperature is an effective means to limit NOx emissions. The dilution effect, combined with replacement of air with the exhaust gases CO_2 and H_2O which have higher heat capacities leads to lower combustion temperatures and hence reduced NOx formation [1]. Advancing the ignition timing in spark ignition engines causes the combustion process to occur close to top dead centre and will cause an increase in the level of NOx emissions. Advancing timing in lean mixture has strong effect on the increase of NOx emissions but has less effect for a rich mixture[13-14].

2.2.2 Carbon monoxide emissions (CO)

When a hydrocarbon fuel burns completely, the oxygen in the air combines with the hydrogen to form water (H_2O) and with the carbon to form carbon dioxide (CO_2). If the burning is not complete, then some of the carbon atoms only combine with one oxygen atom rather than two, to form carbon monoxide (CO), a highly poisonous gas.

During combustion process in an oxygen starved environment, there is a shortage in oxygen present to completely oxidize the carbon atoms of CO in to carbon dioxide (CO_2). If carbon atoms only bond with one oxygen atom, carbon monoxide (CO) will be formed. Emissions of CO are therefore influenced primarily by the air-fuel ratio relative to the stoichiometric proportions. Fuel-rich combustion invariably produces CO, and emissions increase nearly linearly with the deviation from stoichiometric engine operation [15]. Early results reported by Dec 2002 [16] predicted that for low loads, incomplete bulk-gas reactions should play a significant and perhaps dominant role in CO emissions, and contribute to HC emissions.

2.2.3 Hydrocarbon Emissions (HC)

Hydrocarbons escaping the combustion are quite simply, raw unburned fuel. When the engine is misfiring, there is a poor combustion occurring during the engine strokes which results in emitting a huge amount of hydrocarbon from the combustion chamber. Another source of hydrocarbon called wall quenching which occurs when the flame propagation front burns close to the cool walls of the combustion chamber [17]. The wall cooling extinguishes the flame appearance just before most of the fuel is completely burned; leaving behind a very small amount of hydrocarbon to exit through the exhaust valve, some of the excessive hydrocarbons is presented by the deposits of the combustion chamber. As long as these carbon deposits become porous, so the hydrocarbon is pushed into these pores at the same time when the air/fuel mixture is compressed during the compression stroke. During the combustion the existed fuel does not burn; however, at the beginning of the exhaust stroke, these unburned hydrocarbons are forced in to the exhaust stream. The excessive hydrocarbon emission is also affected by the intake air temperature which has a great influence on the air/fuel mixture as it enters the combustion chamber. Any excessive low intake air temperature will lead to poor homogeneity of fuel and air mixture, resulting in partial engine misfire. Essential components of unburned hydrocarbons are aromatics (benzene, toluene, and ethyl benzene), olefin (e.g. propene, ethylene), acetylene and paraffines (e.g. methane).

Varying the geometry of the piston top-land crevice is one of the main factor which could affect the source of the HC emissions using (premixed HCCI using iso-octane) [18]. New way of controlling hydrocarbon emissions at cold start from single cylinder spark ignition engine, using a partially ceramic coated piston, showed that, the coated piston surface temperature has increased up to 100 ºC during the cold start, which will lead to an increase in the air/fuel mixture temperature in the crevice and wall quenching regions. [19]

The influence of modifying the bowl of the piston head to get a narrow spray angle and advanced injection timing using HCCI combustion in dim ethyl ether fuelled diesel, showed that, the injection timing has significant effect on NOx. HC, and CO emissions, NOx emissions after the start of injection show a low value, and the incomplete combustion in the bowl and crevice region is responsible for the increase of HC and CO emissions [20]

HCCI combustion is very sensitive to intake charge temperature and cylinder wall temperature, changing the wall temperature may have less effect on the inlet charge temperature. HCCI combustion stability depends on wall temperature rather than intake temperature, decreasing the intake temperature will retard the timing so the burn rates change primarily as a function of ignition timing and reduce combustion efficiency in HCCI operation. On the other hand, any reduction in wall temperature, will lead to more reduction in the bulk burn rate and higher combustion variations due to retarded ignition [21]. The influence of injection timing and ignition timing on regulated emissions from a direct-injection SI with fuelled methanol were significant, and the affect of injectors nozzle parameters on emissions HC, CO, and NOx were very obvious, the smaller nozzle diameter the lesser HC, and CO emissions [22]. Systems that provide variable timing, for examples inlet valves have a widespread use; advancing the inlet opening timing will in this case yield low HC emissions at high loads. At low loads, retarding the inlet opening is preferable as a means of minimizing HC emissions [23] . Hydrogen addition on combustion and engine-out emissions from SI gasoline engine at lean conditions shows that, brake thermal efficiency was improved at wide range of lean operation after hydrogen addition may hydrocarbon, carbon dioxide emissions were reduced, but NOx emissions increased due to the higher combustion temperature after hydrogen addition[24] .

Use of a catalytic converter currently constitutes the most efficient way of reducing pollutant emissions of spark-ignition engines. The drawbacks of such a system, especially in terms of fuel economy, design complexity and costs, have led to a desire for alternative solutions. One of the solutions was introduced was a lean-burn engine concept, which showed evidence that the NOx and CO components are reduced significantly when operating the engine at an air-fuel ratio of less than 1. Hydrocarbons increase as the air/fuel ratio is raised especially when approaching the misfire limits of the air-fuel mixture. The resulting increase of HC concentrations however is a definite disadvantage [25] .

Another source of HC emissions is combustion chamber deposits (CCD) which are derived from the fuel and oil usually formed on all internal surface of a spark-ignition engine. Interest in combustion chamber deposits (CCD) and their effects on engine emissions has increased as fuel and additives technology to control deposits in other parts of the engine has matured. An increase of up to 25% in NOx emissions, where the observed increase was dependent on the fuel structure. The increase is related to the increase in bulk gas temperature brought about by the CCD [26]. The effect of lubricants oil on CCD formation was stronger than that of the fuel, and most of the CCD come from the detergent dispersant which is used as lubricant oil additives, the influence of CCD formation under low pressure condition is greater than the deposit formed under high pressure [27]. However the effect of CCD on both CO and HC emissions is not clearly established. The high level of the cold-start emissions, particularly HC is influenced by engine design, a careful attention to design is important to minimize crevices associated with the piston ring pack, cylinder head gasket and spark plug. The coolant flow should be also minimized to enhance warm-up as well as variable valve timing should be used to minimize exhaust residual gases at light load [28].

The influence of engine deposit removal by decarbonisation on the exhaust CO and HC emissions from gasoline engines was highly recommended, HC, CO emissions could be reduced using decarbonisation method by 18% for HC and 29% for CO emissions [29].

2.2.4 Carbon Dioxide Emissions (CO2)

With the growing concern over the impact of CO_2 emissions on global climate change, many researchers have attempted to identify and quantify the under lying forces that affect of aggregate CO_2 emissions in a country or region, Carbon dioxide ($CO_{2)}$ contributes to long-term environmental damage caused by atmospheric changes (known as global warming or the greenhouse effect). Carbon dioxide occurs naturally in the atmosphere and is a normal product of combustion. Excessive concentrations may lead to suffocations. Ideally, hydrocarbon fuel combustion should only produce CO_2 and H_2O. The carbon dioxide emissions can be reduced by reducing the fuel's carbon contents, or by improving the fuel efficiency of the engine.

2.2.5 Particulate matter (PM)

The particulate matter (PM) in raw exhaust gas emitted by engines primarily consists of soot which is a complex material with a complex structure. Soot consists of a carbonaceous core with an agglomerate structure that is formed in the combustion chamber by incomplete combustion [30] [31] . The core has a graphite-like structure, ashes from the metals present in the lube oil or from engine wear are enclosed in the carbonaceous core [32]. Components of sulphur present in the fuel and in the lube oil can be adsorbed on the carbonaceous core, but sulphur components also form particles (partially sulphuric acid aerosol droplets). Water from the combustion process is also present on the surface of the carbonaceous core. The relative amounts of these compounds may differ considerably with different engines and engine operating conditions. Some studies about the effect of ethanol blended with diesel on PM emissions and smoke from diesel engine showed that, when increasing ethanol in the blended fuel the PM and smoke get reduced [33] .

2.2.6 Fuel components

Recent studies show that the chemical composition and magnitude of vehicle exhaust emissions can be directly related to the composition of the gasoline used. Gasoline fuel consists mostly of aliphatic hydrocarbons obtained by the fractional distillation of petroleum, enhanced with iso-octane or the aromatic hydrocarbons toluene and benzene to increase its octane rating. Olefins content in the fuel is used to maximize the gasoline yield from crude oil. The amount of olefinic hydrocarbons blended into a finished gasoline can range from 5 to 20% [34].

Olefins have been shown to be more photochemical and active than paraffin. Therefore, olefins in the fuel have been a target for control or reduction in regulated reformulated gasoline composition. Low molecular weight olefins found in exhausts have been proven to be partial combustion products of paraffin. Hence, the removal of fuel olefins is no guarantee of low olefin exhaust emissions. Even highly exaggerated olefin concentrations in a fuel do not significantly alter the ozone forming potential of exhausts, compared with a more conventional paraffinic fuel of the same volatility [34]. Since aromatic hydrocarbons have a research octane number (RON) of more than 100 and a motor octane number (MON) generally greater than 90, the addition of aromatic fractions is one means employed in refining to achieve the knock resistance levels required by modern automotive fuels. As for gasoline in use, some fuel components may has significant amount of ethanol, and some other fuel contain quantities of additives like methyl tertiary butyl ether (MTBE) as an anti-knock agent to increase octane number or as an oxygenate to reduce exhaust emissions [35].

The stability of the aromatic ring means that the exhaust contains a fraction of the benzene in the fuel. This fraction is directly proportional to the content of the fuel. In addition, the aromatics in the fuel play a role in the exhaust emissions of polycyclic aromatic hydrocarbons (PAH), and aromatic aldehydes, which increase with the aromatics, whereas formaldehyde decreases [36]. Pollutant emissions such as benzene are primarily a dealkylation product formed from toluene and xylenes during the combustion process, and an incomplete combustion product of toluene and other alky-benzenes [37]. Unlike other unregulated hydrocarbons, 1,3-butadiene is a photo-chemically reactive compound [38]. It is a by-product of partial HC oxidation, with 90% of the 1,3-butadiene in the engine exhaust coming from common alkanes and aromatic constituents of the fuel. The USEPA has classified 1,3-butadiene as a group B2 carcinogen, which means that it is a probable human carcinogen [10].

2.2.7 Carbonyls

By definition these are compounds containing a carbon atom connected to an oxygen atom (C=O) in their molecule, namely aldehydes and ketones. Ketones are compounds that are practically absent from combustion effluents, especially in exhaust gases. Their presence in the atmosphere is essentially due to their use as solvents. By contrast, aldehydes are products of the incomplete combustion of carbon compounds, gas, gasoline, diesel, etc. hence they are found in automotive exhausts. The main aldehyde most frequently found in air is formaldehyde (HCHO), which is formed in the atmosphere by a reaction between the hydroxyl radical and methane. Formaldehyde is the lightest aldehydes on gasoline-fuelled vehicles emitted in engine-out exhaust [39]. It has been found that aldehydes account for 2.5% by weight of the hydrocarbons emitted in the gasoline engine-out emission[40].

2.3 Health Effects

The contribution of automotive emissions to air pollution and human health is an important issue which cannot be ignored, nor can its potentially harmful consequences with high-risk to people tolarated. Nitrogen oxide (NO) is by itself non-toxic. The harmful effect of NO stems from its role as an NO_2 precursor, and can penetrate deeply in to the pulmonary system [41]. When air is present NO is oxidised to form NO_2 and with high concentration of ultra-violet concentration it forms photochemical smog [42], hazardous effects on people in good health result from concentrations of nitrogen oxides of over 0.05 ppm (expand) for an exposure of 24 hours.

The toxicity of CO is relatively well known, it causes death above 1000ppm. Harmful effects can be caused even at lower concentrations, due to its affinity for blood haemoglobin which is 240 times greater than that of oxygen [43]. This result in reducing the oxygen supply to the tissues causes the human body problems. Human health is mainly affected by unsaturated hydrocarbons. The olefins are liable to undergo partial metabolic conversion, converting them to genotoxic epoxides [44]. Monocyclic aromatics hydrocarbon (e.g. benzene) is a well-known haematotoxic and occupational exposure to it can cause leukemia. The occupational maximum exposure limit in the United Kingdom (MEL) and the United States permissible exposure limit (PEL) was 10ppm based on the association of benzene exposure with aplastic anaemia, but recently was lowered to 5ppm and 1ppm respectively, reflecting a concern about the risk of neoplasia [45]. Based on the epidemiological evidence, benzene is considered as a human carcinogen (group 1) by the LARC, the international agency for research on cancer [8]. Aldehydes are widespread environmental and industrial compounds, which causes tissue damage and carcinogenicity leading to different diseases and visual complications. The unsaturated aldehydes are more toxic than saturated aldehydes [46] .The substances resulting from automotive pollution are mainly formaldehyde (HCHO), acetaldehyde (CH_3CHO), and acrolein ($CH_2=CHCHO$). It has been demonstrated that exposure to formaldehyde alone induces a high nasal cancer response in rats [47].

The US Clean Air Act, promulgated in (1990) has tightened controls on total organic emissions and specified four individual species (formaldehyde, acetaldehyde, benzene, and 1,3-butadiene) as a toxic air pollutants which may cause cancer, and therefore , they will be subject to future controls [48].

2.4 Impact on the environment

The case for stringent mobile source controls has always been driven in large part by the phenomenal volume of air pollution emitted by mobile sources, a factor as important in 2010 as it was in 1970. Despite five decades of regulation, mobile sources continue to be most responsible for the air pollution problems. The contribution of mobile sources to air pollution fall under five areas in particular. First, mobile sources are the single most important cause of ozone pollution; ozone on ground-level is formed when emissions of volatile organic compounds (VOCs) and nitrogen oxides (NOx) react in the presence of sunlight. This happens particularly during the summer when the UV sunlight intensity is greatest [49] .The same NOx emissions that cause ozone pollution also contribute significantly to acid rain and particulate pollution. Roughly one-third of acid rain results from NOx emissions. Acid rain occurs when sulphur dioxide and nitrogen oxides are emitted into the atmosphere, undergo chemical transformations and are absorbed by water droplets in clouds. Acid rain remains a major contributor to the deforestation problem [50].

Mobile sources emit most of the carbon monoxide (CO) pollution-seventy percent and even more than ninety percent in many urban areas. Carbon monoxide is the second most widespread air pollutant in the United States, and is dangerous because it deprives the heart and brain of oxygen. Mobile sources are the single most important source of toxic emissions. Their carcinogenic emissions include diesel particulates, butadiene, benzene, and formaldehyde. In total, mobile source emissions are responsible for more than half of the cancer caused by air pollution. Finally, the automotive industry is one of the biggest contributors to the global air pollution problems of ozone depletion and global warming. The major environmental problems that are caused by nitrogen oxides (NO_x) are: the formation of acid rain and the resultant acidification of aquatic systems, ground-level ozone (smog), and general atmospheric visibility degradation. Acid rain remains a major contributor to the problem of deforestation which is considered one of the most important ecological problems [50]. Ozone is important component in the earth atmosphere, but with on the ground it is a pollutant and has a negative effect on the environment. Twenty six individual volatile organic compounds were measured, alkanes, alkenes, aromatic hydrocarbons, aldehydes, alcohols, and CO by adding them in to reactive organic gas (ROG) – Nox-air environmental chamber irradiations, representing a simple model of photochemical smog system. Results showed that, addition of formaldehyde, methanol, alkenes, and methy benzene increased integrated OH radical concentrations, and caused NO to oxidize and ozone formation per molecule reacted. The dsaturated n-alkanes (C_{6+}) had strong inhibiting effects on HC radicals [51].

Hydrocarbon species have different photochemical reactivity, the reactivity (R) of the exhaust is defined by the product of the total mass (M) of the organic emissions and the specific reactivity (SR) of the grams of ozone formed by photochemical reactions in the atmosphere per gram of organic species emitted by a vehicle. The reactivity of each organic exhaust species has been defined by its maximum incremental reactivity (MIR) factor. As reported by California Environmental

Protection Agency 2010 (CEPA) Table 2.1 present selected hydrocarbon compounds with their maximum incremental reactivity (MIR) values.

Table 2.1 Maximum incremental reactivity factor for selected HC compounds

Organic Compounds	MIR [g ozone/g HC]	MIR Value [g ozone/g HC]
Alkanes	(year 2001)	(year 2010)
Methane	0.01	0.014
Ethane	0.31	0.28
Propane	0.56	0.49
n-butane	1.33	1.15
Iso-butane	1.35	1.23
n-pentane	1.54	1.31
Iso-pentane	1.68	1.45
n-hexane	1.45	1.24
n-heptane	1.28	1.07
n-octane	1.1	0.90
Alkenes		
Ethene	9.08	9.0
Propene	11.58	11.66
1-butene	10.29	9.73
Iso-butene	6.35	6.29
1,3 butadien	13.58	12.61
1-pentene	7.79	7.21
1-hexene	6.17	5.49
Aromatic HCs		
Benzene	0.81	0.72
Toluene	3.97	4.0
Ethyl benzene	2.79	3.04
p-xylene	4.25	5.84
Naphthalene	2.04	2.12
Methyl naphthalene	4.61	3.06
Oxygenated organic		
Formaldehyde	8.97	9.46
Acetaldehyde	6.84	6.54
Acroline	7.60	7.45
Acetone	0.43	0.36
Furan	16.54	9.15
Crotonaldehyde	10.07	9.39
Pentanal	5.76	5.08
C_5 aldehydes	5.76	5.08
Hexanal	4.98	4.35
Benzaldehyde	0.0	0.0
C7 aldehyde	4.23	3.69
C8 aldehyde	3.65	3.16

2.5 Legislative features

Automotive exhaust emissions are covered by regulations in most industrial countries. Over the years, the number of regulated pollutants has steadily increased, and the statutory limits have become more severe. The first regulations in the United States, which were enacted in California in 1959, eliminated crankcase emissions (blow-by) and limited CO and HC [52]. The standards, which initially covered carbon monoxide and unburned hydrocarbon emissions were later extended in 1970 to nitrogen oxides, and particulates, which subsequently covered diesel engines. The latest Clean Air Act Amendment concerns toxic air pollutants, i.e.benzene, 1-3 butadiene, formaldehyde, acetaldehyde, and polycyclic organic matter (POM), and the total content of these pollutants must be reduced by 15% in the future.

Road transport in Europe and elsewhere is the main contributions to air quality problems through automotive emissions, to preserve air quality, vehicles should meet certain standards for engine exhaust emissions before they get approved for sale in the European Union. The new emissions standards already helped achieve significant reduction in air pollution from cars [53]. EURO 5/6 standards (2009/2014) represents the European NO_x, PM, CO, and HC emission standards for light gasoline passenger cars as shown in Figure 2.1and Figure 2.2.

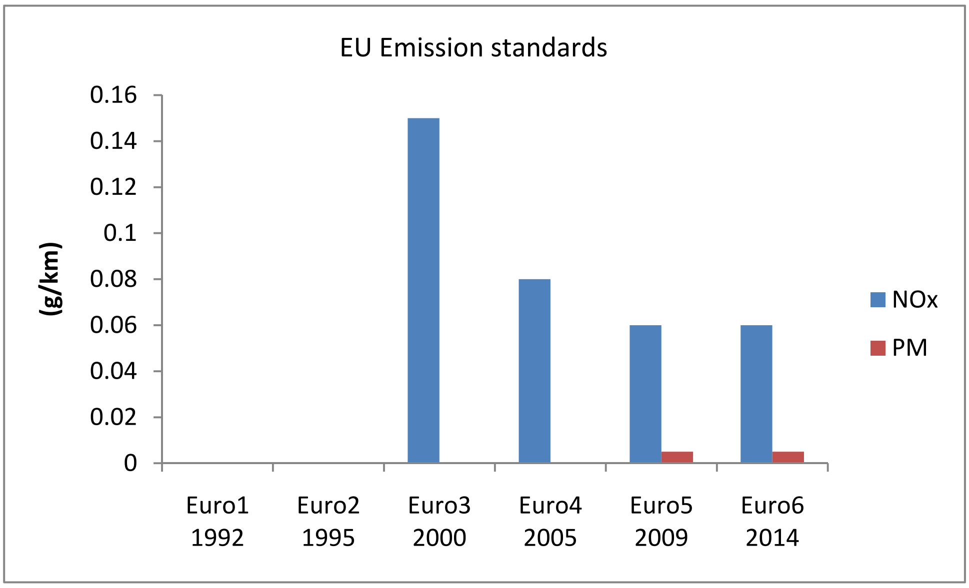


Figure 2.1: European particular matter (PM) and nitrogen oxides (NOx) emission standards for gasoline light passenger cars.

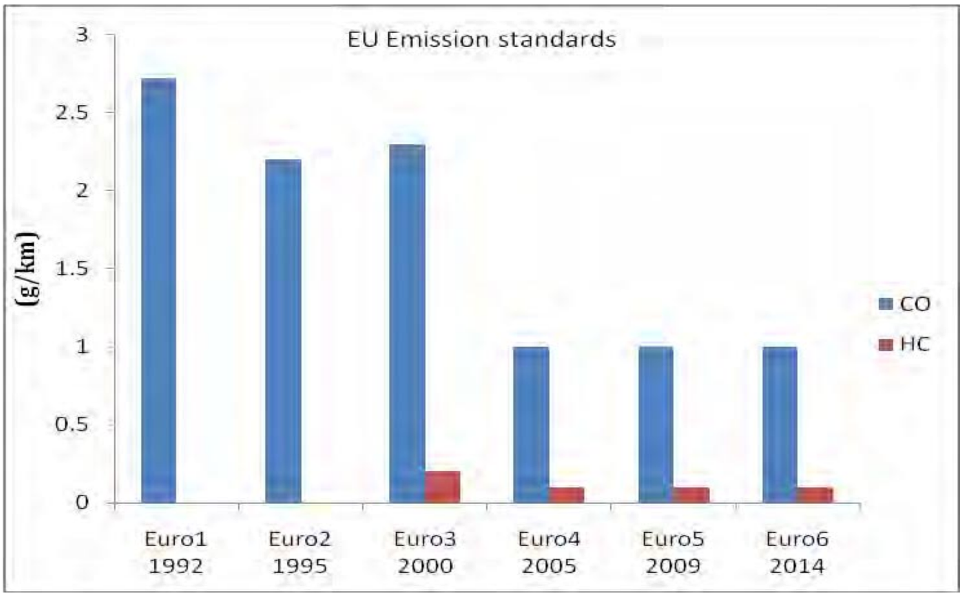


Figure 2.2: European Carbon monoxide (CO) and Hydrocarbon (HC) emission standards for light gasoline passenger car.

2.6 Catalytic converters

Regardless of how perfectly the engine is operating, some harmful combustion products are normally produced. This brings the need to apply a Three-Way Catalytic

(TWC) converter. This catalytic converter normally is located in-line with the exhaust system after the exhaust manifold and is used to bring a desirable chemical reaction to take place in the exhaust flow. Essentially, the use of catalytic converter is to complete fully the oxidation process for carbon monoxide and hydrocarbon (HC), and in addition it works to reduce the oxides of nitrogen (NOx) back to simple nitrogen and nitrogen dioxide. The conventional Three-way catalyst (TWC) converters as seen in Figure 2.3 control CO, HC, and NOx effectively (80 to 90%) efficiency) at or close to the stoichiometric air/fuel ratio which is normally used in the spark ignition engines [12]. With the availability of air NO is oxidised to NO_2, as a rapid conversion takes place at high concentrations. Catalytic converters which are used in most spark-ignition engines are mainly active catalytic material accommodated with a very special designed metal casing; this casing guides the exhaust gas flow through the catalyst bed. The noble metals are used to activate material employed for CO and HC oxidation or NO reduction, these noble metals must be distributed over a very large surface area, so that the mass transfer characteristics which are presented between the gaseous phase and the active catalyst surface is sufficient to achieve high conversion with high catalytic activity. The hydrocarbon adsorption capacity of zeolites has been studied by Kanazawa 2004 on three-way catalyst to meet more stringent environmental regulations, results showed that, the hydrocarbon increased with reducing aluminium content. Zeolites which had a pore size approximately 0.1nm larger than the diameter of the hydrocarbon molecules presented the best performance[54]. Regarding different catalyst types and models, the two most common products presented in the market are ceramic and metallic substrates.

At present, the monolith is the common option for most of the environmental applications where high flow rates and low pressure drop are needed. Foil metallic monolith substrates are becoming more fashionable. Both substrates have relatively low porosity that makes them unsuitable as a catalyst support as seen in Figure 2.4. To overcome this, a thin layer of a porous material is applied to the channel walls. This layer (typically about 20–150 µm thick) is referred to as washcoat. A commonly used washcoat material is γ-Al2O3 with a surface area of about 100 m2/g. A useful review on the preparation technologies for coating ceramic and metallic monoliths may be found in Vergunst et al 2001[55] and Avilla et al 2005 [56].The most important mechanical properties of automotive converter substrates are the thermal shock resistance and the coefficient of thermal expansion. In automotive industry applications, ceramic monoliths are mostly made from synthetic cordierite (2MgO $2Al_2O_3$ $5SiO_2$ – 14% MgO, 35% Al_2O_3 and 51% SiO_2) that have a significantly low thermal expansion coefficient and are highly resistant to fracture due to thermal shock [57]. Cordierite material has high melting temperatures, around 1450 ^{0}C, and is also resistant to oxidation.

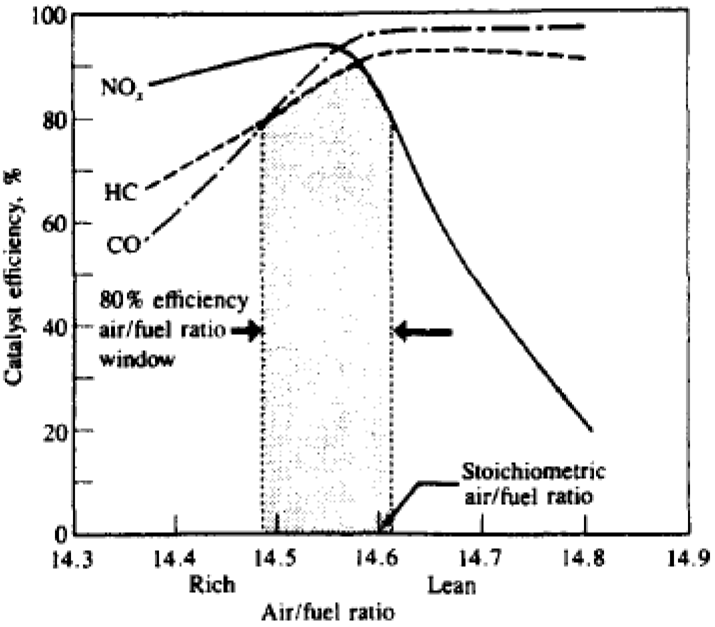


Figure 2.3 : Conversion efficiency of NO, CO and HC as function of the air-fuel ratio in a three way catalytic converter [58].

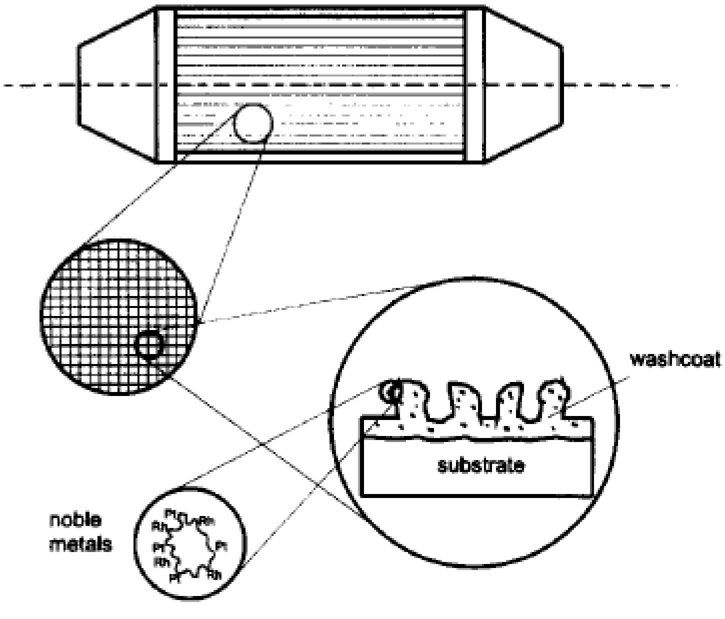


Figure 2.4: Structure of the monolithic catalytic converter

Initial use of ceramic monoliths started in the mid-1970s when the catalytic converters were installed in new vehicles in the USA. Until 1980, all automobile manufacturers used ceramic monoliths in their catalytic converters [59].

Studies reported by Umehara et al, 1997 [60] and Schimdtet al,1999 [61] regarding ceramic substrates showed the benefits to the conversions of increasing geometric surface area by means of both increasing cell density and reducing thermal mass with thin walls. Umehara et al, 2000 [62] found that the effect of cell density varies with the exhaust conditions. Specifically, they found that increasing the geometric surface area is more important under high exhaust flow conditions. Moreover, these authors also concluded that high geometric surface area favours high conversion of pollutants when the conversion rate is controlled by bulk mass transfer.

The majority of the present day monolithic three way emission control catalysts for gasoline engines use a combination of platinum and rhodium as precious metal components. There has been a keen interest lately in replacing a part or all of the platinum content of an automotive catalyst by palladium, mainly as a means to reduce the precious metal cost of the catalyst.

Apart from the precious metals, the 3WCC alumina washcoat also contains some other components, which function as catalytic promoters or stabilizers against ageing. Cerium is normally found in large quantities in the washcoat (order of 30% w. Or 1000g/ft^3) and has multiple functions: stabilization of the washcoat layer and improvement of thermal resistance, enhancement of precious metal catalytic activity, promotion of the water-gas shift reaction and function as an oxygen storage component[63-66].

Several studies carried have been on TWC improvements, for example Brisley et al 1999 [67], compared a new platinum – rhodium TWC with an advanced palladium – rhodium catalyst on an engine test bed. Their results showed that, the new platinum – rhodium catalyst gave equivalent or better performance at similar total precious metal cost. Tamura et al 2001[68], have developed a new NOx-trap catalyst to satisfy the required higher catalyst performance under high- temperature conditions. They used a catalyst containing potassium which is excellent for NOx storage capacity under high temperature region, and they also mixed Zeolite in the catalytic layer to retain potassium stability, as well as coating the substrate with silica. The new catalyst has been proved to have improved NOx conversions efficiency. Hiramoto et al 2003 [69] developed HC- adsorption three way catalyst (TWC) and an adsorption system that reduce cold – start HC emissions , by optimizing the conversion catalyst layer composition to match different catalyst operating conditions. The HC trap efficiency of the new system has improved by at least 50%. Gong et al 2006 [70] based on simulation model studied the impact of monolith geometric parameters, ellipse ratio , and convertor length on three way catalytic converter, they reported that, decreasing the ellipse ratio and, increasing the converter length and cross-section area has a favourable effect on catalyst conversion efficiency.

Santos et al 2007 [71] investigated the ceramic and metallic three way catalyst convertors and compared them to assess the effect of the substrate geometrical and physical parameters on the catalytic conversion of the engine-out exhaust gases.

Their experimental data showed that, at low space velocities, the ceramic substrate presents higher conversions, particularly for HC and CO, as compared to the metallic substrate. On the other hand at high space velocities the metallic substrate presents better conversion as compared to the ceramic one. Tanikawa et al 2008 [72] developed advanced TWC technology by optimizing the washcoat characteristic using thermally durable Ce-Zr mixed oxide material, low thermal mass and macro pores are incorporated in to the washcoat. An experimental result reveals that, the developed catalyst has higher light – off performance and hot – NO conversion efficiency. Aoki et al 2009 [73] developed a double layered TWC loaded with Pt and Rh suppresses Pt-Rh alloying. Results showed a double – layered catalyst capable of lowering the amount of noble metal used by 40% compared with a conventional catalyst. HCCI gasoline engines after treatment study is limited, for example Erlandsson et al 2000 [74] used a Fe Cr alloy mesh – type catalyst to reduce HC and CO emissions from a 4-stroke HCCI engine. They showed that, by using EGR , the resulting exhaust gases can be treated more efficiently in the catalyst due to the lower flow and higher temperature of the exhaust before entering the catalyst. Zeng et al 2007 [75] investigated HCCI engine with piston surfaces which were coated with platinum. The results showed that, due to the catalytic coating the ignition timing is advanced, the emissions of HC and CO are decreased, while NOx emissions are elevated and the fuel conversion rate and the combustion efficiency are increased.

William et al 2008 [76] studied an oxidation catalyst under HCCI and SI operation modes, using a model gas reactor and with natural gas fuelled HCCI and SI engines. They reported that, the HCCI – tailored catalyst exhibits complete conversion of CO under HCCI engine emission conditions with various loads, and high conversion efficiency is observed for methane and non-methane hydrocarbons under SI operation mode. Macrafi et al 2010 [77] investigated the influence of fuel type (e.g. gasoline, diesel, mixture of n-heptan, and toluene), equivalence ratio, and dilution on the emission reduction from HCCI engine. In their study this effect of dilution was considered for gasoline, while the effect of equivalence ratio was considered for all the fuels. Results revealed that no significant amount of NOx was detected; on the other hand CO, O_2 and HC emissions were decreased by reducing the toluene in the fuel components and by decreasing the dilution. The opposite hold for CO_2, in their HC reduction appears to compete with reduction of the CO_2 emissions and diesel seemed to produce less CO and HC than gasoline when auto – ignited.

2.6.1 CO oxidation mechanism

In the presence of excess oxygen in the exhaust gas, an oxidation catalyst helps to conduct the following overall reaction:

$$CO + 1/2O2 \Rightarrow CO2 \quad \text{(2-4)}$$

The oxidation of CO by oxygen is generally considered to take place in four basic steps:

$$CO_{gas} \Rightarrow CO_{ads} \quad \text{(2-5)}$$

$$O2_{gas} \Rightarrow 2O_{ads} \quad \text{(2-6)}$$

$$O_{ads} + CO_{ads} \Rightarrow CO2_{gas} \quad \text{(2-7)}$$

$$O_{ads} + CO_{gas} \Rightarrow CO2_{gas} \quad \text{(2-8)}$$

Reactions (2-7) and (2-8) lead to the formation of CO2. In a rich mixture, however, the high adsorption of CO (highly polar) on noble catalysts would hinder its oxidation by oxygen. A sufficient temperature must be reached (between 100 and 200^0C) for the initiations of CO desorption in order to release catalyst sites accessible to oxygen. The oxygen dissociates, reaction (2-6), and the reaction of type (2-7) begins. This reaction releases new sites and the catalytic oxidation of CO is suddenly triggered [12, 78].

2.6.2 HC oxidation mechanism

In the presence of surplus oxygen and an oxidation catalyst the following overall reactions are carried out:

$$CxHy + (x + y/4)O_2 \Rightarrow xCO_2 + y/2H_2O \qquad \text{(2-9)}$$

The oxidation of hydrocarbon can be described by an expression similar to the one concerning CO, NO and CO tend to exert an inhibiting effect in these reactions [12, 78].

2.6.3 NOx reduction mechanism

Except at very high temperatures, the NO molecule in thermodynamically unstable, it is therefore theoretically subject to decomposition into nitrogen and molecular oxygen according to the reactions:

$$NO \Rightarrow 1/2N_2 + 1/2O_2 \qquad \text{(2-10)}$$

This exothermic reaction is nevertheless very difficult to carry out, both thermally and in the presence of a catalyst. An effective catalyst capable of reducing NO in the presence of oxygen (as in diesel exhausts) still remains to be discovered.

The problem with various catalysts (precious metals, oxides) is the partial dissociation of the adsorbed NO molecule and the dissociation products that remain strongly adsorbed on the surface of the catalysts. Desorption of the oxygen formed, limits the advancement of the reaction elevated temperatures or the presence of chemical reducing agents, which are indispensable of catalyst activity [12, 78]. These reducing agents can be the species that are present in the exhaust accompanying the NO; CO, H_2, and unburnt hydrocarbons. In particular, the hydrogen present may result from the steam reforming of CO (water shift-reaction) catalysed for example by NiO or CeO_2:

$CO + H_2O \Rightarrow CO_2 + H_2$ .... (2-11)

The reactions leading to the destruction of NO are accordingly:

$NO + CO \Rightarrow 1/2N_2 + CO_2$ .... (2-12)

$NO + H2 \Rightarrow 1/2N_2 + H_2O$ .... (2-13)

$NO(2x + y/2) + (CxHy) \Rightarrow (x + y/4)N_2 + (y/2)H_2O + xCO_2$ .... (2-14)

$2NO + 5CO + 3H2O \Rightarrow 2NH_3 + 5CO_2$ .... (2-15)

$2NO + CO \Rightarrow N_2O + CO_2$ .... (2-16)

$2NO + 5H_2 \Rightarrow 2NH_3 + 2H_2O$ .... (2-17)

$2NO + H2 \Rightarrow N_2O + H_2O$ .... (2-18)

For the oxidation of the chemical reducing agents CO, HC, and H_2 competition occurs between the oxygen produced by the dissociation of NO and the molecular oxygen present in the exhaust gas. If the partial pressure of the molecular oxygen substantially exceeds the partial pressure of the NO that is present, the rate of elimination of this NO drops considerably. This is why, with catalysts available today, it is impossible to remove the entire NO from the exhaust gases of engines with excess air (lean-burn spark ignition engines and diesel engines). On the contrary, in a rich mixture where the chemical reducing agents are present in substantial excess, atomic nitrogen resulting from the dissociation of NO can undergo a more through reduction. The main reaction involves the formation of ammonia in one of the following two ways:

$$NO + 5/2H2 \Rightarrow NH_3 + H_2O \qquad (2\text{-}19)$$

$$2NO + 5CO + 3H_2O \Rightarrow 2NH_3 + 5CO_2 \qquad (2\text{-}20)$$

2.7 HCCI Gasoline Engine Technology

The theoretical and practical roots of HCCI combustion concepts are attributed to the pioneering work carried by the Russian scientist Nikolai Semenove and his colleagues in the field of ignition in the 1930s [1]. Later in 1970, this earlier work led to the first controlled-combustion engine developed by Semenove and Gussak [79]. The apparent potential of this type of combustion process to reduce emissions and fuel consumption led to an investigation into the application of the new combustion process to a 4-stroke single cylinder engine by Najt and Foster in 1983 [80]. In 1992, Stockinger et al [81] showed for the first time that a four-cylinder gasoline engine could be operated with auto-ignition within a very limited speed and load range by means of higher compression ratio and pre-heating the intake air. The most significant progress in the adoption of controlled auto-ignition to 4-stroke gasoline engines took place in Europe around the year 2000 [1]. Over the last few years, the residual gas trapping and exhaust gas re-breathing for initiating and controlling HCCI has proved to be increasingly popular with researchers, since it appears to offer the best chance of incorporating HCCI combustion operation into a production gasoline engine.

2.7.1 HCCI operation Principle

Homogeneous charge compression ignition (HCCI) engine takes premixed air/fuel mixture as in conventional spark ignition (SI) engines and ignites the mixture by compressing it in the cylinder without a spark plug, as in conventional compression ignition (CI) engines [1]. Lean burn combustion is achieved through homogeneous mixture formation and compression ignition enabling combustion temperature much lower than that of conventional SI and CI engines as reported by Epping et al 2002[82]. Due to the lean mixture low temperature combustion, nitrogen oxides (NOx) emissions are reduced dramatically and fuel economy is improved. However, greater amounts of hydrocarbon (HC) and carbon monoxide (CO) emissions are released relative to conventional SI and CI engines. The oxidation reactions of HC and CO emissions during the expansion stroke are reduced due to the lower combustion temperature. Unlike the gasoline spark ignition gas engine or diesel engine, the homogenous charge compression ignition (HCCI) produces a low-temperature, flameless release of energy throughout most of the entire combustion chamber. The fuel mixture existed in the combustion chamber are burned simultaneously. These phenomena are able to produce power similar to conventional gas engines, with less fuel needed to do it. Heat is a necessity for the HCCI process to take place, so a traditional spark ignition (SI) mode is needed to be used when the engine is started cold to generate heat inside the cylinders and rapidly heat up the exhaust catalyst and enable HCCI engine operation. HCCI operation builds on the integration of other advanced engine technologies – some of these are already have been in production and can be used to existing gas engines.

2.7.2 Parameters affecting HCCI combustions and emissions

Homogenous charge compression ignition has advantages with regards to high thermal efficiency and low nitrogen oxide emissions and potentially will be a promising combustion method in internal combustion engines. However, HCCI still faces three challenges- ignition control, operating range extent, SI-HCCI transition and HC emissions. Even though HCCI operation at high load may be obtained, the NOx reduction benefit is very small compared with a conventional gasoline engine with a three-way catalyst. Researchers are therefore expending a great deal of effort to overcome some of these challenges. One of these challenges is ignition control , many indirect methods which could influence mixture temperature have been applied to control the ignition of gasoline HCCI combustion, Hyvönen et al 2003 [83] showed that, HCCI combustion timing could be controlled by varying intake temperature and cam phasing, and they also reported, that any increase of effective compression ratio will reduce the required intake air temperature for auto ignition. Christensen et al 1999 [84] used iso-octane and n-heptane as fuel for HCCI engine and found that, the combustion efficiency of HCCI decreased with increased compression ratio due to the lower combustion temperature during the process. They also stated that, almost any liquid fuel can be used in an HCCI engine using variable compression ratio. Fuerhapter et al 2003 [85] mentioned that SI could be used to stabilize the HCCI combustion at low load on HCCI gasoline engine. Milovanovic et al 2004 [86] found that SI might trigger auto-ignition at the transient operation from SI to HCCI under internal exhaust gas recirculation (EGR) conditions. The effect of air/fuel ratio and temperature in homogeneities on HCCI combustion has been also analysed in a hydrogen fuelled HCCI engine by Noda et al 2001 [87]. They reported that, the effect of gas temperature on ignition timing was more dominant than that of air/fuel ratio.

Using a single-cylinder engine fuelled with iso-octane at different engine conditions (e.g. intake temperatures, engine speeds, compression ratio), with premixed and gasoline-type direct injection (GDI) fuelling, the intake temperature was significantly affecting the incomplete bulk- gas combustion, may a minimal effects on engine speed and compression ratio for the used fuel was recorded, on the other hand fuel stratification by late GDI injection was found to have good potential for improving combustion efficiency [17] . Dec et al 2008 [88], conducted further work on a HCCI engine fueled with iso-octane over a range of fuelling rates and over a range of fuel stratification levels. Results show that fuel stratification improves combustion efficiency by reducing the fuel penetration to the crevice and cylinder-wall and boundary-layer regions, also by creating a locally richer mixture which will burn hotter and more completely. Bhave et al 2005,2006, [89-90] found that, CO emissions in HCCI engine are influenced by several events (e.g. fluid-wall interactions, mixing of hot and cold air fuel particles and wall temperature).

Furthermore, the inhomogenetites persisting during the combustion dictated the level of CO emissions out of the exhaust. They also mentioned that, theoretically a possible control strategy for HCCI engine can be applied, as, at low loads intake temperature heating with some residual gas trapping; and at medium loads residual gas trapping alone; and at high loads SI operation. With these conditions a stable engine operation could be achieved over the entire operating range. HCCI combustion with the help of negative valve overlap could be one of the promising implementation strategies of HCCI which is closest to production. Persson et al 2004 [91] used a naturally aspirated in-line six-cylinder operated in HCCI mode using a camshaft with low lift and short duration generating negative overlap. The inlet air temperature variation has a significant effect on HCCI combustion through the negative valve overlap, especially when the engine runs well inside of the HCCI operating range; on the other hand the effect was prominent when the engine is operated close to the border of operating range.

Another study conducted by Olsson et al 2003 [92] focused on the effect of exhaust gas recirculation (EGR) on the total hydrocarbon, NOx, and CO. They used a 6 cylinder gasoline engine modified to HCCI operation working under different operating reigns. Results showed that, CO, HC, and NOx emissions in most cases improved with EGR compared to lean operation and combustion efficiency was also improved with EGR due to lower emissions of CO and HC. Another study regarding EGR is presented by Dec et al 2002 [16] in which they report that, the main effect of EGR is to lower the compressed-gas temperature, which retard the ignition timing and slows the combustion rate, and it could also slow the kinetic rates at a fixed ignition timing. A combination of the two effects will provide maximum smoothing of the heat release. Megaritis et al [93-94] reported that, by applying forced reduction to bioethanol HCCI combustion with residual gas trapping would extend engine load of HCCI operation compared to naturally aspirated operation, they also mentioned, higher load in HCCI combustion could be achieved with lower lambdas at certain boost pressure. Another interesting point raised by them, showing a fixed-rate water ethanol blending of HCCI combustion could reduce pressure rise rate in higher engine load. Yap et al [95] showed that, internal residual gas in HCCI gasoline combustion has significant affects in lowering thermal needs for mixture auto ignition and controlling the engine load range, they also stated that, varying inlet valve timing will affect the combustion phasing which ends up with reduction in maximum pressure rise rates. Hydrogen reforming in HCCI engine combustion could lower the intake temperature to get a stable operation, introducing reformed gas to the engine will extend the lower load boundary of HCCI operation [96]. Bunting [97] investigated the effect of properties and chemistry on the combustion of gasoline HCCI engine operated near lambda = 1.0, equipped with hydraulic variable valve actuation. Results showed that fuels with higher octane sensitivity were found to ignite more easily and burn quicker than fuels with lower octane sensitivity. Many parameters can affect HCCI combustion.

Canakci [98] studied the effect of boost pressure on the performance and emissions of a DI-HCCI gasoline engine under constant air fuel ratio and intake air temperature with different engine speeds. Results showed that, exhaust temperature decreases with increasing boost pressure while combustion efficiency increased with engine speed. However, combustion efficiency was found to be higher in lower boost pressure. With, regard to exhaust emissions, CO emissions have increased with engine speed for each boost pressure, while decreasing with increased boost pressure. On the other hand HC emission decreased with engine speed and increased with boost pressure, and NOx decreased with increasing boost pressure. Marriot et al 2002 [99] investigated the influence of engine load on the HC emission, and found that, HC emissions reduced when shifting to higher load due to the higher combustion temperature which promote to complete oxidation. Another major issue of HCCI is to control the rapid combustion which has no flame propagation, so the quantity of fuel injected could be used to obtain higher power output. Controlling ignition timing is another issue because it is substantially affected by chemical reaction of the fuel. Several approaches have tried to expand the range of stable engine operation, including the use of a blend of two types of fuel with different ignition characteristics. This was studied by Saitou et al 2010 [100], who focused on the use of a mixture of two fuels, with different ignition characteristics, n-heptane (0RON) which is readily auto ignitable fuel and iso-octane (100 RON) as a fuel non conductive to auto ignition. They reported that by using this approach, the fuel injected could be increased while controlling the ignition timing. Starck et al 2010 [101] employed a set of fuels using a base fuel with different cetane numbers (from 33-40) and different chemical compositions (by the addition of reactive products which are olefinic and naphthenic compounds). They showed that, when the fuel has a low cetane number, a high volatility and an appropriate chemical composition could improve the HCCI operating range of more than 30%.

To improve understanding of the possibility of HCCI emissions reduction , Machrafi et al 2008 [102] studied the effect of changing several parameters (e.g. inlet temperature, equivalence ratio, compression ratio, diluting) on the engine-out emissions. They noticed that, any increase of inlet temperature, EGR temperature, the equivalence ratio and the compression ratio, results in to a decrease of CO and HC emissions by up to 75%. On the other hand the emission of CO2 increased by about 50%; the increase of CO2 emissions could be compensated by altering the compression ratio and EGR parameters making it possible to control the emission of the HCCI engine. Komninos et al 2008 [103] simulated the HCCI combustion with a multi zone model to find the source of emissions during combustion; they reported that, most of the HC and CO emissions emitted are coming from the crevice regions, caused by gases flowing into the combustion chamber during expansion which have escaped the main combustion event.

2.8 HC Speciation

In terms of emissions, hydrocarbon speciation is a powerful tool to understand the complex reactions happening inside the cylinder during the combustion process and to observe the effects of varying the fuel composition, fuel additives, and emission control system. Using speciation data enables researchers and scientists to evaluate the relative reactivity of the exhaust and evaporative emissions. Different hydrocarbons in urban air form from differing levels of ozone (smog) which depend on the reactivity of these chemical compounds. To evaluate hydrocarbon impact on ozone formation, HC speciation is required which will also help to determine the presence of toxic emissions from the exhaust tailpipe. Using speciation data has helped researchers to make a number of non-proprietary observations about the relationships between fuel property modifications and automotive emissions.

2.8.1 Unregulated HC in gasoline engines

Internal combustion engines and gasoline have coevolved over the last 100 years, with the primary emphasis on the improvement of power, efficiency, and drivability. Lead was added to gasoline in the past to increase knock resistance and allowing higher compression ratios and greater efficiency. In the past, control has been focused primarily on the engine. Engine design has been revolutionised, most notably through the introduction of computer control. The main change which occurred was related to fuel modification by removal of lead from gasoline and this has allowed the use of catalytic after treatment. The other development was the reduction of gasoline vapour pressure which has a positive effect on the control of refuelling and evaporative hydrocarbon emissions. As we enter 2011, a poor air quality standard, especially in urban areas, is still a big problem and the automotive industry is still a major contributor. An additional effort to reduce motor vehicle emissions is necessary. Gasoline is a middle distillate of petroleum, containing C_4 to C_{12} hydrocarbons. Through catalytic and hydro cracking, modern refineries convert heavy distillates of petroleum in to gasoline-blending components. Because of the extensive gasoline motor vehicle fleet and the gasoline production and distribution infrastructure, it is likely that gasoline will be the dominant motor vehicle fuel well into the next century, aside with diesel even as petroleum reserves are depleted.

In the USA in 2000 the Clean Air Act amendments required the level of toxics in reformulated gasoline to be decreased (benzene, 1,3-butadiene, formaldehyde, acetaldehyde, and polycyclic organic matter) by 25% [104-105]. Reformulated gasoline, which refers to gasoline blend or additives designed to reduce emissions, has been presented as keys to achieving lower emissions. The affects of fuel composition on emissions were known by early researchers and developers of vehicle emissions control. Koehl et al [106] review studies of the relations between fuel composition and emissions conducted over 50 years. Although emissions from gasoline-powered vehicles have been reduced significantly since 1960, we must admit the motor vehicles remain significant contributors of pollutants all around the world.

A lot of studies have been conducted by researchers regarding the HC composition of exhaust gas. One of the earliest speciation studies was done by Walker et al [107] in which mass-spectrometry was applied to the analysis of automobile exhaust gases. Another study was carried out by Coulson [108] when he used mercuric per chlorate and perchloric acid ($HCLO_4$) on granular fire brick, to remove olefins and acetylenes in the gas phase from automobile exhaust gases. Exhaust emissions have often de-emphasized the complex inter-relationship between fuel-combustion chemistry, engine design, and catalytic-convertor performance. In the past combustion- chemistry studies have been mostly limited to simple fuels in specialized laboratory engines or reactors, Olson et al [109] used gas chromatographic technique and computer technology for analysing exhaust gases from a multi cylinder gasoline engine fuelled with complex, petroleum-based fuels. A single-column GC technique was used to characterize C_5-C_{12} hydrocarbon emissions. Kaiser et al [37] conducted an important study using a single-cylinder engine fuelled with single-component fuels. The fuels included gaseous straight-chain alkenes, branched-chain liquid alkanes, toluene, and a five-component liquid-fuel blend. They showed that, both the total engine-out emissions and the distribution of individual hydrocarbon species in the exhaust gas are sensitive to the fuel used.

The percentage contribution of unburned fuel to the hydrocarbon emissions varies by changing engine operation conditions, particularly speed and spark timing. Kaiser et al [110] extended their studies to include two cyclic alkanes (cyclohexane and methylcyclohexane), a mixture of heavier aromatics containing xylenes plus methylbenzene, and a fuel-blend gasoline. They reported from the experiment that the exhaust mole fractions of both unburned fuel and direct combustion products from the fuel mixture could be predicted to within 40%, based on the emissions from the single-components fuels and the known fuel blend composition. From their results it is clear that any emissions studies of single-component fuels can be useful in estimating exhaust species mole fractions from fuel blends. The measurements of engine-out emissions from single-component fuel can provide important information regarding the effect of fuel structure on tailpipe emissions from an engine operation test. Kaiser et al [111] again extended their studies to include olefinic fuels and a mixture of a single-component hydrocarbon with a fully blended gasoline. Olefins fuel (saturated) can comprise a significant fraction of gasoline fuels, and a determination of the types of partial combustion products formed by olefinic fuels is important to gain a better understanding of the fuel effect of fuel structure on hydrocarbon emissions from spark-ignited engines. They examined three olefinic fuels and found that, the total HC emissions increased with the increasing molecular weight of the fuel. They also showed total hydrocarbon emissions from alkenes fuels were lower than those of their conjugate alkanes during lean operation.

Kaiser et al [112] carried out experimental work regarding the effect of fuel structure on emissions from a spark ignited engine. Running the engine at four steady-state conditions, they reported that, the fuel structure and the engine operating conditions affected both the total HC emissions and the reactivity of these emissions for forming photochemical smog in the atmosphere. In their experiments they identified major precursor species of the toxic HC emissions, benzene and 1,3 butadiene. Apart from fuel structure effects on emissions, engine operations play a significant effects on exhaust emissions, Kaiser et al [110], using a single-cylinder gasoline engine showed that, both retarded spark and high-speed could reduce total hydrocarbon emissions by 20-50% depending upon the fuel used. They also reported HC products were affected by air/fuel ratio, the relative abundance of methane and acetylene increased during fuel-rich operation. One more factor was that the oxidation rate of HC increases rapidly with temperature. Kaiser et al [113] used iso-octane as fuel and claimed that, the reduction of unburned iso-octane in the exhaust was as a result of increased engine speeds, whilst on the other hand the sum of olefins combustion products was increased.

The reactivity of engine-out exhaust HC emissions from a single-cylinder, spark – ignited (SI) engine using high resolution capillary GC showed an increased burn-up during retarded spark of high speed running which results in the production of less reactive combustion products (e.g. methane, acetylene, benzene, and toluene) and the specific reactivity actually decreases. Another experimental study done on a gasoline engine by Schuetzle et al [114] showed that, hydrocarbon emissions increase rapidly as fuel and air mixture becomes fuel rich. Natural gas, methanol, liquid petroleum gas (LPG), ethanol, and hydrogen are most likely alternatives as clean substitutes for gasoline, because all these fuels are compatible with current gasoline and diesel designs even with HCCI engine design with modest modifications. The attractiveness of such fuels has resulted from air-quality improvements due to their lower levels of photochemical reactivates.

2.8.2 Oxygenated HC

The hydrocarbon emissions from HCCI engines have been detected and measured as early as HCCI combustion was being investigated. Unfortunately information related to the individual chemical species comprising these emissions is scant. This is because total hydrocarbon is detected and measured using typical exhaust-gas analysers, which measures the total carbon in the exhaust HC and does not give information on species composition. Also the typical HC analysers such as flame ionization detector (FID) or GC-MS are less sensitive to carbon atoms that are bound to oxygen. Therefore oxygenated hydrocarbon (OHC) compounds give a wrong signal or even no signal for species such as formaldehyde, which only have one carbon atom bound to an oxygen atom, and as a result, the OHC compounds were not detected until more recently. Due to the difficulty in measuring OHC species, they were not detected in HCCI exhaust until 2002. Later on more studies were carried out regarding OHC from HCCI exhaust by different authors. Kaiser et al [115] carried out an experimental study of individual species in the engine – out exhaust gas from gasoline fuelled direct – injection compression ignition HCCI engine, which have been measured by GC-MS over different air/fuel ratio, and found a significant increase taking place in the emissions indices of the organic which are formed by the combustion of the major fuels components. These combustion products mole fraction increase as the air/fuel ratio becomes leaner while unburned fuel species increase with lower percentage and formaldehyde was also detected in their results as a product of methyl radical oxidation and alkoxy radical decomposition. In general the high level of formaldehyde formation observed in SI combustion is when using methanol as a fuel. According to the literature[116-117], the main reaction paths for methanol oxidation under typical engine conditions are through H-atom abstraction reactions of methanol, mainly with hydroxyl radicals ($\dot{\mathrm{O}}$ OH), but also, especially under rich conditions, with H-atoms or O-atoms. These abstraction reactions yield hydroxymethyl radicals ($\dot{\mathrm{C}}$ H2OH or $\dot{\mathrm{C}}$ H3O) that generate formaldehyde through further reactions [116]. Another work by Kaiser et al presented emissions data for many compounds of HC and OHC species for gasoline-fuelled HCCI. The trends of the few species they plotted showed that the percentage of fuel carbon in these species increases with decreased fuelling. Further work presented by Dec et al 2002[16] involved carrying out an oxygenated hydrocarbon analysis. Computational results showed that, significant quantities of the OHC species should be found in HCCI exhaust at low loads, and the concentration of these compounds should increase with reduced fuelling, due to incomplete bulk-gas combustion. With subsequent work, Dec and Sjoberg [17] detected and identified the most prevalent of these species as formic acid, formaldehyde, acraldehyde, and acetaldehyde, based on the computational results for the iso-octane. Another work related to HC speciation was presented by Poulopulose et al [118] using an internal combustion engine operating on ethanol – containing fuels, they reported an ethanol was identified in the exhaust gases only when it was present in the fuel, on the other hand acetaldehyde engine – out emission increased when ethanol was added to the fuel.

2.8.3 Oxidation processes

Under low temperature combustion, based on previous studies[119-121], there is a low- temperature reaction scheme from straight- chain saturated hydrocarbons take place as shown in Figure 2.5. The reaction is initiated by H abstraction by O2 to form the alkyl radical $\dot{R}$, then first O2 addition to $\dot{R}$ (reaction 1) and isomerisation of alkylperoxy radicals $R\dot{O}2$ (reaction 2) occur, which results in hydroperoxyalkyl radicals $\dot{Q}$OOH. Subsequently, second O2 addition to $\dot{Q}$OOH occurs (reaction 3) to form $\dot{O}$2QOOH radicals and leads to decomposition to ketohydro- peroxides (KETO) and the $\dot{O}H$ radical (reaction 4). Furthermore, KETO decomposes to aldehydes, ketones and the $\dot{O}H$ radical (reaction 5). $\dot{Q}$OOH also decomposes to cyclic ethers and $\dot{O}H$ radical by O–O scission (reaction 6), to olefins, aldehydes and $\dot{O}H$ by β-scission (reaction 7) and to olefins and the hydroperoxy radical $H\dot{O}2$ (reaction 8).

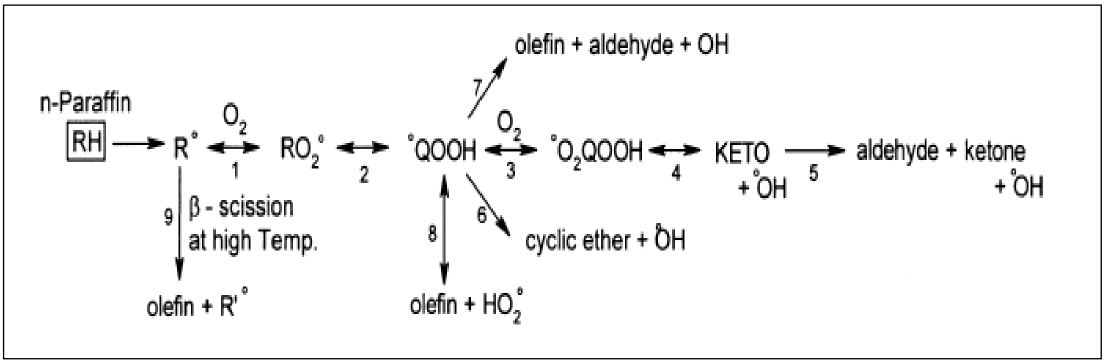


Figure 2.5: Oxidation scheme for n-paraffin fuel [120].

2.9 Sampling Techniques

The sampling technique used in gas analysis tests depends on the kind of sample analysis needed to be adopted. Sampling methods vary in their procedures which make their performance difficult to compare. All test samples in this work are related to the gases species, so sampling methods will focus on gas sampling.

2.9.1 Gas sampling

The level of interest in efficient and accurate gas sampling techniques is currently a very high priority in our study. Proper knowledge and correct implementation of methods of sampling will provide quality and high standards of HC gas analysis.

2.9.1.1 Bag sampling

Bag sampling technique could be used temporarily to store the tested sample, This method is also called (Grab Sampling). The test sample is collected in an impermeable container (evacuated bottles, syringes, and plastic, Tedlar bags), and samples should be taken direct to the analysis instrument. However some detected species are not stable if they get stored in the bag for long periods, (e.g. 1,3 butadiene) is not a stable compound if it was stored for long time [122].

2.9.1.2 On-line Sampling

The gas sample with a flow suitable to the analysis technique is transferred directly from the exhaust pipe via heated line to the gas analyzer. The heated line temperature depends on the gases being analysed. Detected species (C_1-C_{11}) should be transferred by 180 ^{0}C heated line. The sampling heated line must be heated to the desired temperature in order to prevent water condensation and minimize the sample losses, also to keep the HC sample in the gas phase state [110].

2.9.1.3 Midget Impingers and Cartridge Sampling

The midget impinger sampling technique is an essential method when sampling trace of aldehyde and ketone. Sampling procedure involves stabilizing reactive carbonyls by combining them with a derivatizing reagent during the sample process. Reagents used during the process are normally held in an impinger or on a solid adsorbent seated in a cartridge. In general, the gas sample is drawn through midget impinger which is placed in an ice bath, maintaining the sample temperature at 0 ^{0}C lowers the vapour pressure of the absorbing solution and preventing any major vapour losses. After derivatization, solvent extraction is used to recover the detected species, followed by chromatographic analysis procedures. Derivatization using 2,4-dinitrophenylhydrazine (DNPH) followed by liquid chromatographic separation is highly recommended. This method has the ability to detect the time-weighted carbonyl concentrations as low as a few parts per billion (PPB) [123]. Cartridges mainly are built from polyethylene or plastic. They have a solid inorganic sorbent which is placed as situated between mesh screens placed at the cartridge inlet and out let. The inorganic sorbents are essential medium to collect gases; the cartridge comes as blank or precoated with acidified DNPH.

2.9.1.4 In Cylinder Sampling Technique

In-cylinder sampling is a technique that can provide information on events that transpire in the cylinder, the samples get extracted from cylinder while the engine is operating, then samples are analysed to determine their composition, samples could be taken at different times throughout the engine cycle to measure and investigate how composition during the engine operation are changing with crank angle in the region being sampled, also samples could be taken at different locations in the cylinder. Three different types of valves are utilized, large valves with high flow and long duration to extract bulk quantity, and fast sample valve with low flow and short duration to extract a small portion of the cylinder mass over a short duration in order to provide crank angel resolution of cylinder composition. The last type is check valve which is implemented in applications if the pressure profile at the sampling location could be used to open and close the valve.

2.9.1.5 Adsorption Method

In this process a gas is adsorbed over the surface of solid particles. It is mainly a physical process rather than chemical one, during this process species could be removed by a solvent then analysed. Adsorption technique could be efficient as long as it allows trace components to become concentrated before analysis. Adsorption process includes activated charcoal, silica gel and porous polymers. This technique is of limited use in exhaust gas analysis, due to some gases which are not easily adorable such as, hydrogen, nitrogen, and carbon monoxide.

2.9.1.6 Condensation (Cryogenic collection)

During this process the sample is cooled down to the temperature below the boiling point, or to the freezing points of the gaseous components. In case of the hydrocarbon components exhaust gases, this is not complicated process but for a full analysis regarding other gases such as Nitrogen, Oxygen process becomes more difficult. The sample is dried before collection to prevent any water vapour could affect the results, by using liquid nitrogen as a cooling medium, plenty of gases components could be condensed.

2.10 Chromatographic Methods

The term chromatography was used for the first time by the Russian chemist Tswett (1872-1919) to describe his work on the separation of coloured plant pigments into bands on a column of chalk. The 1940s saw a lot of development regarding partition chromatography and paper chromatography with gas chromatography following in 1950. There was a rapid rise in the 1960s in the routine use of chromatography as a universal technique, especially in field of chemistry, biology and medicine [124-125]. Chromatography is a flexible powerful procedure for analysis and chemical technique for separating mixtures. The international union of pure and applied chemistry has defined chromatography as a method used primarily for the separation of the chemical components of a sample, and the components are distributed between two phases, one of which is stationary while the other one is a mobile phase which it moves. The stationary phase may be a solid, or a liquid supported on a solid, or a gel. The stationary phase may be packed in a column, spread as a layer, or distributed as a film; in these definitions “chromatographic bed” is used as a general term to denote any of the different forms in which the stationary phase may be used. The mobile phase may be gaseous or liquid [126]. The stationary phase consists of small solid particles (usually less than 150µm in diameter) with a micro porous surface, which may be packed into a column or coated on to a plate. These particles are sometimes coated with an inert chemical agent to modify the surface properties. The mobile phase serves to carry the sample component molecules through the chromatographic system. During this process the component or solute molecules in the mobile phase come into contact with the stationary phase, there is now competition between the two phases for the solute molecules which depends on their physical properties and affinity for stationary phases. This process is termed partition with each component distributed between the stationary phase and mobile phase. Data from chromatography may be used to obtain the relative concentrations of components in a mixture, providing good resolution is achieved. Peak area from integration of the detector signal during elution of a component, is proportional to concentration of that component. However, the response of detectors varies from one compound to another.

2.10.1 Gas Chromatography

It was a rapid development particularly during the 1960s, producing sweeping changes in analytical chemistry and in many areas of research and development. It was now possible to separate, quantify, and subsequently identify components in a mixture from permanent gases. Gas chromatography offers a method of obtaining very pure compounds and is used commercially in the manufacture of laboratory reagents. The instrumentation for gas chromatography incorporates the features common to all forms of chromatography, namely a mobile phase, a stationary phase and a detection system. GC utilizes a column containing the stationary phase, but requires a gaseous mobile phase, the carrier gas and a sample introducing or injection system. The detector requires an amplifier for signal processing; the variable parameters, for example, column and injection temperature, are electronically controlled. This instrument has been used for some time. Uchida et al [127] developed a GC-FID system which utilize two chromatographic columns, which has an analytical time of 2 minutes and a minimum measurement range of 0-10ppm. Another development for GC was shown by Olson et al [128] when they used a rapid gas chromatography (GC) instrument to separate light (C_2-C_4) and the midrange (C_5-

C_{12}) hydrocarbons in less than 10 minutes. Kaiser et al [129], conducted experimental tests on an HCCI engine and presented speciation data using gas-chromatography combined with aflame ionising detector (FID) or a mass spectro matography (GC-FID) and (GC-MS). They identified some individual aldehydes species (e.g. formaldehyde, acetaldehyde, and benzaldhyde). Farrugia et al [130] used a high-resolution gas chromatography (GC) instrument for speciation of individual hydrocarbons vapours in vehicle exhaust and improved it to be able to extend its application to include exhaust from low emission gasoline-fuelled vehicles. Another experimental work was conducted by Elghawi et al [131], using GC-MS technique, when they carried out a quantitative analysis of individual hydrocarbons in the range of (C1-C6) emitted in the exhaust gas of a V6 gasoline direct injection engine. Lewis et al [132] used high pressure liquid chromatography mass spectrometry (LC-MS) to speciate carbonyls as large as C_9 from light-duty diesel engine. There are several methods for hydrocarbon speciation using different columns by following two approaches, one of these approaches uses a capillary columns with liquid films (e.g., DB-1, J&W Scientific; Folsom, CA) and sub ambient injection, the other approach uses a porous-layer open-tubular (PLOT) columns which is composed of fused silica coated with aluminium oxide and deactivated with potassium chloride. The Auto-Oil Air Quality Improved Research Program (AQIRP) [106, 133] utilized a 60-mx0.32-mm DB-1 column (J&W Scientific) with a1-µm film thickness. More than 140 chemical compounds were included in the method in the C_1-C_{12} range. This type of single column approach was also used in Europe [134] and extensive results were reported by the automotive industry (Ford) in USA [37, 110, 135-136]. On the other hand further application in Europe has subsequently used PLOT columns for exhaust speciation. By combining

PLOT and liquid-film column technology, the range of compounds analysed could be extended. For example AQIRP has improved the sensitivity of the method they used, several solutions have been resolved, and the number of chemical compounds analysed was extended[137]. The improved method requires three gas chromatographs (GCs) and utilizes a PLOT column for (C_1-C_4) species. The AQIRP method uses a pre column to protect the PLOT column from heavy hydrocarbons and water; similar approach was reported by Olsen et al 1993[109].

2.10.2 High performance liquid Chromatography

The pioneering work of Martin and Synge [124] led to the development of gas liquid chromatography. The developing stature and importance of High Performance Liquid Chromatography (HPLC) is evidenced by the vast growth in published scientific papers which cite the technique as the chosen method of analysis. In comparison with GC, HPLC is not limited in applicability by component volatility or thermal stability, which makes it the method of choice for many chemical compounds and thermally unstable materials. Furthermore comparable, if not greater, separation and column efficiency can be achieved due to the greater control and choice of both stationary and mobile phase. Many detectors used in HPLC are non-destructive, thus facilitating sample recovery and providing the opportunity for subsequent spectra analytical studies. Sample introduction can be automated and detection and quantisation can be achieved by the use of continuous flow detectors; these features lead to improved accuracy and precisions of analysis. Thus it would seem that the stature of the technique is assured and it may be that it will supplant (substitute) gas chromatography as the most useful and expedient of chromatographic methods in the coming decade. Oberdorfer 1967 [138] separated total aldehydes into individual, identifiable components by chromatographic techniques from automobile exhaust gas. Later on 1979 Harrenstien [139] measured individual aldehyde and acetone emissions from the exhaust gas of a premixed multi cylinder ignition engine, using a gas chromatographic instrument. Mori et al 1995 [140] detected formaldehyde using HPLC method in tailpipe exhaust emissions from methanol fuelled-heavy-duty vehicle under steady-state driving conditions. Galante-Fox 2008 [141] conducted experimental work using HPLC to measure the concentration of an organic acide in E-85 fuel. An internal standard (maleic acid) was used to monitor HPLC system stability and peak retention time stability. This method utilizes an ultra violet (UV) detector to detect and quantify the levels of each acid in E-85 fuel.

2.11 Summary

Legislations to control hydrocarbon emissions from gasoline line and diesel vehicles have been enacted throughout the developed world. Current restrictions control the total mass of emitted non-methane hydrocarbons, CO, and oxides of nitrogen. Generally, the legislation does not require any chemical analysis of hydrocarbons. Possible future requirements may regulate the photochemical reactivity of these emissions in the atmosphere, and such a change would require the control of specific hydrocarbon species in the exhaust in addition to the total mass. Thus it is possible that new regulatory requirements might be considered for selected compounds including polycyclic organic material (POM), benzene, 1,3 butadiene, and aldehydes [142]. In addition the US Clean Air Act, promulgated in 1990 [143], has tightened controls on total organic emissions while benzene, and 1,3 butadiene as toxic air pollutants may be subject to future control. To design a power pack system to comply with the emissions standards, it is hard to understand the combined effect of engine design, catalyst design, and fuel composition on regulated emissions. A lot of effort has been expended in exploring the effects of variables related to engine design (e.g. air fuel ratio, variable valve timing, piston top land geometry and fuel injections) on hydrocarbon emissions [17-18, 89, 144]. However, individual hydrocarbons can have vastly different inherent toxicities and photochemical reactivates (or ozone-forming potentials). In USA the Californian authorities brought up a concept called " Reactivity Adjusted Emissions" [145]. In this concept the hydrocarbons are chemically analysed in order to assess effects on urban ozone formation. This legislative approach recognises for example, that the photochemical reactivity of alkenes can be much greater than that of alkanes.

The individual HC species analysis in this research covered fuel components from C1-C11, the heavier HC with C12 and above needed standards with Known concentration and identified retention time to detect more species in the engine out emissions and upstream the catalyst from HCCI/SI engine modes which was not available for this research.

CHAPTER: 3

EXPERIMENTAL LAYOUT AND TECHNIQUE

This chapter describes the experimental facilities and the emissions instruments used in this work. The description includes the experimental engine, prototype three way catalytic (TWC) converter, and emissions equipments.

3.1 Jaguar V6 HCCI Gasoline Engine

The experimental engine used in this work is a Homogeneous Charge Compression Ignition engine (Jaguar gasoline V6 directs injection), with 4 valves per cylinder (wall guided) and 3 litres swept volume as shown in Figure 3.1. The fuel used in this study was standard unleaded gasoline of RON 95, H/C=1.86; composition: alkanes = 48.26%, alkenes = 16.2%, napthenes = 3.66%, aromatics = 30.2%.

The engine is coupled with a Froude EC 38 eddy current dynamometer. The connection between the engine and the dynamometer is made by a shaft with universal CV joints at both ends. The valve-train was modified to permit operation in HCCI mode by the provision of a cam profile switching mechanism. This cam profile switching (CPS) system is used to switch between SI and HCCI modes. The variable valve timing system of the engine makes it possible to change the valve timing for the inlet and exhaust valves. An engine specification summary is presented in Table 3.1.

The use of trapped residual gas to heat up the intake charge is important to improve the mixture operation in HCCI mode. To switch between SI and HCCI modes of operation, the cam profile switching system is used. This system allows on-line switching of valve lift from 9mm (SI operation) to 3mm (HCCI) operation. The HCCI operation is achieved by internal exhaust gas recirculation (EGR), using negative valve overlap which traps exhaust gases in order to retain enough energy for auto-ignition. Exhaust gas trapping (Residual) could be a significant tool due to its application flexibility for a lot of different engine configurations; it can be also combined with the other methods for HCCI control. Implementing HCCI operation by trapping EGR leads to a typical limitation of HCCI window, at low boundary it is limited by misfire due to limited tolerance of internal EGR, for higher boundary the limitation is due to knock tendencies. The limited operating window brings the needs for the use of SI combustion outside the HCCI operating region, which forces the use of a cam profile switching (CPS) system in order to switch to internal EGR trapping. The HCCI mode starting procedure involves a warming-up period; this can be done by first operating the engine in SI mode until the crankcase lubricant and coolant temperatures reach 90^{o}C. The temperature of the intake air was controlled by a thermal management system. In HCCI mode the engine is operated with a wide open throttle. The temperature in the intake stroke at IVC is typically about 500 to 600K, about 250K higher than it would be in SI mode. To keep a stable HCCI operation during testing, the coefficient of variations (COV) of net mean effective pressure (NMEP) should be kept below 5%. A dSPACE- based system coupled to a computer using MATLAB/SIMULINK software is used to control the engine parameters during operation and to record data. Fuel flow was measured by an AVL controls gravimetric meter, and fuel injection pulse width is adjusted by the engine management system to maintain the required air/fuel ratio

Figure 3.1: The V6 SI/HCCI Research Engine

Table 3.1: Engine specification summary

Description	Specification
Engine type:	Jaguar research V6, 24-V, GDI
Bore:	89mm
Stroke:	79.5mm
Fuel:	Gasoline, RON 95
Compression ratio:	11.3
Intake valve timing:	Variable CA
Exhaust valve timing:	Variable CA
Intake temperature:	Variable

3.2 Three way catalytic converter

A prototype three-zone monolith catalyst as shown in Figure 3.2 (supplied by Johnson Matthey) was connected to the actual engine exhaust manifold. The first zone was designed to reduce HC and NOx under lean and stoichiometric engine conditions at high temperatures >400°C, the second zone was designed to reduce NOx by reaction with HC under lean engine operation over a temperature range of 250°C – 400°C, while the third catalyst zone was designed to control part of the exhaust hydrocarbons and CO at temperatures below 300°C. During preliminary testing it was observed that the middle zone catalyst was not very sensitive to the type of hydrocarbons (e.g. chain length) in NOx reduction, while over the first zone catalyst NOx reduction activity was improved with long chain hydrocarbons. The overall dimensions of the three-zone catalyst, and hence its volume, were the same as the production three-way catalyst with which the engine was originally equipped.

Figure 3.2: Prototype three-zone monolith catalyst

3.3 Regulated Emissions

A Horiba MEXA 7100 DEGR equipped with a heated intake line was used to measure total hydrocarbons, carbon monoxide, carbon dioxide, NOx and oxygen..The heated line and pre-filter are maintained at 190ºC. The analyzer equipped with flame ionization detector (FID) was used to measure total hydrocarbon in ppm methane (CH_4) equivalent. The measurement of HC represents wet HC concentration. Carbon monoxide (CO) and carbon dioxide (CO_2) were analysed by non-dispersive infrared (NDIR) detector and NOx by a chemiluminescene detector (ClD). The λ (air/fuel ratio relative to stoichiometric), temperature and pressure of the exhaust gases at the engine exhaust manifold were also measured. The system should be calibrated using suitable bottled span and zero calibration gases.

3.4 Engine Data processing

The data processing procedure involves averaging over 100 consecutive pressure cycles (including pressures other than in-cylinder), temperatures, fuel consumption and other parameters. Parameters such as: NMEP, rate of pressure rise, COV of NMEP and fuel consumption are calculated in the SIMULINK model; only an averaged value is calculated during data processing. All data processing has been accomplished using MATLAB software. Since data is acquired with quite a large variation of ambient conditions, standardisation to normal conditions has to be calculated.

3.5 Gas Chromatography (GC)

For this study the Hewlett-Packard HP 5890 GC instrument with oven temperature program capabilities with maximum temperature of 300°C was used Gas chromatography is capable of providing quantitative and qualitative analysis of hydrocarbon compounds present in the sample. The compounds are carried out through a GC column as gases, either because the compounds are normally gases or they can be heated and vaporized into a gaseous state.

The compounds partition between a stationary phase (solid or liquid) and mobile gas phase, the differential partitioning into the stationary phase allows the compounds to be separated in time and space. The gas chromatography basic components are shown in Figure 3.3.

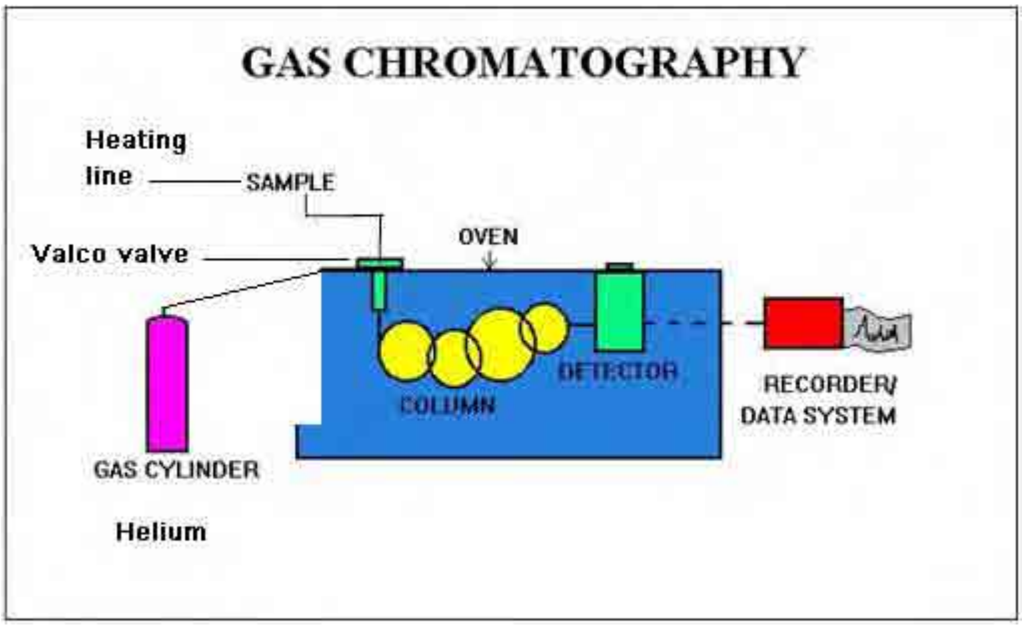


Figure 3.3: Gas Chromatographic – Basic Components

3.5.1 Carrier gas (Mobile phase)

The carrier gas is usually helium, hydrogen or nitrogen. The carrier gas serves as the mobile phase; in our study it was helium which carries the sample through the column. The carrier gas has to be chemically inert, must not interfere with the mass spectral pattern, should be enriched of the eluent and should not contribute to the total ion monitor signal [124]. The carrier gas flow is quantified by volumetric flow rate, expressed in ml/min and the flow rate is dependent on the column diameter.

3.5.2 GC-Column

The capillary GC column is the heart of the system; it is coated with a stationary phase which has a great effect on the separation of the compounds. The structure of the stationary phase affects the amount of time the compounds take to move through the column. Columns are available in many stationary phases' sizes. A typical capillary column is 15-60m in length and 0.25-0.32mm ID, 0.1-2.5 micrometer film thickness. As the literature survey showed different columns have different applications, the component with shorter retention time, will appear first and will have lower heat of solution in the stationary phase. For our work the Pora plot-Q column was used because it is suitable for (C_1-C_7) hydrocarbon speciation, on the other hand the DB-1 column was suitable for (C_5-C_{11}) hydrocarbon speciation.

3.5.3 GC-Oven

The aforementioned column is placed in an oven where the temperature can be controlled very accurately over a wide range of temperatures. Typical GC oven temperatures range from room temperature to 300^0C.

3.5.4 Data processing

A data recorder plots the signal from the detector over time. The plot is called a chromatogram. The retention time, which is when the component elutes from the GC system, is qualitatively indicative of the type of compound. The data recorder also has an integration component to calculate the area under the peaks or the height of the peak. The area or height is indicative of the amount of each component. When the component elutes from the GC column the signal from the detector will increase, a detected components peak will appear for each component as shown in the total ion chromatogram of Figure 3.4.

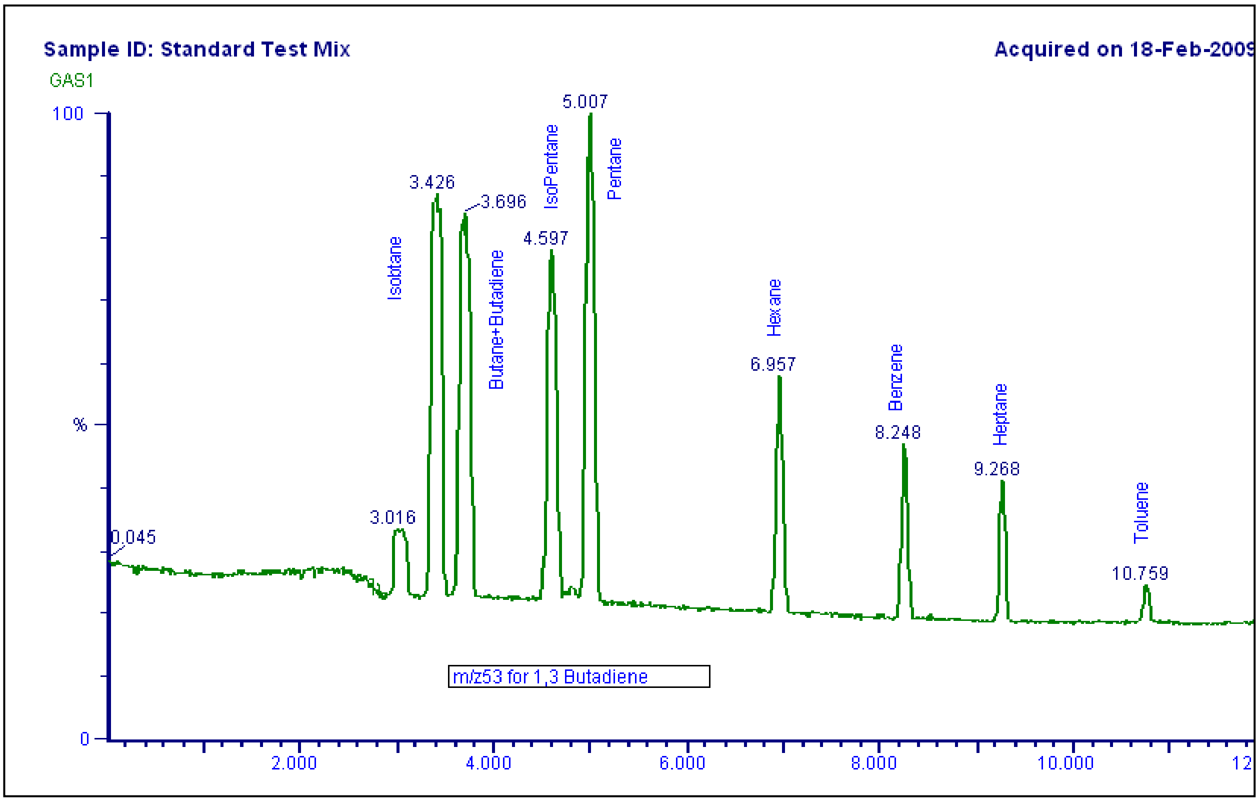


Figure 3.4: Standards gas peaks in the total ion chromatogram

3.6 Flame Ionization Detector (FID)

The flame ionization detector is one of the most sensitive gas chromatographic detectors for hydrocarbon components, and it is the most widely and successfully used gas chromatographic detector for volatile hydrocarbon containing compounds. The presence of oxygen atoms in the molecule decreases the detectors response. For instance, the FID detection of methane CH_4 is excellent but formaldehydes CH_2O detection is poor. So for oxygenated hydrocarbon it is not recommended to use FID instead there are some other methods which could be used such as the High Performance Liquid Chromatography (HPLC) method. The FID basic components are shown in Figure 3.5.

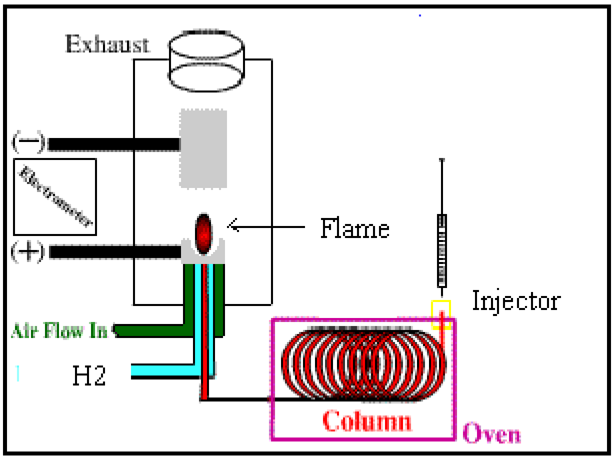


Figure 3.5: Flame Ionizing Detector – Basic Components

The small diameter capillary column is fitted directly in to the bottom of the detectors flame jet. Eluents of gases coming out from the column are mixed with separately plumbed in hydrogen and air, all of which gets burned on the jets tip. After H_2 and oxidant O_2 in air started, the flame is lit using an electronic ignition. The charged particles presented in the combustion process create a current between the detectors electrodes. The metallic jet itself represent one electrode, the other one is close by and above the jet. The gaseous products exit the detector chamber via the exhaust. The detector casing is heated so that gases produced by the combustion (mainly water) do not condense in the detector before leaving the detector chimney.

In our study Hydrocarbons speciation C_1–C_7, was performed by a gas chromatograph (Hewlett – Packard Model 5890 Series II Plus) equipped with an Agilent flame ionization detector (FID) Figure 3.6. Data acquisition was achieved by employing an Agilent Chem-Station (ver.3.08b) to control and monitor the analysis. The gas sampling temperature was kept at 190^{o}C, where the gas entered a six port Valco valve fitted with a 250µl sample loop. A 25 m long x 0.32mm i.d. capillary column with 10µm film thickness PoraPLOT Q was used, which allowed the polar and non-polar compounds to be detected simultaneously. The column head pressure was kept at 10Psi. The helium carrier gas flow rate was pressure controlled with a flow rate of 5.5ml/min. Hydrogen and oxygen supplied to the FID was kept at a ratio of 10:1. The repeatability of the chosen 15 species Table 3.3 was consistently within ±1.5%.

The temperature programme settings as seen in Table 3.2 permitted the heavier hydrocarbons (C_7+) to be flushed out, to cope with different engine operational modes. Standard mixtures of paraffins and olefins and aromatics from C_1 to C_7 with known concentrations were used to calibrate the chromatograph. The retention times of the key species were calibrated daily before each set of experiments by the analysis of 15 component gases in a reference mixture. The total run time was 28.5mins, and the individual retention times are listed in Table 3.3.

Table 3.2: Gas Chromatographic Parameters

Instrument	HP 5890 series II
Column	Pora PLOT Q 25m; 0.32mm ID; 10µm film
Detector	FID Source 200°C
Oven Temp	50°C initial; 0.5 min hold 7.5°C/min to 250°C; 5min hold
Flow Rate	5.5ml/minute ; He

Table 3.3: Retention Time of Different Standards Compounds

Peak Number	Compound	Retention Time (minute)
1	Methane (CH_4)	0.845
2	Ethylene (C_2H_4)	1.353
3	Propylene (C_3H_6)	3.861
4	Propane (C_3H_8)	4.141
5	iso-Butane (C_4H_{10})	7.638
6	1-Butene (C_4H_8)	8.066
7	1,3-Butadiene (C_4H_6)	8.395
8	n-Butane (C_4H_{10})	8.556
9	iso-Pentane (C_5H_{12})	12.271
10	1-Pentene (C_5H_{10})	12.613
11	n-Pentane (C_5H_{12})	12.944
12	n-Hexane (C_6H_{14})	16.732
13	Benzene (C_6H_6)	17.253
14	n-Heptane (C_7H_{16})	20.197
15	Toluene (C_7H_8)	20.93

Figure 3.6: GC–FID Instrument

3.7 Mass Spectrometry

Mass spectrometry (MS) is a powerful tool used with an analytical technique that measures the charged particles and the mass-to-charge ratio of the chemical compound. It is used for the identification of organic compounds and determining the elemental composition of a sample or molecule. The principle of MS is to ionize a chemical compound (sample) introduced in the gaseous state to generate charge molecules or molecule fragments and measurements of their mass-to- charge ratio. When the sample is loaded onto the MS instrument, and under goes vaporization, the components of the sample are ionized by impacting them with an electron beam which results in the formation of charged particles (ions).These ions are extracted in to the analyser region of the mass spectrometer where they are separated according to their mass (m) - to-charge (z) ratio (m/z). The separated ions are detected and this signal sent to a data system where the m/z ratios are stored together with their relative abundance for presentation in the format of an m/z spectrum. The m/z values of the ions are plotted against their intensities to show the number of components in the sample, the molecular mass of each component, and the relative abundance of the various components in the sample. The analyser and detector of the mass spectrometry and the ionization source are maintained under high vacuum to give the ions enough time to move from one end of the instrument to the other end without obstructing from air molecules. For the GC-MS used in this work the computer is linked to the National Institute of Standard and Technology (NIST) mass spectra library which helps to identify an unknown chemical in the sample mixture. The library compares the identified mass spectrum of a sample component and compares it to the mass spectra in the library; it reports a list of most likely identifications along with the statistical probability of the match.

In our study hydrocarbon speciation C_5 - C_{11} compounds was performed by a GC-MS. GC 8000 series was connected to Fisons MD 800 (mass spectrometer detector) Figure 3.7. The gas samples were introduced via the heated line into a six port valco valve outfitted with a 0.1ml sample loop. The gas sampling apparatus was kept at a constant temperature of 200 ^{o}C. A 30 meter long x 0.53mm i.d. DB-1 capillary column with a 3µm film thickness was used, this type of column allows for separation of both the polar and non-polar compounds. The column head pressure was kept at 10Psi. The helium carrier gas flow rate was pressure controlled with a flow rate of 6ml/min. The temperature programme settings, Table 3.4, allows the heavier hydrocarbons to be flushed out, allowing the analysis to cope with exhaust analysis from the different engine operational conditions and combustion modes. Standard mixtures of paraffin’s, olefins and aromatics with known concentrations were used to calibrate the chromatograph; the components of the standards sample were generally stable under the operation conditions used in this analysis. The retention time~~s~~ of each species were calibrated daily before each set of experiments, by the analysis of a 15component reference gas purchased from British Oxygen Company (BOC). The total run time was 20 minutes. The area under the peak of each specific component in the chromatogram is proportional to the concentration of that component. The VG Mass-Lab software was used to acquire and integrates the basic GC-MS data.

Table 3.4: Gas Chromatographic Parameters

Instrument	GC 8000 series
Column	DB-1, 30m; 0.53mm ID; 3μm film
Detector	MS, Source 200°C
Oven Temp	40°C initial; 5 min hold 10°C/min to 240°C; 5min hold
Flow Rate	5ml/minute ; He

Figure 3.7: GC–MS Instrument

3.8 High Performance Liquid Chromatography (HPLC)

A high performance liquid chromatography (HPLC) system consists of different components Figure 3.8 where the process is accomplished by the injection of a small amount of liquid sample in to a moving stream of liquid (called the mobile phase) that passes through a column packed with particles of stationary phase. Separation of a mixture into its components depends on the different degree of retention of each component in the column. The extent to which a component is retained in the column is determined by its partitioning between the liquid mobile phase and the stationary phase. Since the compounds have different molecules, they exit the column at different times, so they have different retention times. The retention time is the time between injection and detection. There are numerous detectors which can be used in liquid chromatography. It is a device that senses the presence of components different from the liquid mobile phase and converts that information into an electrical signal. For qualitative identification one must rely on matching the retention times of known compounds with the retention times of components in the unknown mixture. Thus HPLC is most often used when one is performing specified compounds analyses, when one has a good idea of the compounds present in the mixture so that reference standards can be used for determining retention times.

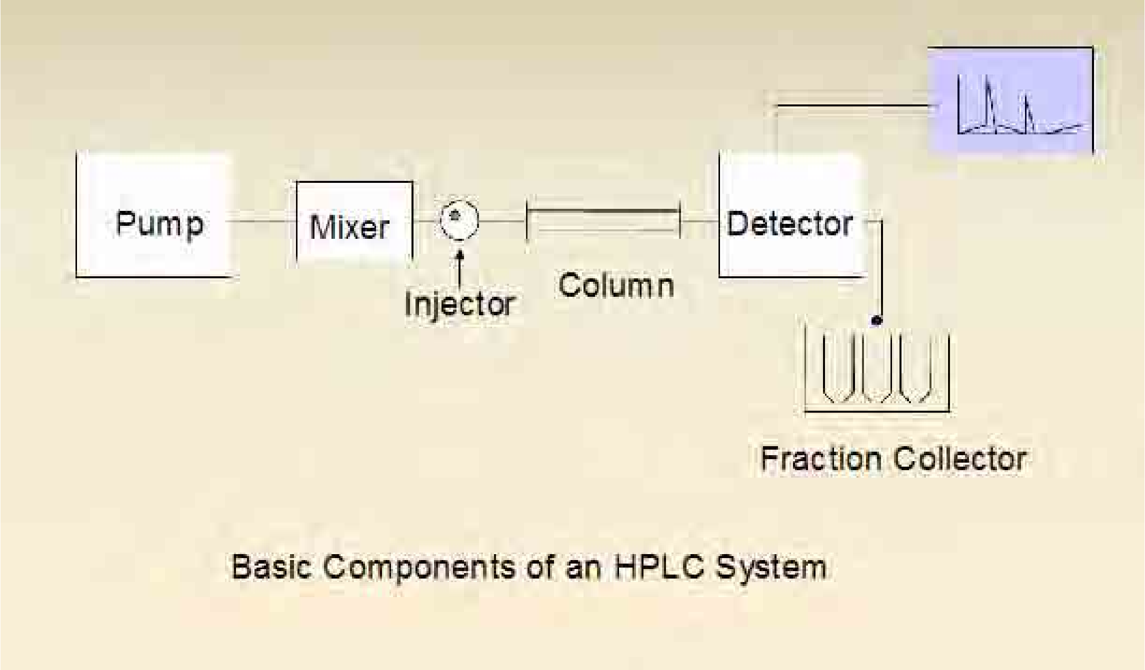


Figure 3.8: Basic components of HPLC system

For a sample of largely unknown composition qualitative identification can be determined by liquide chromatography mass spectrometry (LC-MS). A mass spectrum of any or all peaks in the chromatogram is compared with spectra contained in spectral libraries on the systems computer.

The apparatuse consists of a mobile phase reservoir which is just a clean solvent jug, a solvent delivering precise, reproducible and constant amount of mobile phase, a sample inlet, the column, a detector with associated electronics, and some kind of interface to the outside world such as a computer.

3.9 Sampling of aldehydes compounds

Aldehydes are a class of highly reactive organic chemical compounds that contain a carbonyl group (in which a carbon atom is double-bonded to an oxygen atom) and at least one hydrogen atom bonded to the alpha carbon atom. Molecules that contain aldehyde group can be converted to alcohols by the addition of two hydrogen atoms to the central carbon oxygen bond. One of the most intensively used techniques is High Performance Liquid Chromatography (HPLC) analysis with 2,4 dinitrophenyl hydrazine (DNPH) derivatives of aldehydes and ketones. The analysis of aldehydes and ketones was performed by reversed phase HPLC. The gas sample is drawn with flow rate of 1.0L/min, through midget impinger with 25ml of DNPH solution. The impinger is placed in an ice bath, maintaining the sample temperature at 0 ^{0}C lowers the vapour pressure of the absorbing solution and preventing any major vapour losses. The exhaust gas bubble inside the DNPH solution reagent for 20 minutes. After derivatization, solvent extraction is used to recover the detected species, followed by chromatographic analysis procedures. When the exhaust gas bubbles in the DNPH solution the aldehydes and keton react with the reagent to produce DNPH-carbonyl derivatives. This method of sampling and measurements was carried out before by Lipari and Swarin [123]. Each sample was kept in the fridge below 4^{0}C until HPLC analysis. HPLC Dionex Acclaim 120 system was used, separation of the sample components was achieved on a 250mm x 4.6mm ID. Column with 5µm C18 was used in this study. A UV detector was used and the wavelength was set to

365nm.A mobile phase solvent gradient of acetonitrite and deionised water was (10:90v/v) used as an eluent, the flow rate of the eluent was adjusted to 1.0 ml/min. The mixing ratio was changed linearly to reach 75:25 v/v acetonitrile to deionised water at 60 min, and then kept constant to the end of the run. Analysing time for the a single measurement was 70 minutes. The acidified solution of 2, 4 DNPH was obtained from Sigma Aldrich Company, and 15 different carbonyl standards were used for chromatography calibrations. Figure 3.9 shows the experimental setups for the arrangement of the carbonyl trapping method and HPLC system.

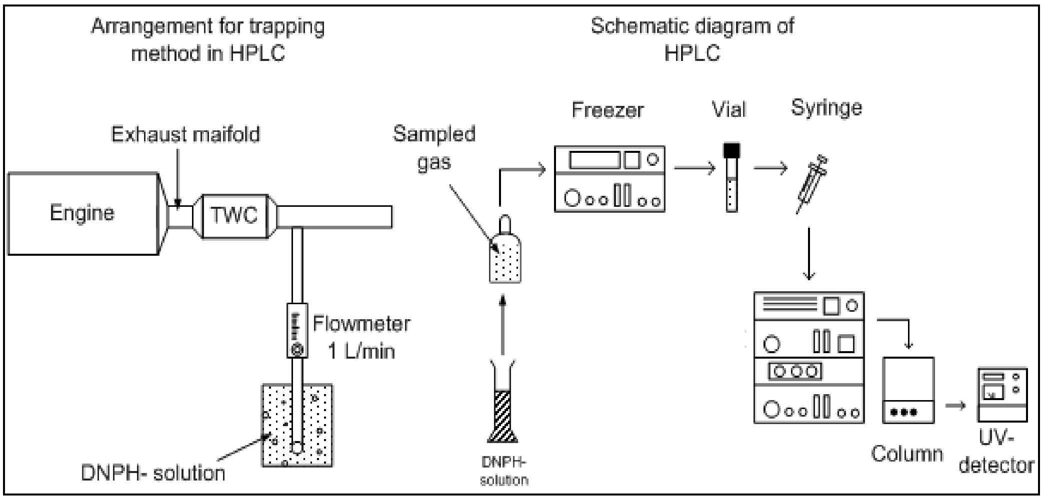


Figure 3.9: Schematic of Experimental setup

The HPLC programme settings are shown in Table 3.5. Fifteen (15) Standards of carbonyl compounds were used as reference materials to compare the detected aldehydes and ketons from the exhaust gases. Table 3.6 shows the retention time of each peak corresponds to the concentration level of that specific compound.

Table 3.5: HPLC Parameters

Instrument Parameters	Dionex Acclaim 120
Column	C18 250mmx4.6mm ID; 5µm film
Detector	UVD 170s Wave length 365nm
Pump	P 580 quaternary low pressure
Flow Rate	1.0ml/minute, eluent

Table 3.6: Retention Time of different Carbonyls Standards Compounds

Peak Number	Compound		Retention Time (minute)
1	Formaldehyde	HCHO	32.65
2	Acetaldehyde	CH3CHO	42.88
3	Acrolein	CH3CH=CHCHO	53.42
4	Acetone	CH3COCH3	54.63
5	Propionaldehyde	CH3CH2CHO	58.34
6	Crotonaldehyde	CH3CH=CHCHO	69.14
7	Butyraldehyde	CH3(CH2)2CHO	70.05
8	Bnzaldehyde	C6H5CHO	80.38
9	Isovaleraldehyde	(CH3)2CH(CH2)CHO	83.80
10	Pentanal	CH3(CH2)3CHO	85.57
11	o-Tolualdehyde	CH3(CH6H4)CHO	88.74
12	m-Tolualdehyde	CH3(C6H4)CHO	89.58
13	p-Tolualdehyde	CH3(C6H4)CHO	90.13
14	Hexanal	CH3(CH2)4CHO	94.98
15	2,5-Dimethylben	(CH3)2(C6H4)CHO	96.91

CHAPTER 4:

CATALYST DESIGNED FOR HC, CO, AND NOX EMISSIONS REDUCTION IN GASOLINE SI/HCCI ENGINE

4.1 Introduction

This chapter presents a study on a new catalytic converter design, which aim to control total hydrocarbon (THC), carbon monoxide (CO) and NOx emissions under lean (excess oxygen) SI/HCCI engine operation. The experiments were conducted on a Jaguar V6 gasoline engine equipped with the prototype catalyst at the one bank. The effects of engine load, speed, boost pressure and space velocity and air/fuel ratio on exhaust emissions and catalyst performance were explored. A prototype three-zone monolith catalyst as described in section 3.2 was used Figure 4.1.The THC, CO, and NOx emissions of the exhaust gases produced from HCCI/SI engine lean operation mode was carried out under different engine loads and three different speeds upstream and downstream the catalyst . The effect of boost pressure on engine-out emissions was also investigated. The air/fuel ratio is represented by λ (1.2, 1.4, and 1.6). The experimental conditions of the V6 gasoline engine are listed in Table 4.1 and Table 2.1. Hydrogen was added upstream of the catalyst under HCCI lean engine operation at a speed of 1500rpm to assess its ability to promote NOx reduction.

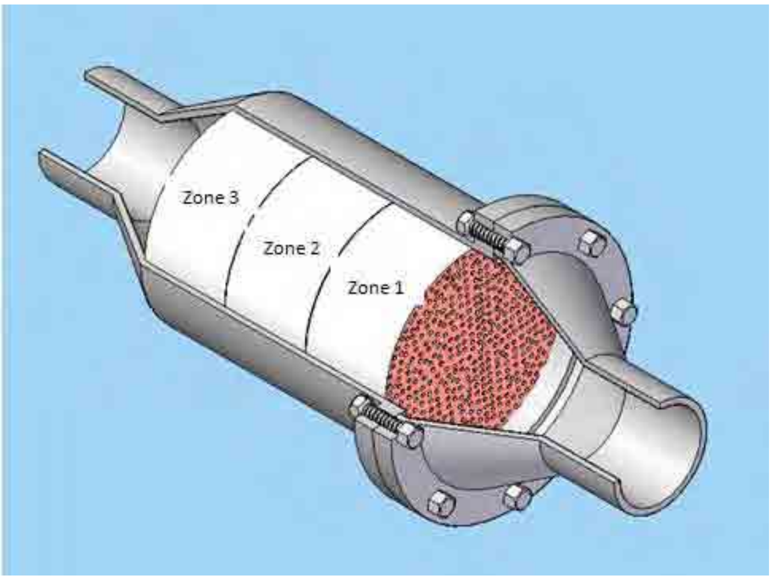


Figure 4.1: Prototype Catalyst After treatment - 3 Zones

Table 4.1: Engine test conditions (3-4bar NMEP)

Air/Fuel ratio (λ)	Engine Speed (rpm)	Exh. Temp. (^{0}C)	Oxygen (%)	Load NMEP (bar)	GHSV (kh^{-1})
1.2	1500	370	4.08	3	26
	2000	355	4.10	3	30
	2500	340	4.30	3	24
1.4	1500	350	6.50	3.5	27
	2000	355	6.55	3.5	31
	2500	345	6.80	3.5	30
1.6	1500	355	8.31	4	33
	2000	350	8.84	4	35
	2500	360	8.28	4	36

Table 4.2: Engine test conditions (4-5bar NMEP)

Air/Fuel ratio (λ)	**Engine Speed (rpm)**	**Exh. Temp. (^{0}C)**	**Oxygen (%)**	**Load NMEP (bar)**	**GHSV (kh^{-1})**
1.2	1500	400	3.80	4	28
	2000	405	4.20	4	31
	2500	420	3.80	4	33
1.4	1500	375	6.13	4.5	31
	2000	382	6.83	4.5	33
	2500	390	6.43	4.5	34
1.6	1500	370	8.34	5	34
	2000	393	8.45	5	38
	2500	385	8.23	5	41

4.2 HCCI engine-out emissions

4.2.1 Effect of engine load on engine-out emissions, λ=1.2, (3-4bar NMEP)

HC and CO emissions are influenced by the in-cylinder conditions (i.e temperature) and the homogeneity of the fuel with air. Increasing engine load from 3 to 4bar NMEP improves HC and CO oxidation, Figure 4.2 and Figure 4.3, which in turn leads to significant reduction of HC and CO engine emissions. On the other hand the opposite trend is seen in the case of NOx emissions when the engine load was increased. In the case of HC emissions this was presumably because of crevice loading of HC, with lower load 3bar, this is having a bigger effect on HC emissions than that with higher load 4bar. The exhaust gas temperature at low engine load was 340^{0}C, Table 4.1, which seems to be too low for the hydrocarbons to be oxidized during the expansion stroke, compared to the higher gas temperature of 420^{0}C, Table

4.2, at higher engine load. The lower gas temperature is not favourable for HC oxidation in the exhaust ports. Furthermore, the low combustion gas temperature presented at lower load can result in an incomplete of the combustion process and cause higher HC emissions [146]. Similarly at lower load CO emissions increased. This rapid increase resulted from the quenching of the CO oxidation process at lower load as the gas temperature dropped. Dec [16] predicted that for low loads, incomplete bulk-gas reactions should play a significant and perhaps dominant role in CO emissions, and contribute to HC emissions. NOx reduction has been a result of lower combustion temperature in the homogeneous combustion. The conversion efficiency of the catalytic converter is defined as:

Conversion efficiency = emissions (upstream the catalyst – downstream the catalyst) divided by the emissions upstream the catalyst.

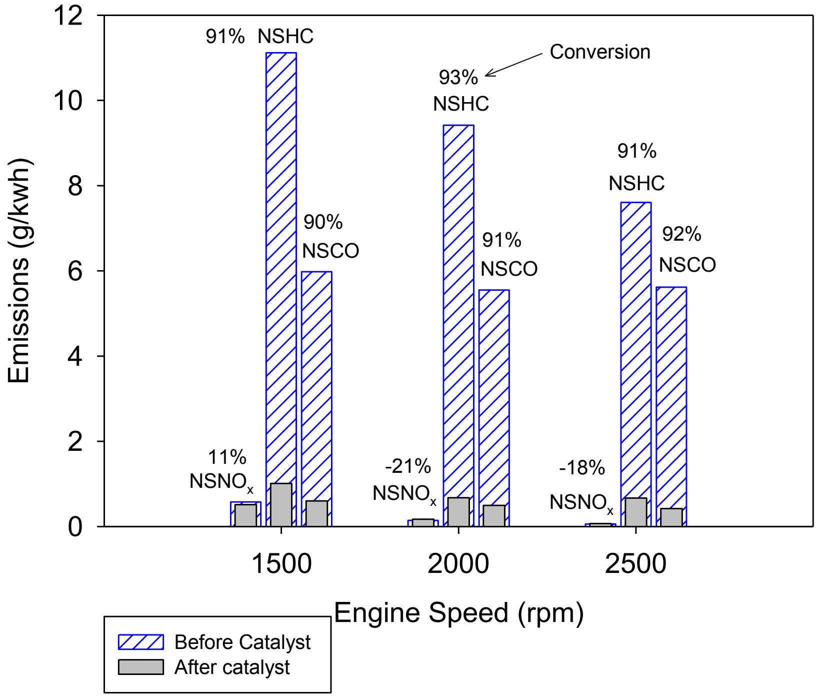


Figure 4.2: Engine-out emissions and catalyst efficiency in reducing HC, CO, and NOx (3bar NMEP), HCCI, lambda 1.2

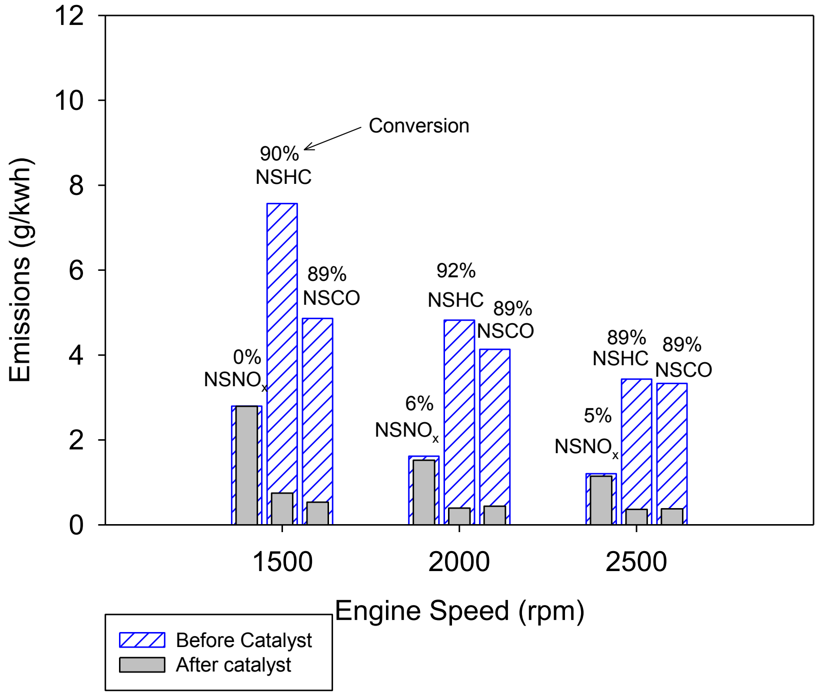


Figure 4.3: Engine-out emissions and catalyst efficiency in reducing HC, CO, and NOx (4bar NMEP), HCCI, lambda 1.2

4.2.2 Effect of air fuel ratio on engine-out emission, λ=1.2, 1.6(4bar)

As the air-fuel ratio is increased, Figure 4.3 and Figure 4.4, (leaner operation) the fresh charge becomes colder which leads to lower combustion temperature and therefore lower NOx emissions. When (λ) was increased further, the cold charged will lead to deterioration of auto-ignition and resulted in slightly higher HC and CO emissions. Also the total heat release and average combustion temperature are reduced. As a result, fuel/air mixtures are subject to low combustion and post-oxidation temperature and less complete oxidation of HC and CO to CO_2 [88].

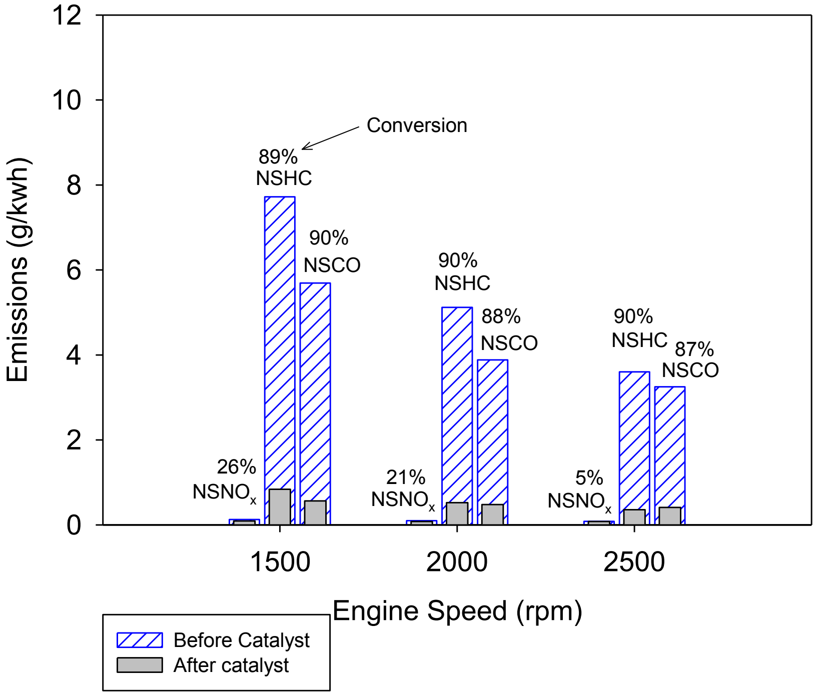


Figure 4.4: Engine-out emissions and catalyst efficiency in reducing HC, CO, and NOx *(4bar NMEP), HCCI, lambda 1.6.*

4.2.3 Effect of engine speeds on engine-out emission, λ=1.4, (3.5-4.5bar)

Increasing engine speeds reduces engine out HCs emissions but does not significantly influence CO emissions Figure 4.5 and Figure 4.6. This fact has been ascribed to thermal conditions under which the HCCI engine operates. Increasing engine speed increases heat flux from the engine; therefore the air charge was warmer and the in-cylinder temperature at the end of compression stroke was higher. Furthermore, combustion efficiency has increased and as a result, HC emissions have decreased. NOx emissions tend to be reduced with increasing engine speed, this is mainly due to an improved mixing process that in turn improves charge homogeneity and reduces NOx emissions.

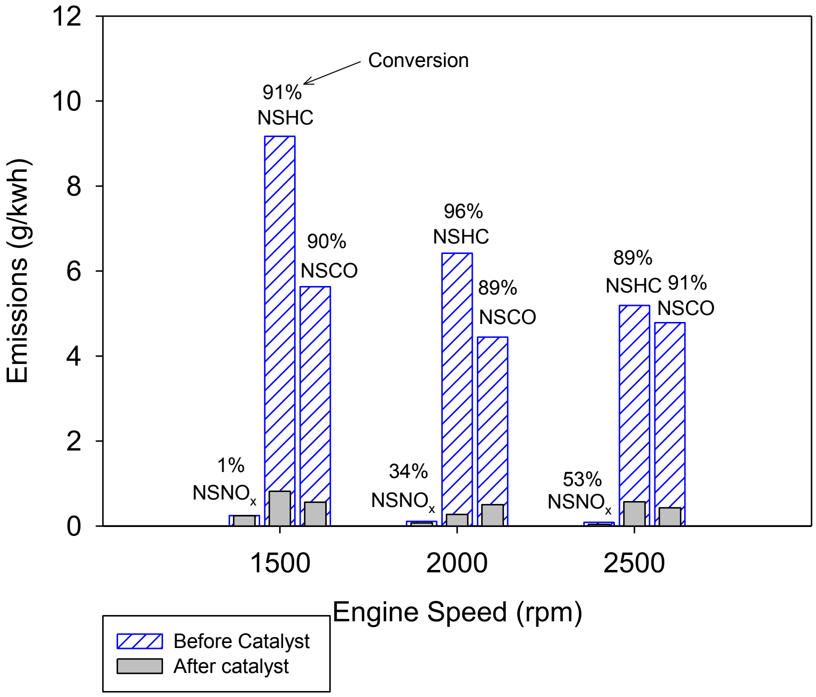


Figure 4.5: Engine-out emissions and catalyst efficiency of HC, CO, and NOx *(3.5bar NMEP), HCCI, lambda 1.4.*

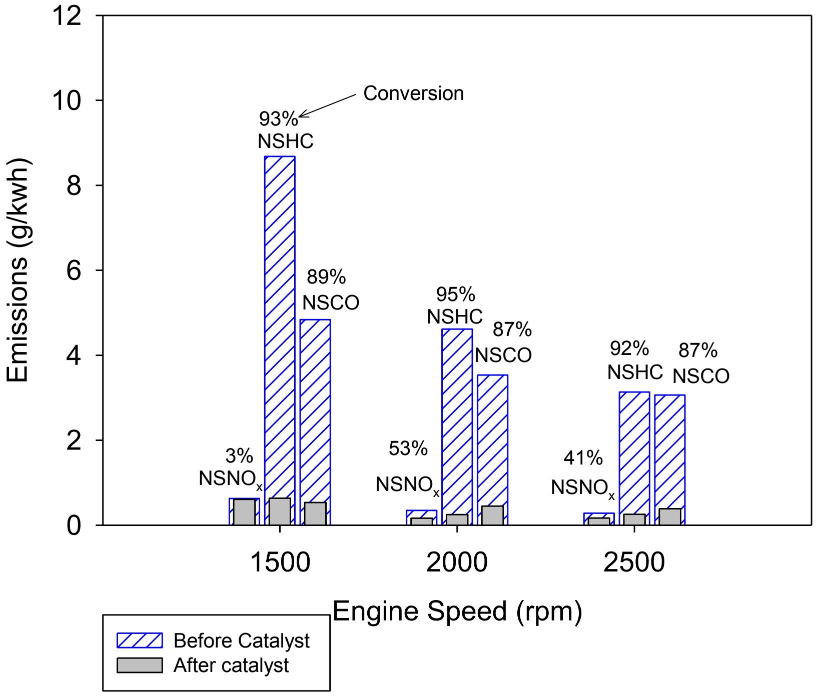


Figure 4.6: Engine-out emissions and catalyst efficiency in reducing HC, CO, and NOx (4.5bar NMEP), HCCI, lambda 1.4.

4.2.4 Effect of Boost Pressure on engine-out emission, λ=1.4, (5bar)

Higher boost pressure in HCCI combustion was achieved by introducing more air into the cylinder by means of using turbocharger; this resulted in increased cylinder pressure during the compression stroke. This increase in the mass of trapped air requires an increase in the rate of trapped residuals gas for stable HCCI operation at higher loads. The higher amount of residual gas can be reached by advancing the exhaust valve timing, which leads to a higher in-cylinder pressure during the re-compression stroke. However, since part of the higher in-cylinder pressure has been due to a higher trapped residual rate, there will be a benefit with respect to hydrocarbon emissions Figure 4.7. Christiansen et al [147] reported that HC emissions decrease when increasing exhaust gas recirculation (EGR) and load.

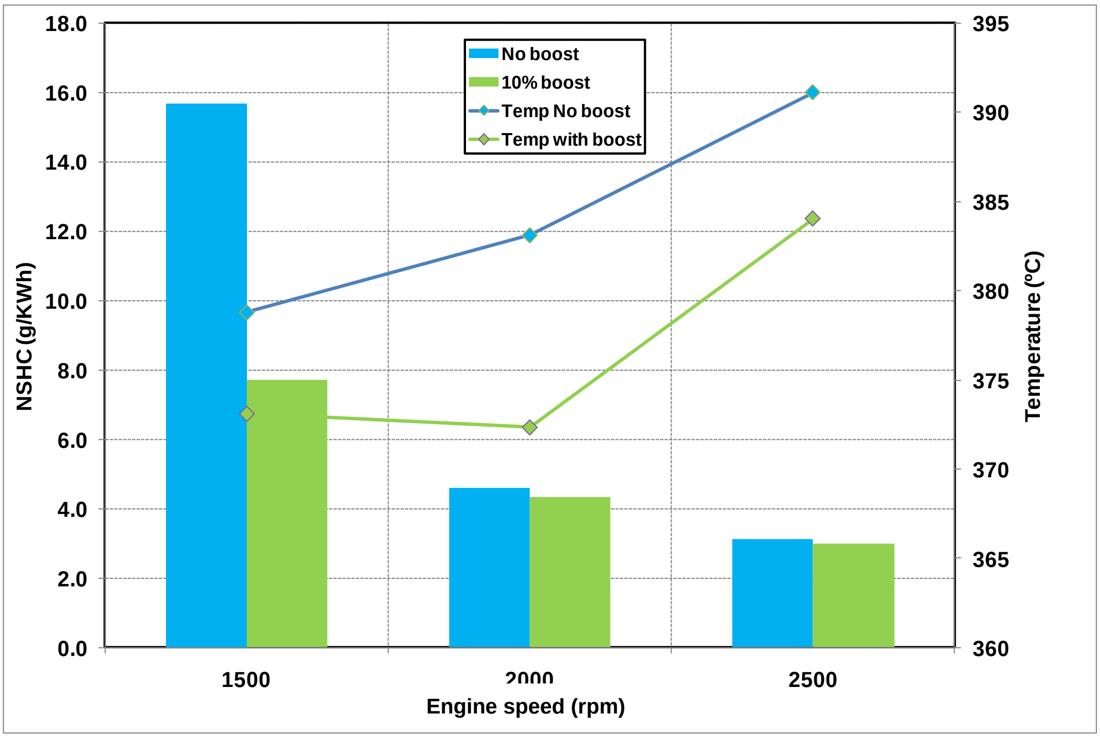


Figure 4.7 :HC emissions at different engine speeds with no boost pressure and with 10% boost pressure(5bar NMEP)

It is clear that even a relatively small boost pressure such as 10% can produce a good improvement in terms of exhaust emissions.

The residual exhaust decreases the in-cylinder temperature and lowers engine out NOx emissions Figure 4.8. These results are in accordance with results reported by Yap et al [148] from their work in applying boost pressure to a single cylinder engine. These emission improvements could be attributed to the effect of charge heating and dilution by residual exhaust, which is responsible for the advanced auto ignition timing, and increased heat capacity of the mixture which leads to extended combustion duration [149]. Also the higher amount of retained exhaust gases in the cylinder led to a higher temperature in the mixture which triggers the fuels tested, to burn within a few crank angle degrees [150].

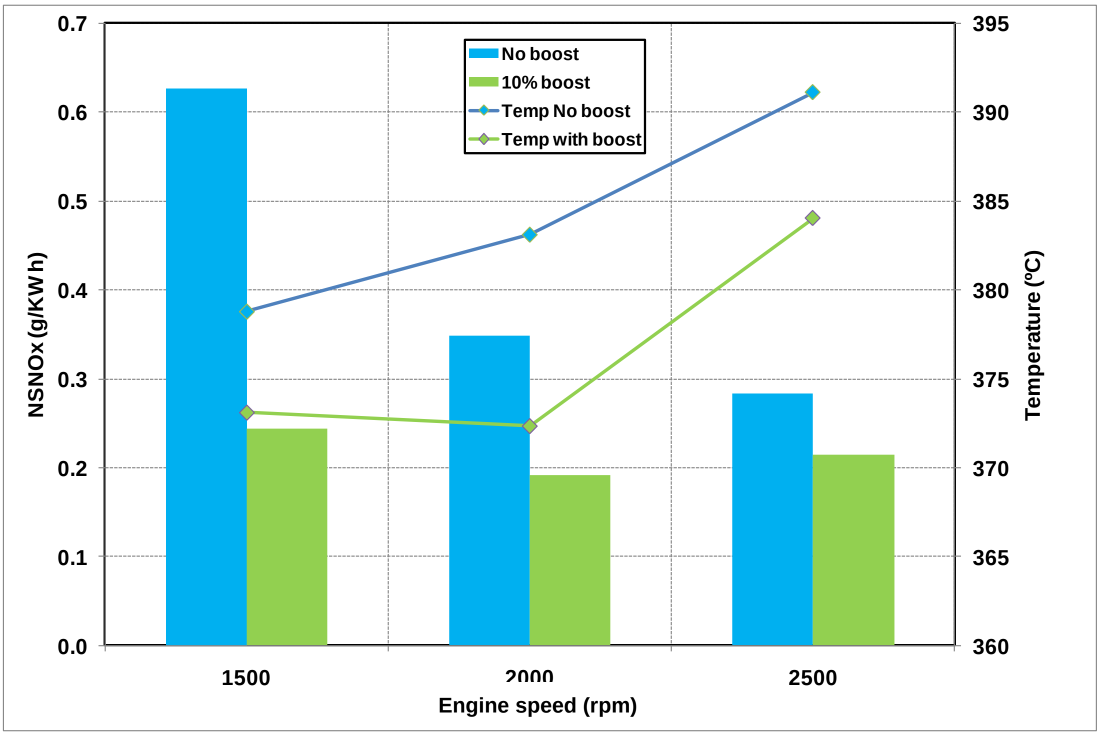


Figure 4.8 : NOx emissions at different engine speeds with no boost pressure and with 10% boost pressure (5bar NMEP)

On the other hand CO emissions increased, Figure 4.9, and this could be attributed to the lowered combustion temperature existing in this condition which was not enough to complete the oxidation of CO to CO_2. These results are in accordance with results reported by Zhao et al [1].

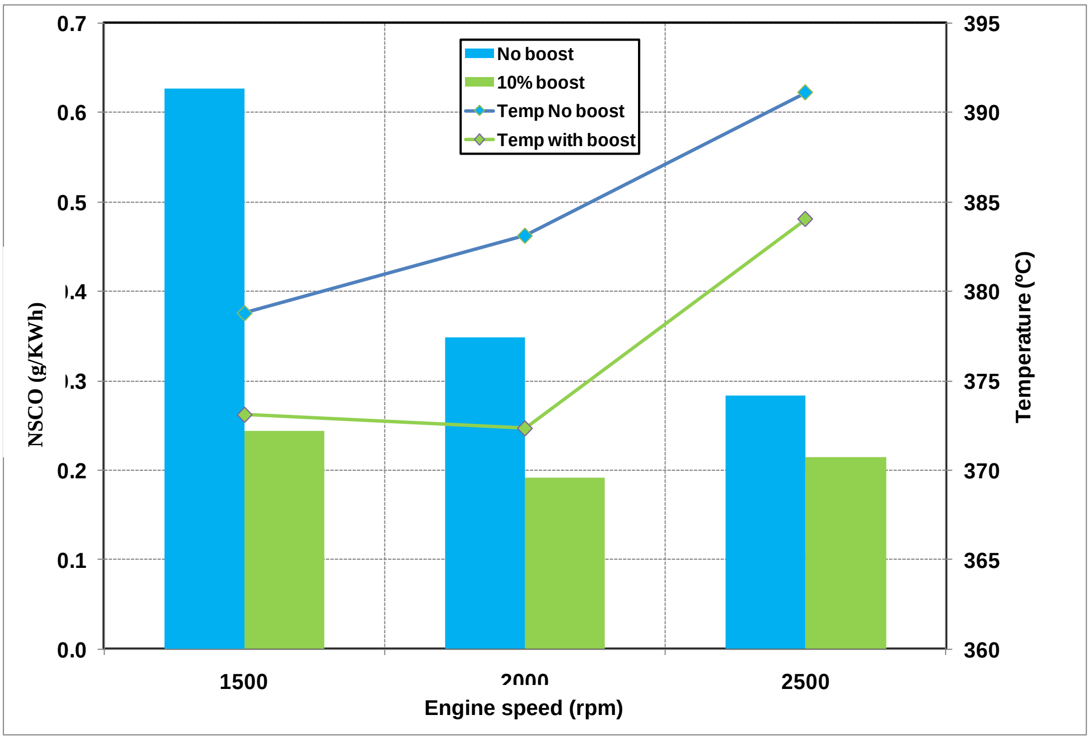


Figure 4.9:CO emissions at diferent engine speeds with no boost pressure and with 10% boost pressure (5bar NMEP)

4.3 Catalyst Efficiency

Under most engine operation, the prototype catalyst covered a wide range of engine conditions. Shifting the engine operation to leaner combustion from λ=1.2 to1.6, and increasing engine load NMEP from 3 to 4.5bar respectively does not influence the engine exhaust gas temperature significantly. The HC and CO conversions ranged from 90-96% over the catalyst independently from in-cylinder conditions. This is the effect of interference of three parameters: retention time (space velocity), exhaust temperature, and exhaust gas composition (HC, CO, and CO_2 due to high heat capacity).

The most important factor affecting CO conversions correlated to the retention time (space velocity-engine flow rate) – the highest conversion up to 92% was achieved when engine flow rate was low in HCCI lean operation Figure 4.2. At λ=1.2 and 2500rpm (load limited), results revealed that the highest conversion rate happened at the lowest space velocity of 24kh^{-1} Table 4.2. Even at higher exhaust gas temperatures the increase in the engine load cannot cover the increase in the flow rate and hence, conversion efficiency is generally lower. However, the prototype catalyst has shown excellent HC and CO conversion regardless of the exhaust gas temperatures.

Minimal catalytic conversion of NOx emissions, up to 55% efficiency, occurred at HCCI mode, this is correlated with CO and HC emissions. When CO and HC emissions are relatively low (and exhaust temperature is low) the CO oxidation deteriorates and allows higher efficiency of NO_x reduction (more CO is available for the reduction reaction). There is the possibility of a similar effect with H_2 in the exhaust gas. An optimal flow rate is required for the best NOx conversion, in this case, the most effective flow rate oscillates around space velocity of 33 kh^{-1}. Despite the catalyst lower NOx conversion efficiencies under HCCI mode, NOx emissions after the catalyst were kept at lower values compared to SI.

4.3.1 Catalyst performance with H_2= 2400ppm addition upstream the catalyst, HCCI operation of engine load 3bar, λ = 1.2, 1.4, 1.6

Hydrogen addition upstream of the catalyst has strongly affected NOx conversion in HCCI lean operation, as seen in Figure 4.10. The NOx conversion is highly dependent on the reaction temperature and gas composition (e.g NOx and HC concentrations in the exhaust). Regarding the NOx conversion without H_2 addition (2400ppm) at HCCI lean λ=1.2 the maximum conversion achieved was 17% and a sharp deterioration in the NOx conversion was observed when changing to leaner mixture with λ=1.4. The increased of NOx after catalyst in the lean operation could be attributed to the low consumption of NOx by the reducing species present in the exhaust, such as CO, HC or H2 which is the preferred catalyst process, These phenomena observed are due to the HC oxidation over the catalyst, no H2 was added upstream the catalyst in case of λ=1.6.

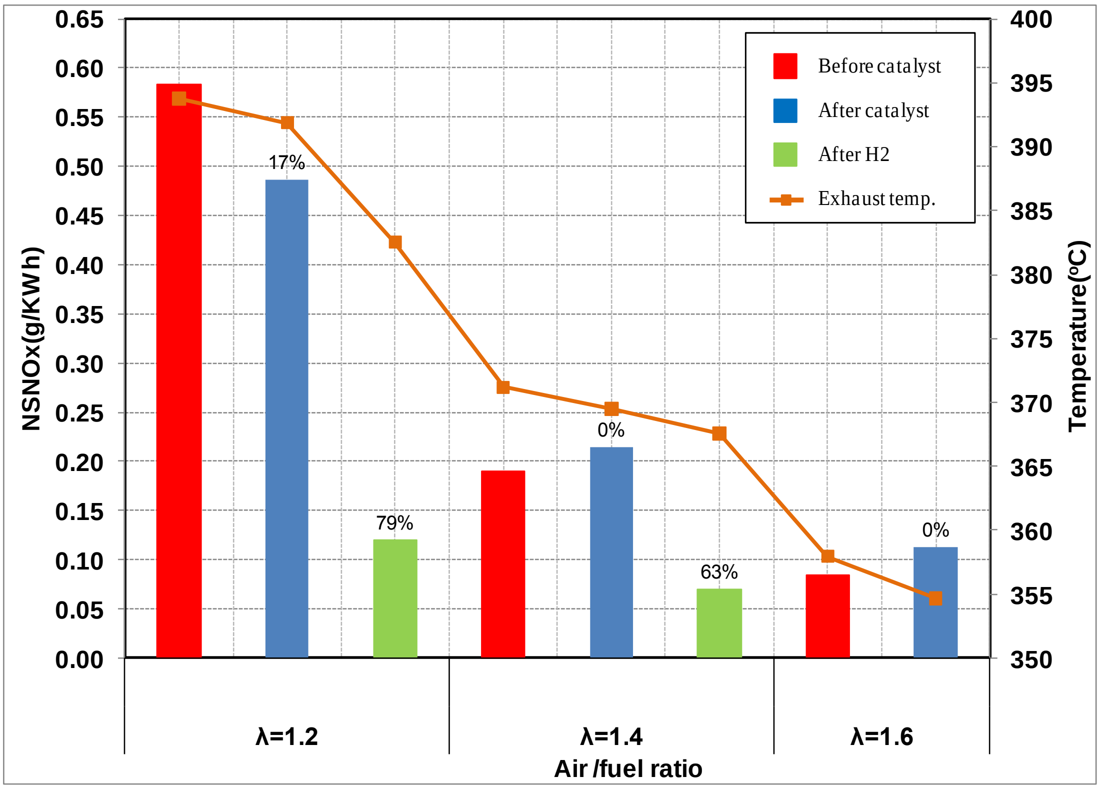


Figure 4.10: NOx conversion efficiency over catalyst with H_2 addition (3bar NMEP), HCCI lean operation, engine speed 1500rpm.

H_2 addition upstream the catalyst has improved NOx conversion from 17% to 79% at λ=1.2 and to 63% for λ=1.4 at the same engine load of 3bar. It can be observed that H_2 addition shifts the peak of the maximum NOx conversion to a lower temperature region. However H_2 addition has an insignificant effect on NOx conversion in the higher temperature region. The conversion of NOx in the low temperature region in the case of the H_2 addition is elucidated to the increased bed temperature from the oxidation of hydrogen. The existed hydrocarbon in the engine-out exhaust such as toluene could help in reducing NO to N_2, with high selectivity and without very large formation of N_2O when compared to other commonly used hydrocarbons [151-152]. Regarding the influence of H_2 addition on HC conversion, a minimum effect on HC conversion of only 1% improvement was achieved downstream of the catalyst, Figure 4.11.

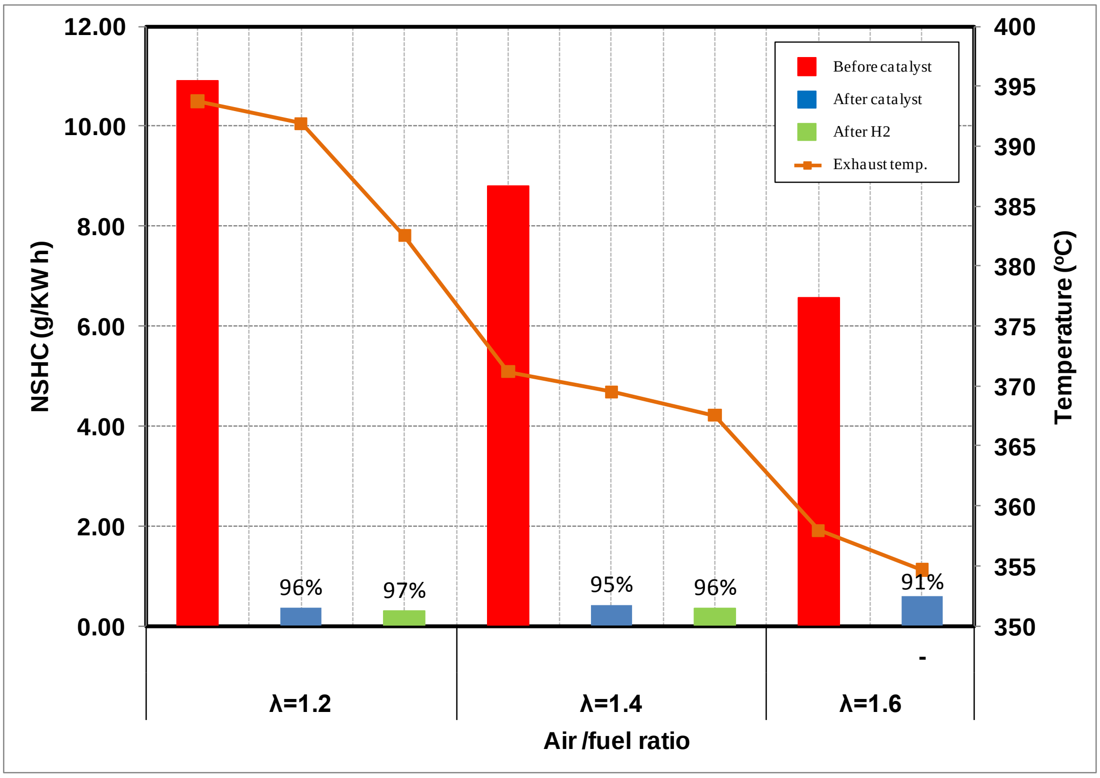


Figure 4.11: HC conversion efficiency over catalyst with H_2 addition (3bar NMEP), HCCI lean operation, engine speed 1500rpm.

When combustion takes place in an oxygen starved environment, there is insufficient oxygen present to fully oxidize the carbon atoms in to carbon dioxide (CO_2). Carbon monoxide (CO) conversion over the catalyst reached 100% without the interference of H_2 additions Figure 4.12.

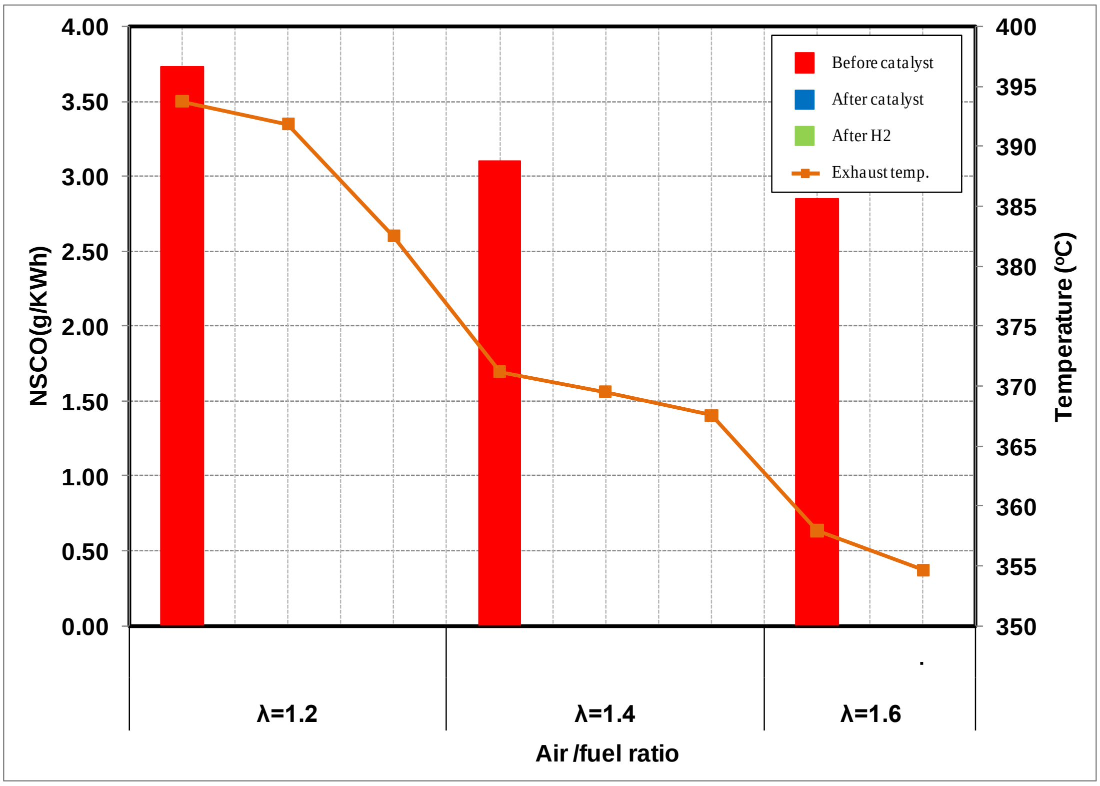


Figure 4.12: CO conversion efficiency over catalyst with H_2 addition (3bar NMEP), HCCI lean operation, engine speed 1500rpm.

On the other hand, as seen in Figure 4.13, a high concentration of CO_2 presented downstream the catalyst due to the oxygen in the catalyst combining with the carbon to form carbon dioxide (CO_2). The high concentration of CO_2 in the tail pipe after CO conversion reflects the catalyst power of converting CO to CO_2 under such conditions.

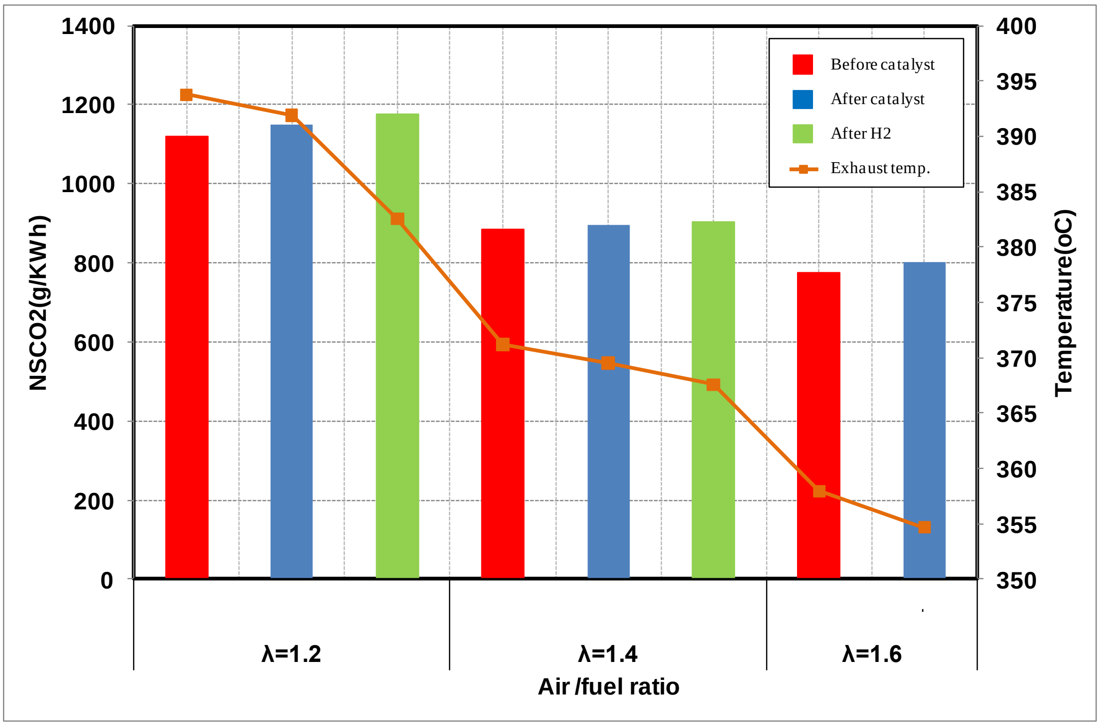


Figure 4.13: CO_2 conversion efficiency over catalyst with H_2 addition (3bar NMEP), HCCI lean operation.

CHAPTER 5:

EFFECT OF COMPOSITE AFTER TREATMENT CATALYST ON ALKANE, ALKENE AND MONOCYCLIC AROMATIC EMISSIONS FROM AN HCCI/SI GASOLINE ENGINE

5.1 Introduction

The present work in this chapter assesses the performance efficiency of a three-zone prototype catalytic converter in reducing exhaust emissions from a gasoline engine, operating in Homogeneous Charge Compression Ignition (HCCI) and Spark Ignition (SI) mode under lean and stoichiometric conditions. The experimental setup for this work is shown in Figure 5.1. This chapter mainly focus on the quantitative analysis of C_1-C_7 hydrocarbon compounds before and after the catalytic convertor. Therefore one of the objectives of this study was to see whether the prototype catalyst has the potential to reduce 1, 3 butadiene and benzene emissions together with the other hydrocarbons, CO and NOx, in HCCI/SI modes under lean and stoichiometric engine operation. Emission measurements and C_1-C_7 hydrocarbon speciation of the exhaust gases from HCCI/SI engine operation have been carried out at five engine conditions before and after the catalyst. A 25 m long x 0.32mm i.d. capillary column with 10µm film thickness PoraPLOT Q was used, which allowed the polar and non-polar compounds to be detected simultaneously.

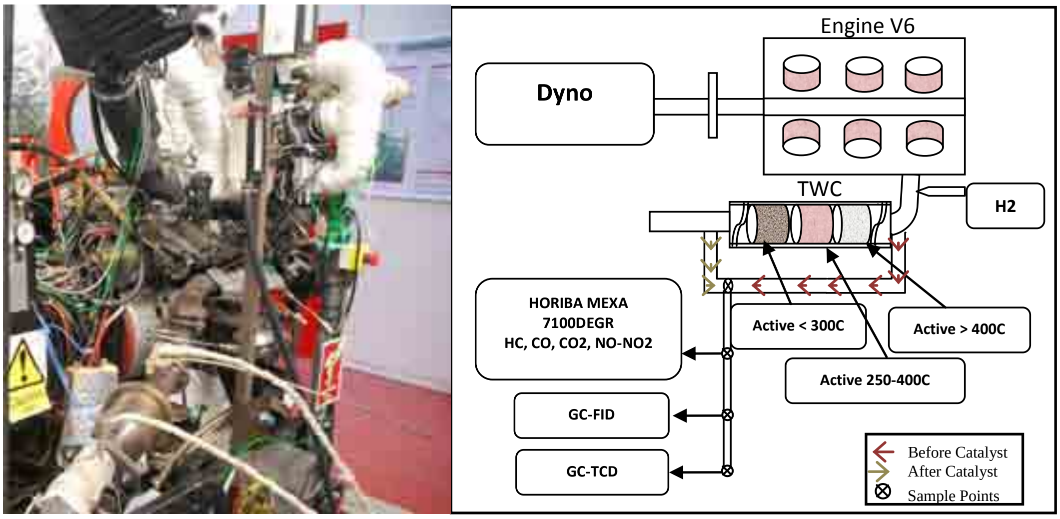


Figure 5.1: Research Engine and TWC System (showing the three catalyst zones)

5.2 Engine operation conditions

Results presented in this study were obtained from SI and HCCI mode when the engine was fully warmed up, the engine was operated in SI mode first until the crankcase lubricant and coolant temperatures reached 90^{o}C.The variable valve timing system of the engine made it possible to change the valve timing for the inlet and exhaust valves within a 60 crank angle degree range. The HCCI operation was enabled by exhaust residual trapping, using negative valve overlap, which trapped exhaust gases in order to retain enough energy for auto-ignition. The variables studied here have been a) engine load effect under HCCI stoichiometric operation, b) air to fuel ratio, c) HCCI and SI combustion modes under the same load, and d) hydrogen addition upstream of the catalyst. The specific engine conditions are presented in Table 5.1.

Table 5.1: Engine Conditions and Emissions under HCCI and SI modes at engine speed 2000 rpm

Engine Condition			**Engine Mode**	**Engine Emissions**			
Conditions	λ	NMEP (bar)		THC (C1 ppm)	CO (%)	NOx (ppm)	O2 (%)
1	1	3.0	HCCI	3065	0.56	12	1.2
2	1	4.0	HCCI	2196	0.63	104	1.2
3	1.4	3.5	HCCI	2622	0.09	12	6.29
4	1.4	4.5	HCCI	2106	0.08	43	6.55
5	1	4.0	SI	1651	0.75	1035	1.06
6	1.4	4.5	HCCI+H_2	2106	0.09	45	6.55
7	1.4	4.0	HCCI	2300	0.07	24	6.13
8	1.6	4.0	HCCI	2479	0.08	11	8.28

5.3 Regulated Emissions

The engine-out total hydrocarbon (THC), CO and NO_X emissions for the same set-point conditions under SI and HCCI mode are shown in Table 5.1. Emissions of NOx were significantly lower than at the same load conditions during HCCI combustion, and were affected by the engine load and air-to fuel ratio. The reduction of NOx emissions over the catalyst under HCCI mode was in the range of 30- 54%, and reached approximately 95% under SI engine operation. Despite the anticipated lower NOx conversion efficiencies under HCCI mode, the lower engine-out emissions meant that the post-catalyst NOx concentration was still lower than that during SI.

The CO emissions during the SI mode were approximately 12% higher when compared to the HCCI mode under an equivalent engine condition. In part, this can be explained by the fact that HCCI combustion (with residual gas trapping) enhances

CO oxidation to CO_2 from one cycle to another [1]. The catalytic conversion efficiency for CO was in the range of 86-91% for HCCI and 100% for the SI engine operation.

The main benefit of the HCCI engine operation is the saving in fuel consumption (g/hr). From Table 5.2 it can be observed that under the same engine load 4bar NMEP (i.e. same power) the fuel consumption for HCCI operation was approximately 21% lower when compared to SI engine operation. This is mainly a result of reduced pumping losses due to fully open throttle operation.

The magnitude of the total HC emissions was strongly affected by the engine operation modes, air fuel ratio, and engine loads as seen in Table 5.2.The results also show that THC emissions in the SI mode were much lower than in the HCCI mode. Catalyst conversion efficiency in reducing HC emissions was in the range of 92 to 96%, except during engine operation at 3 bar NMEP stoichiometric HCCI, where the HC conversions were approximately 60% as a result of the lower oxygen availability and lower exhaust gas temperatures.

Table 5.2: Catalyst efficiency from optimised catalyst arrangements (HCCI modes and SI mode) and fuel consumption at an Engine Speed of 2000rpm

Engine Condition				**Catalyst Conversions (%)**			**Fuel Cons g/hr**	**$T_{Ex.}$ °C**
Cond.	λ	Mode	NMEP (bar)	NSHC	NSCO	NSNOx		
1	1	HCCI	3.0	60	91	30	3000	385
2	1	HCCI	4.0	93	90	36	4100	413
3	1.4	HCCI	3.5	96	88	40	3900	349
4	1.4	HCCI	4.5	95	86	54	4800	386
5	1	SI	4.0	95	100	94	5200	661
6	1.4	HCCI +H_2	4.5	91	87	40	4800	406
7	1.4	HCCI	4.0	95	87	60	3714	383
8	1.6	HCCI	4.0	90	87	30	4075	353

NS= Nett (indicated) specific
NMEP=Nett Mean Effective Pressure

5.4 Hydrocarbon Speciation

The concentration of C_1 to C_7 HC species measured in the exhaust was in the range of 52 – 77% of THC for the HCCI combustion and approximately 81% for the SI engine operation Table 5.3. The rest of the hydrocarbons (i.e. >C7) can be assumed to be uncombusted fuel fractions.

The variation in concentrations of the majority of the alkanes, alkenes and aromatic compounds followed a very similar trend in all of the tests Table 5.3. These species all decreased in concentration as a function of increased engine load and combustion temperature. The highest concentration levels of ethylene and propylene were seen in the SI engine exhaust. All the hydrocarbon species measured before or after the catalyst are listed in Table 5.3

Table 5.3: Hydrocarbons (C_1 – C_7) before and After the Catalyst for the Different Engine Conditions at 2000rpm

Compound	**HCCI λ=1, 3.0bar (ppm)**		**HCCI λ =1, 4.0bar (ppm)**		**HCCI λ =1.4, 3.5bar (ppm)**		**HCCI λ =1.4, 4.5bar (ppm)**		**SI λ =1, 4.0bar (ppm)**		**HCCI+H_2 λ =1.4, 4.5bar (ppm)**	
	Bcat	Acat	Bcat	Acat	Bcat	Acat	Bcat	Acat	Bcat	Acat	Bcat	Acat
Methane	67	45	45	37	60	5	27		72	3	27	30
Ethylene	190	72	128	4	191	2	113	0.0	230	9	113	0.0
Propylene	143	98	88	3	132	2	90	0.0	298	4	90	0.0
Propane	3	1	0.0	0.0	2	0.0	1	0.0	0.0	0.0	1	0.0
Iso-butane	48	18	26	7	51	0.0	41	0.0	11	0.0	41	0.0
1-butene	60	32	38	0.0	51	0.0	40	0.0	46	0.0	40	0.0
1,3 butadiene	39	6	27	0.0	33	0.0	25	0.0	20	2	25	0.0
n-butane	86	32	47	13	87	3	71	0.0	14	0.0	71	9
Iso-pentane	173	62	93	17	172	5	141	4	40	0.0	141	5
1-pentene	47	10	25	0.0	49	0.0	39	0.0	28	0.0	39	0.0
n-pentane	108	35	59	7	106	2	85	0.0	47	0.0	85	2
n-hexane	103	35	56	6	98	2	83	0.0	34	0.0	83	1
Benzene	93	46	70	9	102	0.0	65	10	146	3	65	0.0
n-heptane	58	21	33	0.0	109	13	35	4	12	19	35	0.0
Toluene	590	188	417	55	781	25	531	16	340	32	531	51
Total C_1-C_7	1813	706	1156	158	2028	59	1391	35	1338	72	1391	100
Total HC (ppm)	3065	1212	2196	133	2622	92	2106	85	1651	81	2106	196
C_1-C_7 (% of THC)	60		52		77		66		81		66	

The individual compounds that are quantified in this study such as 1,3 butadiene and benzene are carcinogenic and they were chosen because of the impact they have with the other species on air quality and ultimately human health. The Occupational Safety and Health Administration (OSHA) have introduced exposure limits for different chemicals. These limits (time weighted average) are called permissible exposure limits (PELS), which are calculated based on an exposure time of 8 hours. These exposure limits are listed in Table 5.4.

Table 5.4: MSDS, Material Safety Data Sheet: Chemical Compounds Exposure Limits[153].

Chemical Compounds	**Exposure Limits (ppm) TWA**
Methane	N.A
Ethylene	200
Propylene	500
Propane	1000
Iso-butane	800
1-butene	N.A
1,3 butadiene	2
n-butane	800
Iso-pentane	1000
1-pentene	N.A
n-pentane	1000
n-hexane	500
Benzene	1
n-heptane	500
Toluene	200

TWA: Time Weight Average

5.4.1 Catalyst performance under HCCI operation, effects of engine load, 3 4bar NMEP, λ = 1.

The effect of engine load on the production of C_1 to C_7 hydrocarbon species at stoichiometric ratio (λ = 1) of HCCI mode are compared in Figure 5.2 and Figure 5.3. The individual HC distribution observed from the high HCCI engine loading of 4bar NMEP is similar to that at the low load condition of 3bar NMEP, except that the concentrations are significantly lower at the higher load of 4bar NMEP conditions both, before and after the catalyst. As expected, hydrocarbon reduction efficiency over the catalyst was significantly improved at higher engine load conditions, as a result of the higher exhaust gas temperatures and oxygen availability. The average individual HC conversion over the catalyst at low and high engine loads is 60% and 85%, respectively. Note that the relatively high methane concentration is believed to be the direct result of ethylene and propylene break down, while its low conversion reflects the low rate of methane oxidation by the catalyst in this temperature range.

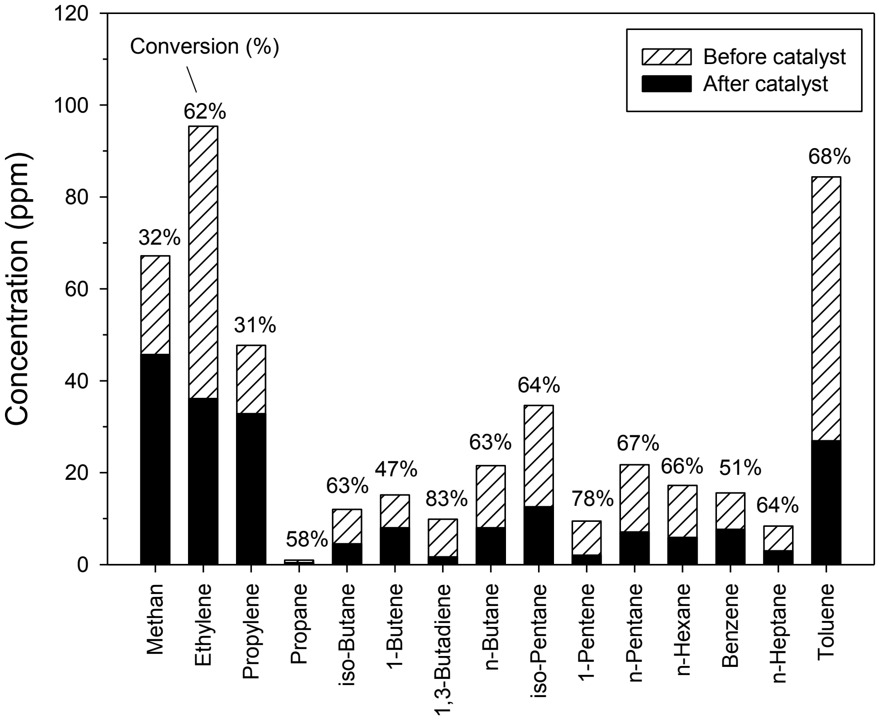


Figure 5.2: Catalytic Efficiency and C_1-C_7 Hydrocarbon Speciation (3bar NMEP, HCCI, Lambda 1)

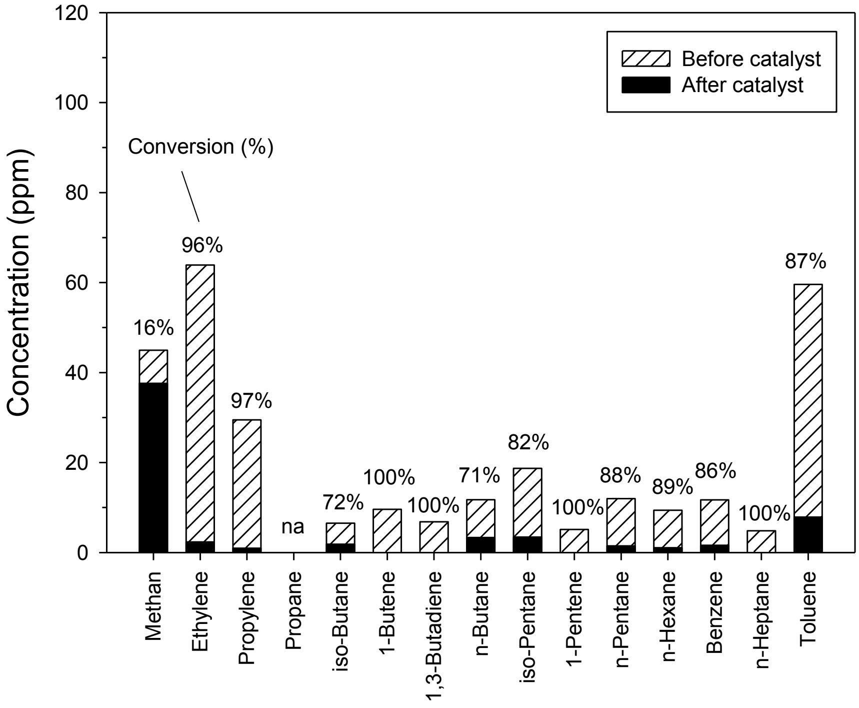


Figure 5.3: Catalytic Efficiency and C_1-C_7 Hydrocarbon Speciation (4bar NMEP, HCCI, Lambda 1)

5.4.2 Catalyst performance under SI and HCCI operation, engine load 4bar NMEP, $\lambda = 1$.

The catalyst efficiency in reducing THC emissions and its effects on the hydrocarbon speciation during stoichiometric HCCI and SI combustion modes are compared under the same load of 4bar NMEP in Figure 5.3 and Figure 5.4 , respectively. Approximately 24% less THC was released during the SI operation when compared to the HCCI mode Table 5.1. The higher HC concentrations during HCCI combustion are mainly attributable to C_4-C_7 species, arising from unburned fuel fractions and the break-down of toluene and other aromatics.

An average C_1-C_7 HC reduction of 94% and 85% was observed over the catalyst during the SI and HCCI mode, respectively. In SI mode the catalyst benefited from the high exhaust gas temperature of 661^{o}C, compared to 413^{o}C exhaust temperature during HCCI mode. GC-FID Chromatogram of SI chemical compounds, before and after catalyst are shown in Figure 5.5 and Figure 5.6 .

Furthermore, the lower combustion temperature of HCCI led to less efficient fuel combustion. As a result, the amount of total olefins traces (e.g. ethylene) was significantly lower than produced in the SI mode. The experimental results suggest that approximately 50% of the total engine HC emissions are typically from C_5 and above.

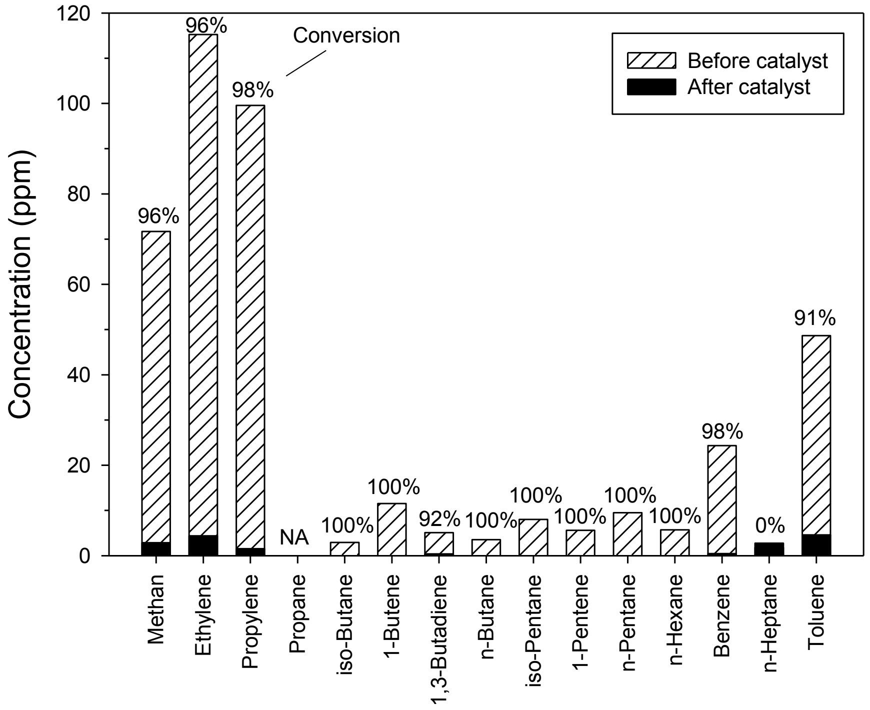


Figure 5.4: Catalytic Efficiency and C_1-C_7 Hydrocarbon Speciation (4bar NMEP, SI, Lambda 1)

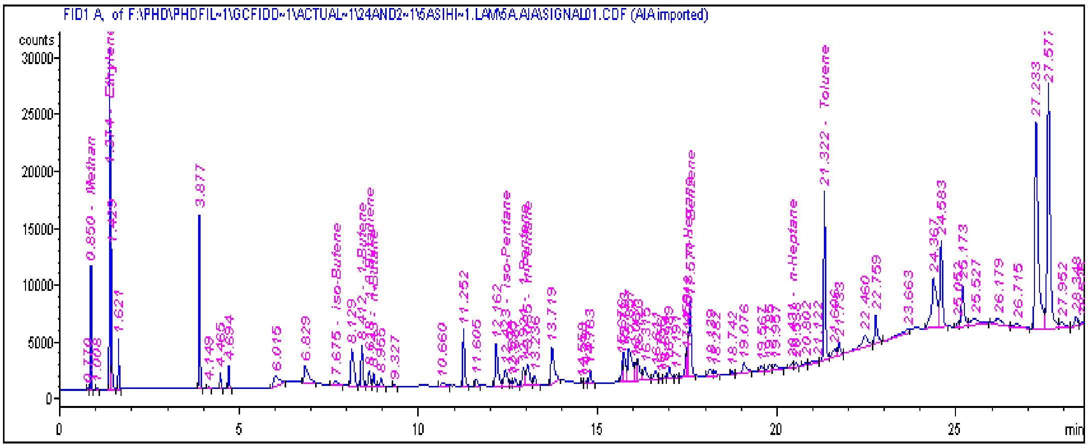


Figure 5.5: GC-FID Chromatogram of SI chemical compounds, Lambda 1, and 4.0 bars before catalyst

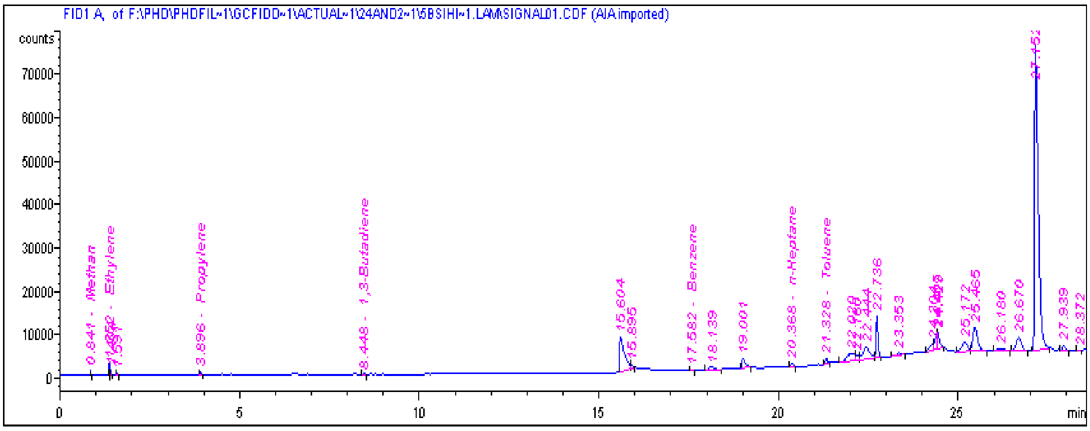


Figure 5.6: GC-FID Chromatogram of SI chemical compounds, Lambda 1, and 4.0 bars after catalyst

5.4.3 Catalyst performance under HCCI operation of engine loads 3.5-4.5bar, $\lambda = 1.4$.

Under lean HCCI combustion (i.e. $\lambda = 1.4$), the different engine load conditions had less effect on either the individual HC distributions or concentration levels Figure 5.7 and Figure 5.8 when compared with the stoichiometric conditions (i.e. condition 1 and 2). GC-FID Chromatogram of HCCI lean, chemical compounds before and after catalyst is shown in Figure 5.9 and Figure 5.10. The catalytic combustion efficiency was improved by the excess oxygen available, as shown by the HC conversion, which was approximately 98% for both conditions (i.e. 3.5 and 4.5bar).

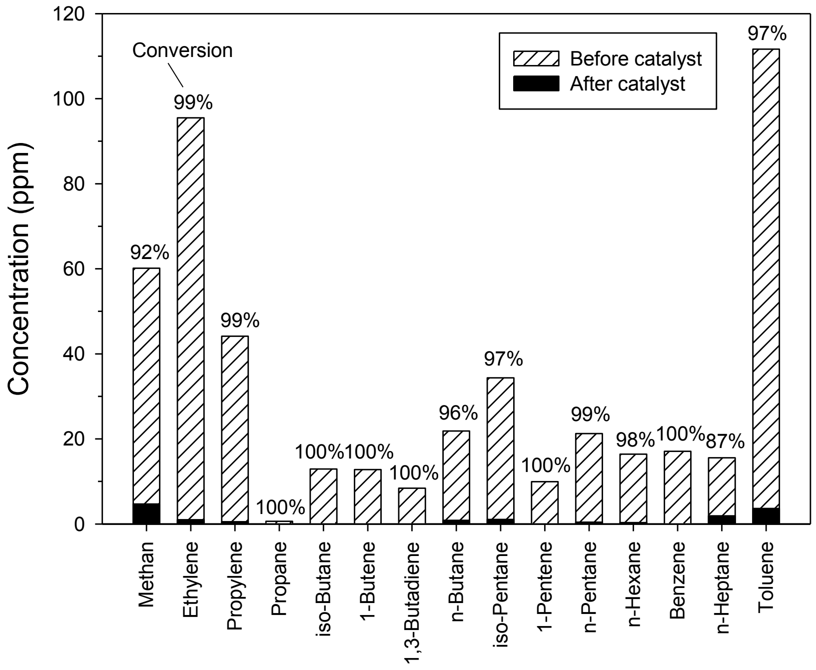


Figure 5.7: Catalytic Efficiency and C_1-C_7 Hydrocarbon Speciation (3.5bar NMEP, HCCI, Lambda 1.4)

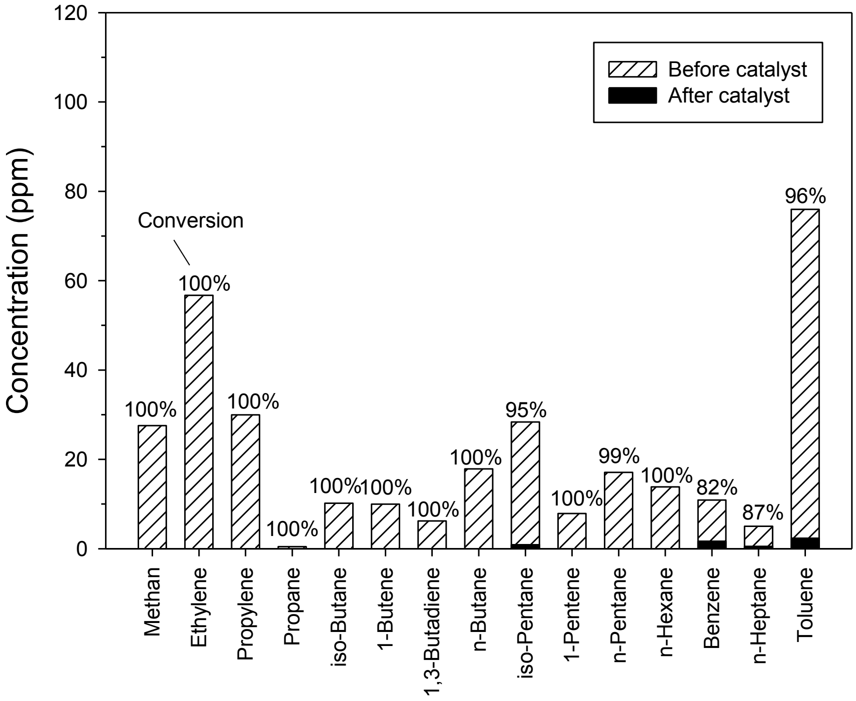


Figure 5.8: Catalytic Efficiency and C_1-C_7 Hydrocarbon Speciation (4.5bar NMEP, HCCI, Lambda 1.4)

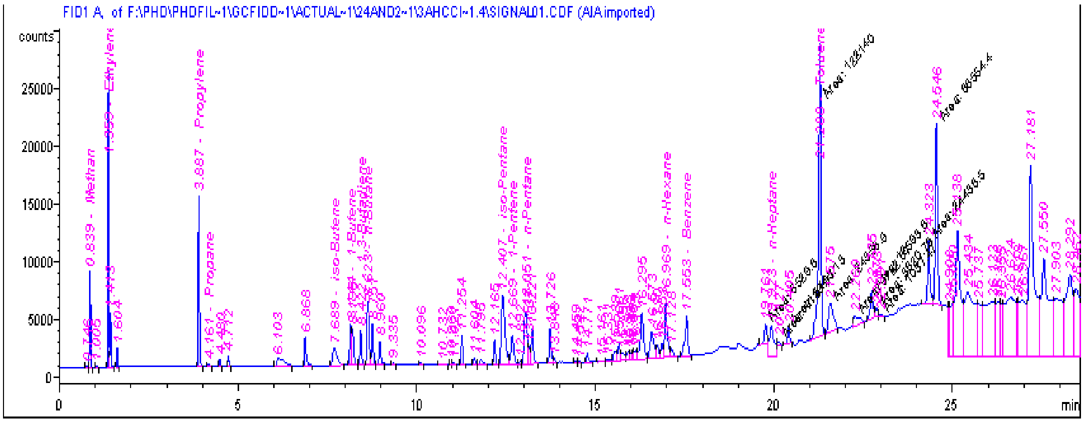


Figure 5.9: GC-FID Chromatogram of HCCI lean chemical compounds, Lambda 1.4, and 3.5 bars before catalyst

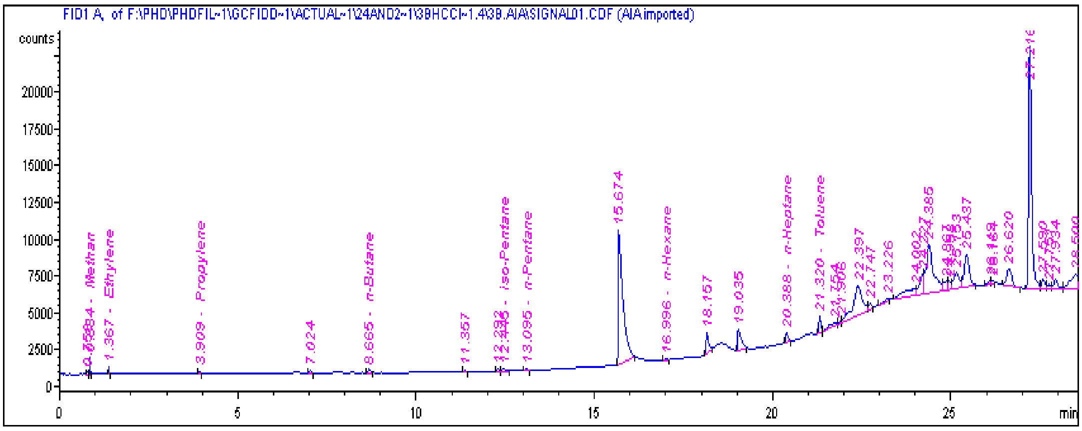


Figure 5.10: GC-FID Chromatogram of HCCI lean chemical compounds, Lambda 1.4, and 3.5 bars after catalyst

5.4.4 Catalyst performance with H_2= 2400ppm addition, HCCI operation of engine load 4.5bar, $\lambda = 1.4$

Under the same engine operating condition Figure 5.11 (HCCI, λ = 1.4, 4.5bar NMEP) hydrogen addition, 2400ppm in this case, has no beneficial effects on catalyst performance. In fact, the THC conversion over the catalyst was reduced from 97% to 91%. This could be due to the hydrogenation affect, where H2 reacts with aromatic species to form saturated HC species which could be affected HC conversions over the catalyst.

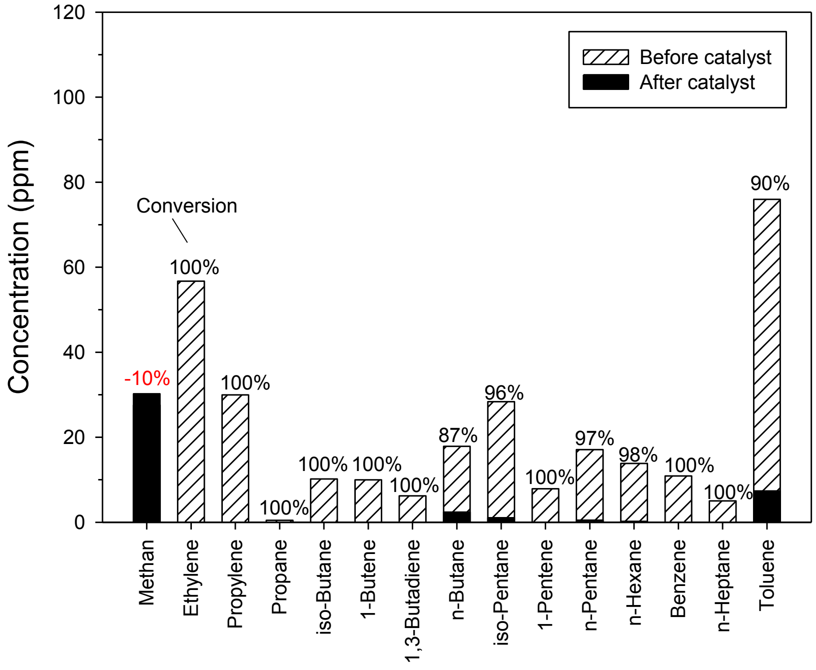


Figure 5.11: Catalytic Efficiency and C_1-C_7 Hydrocarbon Speciation (4.5bar NMEP, HCCI, Lambda 1.4, H2 Addition= 2400ppm)

5.5 Further Discussion on C_1 to C_7 HC Speciation

5.5.1 Alkanes

Engine-out emissions of methane, propane, iso-butane, n-butane, iso-pentane, n-pentane and n-hexane were all within the range of 0-67 ppm in the HCCI combustion mode Table 5.3. The concentrations of these saturated hydrocarbons increased as the engine load and combustion temperatures were reduced. Switching to SI mode, the concentration of most of these species were reduced to less than 15 ppm as a result of the higher combustion temperatures, with the exception of methane. The concentration of this greenhouse gas was much higher (72 ppm) than during HCCI stoichiometric combustion Figure 5.12.

Breakdown of higher HC species during high temperature combustion is one of the main reasons suggested by Horn et al 2006 and Williams et al [154-155]for the formation of methane.

Conversion efficiencies of the alkanes over the catalyst were in the range of 71-100% for both engine modes, except for methane at HCCI stoichiometric conditions where methane conversion was 32% and 16%, respectively. The addition of H_2 at the inlet of catalyst did not have the expected impact on alkane conversion. It is believed that the low flash point of H_2 has a negative effect, as it consumes part of the oxygen and promotes the oxidation of lighter unsaturated species instead of the alkanes species (i.e. iso-butane, n-butane). The increase of methane after the catalyst shows its resistance to oxidation, and also indicates its formation from the breakdown of the heavier HCs over the catalyst.

5.5.2 N-heptane

N-heptane - is a straight chain alkane which is considered toxic to aquatic organisms, its toxicity to fish is EC50/84h/Daphnia = 1.5 mg/L [156]. The n-heptane concentration in the exhaust was dependent on the engine combustion temperatures, and therefore increased as the engine load was reduced. Catalyst efficiency in reducing n-heptanes reached 100% at 4bar NMEP for HCCI stoichiometric operation as a result of the higher exhaust temperature, regardless of the differences in air/fuel ratio.

5.5.3 Alkenes

Alkenes (i.e. ethylene, propylene, 1-butene, 1-pentene). Without the influence of the catalyst, higher concentrations of ethylene and propylene were produced during HCCI operation, at low engine loads, regardless of the air/fuel ratio, in agreement with the results of Li et al [157] from their studies using n-heptane as fuel. A similar trend has been observed from 1-butene and 1-pentene species. The alkenes content in the exhaust is attributed to the incomplete combustion of the alkanes in the fuel. In SI engine operation ethylene and propylene concentrations were higher than during HCCI engine operation, as a result of the higher combustion temperatures, promoting paraffinic species conversion into olefins (e.g. ethylene) by H-atom abstraction, in agreement with the results reported by Elghawi et al [131].

The prototype catalyst showed excellent performance in oxidising alkenes, with the catalyst conversion efficiency lying within the range of 96-100% in most cases, except during engine operation at the HCCI stoichiometric condition with load of

3bar NMEP. Despite the relatively high exhaust gas temperature of 385°C, the low oxygen content in the exhaust restricted the alkene conversion to 32-78 %. Under all other test conditions with even lower exhaust gas temperature of 349°C (condition 3, Table 5.2), 96% reduction was achieved, a result that shows the correlation between the oxygen concentration and the conversion of alkenes.

5.5.4 1,3Butadiene

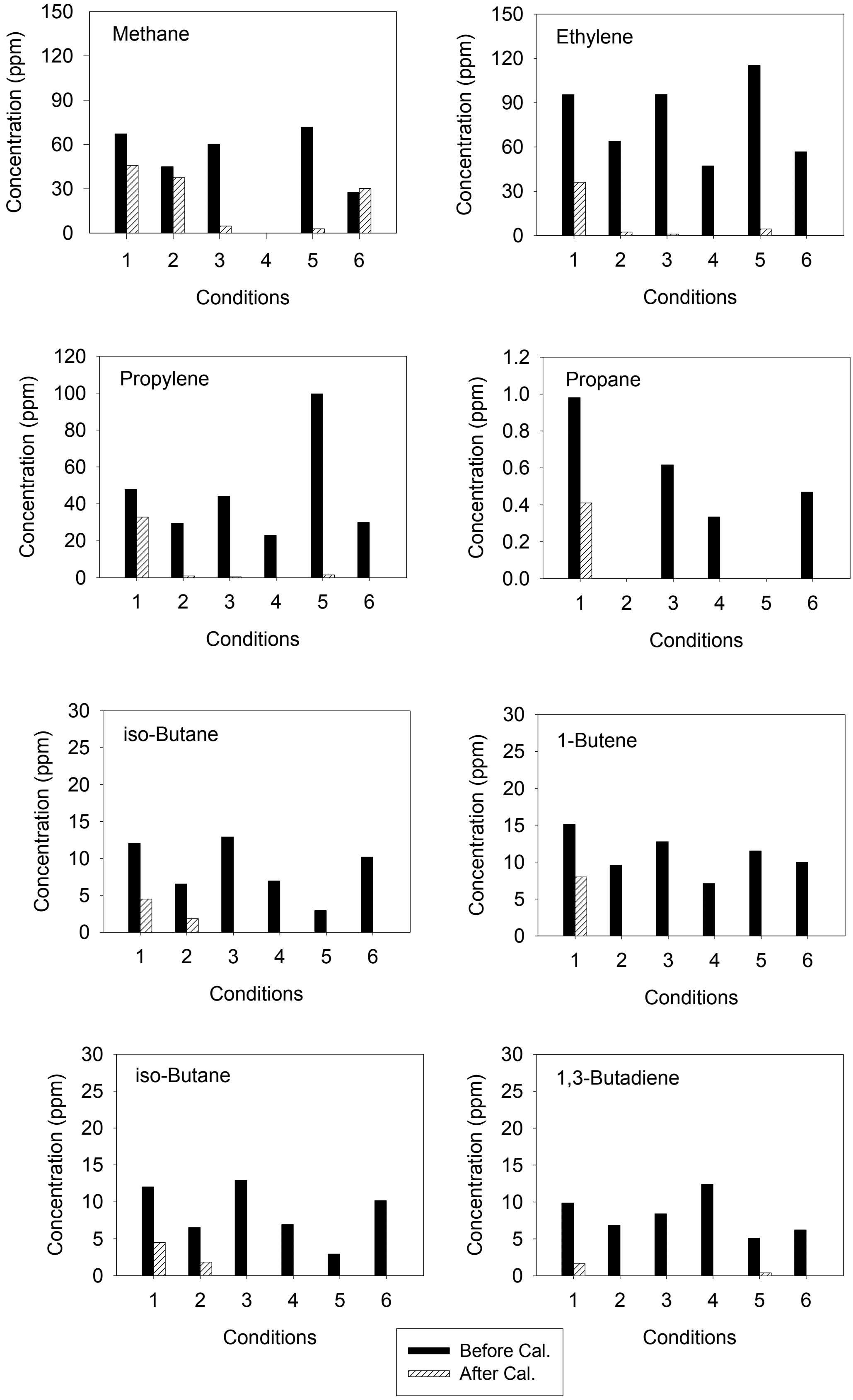
1,3Butadiene - Unlike other unregulated hydrocarbons, 1,3-butadiene is a photo-chemically reactive compound [38]. It is a by-product of partial HC oxidation, with 90% of the 1,3-butadiene in the engine exhaust coming from common alkanes and aromatic constituents of the fuel. The US EPA has classified 1,3-butadiene as a group B2 carcinogen, which means that it is a probable human carcinogen (EPA, 2000) [10]. The highest trace of 1,3-butadiene was produced during HCCI engine operation, mainly because of the low combustion temperatures compared to SI, making alkenes less likely to be oxidised or decomposed. The catalyst eliminated all the 1, 3-butadiene, except during HCCI stoichiometric operation at 3 bar NMEP, where a concentration of 2 ppm was recorded.

5.5.5 Aromatic compounds - (benzene, toluene)

Benzene - is primarily a dealkylation product formed from toluene, alkylbenzenes and xylenes during incomplete combustion [37, 158]. A risk assessment by Johnson et al indicates that an exposure of 1-5 ppm in ambient air for 40 years is associated with an increased risk of acute myeloid leukaemia [159]. Based on the epidemiological evidence, benzene is considered as a human carcinogen (group 1) by LARC, the international agency for research on cancer [8].

In our work, the concentration of benzene ranged from 10 ppm to 24 ppm with the highest concentration being for the engine operating in SI mode Figure 5.12 condition 5. This is due to the increased post-flame oxidation, which also explains why in the SI mode benzene formation is favoured over toluene [160]. High conversion of benzene over the catalyst was achieved in the SI mode, in contrast to HCCI where the benzene conversion over the catalyst was as low as 51%, giving benzene traces above the recommended limit. Toluene - Although pronounced toxic effects of high and long-term toluene exposure are well-known [161], the health effects of short-term exposure remain uncertain. Although it is a non carcinogen (category: 3A), its appearance is often related to the formation of benzene due to its related aromatic structure. For example, Schuetzle et al 1994 [114] have shown that a substantial increase in benzene emissions is observed when toluene or xylene is added to gasoline fuel.

Throughout our tests, toluene was present at relatively high concentrations compared to the rest of the measured compounds in this group. The highest and lowest toluene traces of 112 ppm and 49 ppm as seen in Figure 5.12 were found in SI mode and at HCCI lean mixture with 3.5bar NMEP, respectively.


Methane
Concentration (ppm)
150
120
90
60
30
0
1 2 3 4 5 6
Conditions
Ethylene
Concentration (ppm)
150
120
90
60
30
0
1 2 3 4 5 6
Conditions
Propylene
Concentration (ppm)
120
100
80
60
40
20
0
1 2 3 4 5 6
Conditions
Propane
Concentration (ppm)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
1 2 3 4 5 6
Conditions
iso-Butane
Concentration (ppm)
30
25
20
15
10
5
0
1 2 3 4 5 6
Conditions
1-Butene
Concentration (ppm)
30
25
20
15
10
5
0
1 2 3 4 5 6
Conditions
iso-Butane
Concentration (ppm)
30
25
20
15
10
5
0
1 2 3 4 5 6
Conditions
1,3-Butadiene
Concentration (ppm)
30
25
20
15
10
5
0
1 2 3 4 5 6
Conditions
Before Cal.
After Cal.

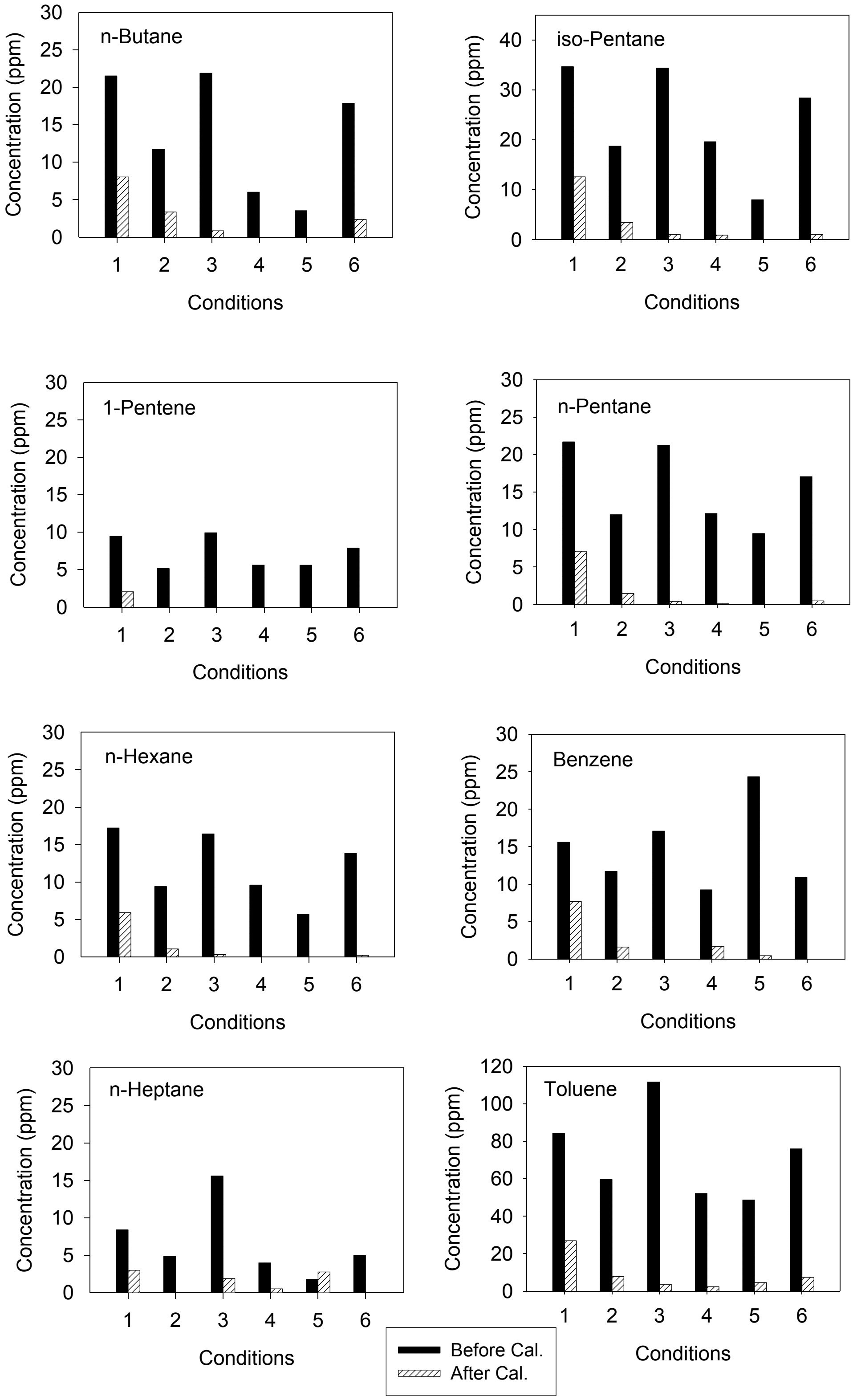


Figure 5.12: Engine emissions C_1-C_7 before and after the catalyst: 1) HCCI, 3bar λ=1; 2) HCCI, 3.5bar λ=1; 3) HCCI, 3.5bar λ=1.4; 4) HCCI,4.5bar λ=1.4; 5) SI, 4bar λ=1; and 6) HCCI+ H2, 4.5bar λ=1.4.

CHAPTER 6:

DETERMINATION OF HYDROCARBONS SPECIES (C5-C11) FROM HCCI/SI GASOLINE ENGINE, EQUIPPED WITH PROTOTYPE CATALYST

6.1 Introduction

This chapter describes a study on the performance of a three way catalytic converter in reducing heavy hydrocarbon species in the engine exhaust under lean and stoichiometric SI and homogeneous charge compression ignition (HCCI) engine operating conditions. A qualitative and quantitative analysis of hydrocarbon compounds ranging from C_5-C_{11}, before and after the catalytic converter, was conducted using Gas Chromatography-Mass Spectrometry (GC-MS). The experimental setup for this work is shown in Figure 6.1. The following compounds were monitored at engine and catalyst outlet; Iso-pentane, benzene, toluene, ethyl benzene, p-xylene, iso-octane, naphthalene and methylnaphthalene.

A 30 meter long x 0.53mm i.d. DB-1 capillary column with a 3μm film thickness was used, this type of column allows for separation of both the polar and non-polar compounds.

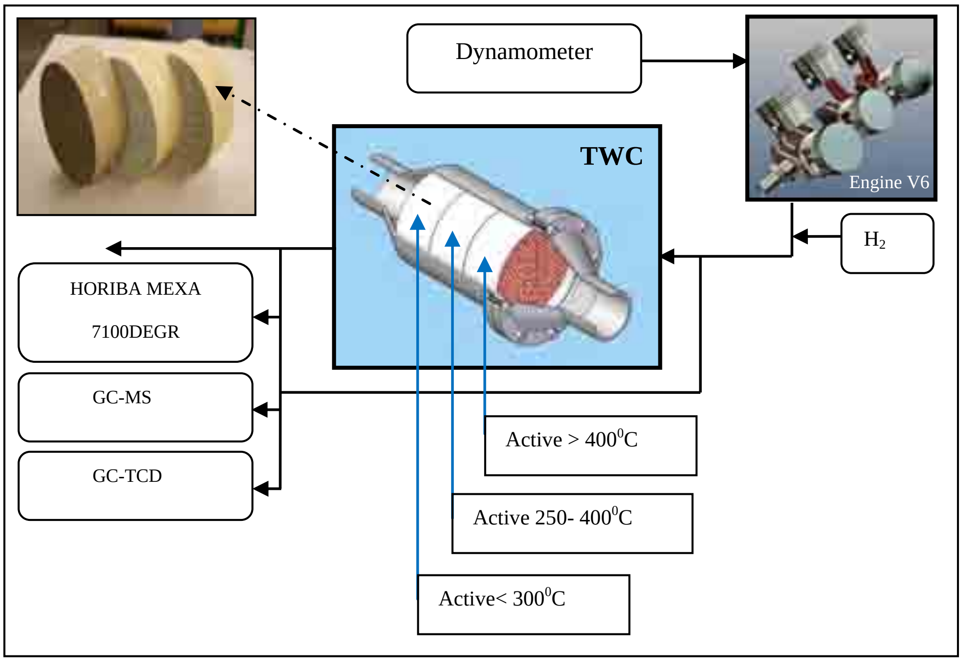


Figure 6.1: Schematic of Experimental setup

6.2 Engine operation conditions

The operating window of the HCCI/SI research engine is limited by misfire at low load or knocking at high load. A broader discussion about the HCCI operating window has been described in previous publications [162-163]. Six engine conditions were selected for the emission speciation upstream and downstream the catalyst as shown in Table 6.1. To be able to switch to HCCI operation the valve-train was modified to permit operation in HCCI mode by the provision of a cam profile switching mechanism. This cam profile switching (CPS) system is used to switch between SI and HCCI modes. This system allows on-line switching of valve lift from 9mm (SI operation) to 3mm (HCCI) operation. The HCCI operation is achieved by internal residual gases, using negative valve overlap which traps exhaust gases in order to retain enough energy for auto-ignition. The variable valve timing system of the engine makes it possible to change the valve timing for the inlet and exhaust valves within a 60 crank angle (CA) degree range. The conditions studied here are a) engine load effect under HCCI stoichiometric conditions; b) air to fuel ratio (stoichiometric and lean), c) HCCI and SI combustion modes under the same load and d) hydrogen addition upstream of the catalyst.

Table 6.1: Engine conditions and emissions under HCCI and SI modes at 2000 rpm speed.

	Mode	HCCI	HCCI	HCCI	HCCI	SI	HCCI+H2
Engine Condition	Condition No	1	2	3	4	5	6
	λ	1.0	1.0	1.4	1.4	1.0	1.4
	NMEP / bar	3.0	4.0	3.5	4.5	4.0	4.5
Emissions	THC/ ppm	3065	2196	2622	2106	1651	2106
	O_2 / %	1.2	1.2	6.29	6.55	1.06	6.55
	CO_2%	12.31	13.92	10.31	10.34	13.81	10.34
	Fuel Cons./gh^{-1}	3000	4100	3900	4800	5200	4800
	T_{Ex}./ °C	385	413	349	386	661	406

The speciation of C_5-C_{11} hydrocarbon species from the collected samples of both engine modes produced eight compounds with different concentrations. The aromatic species were dominating the engine out emissions from HCCI mode followed by alkane species, benzene was the only compound dominant in SI mode. Each compound has different retention time as shown in Table 6.2.

Table 6.2: Retention Time of detected Compounds

Peak NO	Compound	Retention Time (minute)
1	iso-pentane (IP) C_5H_{12}	3.77
2	Benzene (Bz) C_6H_6	7.04
3	iso-octane (Io) C_8H_{18}	7.85
4	Toluene (T) C_7H_8	9.42
5	ethyl benzene (EBz) C_8H_{10}	11.54
6	p-xylene (Px) C_8H_{10}	11.72
7	Naphthalene(Na) $C_{10}H_8$	18.19
8	Methylnaphthalene (MeNa) $C_{11}H_{10}$	20.66

6.3 Engine-out speciated hydrocarbon emissions

In both lean (λ=1.4) and stoichiometric HCCI operation, when increasing engine load, HC species emissions were reduced. For the same conditions (speed and load) under stoichiometric SI and HCCI, THC emissions were found to be approximately 25% lower for SI combustion compared to HCCI. This shows that the magnitude of THC emissions is highly affected by engine load, air/fuel ratio, and combustion mode.

Hydrocarbon emissions are highly dependent on the engine load and tend to be high at low load engine conditions Table 6.1, where the in-cylinder mean gas temperatures are also low and combustion is less efficient [112] . At low exhaust gas temperatures the catalyst efficiency in reducing these emissions is also lower. Individual HC species such as benzene appeared to be produced primarily by the dealkylation of toluene and xylene during combustion. Another source of benzene formation could come from cyclohexan (C_6H_{12}) which is the only non-aromatic component in the fuel which could produce significant levels of benzene.

Furthermore, the lower HCCI combustion temperature led to less efficient fuel combustion which reduced oxidation post combustion. Increasing the engine load to 4bar, Figure 6.2 (conditions 1 and 2), has the greatest effect on the hydrocarbon species in the range of C_5 to C_8. There was a reduction of approximately 100% for iso-octane and 19% for both benzene and ethyl benzene. Compared to all of the measured species, toluene generally had the highest concentration at low load, and was reduced by approximately 30% as the engine load was increased. In contrast some compound species such as naphthalene, and methylnaphthalene showed a reverse trend when the load was increased, for both SI and higher load HCCI where the in-cylinder and exhaust temperatures are higher. This phenomenon could be attributed to two benzene rings joining together by sharing a pair of carbon atoms to form the polycyclic aromatic hydrocarbon naphthalene ($C_{10}H_8$). Further reaction pathways make it possible for the hydrogen atoms to be interchanged with methyl groups [164].

Under lean HCCI combustion (i.e. $\lambda = 1.4$) increasing engine load has relatively less effects on C_5 - C_7 hydrocarbons compared to C_8 - C_{11} hydrocarbons Figure 6.2 (conditions 3 and 4). Increasing engine load has a significant effect on the heavier aromatic hydrocarbons (e.g. p-xylene, naphthalene and methylnaphthalene), which are reduced by 38%, 65% and 51% respectively.

Hydrocarbon species measured in the engine exhaust under HCCI and SI stoichiometric combustion modes were compared for the same load of 4bar NMEP as shown in Figure 6.2 (conditions 2 and 5). The toluene concentration in HCCI mode was found to be 18% higher than in SI mode and is one of the major volatile compounds in the atmosphere [165]. Toluene and xylene are not currently listed as carcinogens, with their appearance often being related to the formation of benzene, due to its aromatic based structure. On the other hand benzene and ethyl benzene are found to be higher in SI mode, this could be attributed to the breakdown of toluene and p-xylene during the combustion process.

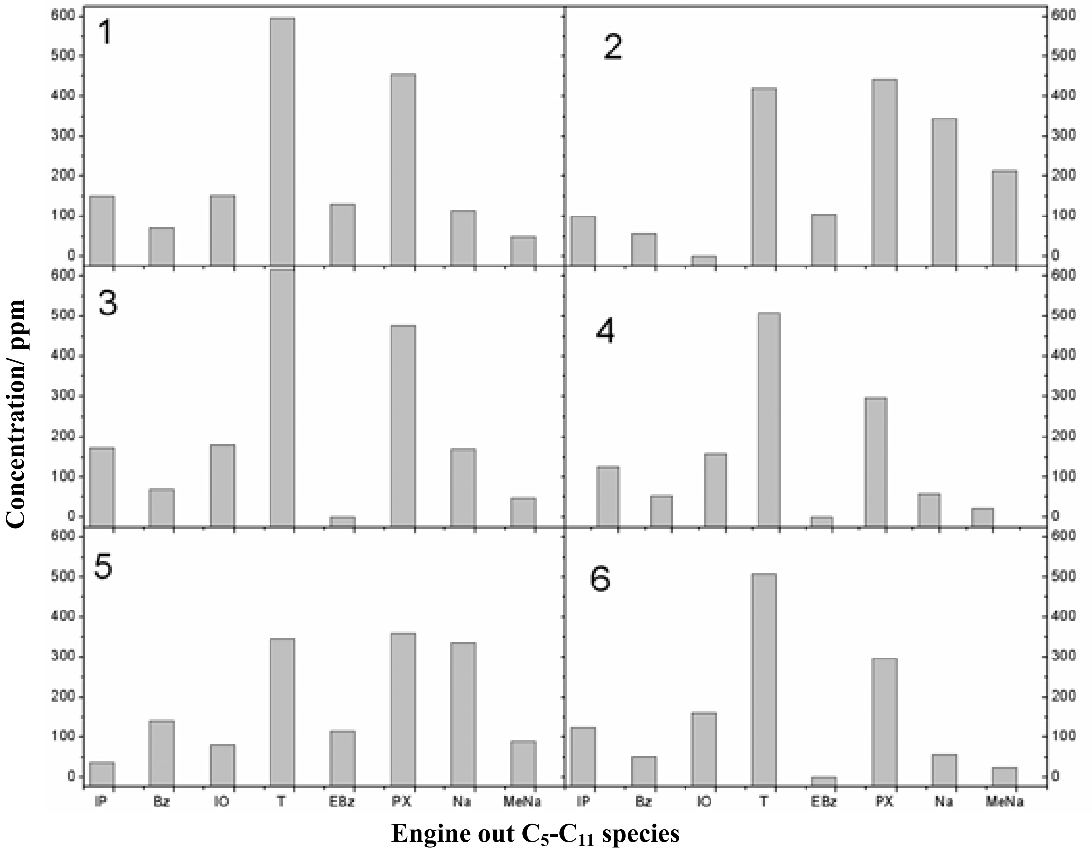


Figure 6.2: Engine out C_5-C_{11} species emissions: 1) HCCI, 3bar, λ=1, 2) HCCI, 4bar, λ=1; 3) HCCI 3.5, λ=1.4; 4) HCCI 4.5bar, λ=1.4; 5) SI 4bar, λ=1; and 6) HCCI+ H2, 4.5bar, λ=1.4.

The increase in HC species concentration for HCCI combustion is mainly caused by C_5 to C_{10} hydrocarbons, Table 6.3. This can be attributed to the unburned fuel and break-down of toluene and alkenes compounds. As a result, the total amount of aromatic species, i.e. toluene, p-xylene, naphthalene and methyl naphthalene is higher than that for SI mode. The detected HC species exposure limits are shown in Table 6.4.

Table 6.3: Hydrocarbons species (C_5 – C_{11}) before and after the catalyst for the different engine conditions at 2000rpm engine speed

Compound	HCCI λ=1, 3.0bar (ppm)		HCCI λ =1, 4.0bar (ppm)		HCCI λ =1.4, 3.5bar (ppm)		HCCI λ =1.4, 4.5bar (ppm)		SI λ =1, 4.0bar (ppm)		HCCI+H_2 λ =1.4, 4.5bar (ppm)	
	B	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**B**	**A**
Iso-pentane	150	55	100	15	174	15	125	8	36	6	125	39
Benzene	72	25	58	2	68	0	52	4	140	10	52	27
Iso-octane	151	52	N.A	N.A	180	39	160	27	80	0	160	N.A
Toluene	597	144	420	41	616	30	508	14	345	34	508	40
Ethyl benzene	130	29	105	19	N.A	N.A	N.A	N.A	115	19	N.A	N.A
p- xylene	454	115	442	46	476	20	296	39	360	63	296	27
Naphthalene	114	55	344	69	170	144	58	44	335	159	58	0
Methylnapthalene	50	33	214	66	47	42	23	23	89	89	23	0
Total C_5-C_{11}	1718	508	1683	258	1731	290	1222	178	1500	384	1222	133
Total HC (ppm)	3065	1212	2196	133	2622	92	2106	85	1651	81	2106	196
C_5-C_{11} (% of THC)	56		76		66		58		90		58	

B- before catalyst
A- after catalyst

Table 6.4: Permissible Exposure Limits [153]

Chemical Compounds	Exposure Limits (ppm) TWA
Iso-pentane	1000
Benzene	1
Iso-octane	300
Toluene	200
Ethyl benz	100
p-xylene	150
Naphthalene	10
Methyl napth	N.A

TWA- time weighted average

6.4 Catalyst conversion efficiency

The average hydrocarbons species conversion over the catalyst under HCCI and SI combustion was over 90% for all engine conditions except for HCCI stoichiometric at lower load where the HC species conversion reduced to 60% as seen in Table 6.3. At low exhaust gas temperatures only the 3rd (bottom) catalyst layer is active in C-containing species oxidation (Table 6.1 and Figure 6.1). Under these conditions the space velocity (SV) is significantly high as only 1/3 of the catalyst is active, which also explains the reduced HC oxidation. As expected, hydrocarbons species reduction efficiency over the catalyst was significantly improved across the high engine load conditions, as a result of the higher exhaust gas temperatures. Under these exhaust temperature conditions all the three catalyst layers are active in HC oxidation.

The conversion of Iso-pentane was approximately 63% for HCCI stoichiometric and improved up to 93% at HCCI lean operation Figure 6.3 this is despite the compound being a saturated alkane (single C-C bonds). Iso- octane conversion was approximately 66% in HCCI stoichiometric operation lower load (3bar) condition 1, as the temperature increases (i.e in the SI mode) Figure 6.3 condition 5, the net conversion rose 100%. The concentration of aromatic hydrocarbon, i.e. benzene and toluene was reduced in the conversion process for most engine conditions. For the aromatic hydrocarbon p-xylene (a benzene ring with two methyl substituent) an average of 85% catalyst efficiency was achieved.

For heavier aromatics compounds such as naphthalene and methylnaphthalene, the catalyst conversion was in the range of 15-80%, this low conversion could be due to the high stability of the aromatic rings which are more susceptible to further dehydrogenation than to combustion. As a result, the contact time required for catalytic combustion of heavy aromatic species is longer than that for saturated HCs, which reduces the probability of naphthalene and methylnaphthalene decomposition to smaller hydrocarbon species [120, 166]. Conversion was improved at higher temperatures as the kinetic limitations to combustion were overcome[167].

In SI mode the catalyst activity improved because of the high exhaust gas temperature that was reached (661^{o}C compared to 413^{o}C for stoichiometric HCCI at 4bar NMEP Table 6.1), as many species were identified in the tailpipe emissions. The conversions of the individual compounds over the catalyst are shown in Figure 6.3.

6.5 Catalyst performance with H_2= 2400ppm addition upstream the catalyst, HCCI lean operation

In order to investigate the potential benefit of fuel reforming processes on catalyst performance in reducing HC species emissions, approximately 2400 ppm of hydrogen was injected upstream of the catalyst. A comparison is drawn between the same engine operating condition with and without hydrogen addition, Figure 6.3, (conditions 4 and 6).

Hydrogen enhances the catalyst performance in reducing emissions such as naphthalene and methyl naphthalene. Hydrogen oxidation over the first catalyst layer increases the catalyst temperature and enhancing the oxidation reaction rate of the aromatic hydrocarbon Figure 6.3. Hydrogenation is another possibility where H_2 reacts with aromatic compounds to form other saturated hydrocarbons e.g. hydrogen addition could cause a reaction over the catalyst in which hydrogen atoms are added to the aromatic ring to form increasingly saturated hydrocarbon species, such as cycloalkane which are easier to combust. Although the hydrogenation reactions are overall exothermic, because of the strength of all the new carbon-hydrogen bonds being made, there is a high activation barrier to the reaction [168].

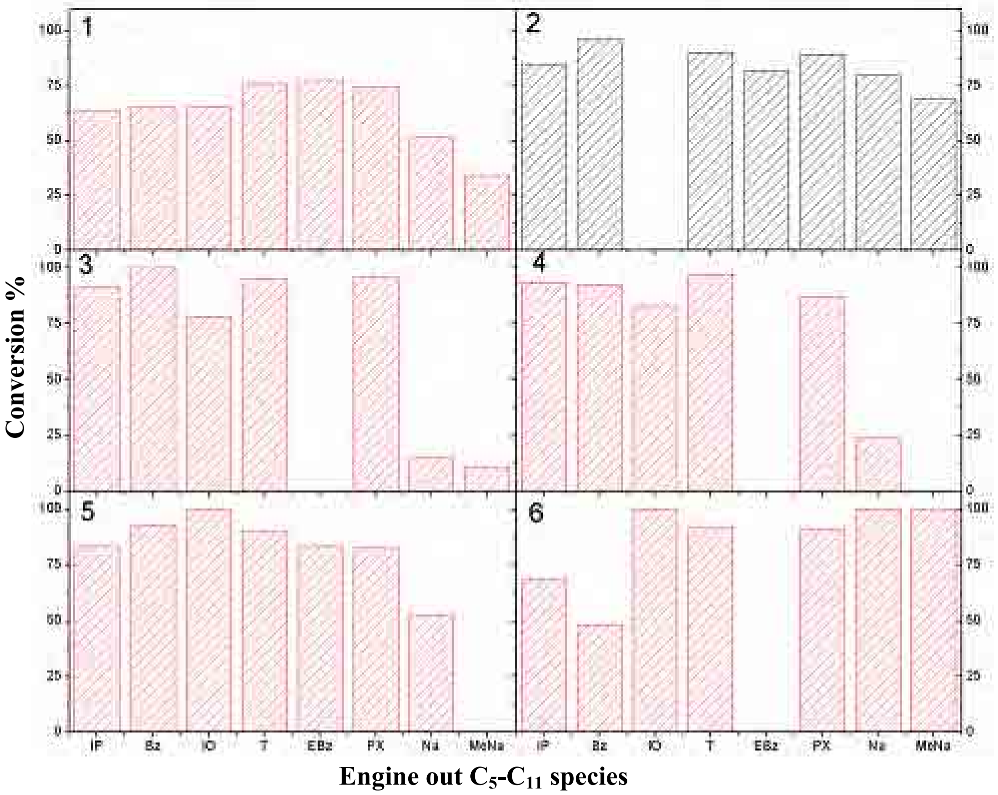


Figure 6.3: Catalyst efficiency: 1) HCCI, 3bar, λ=1; 2) HCCI 4bar, λ=1; 3) HCCI, 3.5bar, λ=1.4; 4) HCCI, 4.5bar, λ=1.4; 5) SI, 4bar, λ=1; and 6) HCCI+ H2, 4.5bar,λ=1.4

The GC-MS Chromatogram of HCCI with engine load of 4bar, λ=1, before and after catalyst is shown in Figure 6.4 and Figure 6.5. The GC-MS chromatogram of SI mode, higher load before and after catalyst is presented in Figure 6.6 and Figure 6.7.

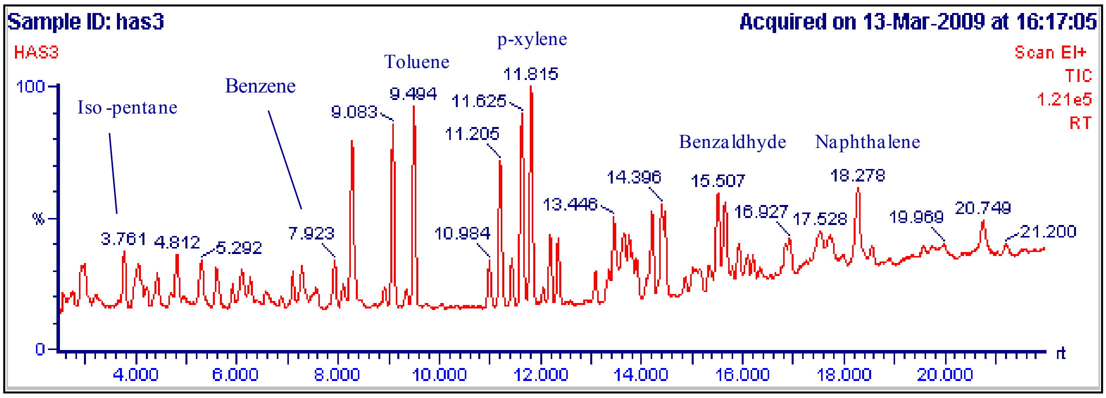


Figure 6.4 : GC-MS Chromatogram of HCCI Stoichiometric before catalyst 4.0 bar

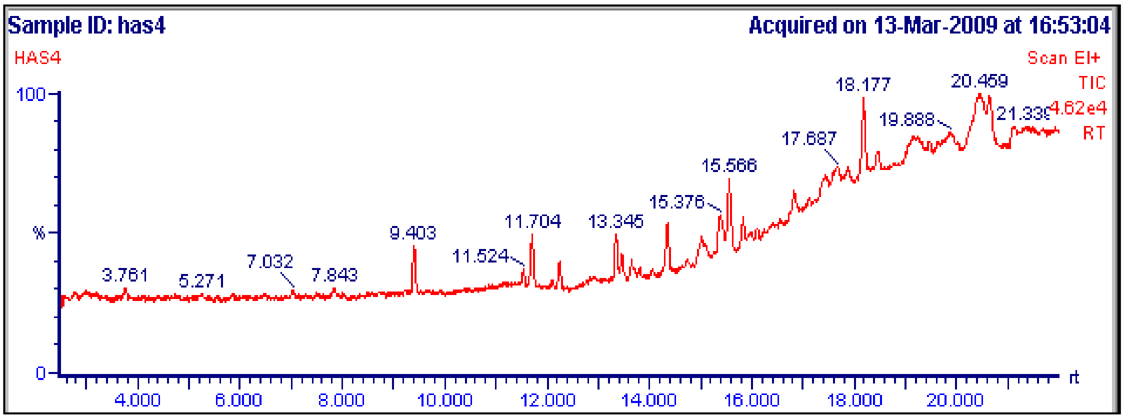


Figure 6.5: GC-MS Chromatogram of HCCI Stoichiometric after catalyst 4.0 bar

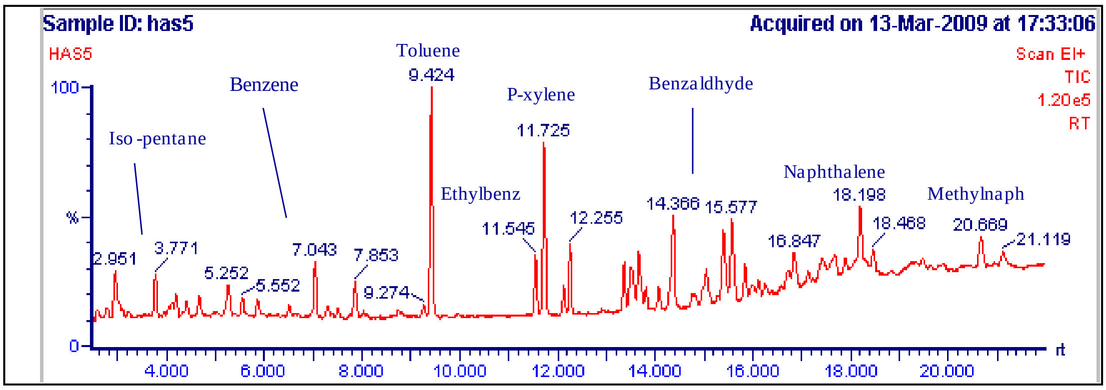


Figure 6.6: GC-MS Chromatogram of SI mode before catalyst, 4.0 bar

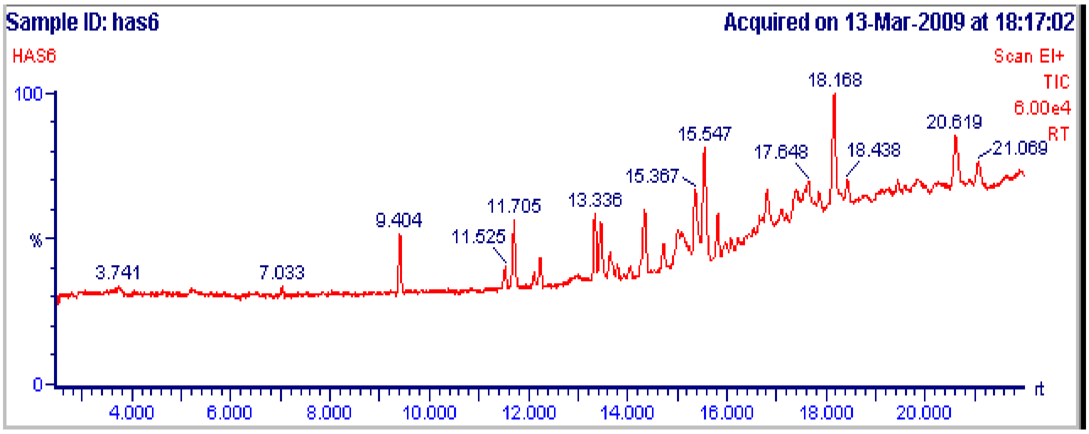


Figure 6.7: GC-MS Chromatogram of SI mode after catalyst, 4.0 bar

6.6 Further Discussion on C_5-C_{11} HC speciation

6.6.1 Iso-octane

Iso-octane – the branched alkanes such as isooctane is a major component in typical gasoline, increasing the engine load results in a decrease in the percentage of unburned isooctane fuel in the exhaust. For HCCI lean engine operation Figure 6.8, increasing engine load reduces iso-octane emissions by 11%. For HCCI stoichiometric operations at higher load (4bar) no emissions were detected. Isooctane produce higher levels of methane compared to similar higher straight chain hydrocarbons [167]. This finding supports previous results found regarding the high concentration of methane presented in HCCI stoichiometric operation[169]. Average catalyst efficiency of iso-octane conversion ranged between 78-100% for all conditions except for low load stoichiometric HCCI operation where the efficiency dropped to 66%. This could be due to the shortage of oxygen in the exhaust stream for this condition 1 (see Table 6.1).

6.6.2 Ethyl Benzene

Ethyl Benzene- this organic compound is a major combustion by-product of aromatic fuel. Formation of ethyl benzene during combustion could be attributed to the Xylene isomers (ortho-, meta-and para) as reported by Gregory et al 1999 [170]. The International Agency for Research on Cancer (IARC) recently evaluated ethyl benzene, and based on evidence of its carcinogenicity in animals, it has been classified as a possible human carcinogen (Class 2B) [8, 171]. It is involved in the formation of polycyclic aromatic hydrocarbons (PAHs), not only because it is present in the fuel, but also because it serves as a common intermediate in the combustion of other aromatic compounds, such as benzene and toluene [172]. During HCCI stoichiometric operation the concentration of this compound is a reverse function of engine loads, with a 19% reduction observed as the engine load was increased. There was not a significant difference in emissions level between HCCI and SI modes, at the same load conditions. Catalyst conversion efficiency of this compound ranged between 78-83% for all engine conditions.

6.6.3 P-xylene

P-xylene – is an aromatic hydrocarbon, in which two methyl groups are bonded to opposite C-atoms on a benzene ring. The formation of this isomer could be attributed to the substitution of two hydrogen atoms in benzene during combustion, by two methyl groups, which gives C_6H_4 (CH_3) as di-methyl benzene (xylene) [164]. This compound is present in relatively high concentration in almost all conditions. For HCCI lean operation the emissions level is a reverse function of engine load, this could be attributed to the higher exhaust gas temperature presented at higher engine load (4.5bar) , so that 38% less is emitted when the load is increased. At engine load of 4bar, SI operation, the concentration of p-xylene emitted was 18% lower than that for stoichiometric HCCI operation while 83% to 94% catalytic conversion was achieved in all conditions.

6.6.4 Naphthalene

Naphthalene – is formed when two or three benzene rings are joined together, with naphthalene ($C_{10}H_8$) being the simplest and most abundant example in polluted urban atmospheres [173]. According to Anderson et al [174] naphthalene formation is achieved when an H atom is removed from the ring of phenyl acetylene by another H atom, this is followed by an acetylene being added to the ring and the side chains of the disubstituted aromatic joining to form the naphthyl radical. The naphthyl radical is itself converted into naphthalene by abstracting an H atom from another hydrocarbon. The phenyl acetylene is formed either from acetylene or benzene.

Naphthalene is defined as a hazardous air pollutant by the US environmental protection agency [10]. The international agency for research on cancer (IARC) has classified naphthalene as possibly carcinogenic to humans [8]. The highest concentrations were seen for stoichiometric HCCI and SI mode at an engine load of 4bar NMEP, for low load, the emitted levels were significantly lower. The naphthalene concentration for HCCI lean operation is significantly less than that for stoichiometric HCCI. Formation of naphthalene mainly occurs in the post-combustion phase of the cycle as the gas is expanding and cooling [175]. The catalyst achieved higher conversion efficiencies for higher engine loads, up to 79% for HCCI and 53% for SI mode. Naphthalene with the strong joined pair of benzene rings and shared two atoms make it more stable and offer more resistance to oxidation process.

6.6.5 Methyl naphthalene

Formation of methyl naphthalene is possible when two benzene rings join together during combustion to form polycyclic aromatic hydrocarbons; simultaneously hydrogen from this compound can be interchanged with methyl group to form methylnaphthalene. These aromatic hydrocarbon emissions are only present at low concentrations for all conditions except stoichiometric HCCI operation with a load of 4bar NMEP. For this condition the concentration was approximately 58% more than any other conditions. Catalyst conversion efficiency ranged from 0-69% for all engine conditions.

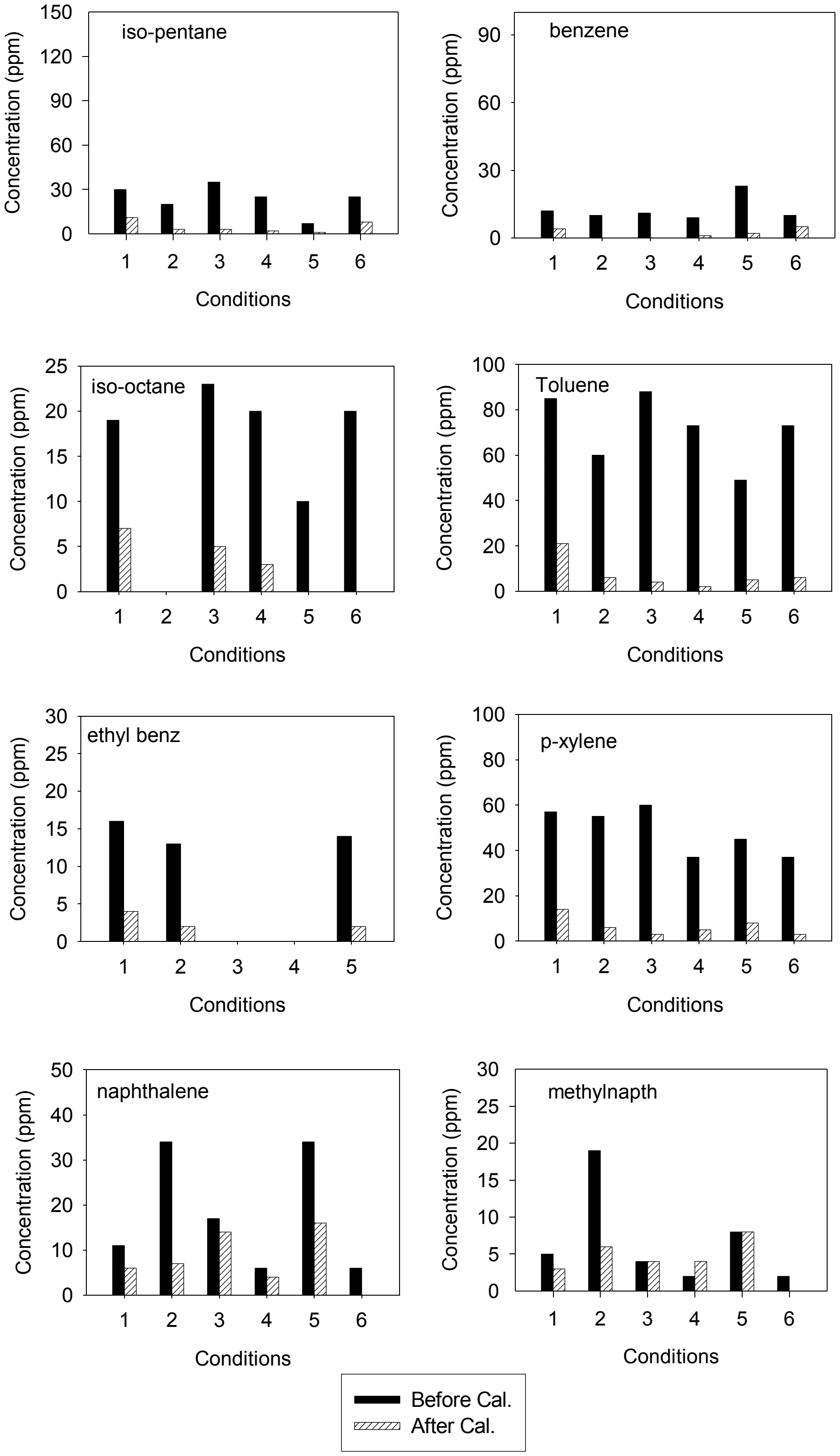


Figure 6.8: Engine emissions C_5-C_{11} before and after the catalyst: 1) HCCI, 3bar, λ=1; 2) HCCI, 4bar, λ=1; 3) HCCI, 3.5bar, λ=1.4; 4) HCCI, 4.5bar, λ=1.4; 5) SI, 4bar, λ=1; and 6) HCCI+ H2, 4.5bar, λ=1.4.

CHAPTER 7:

DETERMINATION OF CARBONYL SPECIES WITH 2,4-DINITROPHENYL-HYDRZINE METHOD FROM HCCI/SI GASOLINE ENGINE, EQUIPPED WITH PROTOTYPE CATALYST

7.1 Introduction

Carbonyl compounds are an important class of vehicular total hydrocarbon (THC) emissions. In urban atmospheres, carbonyls are mainly emitted from vehicular exhaust [176], some carbonyls are toxic, mutagenic, and even carcinogenic to the human body [177-178]. Therefore carbonyls emission from vehicular exhaust is of special importance to our study.

The main objective of the work described in this chapter is to investigate the quantitative and qualitative analysis of aldehydes and ketones from HCCI/SI gasoline engine using high performance liquid chromatography (HPLC) analysis. Twelve samples of Aldehyde and ketons were collected in an acidified acetonitrite solution of 2, 4 dinitrophenyl hydrazin (DNPH). Samples were cooled in an ice bath during the sampling for 20 minutes and were kept below 4^0C before HPLC analysis. To identify and quantify carbonyl groups from exhaust gas emissions upstream and downstream the catalyst, a 250mm x 4.6mm ID Column backed with 5µm C_{18} Acclaim 120 was used. The bubbled carbonyl species from the exhaust gets in the acidified acetonitrite solution to react with DNPH reagent to produce DNPH-carbonyl derivatives Figure 7.1.

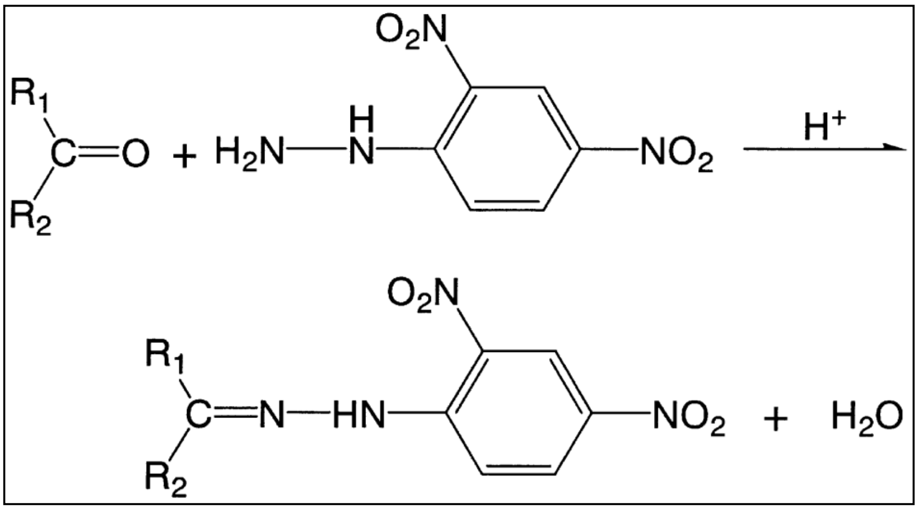


Figure 7.1: Schematic of carbonyl derivatives

The main carbonyl species in the engine-out emissions before the catalyst were Acetaldehyde (CH_3 CHO), benzeldehyde (C_6H_5CHO), formaldehyde (HCHO), and acroline (H_2=CHCHO). The other carbonyl aldehydes (e.g. o-tolualdehyde, pentanal, 2,5-Dimethylben, and hexanal) were observed but at low concentrations. Formation of unsaturated aldehyde was most significant in HCCI lean engine operation (low combustion temperature), on the other hand aromatic aldehydes were observed more during the SI mode and HCCI higher load operation. All aldehydes were identified and quantified by the ultraviolet (UV) detector after derivatization with 2, 4 dinitrophenyl-hydrozine.

7.2 Engine operation conditions

Results presented in this study were obtained from HCCI/SI gasoline research engine upstream and downstream of the prototype catalyst. A positive displacement supercharger is connected to the engine to be used when needed, but throughout this research natural aspiration was implemented. A broader discussion about the HCCI operating window has been described in previous chapters and publications [162-163]. The variable engine conditions studied are a) the engine load effect under HCCI stoichiometric operation, b) the air to fuel ratio, c) the combustion modes (HCCI vs. SI) under the same load, and d) the hydrogen addition upstream of the catalyst.

Six engine conditions were selected for the carbonyl group emission speciation upstream and downstream the catalyst as shown in Table 6.1

15 carbonyl compounds were used as reference materials to compare the detected aldehydes and ketons from the engine exhaust gases and downstream the catalyst. Table 7.1 shows the retention time of each peak corresponds to the concentration level of that specific compound. The chromatograms of carbonyl references components using DNPH derivative are shown in Figure 7.2.

Table 7.1: Retention Time for the reference Carbonyls Compounds

Peak Number	Compound	Compound Formula	Retention Time (minute)
1	Formaldehyde	HCHO	32.65
2	Acetaldehyde	CH3CHO	42.88
3	Acrolein	CH3CH=CHCHO	53.42
4	Acetone	CH3COCH3	54.63
5	Propionaldehyde	CH3CH2CHO	58.34
6	Crotonaldehyde	CH3CH=CHCHO	69.14
7	Butyraldehyde	CH3(CH2)2CHO	70.05
8	Bnzaldehyde	C6H5CHO	80.38
9	Isovaleraldehyde	(CH3)2CH(CH2)CHO	83.80
10	Pentanal	CH3(CH2)3CHO	85.57
11	o-Tolualdehyde	CH3(CH6H4)CHO	88.74
12	m-Tolualdehyde	CH3(C6H4)CHO	89.58
13	p-Tolualdehyde	CH3(C6H4)CHO	90.13
14	Hexanal	CH3(CH2)4CHO	94.98
15	2,5-Dimethylben	(CH3)2(C6H4)CHO	96.91

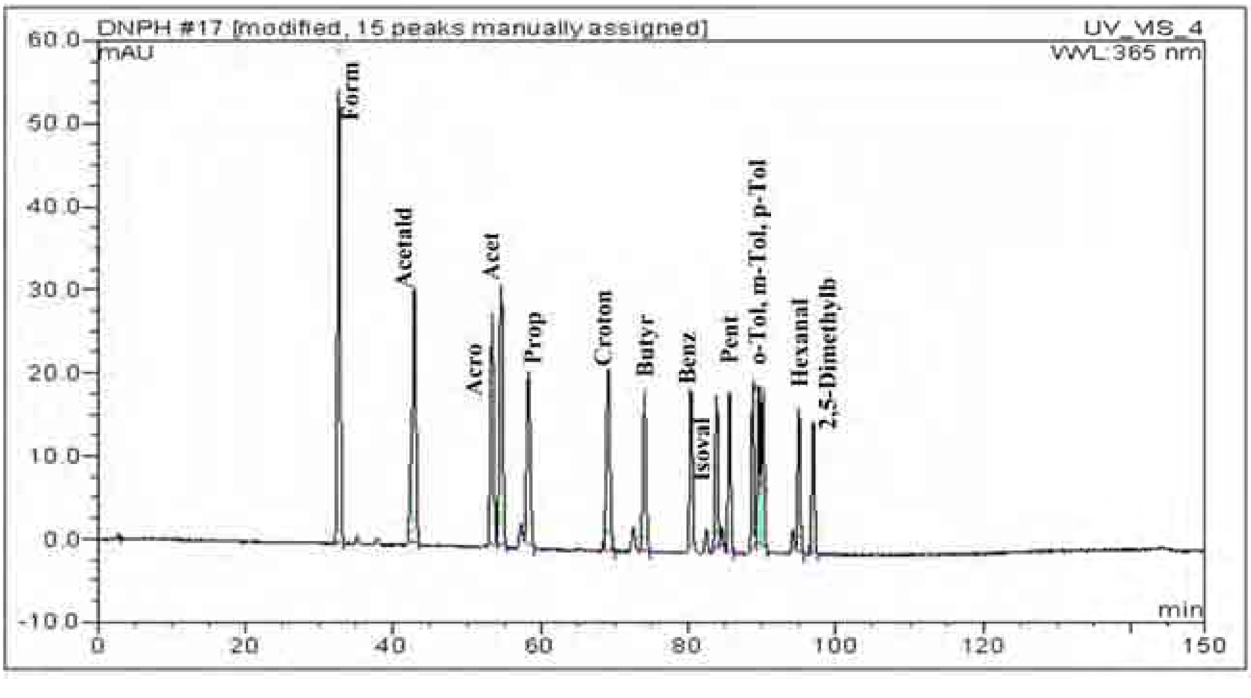


Figure 7.2: Chromatogram of carbonyl standards components using DNPH

7.3 Carbonyl Speciation upstream and downstream the catalyst

Carbonyl species are most likely to be formed as a result of partial oxidation of the fuel components. Detected carbonyl species were measured in ppm and calculated on a C_1 basis equivalent to formaldehyde.The concentration of carbonyl species measured in the exhaust was in the range of 2.6 to 8.4% of the total hydrocarbon for the HCCI combustion and approximately 12% for the SI engine operation, Table 7.2.

Table 7.2: Carbonyls detected using DNPH method* before and after the catalyst* at different engine conditions and speed of 2000rpm.

Compound	**HCCI λ=1, 3.0bar (ppm)**		**HCCI λ =1, 4.0bar (ppm)**		**HCCI λ =1.4, 3.5bar (ppm)**		**HCCI λ =1.4, 4.5bar (ppm)**		**SI λ =1, 4.0bar (ppm)**		**HCCI+H_2 λ =1.4, 4.5bar (ppm)**	
	B	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**B**	**A**
Formaldehyde	10	3	3	0	2	0	20	4	18	0	20	7
Acetaldehyde	66	76	64	79	66	84	47	74	45	82	47	74
Acrolein	5	3	10	5	20	2	27	0	9	0	27	0
Crotonaldehyde	0	0	0	0	3	0	6	0	4	1	6	0
Bnzaldehyde	0	0	14	0	26	0	45	0	53	0	45	0
Pent anal	3	8	5	0	11	15	0	6	0	0	0	0
o-Tolualdehyde	0	0	3	0	6	0	0	0	12	0	0	0
m-Tolualdehyde	0	0	5	0	12	0	34	0	45	10	34	0
Hex anal	0	0	0	0	0	0	0	0	8	0	0	0
2,5-Dimethylben	0	0	0	0	0	0	5	0	9	0	5	0
Total aldehyde	84		104		146		184		203		184	
Total HC (ppm)	3065	1212	2196	133	2622	92	2106	85	1651	81	2106	196
Aldehyde (% of THC)	2.6		4.5		5.5		8.4		12		8.4	

B- before catalyst
A- after catalyst

7.3.1 Engine –out carbonyl emissions and catalyst performance under HCCI operation, effects of engine load, at stoichiometric condition, $\lambda = 1$.

The identified carbonyl compounds and their concentrations upstream and downstream the catalyst at engine loads of 3 and 4bar NMEP are compared in Figure 7.3 and Figure 7.4, respectively. Four carbonyl compounds were identified in HCCI engine – out exhaust at low engine load of 3bar while more carbonyl species were found in higher load of 4bar in HCCI operation. Formaldehyde concentrations were reduced significantly at higher engine load; on the other hand acetaldehyde only reduced by 3%. Seven carbonyl species in higher load were identified in engine – out exhaust while only 2 species were found in tailpipe emission. High catalytic conversion efficiency was achieved for formaldehyde, benzaldhyde, pentanal and o-tolualdehyde. The conversion efficiency for acetaldehyde (CH_3CHO) over the catalyst was very poor Figure 7.3 for both engine modes and operating conditions. This can be attributed to the precursor of the other carbonyls in the engine-out emissions to be further oxidized to acetaldehyde and affected its conversions over the catalyst. [118, 179-180]. Another possibility comes from ethylene oxidation over the catalyst to produce ethylene oxide or ethanol which oxidizes to form acetaldehyde. The percentage contribution of carbonyl species to the THC emissions in this condition ranged from 2.6 to 4.5%.

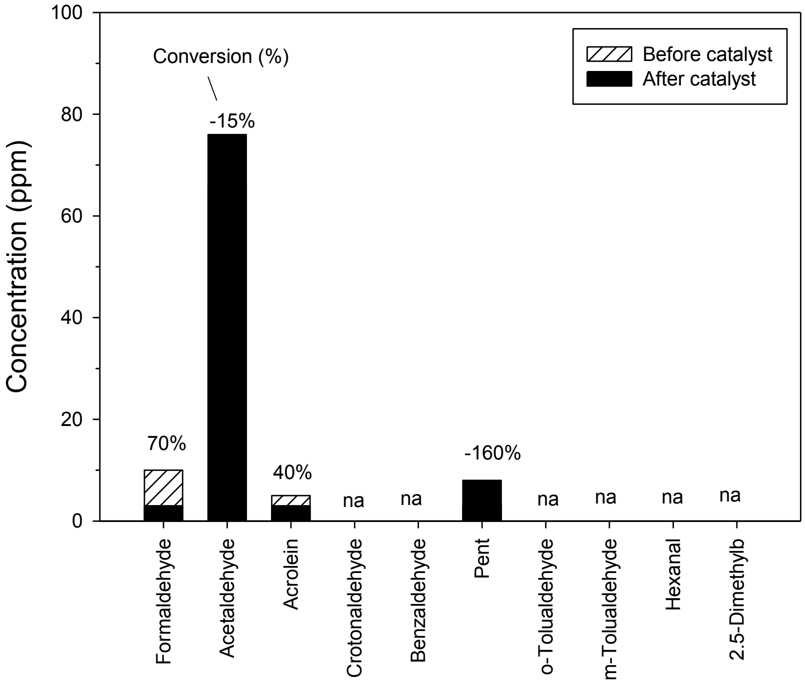


Figure 7.3 : Engine-out emissions and catalyst efficiency in reducing carbonyl species (3bar NMEP, HCCI, lambda 1).

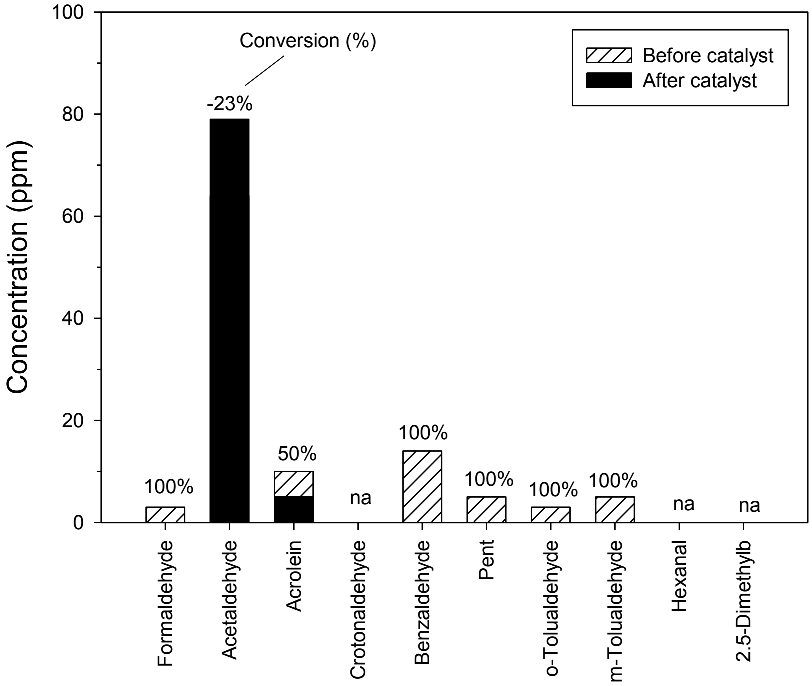


Figure 7.4: Engine-out emissions and catalyst efficiency in reducing carbonyl species (4bar NMEP, HCCI, lambda 1.

7.3.2 Engine –out carbonyl emissions and catalyst performance under SI and HCCI operation, engine load 4bar NMEP λ = 1.

Carbonyl species from the HCCI stoichiometric and SI combustion modes are compared under the same engine load of 4bar NMEP in Figure 7.4 and Figure 7.5, respectively. Aromatic aldhydes (benzaldhyde, o-tolualdehyde, and m- tolualdehyde) were found to be the dominant components which accounted for 54% in SI mode compared to 21% found in HCCI mode under the same engine conditions. Approximately 30% less acetaldehyde emissions were released from the SI operation when compared to HCCI mode Table 7.2. Formaldehyde and aromatic aldehydes in engine out emission could come from the incomplete combustion of saturated aliphipatic hydrocarbons[181-183].

Acrolin reduction of 100% and 50% is observed over the catalyst from the SI and HCCI mode, respectively. In SI mode the catalyst was mainly benefited from the high exhaust gas temperature of 661^{o}C compared to 413^{o}C exhaust temperature at HCCI mode Table 6.1.

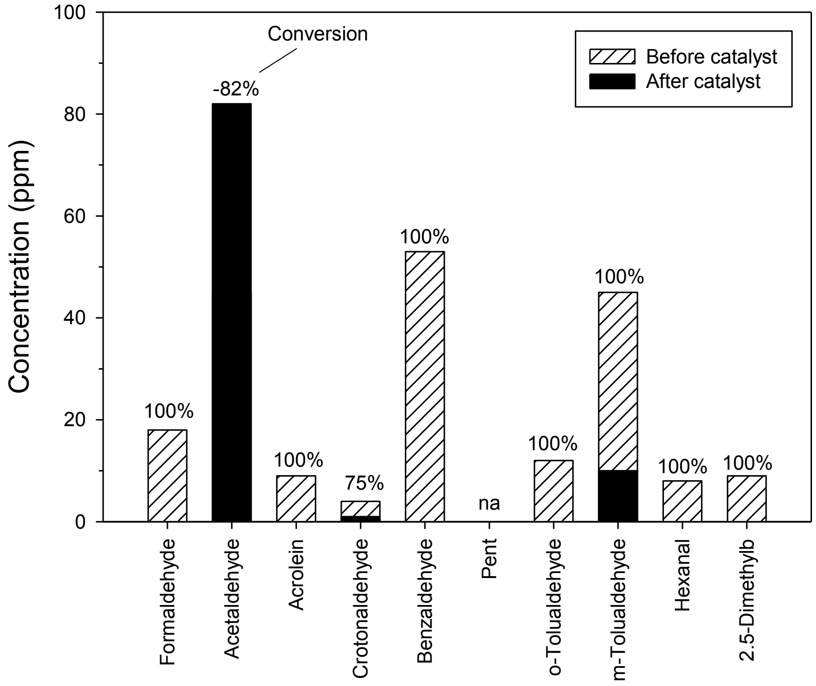


Figure 7.5 : Engine-out emissions and catalyst efficiency in reducing carbonyl species (4bar NMEP), SI, lambda 1.

7.3.3 Engine –out carbonyl emissions and catalyst performance under HCCI operation of engine loads 3.5 to 4.5bar, λ = 1.4.

Under lean HCCI combustion (i.e. λ = 1.4), engine load has significant effects on either the carbonyl species distributions or concentration levels.

Figure 7.6 and Figure 7.7, are compared at engine load of 3.5 and 4.5bar. Carbonyl species such as formaldehyde, crotonaldehyde, benzaldehyde, and m-tolualdehyde, were significantly increased at engine load of 4.5bar. At lean HCCI engine operation, incomplete combustion would still happen regardless of changing engine load due to deficient air at high air/fuel ratio (λ = 1.4), which led to high carbonyls emissions. Despite the low catalyst temperature at these conditions, carbonyl species were significantly reduced over the catalyst (i.e. condition 3 and 4). The conversion efficiency for acetaldehyde for all engine conditions was poor in most cases, these results were also found by Song et al 2006 [180]. The emissions of carbonyl species in the tailpipe exhaust at both engine loads were extremely low with decreases of almost 100% while acetaldehyde increases. The reason for this phenomenon may be that the precursor of the other carbonyls in the engine-out emissions can be further oxidized to acetaldehyde and increases its concentration after catalyst [179, 184].

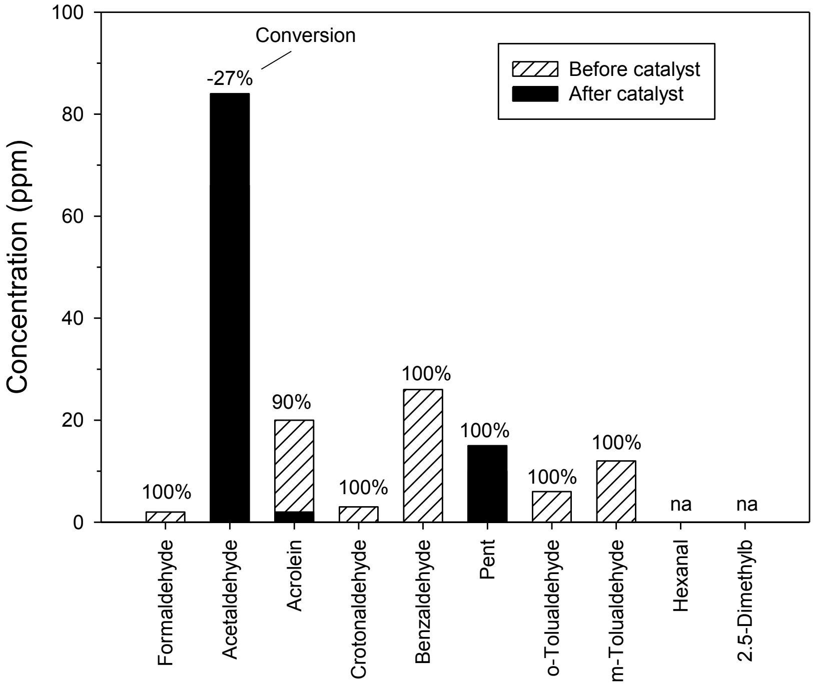


Figure 7.6: Engine-out emissions and catalyst efficiency in reducing carbonyl species (3.5bar NMEP), HCCI, lambda 1.4

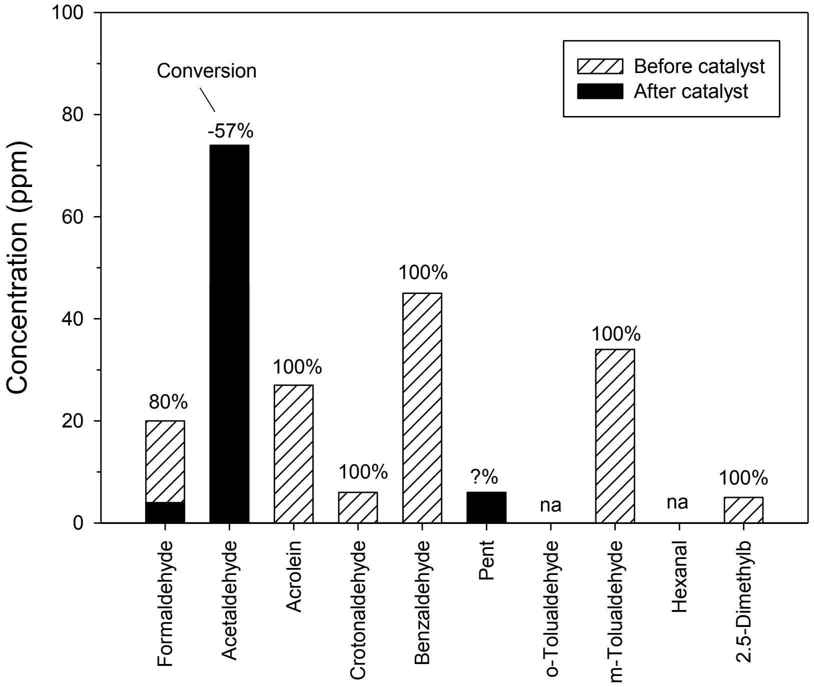


Figure 7.7 : Engine-out emissions and catalyst efficiency in reducing carbonyl species (4.5bar NMEP), HCCI, lambda 1.4

7.3.4 Catalyst performance in reducing carbonyl species with H_2= 2400ppm addition, HCCI operation of engine load 4.5bar, λ = 1.4

In order to investigate the influence of H_2 on catalyst performance in reducing carbonyl emissions, approximately 2400 ppm of hydrogen was injected in the engine exhaust upstream the catalyst. Under the same engine operating condition Figure 7.8, hydrogen addition has no beneficial effects on catalyst performance as formaldehyde conversion over the catalyst was reduced by 15%. This could be resulting from the reaction of carbon monoxide and hydrogen over the catalyst which led to increases in the concentration of formaldehyde.

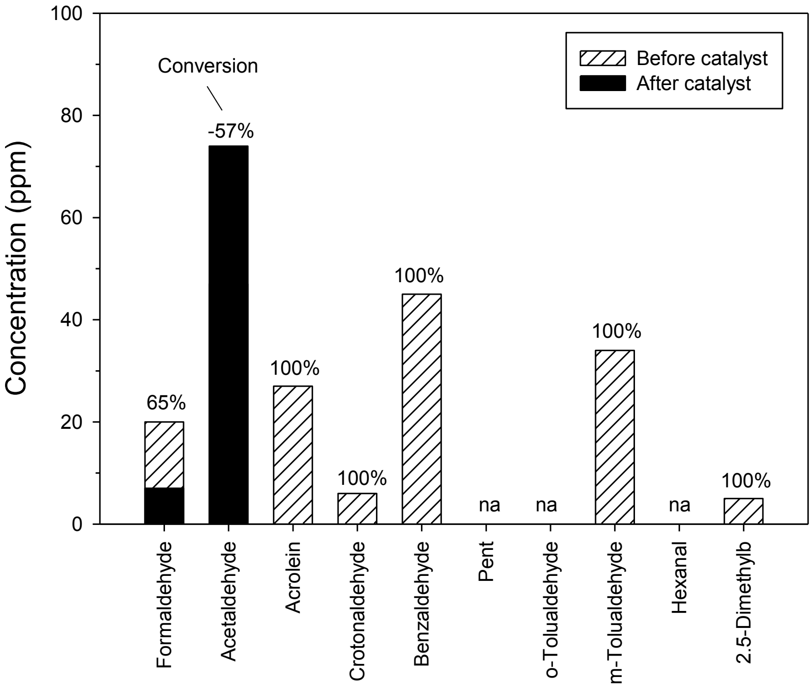


Figure 7.8 : Engine-out emissions and catalyst efficiency in reducing carbonyl species (4.5bar NMEP), HCCI, lambda 1.4, H2 addition= 2400ppm

7.4 Further Discussion on Carbonyl Compounds

7.4.1 Saturated Aldehyde

7.4.1.1 Formaldehyde

The maximum yield of formaldehyde was observed in HCCI lean operation Figure **7.9** at engine load of 4.5bar; its concentration was about 20 ppm. Formation of formaldehyde is relatively low compared to acetaldehyde which was 47ppm in this condition, Figure 7.9. According to Schrewe et al 2007[185], formaldehyde forms as an intermediate species of the combustion process. They also stated, during HCCI combustion, formaldehyde was found adjacent to the wall near the combustion chamber. Conversion efficiencies of formaldehyde over the catalyst were in the range of 80% to 100% for both engine modes. The lower formaldehyde conversion in HCCI lean operation could be attributed to the partial oxidation of methane to formaldehyde over the catalyst[186].

7.4.1.2 Acetaldehyde

The highest yield of acetaldehyde was observed in HCCI combustion mode, its concentration levels ranged from 45ppm to 66ppm Figure 7.9. The yield of acetaldehyde was reduced up to 30% when engine was operated in SI mode under similar engine conditions. Acetaldehyde formation could be attributed to the oxidation of ethylene over the catalyst. Ethylene is one of the main gases in organic chemistry, because ethylene reacts with several kinds of other gases to produce many derivatives such as ethylene oxide or ethanol[187]. With the increase of engine load, tail pipe temperature increase, and it helps the formation of acetaldehyde from ethanol oxidation over the catalyst. The trend is consistent with previous combustion studies where ethanol used as fuel or blended in gasoline fuel [180, 182, 184, 188].

7.4.2 Unsaturated aldehyde

7.4.2.1 Acroline

The concentrations of acroline species are influenced by the engine load and air/fuel ratio. Acroline species ranged from 5ppm under HCCI stoichiometric to 27ppm under engine lean operation Figure 7.9 . The production of acroline at engine load of 3bar in HCCI mode was very low (only 6% of total carbonyls), this percentage increased to 14% when the engine was operated on HCCI lean operation at 4.5bar. In addition fuel composition can significantly influence the emission of carbonyl compounds [37, 189]. It was also found that the conversion efficiency of carbonyls over the catalyst (e.g. acroline) has a positive correlation with increase in engine load Figure 7.9. The influence of the exhaust temperature promotes the conversion of carbonyls over the catalyst.

7.4.2.2 Crotnaldehyde

Unlike other carbonyl species, emissions of crotonaldehyde were below the detectable limit (≤ 1ppm) when the engine was operating in HCCI stoichiometric for both engine loads. As expected when shifting to HCCI lean operation (λ= 1.4), crotonaldhyde emissions reached a concentration of 6ppm. In general oxygenates fuel yields lower contronaldhyde levels than the regular gasoline, this could be due to the absence of 1-hexene and cyclohexane in gasoline which are reportedly sources for the formation of crotonaldehyde [189].This explanation also holds for the levels observed from the aliphatic gasoline, since this fuel has a low total content of hexane. Since each carbonyl emission varied to different extents after passing through the catalyst, the proportion of each component to the total carbonyls varied correspondingly in tail pipe exhaust. Downstream of the catalyst crotonaldhyde species were 100% eliminated, except for the SI mode, where 1ppm was recorded.

7.4.3 Aromatic aldehyde

7.4.3.1 Benzaldehyde

The production of benzaldehyde was dependent on the combustion temperature, under HCCI stoichiometric mode there was a very low benzaldehyde concentration below the detectable limit; the percentage of the total carbonyl species was increased by approximately 13% at higher engine load of 4.5bar and increased to 26% for the SI engine operation Figure 7.9. The H–aromatic bond contains higher energy than the H-aliphatic bond, therefore at HCCI stoichiometric (lower load 3bar) hydrogen is unlikely to be abstracted from aromatics, it will be abstracted more easily from the aliphatic compound which is already competing. So the production of benzaldehyde was enhanced in SI and HCCI (higher load 4bar), where the in-cylinder temperature was higher. These results showed very clearly the importance of combustion temperature for aromatic carbonyl formation. The phenomenon of benzaldhyde predominating in SI mode as observed in this study agrees with other gasoline engine studies, Magnusson et al 2011 [181-182]. The formation of benzaldehyde could result as a combustion product of gasoline aromatics which are formed by the reaction of substituent groups on the ring. Oxygen addition to toluene could produce benzaldehyde as a combustion product, and this result is also reported by Zervas et al 2004 [190].

The relatively high exhaust gas temperature at HCCI higher load and SI mode, in addition to sufficient oxygen, helped the catalyst to adsorb the benzaldehyde on to its high activity surface and allowed the benzaldehyde to oxidise and clear its entire species downstream of the catalyst. Emissions of benzaldehyde in tail pipe exhaust were extremely low (the concentration was lower than the detection limits of our system) with a decrease of 100% under in all engine conditions.

7.4.3.2 O/m-tolualdehyde

The majority of aromatic aldehydes were not detected below 1ppm when the engine was operated in lower load 3bar, HCCI mode. Different trends were observed when the engine shifted to the higher load 4bar, in HCCI mode or switched to SI mode. The contribution of o-tolualdhyde in HCCI mode was very low (2-4% of total carbonyl), on the other hand 5-18% was found for m-tolualdehyde. The percentage of the m-tolualdehyde concentration increased to 22% of total carbonyl when the engine was operating in SI mode. The formation of o/m tolualdehyde can be produced from oxygen addition to Xylenes [131]. The identified o/m tolualdehyde species in the engine- out and tail pipe exhausts at different load levels and different air/fuel ratio are shown in Figure 7.9. 100% catalytic conversion was achieved when the engine was operating in HCCI lean and stoichiometric for both engine loads.

7.4.3.3 dimethyl benzeldehyde

Few species of 2, 5 dimethy benzeldehyde approximately 5ppm were found in HCCI lean operation at an engine load of 4.5bar and increased to 9ppm at SI mode Figure 7.9. The contribution of this compound to the total carbonyl species ranged from 2% in HCCI mode to 4% in SI mode. By having sufficient oxygen and high exhaust gas temperature 2, 5 dimethy benzaldehyde, as with most aromatic aldehydes was easily oxidized over the catalyst, 100% catalytic conversion was achieved for all engine conditions.

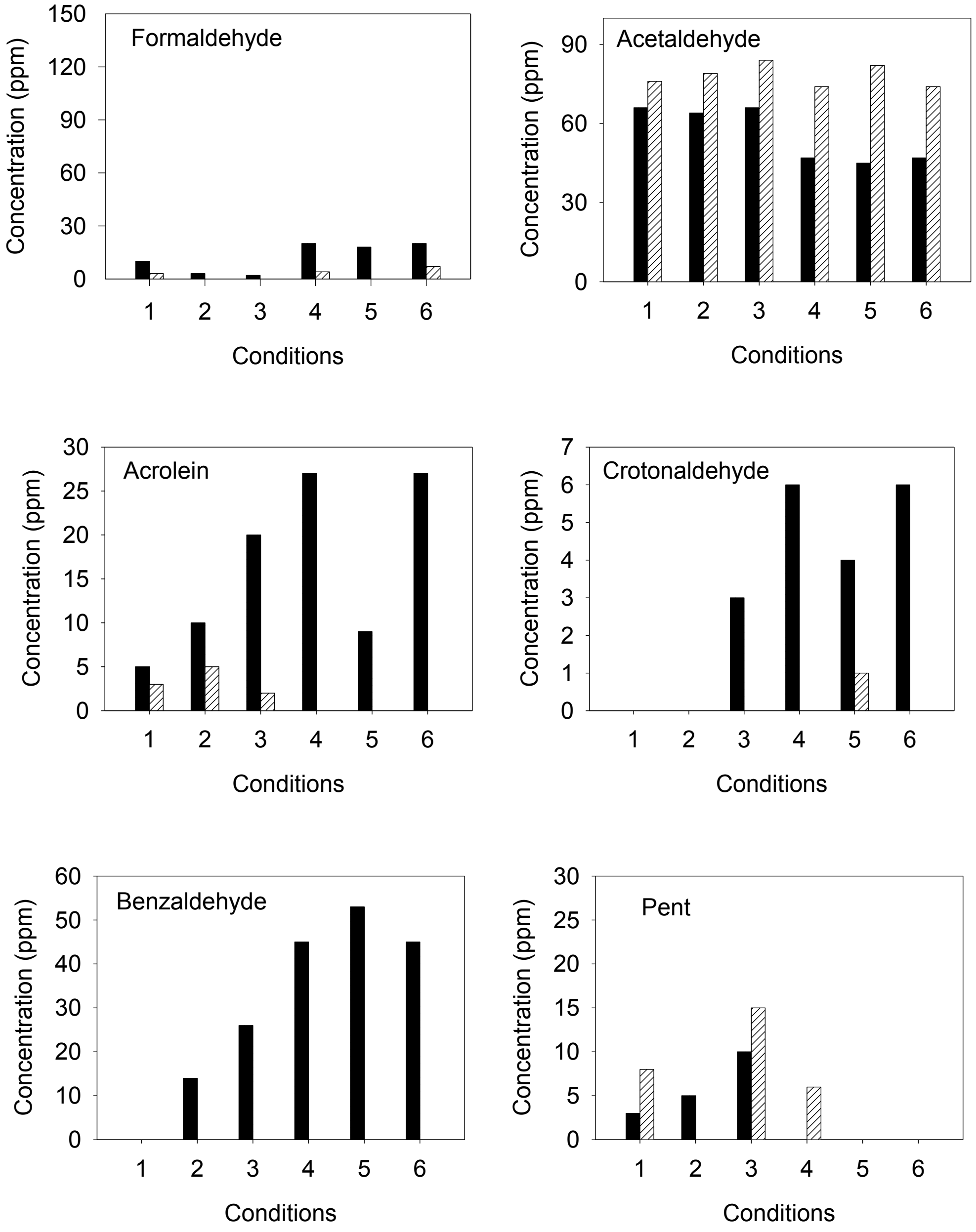
7.4.4 Alkyl aldehyde

7.4.4.1 Pentanal

The formation of alkyl aldehyde (pentanal) presented only in the exhaust of the HCCI engine operation. The concentration of these species was 3–14ppm for HCCI stoichiometric and lean operation Figure 7.9. These species increase as a function of decreased exhaust temperature. Togbe et al 2011 [191] used 1-pentanol in a jet-stirred reactor over a range of equivalence ratio and temperature, by extended detailed chemical kinetic reaction, the consumption of the fuel occurs above 770K accompanied with rapid formation of pentanal, formaldehyde, and ethylene. This compound showed resistance to oxidation over the catalyst especially at low exhaust temperatures under HCCI mode with lower engine loads. Under low-temperature catalytic oxidation of aldehyde, Pentanal could be formed as end products of hexanal oxidation [192].

7.4.4.2 Hexanal

Hexanaldhyde is an alkyl aldehyde which is found in a low concentration of 8ppm, this combustion product is only produced at high temperature at SI mode, Figure 7.9. Hexanal whose bond requires less energy than other volatile aldehydes, could follow a less energetic mechanism on the active sites of the catalyst where mobile oxgen species are involved. At a high temperature as in SI exhaust temperature, the above mentioned mobile species are no longer anchored to the catalyst surface, and oxygen vacancies are likely to be present. In this condition the activation of the hexanal bonds may be characterised by a more energetic mechanism on a greater number of available sites of the catalyst, so hexanal species were fully reduced over the catalyst. The HPLC Chromatograms of detected carbonyl compounds, HCCI lean, 4.5bar before catalyst and after catalyst are shown in Figure 7.10 and Figure 7.11.



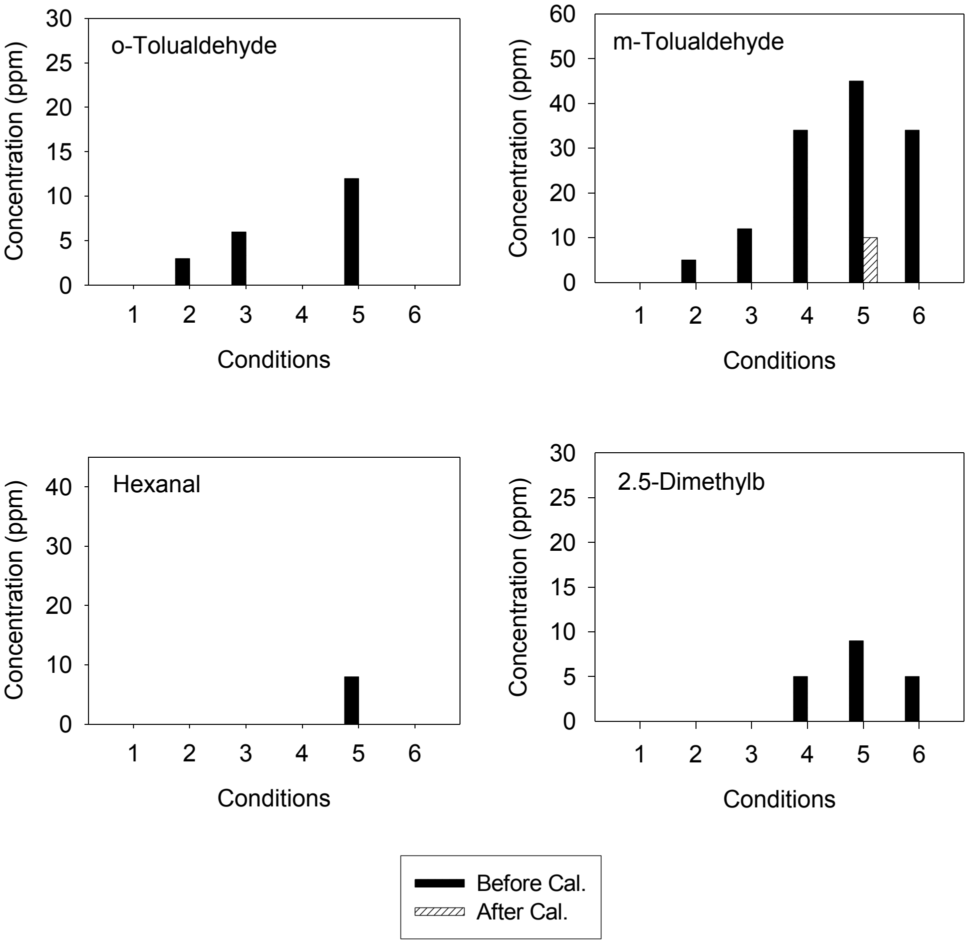


Figure 7.9: Carbonyl emissions before and after the catalyst: 1) Low load HCCI, λ=1, 2) High load HCCI, λ=1; 3) Low load HCCI, λ=1.4; 4) High load HCCI, λ=1.4; 5) High load SI, λ=1; and 6) High load HCCI+ H2, λ=1.4.

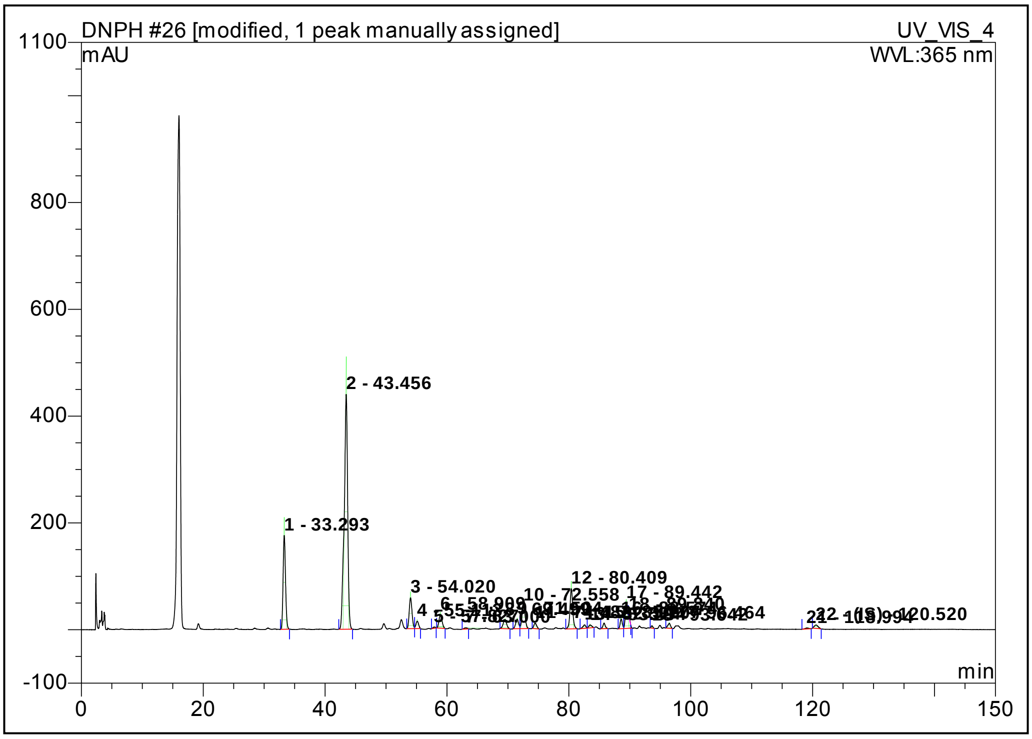


Figure 7.10: HPLC Chromatogram of detected carbonyl compounds, HCCI lean, 4.5bar before catalyst.

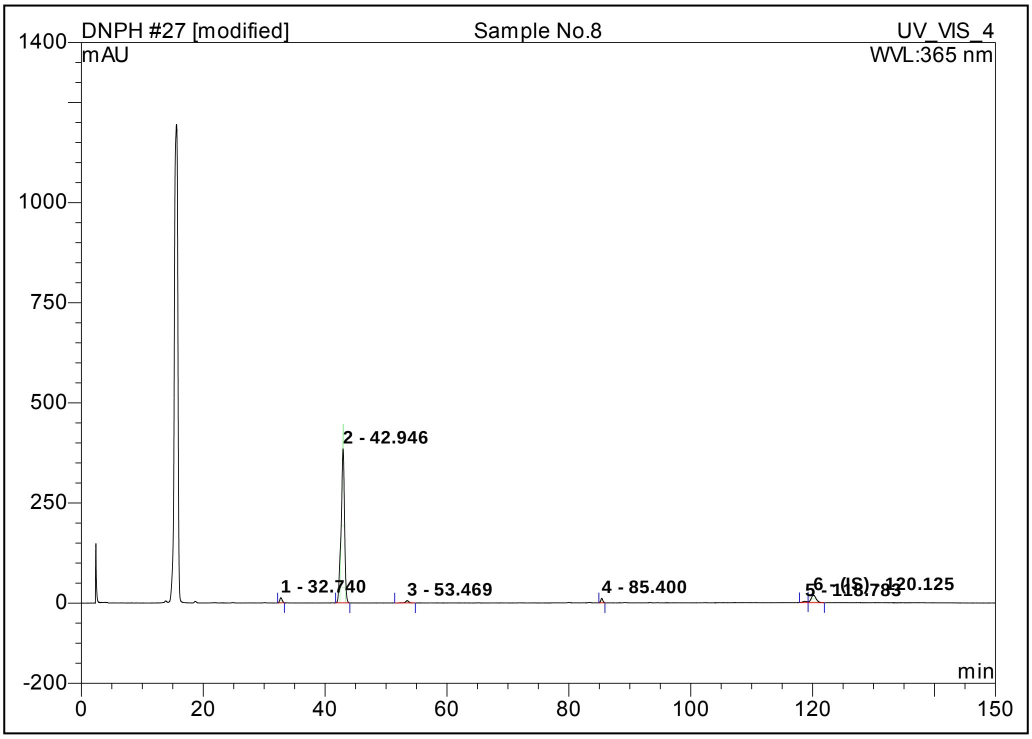


Figure 7.11: HPLC Chromatogram of detected carbonyl compounds, HCCI lean, 4.5bar after catalyst.

CHAPTER 8:

CONCLUSIONS AND FUTURE WORK

As seen from the previous chapters, the combustion mode has a strong effect on hydrocarbon species from HCCI/SI combustion. Most of the unsaturated species (e.g. ethylene, propylene) are combustion products of the SI mode, while saturated species (e.g. methane, iso-octane) are combustion products of HCCI mode. On the other hand some aromatic species (e.g. benzene, toluene) have escaped the combustion process in both engine modes. In addition with HCCI combustion a lot of low temperature reactions take place producing intermediate products, which make it difficult to understand fully the formation of chemical species in the HCCI mode. This work main contribution will be summarised in this chapter and the suggested future work will follow.

8.1 Main Findings

8.1.1 Catalyst Design for HC, CO and NO_x Emissions Reduction in Gasoline bi-mode SI/HCCI Engine

The prototype catalytic converter used in this study under HCCI lean operation was very effective in reducing total hydrocarbons and carbon monoxide emissions over variable engine conditions. NOx conversion over the catalyst was low, it was significantly improved by H2 addition upstream the catalyst. The prototype catalyst consisted of a 3-zone ceramic monolith which is accommodated in stainless steel cylindrical casing. The monoliths were isolated from the internal casing surface using non conductive materials. The catalyst was supplied by Johnson Matthey.

Hydrocarbon and carbon monoxide emissions were reduced over catalyst by approximately 90%. Engine load has a very strong effect on engine-out emissions, engine speed was another major factor which affected emissions reduction, alongside with air/fuel ratio. Retention time (Space Velocity) was one of the main factors that affect catalyst conversion efficiency. The optimum catalytic conversion of the three compounds investigated here, (HC, CO, and NOx) occurred under the same exhaust gas conditions at approximately $33kh^{-1}$. This could be related to the relatively high exhaust temperature, high oxygen concentration, and retention time presented under this condition. The strategy of residual gas trapping (negative valve overlap) is a powerful tool of controlling HC, CO, and NOx in HCCI engine-out emissions; this could be achieved by advancing the exhaust valve timing. Hydrogen reforming is another strategy which strongly effected NOx reduction under HCCI lean operation.

8.1.2 Effect of composite after treatment catalyst on alkane, alkenes and monocyclic aromatic emissions from an HCCI/SI gasoline engine

The hydrocarbon species found in the engine exhaust are dependent on the engine condition and combustion mode (i.e. HCCI or SI). Alkane concentrations were found to be higher in the HCCI mode, while alkene species were mainly found in the exhaust of the SI engine mode. Analysis showed that the hydrocarbon content of the HCCI exhaust contained more of the heavier species (e.g. toluene, n-heptane, benzene) than during SI operation.

The prototype TWC catalytic converter undergo reduction-oxidation reactions to combine the catalytic functions required to oxidise CO and hydrocarbons, while simultaneously reducing NOx, over the expected range of exhaust-gas temperatures under both engine modes. During HCCI lean operation, the catalyst showed more efficient conversion of alkenes and aromatic species compared to alkanes. As an example, ethylene was readily oxidized while methane showed the most resistance to catalytic combustion. 100% elimination of carcinogenic species, such as 1, 3-butadiene and benzene were achieved, except under low load conditions where conversions of 83% and 51% were observed respectively. Hydrogen addition during HCCI lean operation did not have any beneficial effects on catalytic HC combustion. Instead, the conversion reduced from 97% to 91%.

8.1.3 Determination of Hydrocarbons Species C_5-C_{11} from HCCI/SI Gasoline Engine, Equipped with Prototype Catalyst

The hydrocarbon species are strongly affected by the engine operation and combustion mode. Naphthalene and methylnaphthalene concentrations were found to be higher in stoichiometric HCCI operation while lighter HC species were higher in lean HCCI operation. Aromatics hydrocarbon concentrations were found to be higher for HCCI operation; high aromatic components were present in the fuel used, which explained the observed increase of aromatic emissions in the exhaust. On the other hand benzene, iso-octane and ethyl benzene species are mainly found in the exhaust of SI combustion. Analysis shows that the hydrocarbon content of HCCI exhaust contains more of the heavier species (e.g. toluene, p-exylene, naphthalene methylnaphthalene) than that of SI operation.

The prototype catalyst has the potential to reduce most of the chemical compounds during engine operation for both combustion modes (HCCI and SI). The emissions of heavy hydrocarbon species downstream the catalyst were extremely low except for some aromatic species (i.e. naphthalene and methylnaphthalene) which were high. This shows that the catalyst has less capability of activating a fused pair of benzene rings during the lean HCCI operation mode. So for example iso-octane is readily oxidised while naphthalene shows most resistance to catalytic conversion. Hydrogen addition during HCCI lean operation can enhance the catalytic conversion efficiency in reducing naphthalene and methylnaphthalene species. This could be attributed to two different mechanisms. The first of these is the H_2 oxidation, which could increase the temperature and promote these hydrocarbon species oxidation reaction rates. The second is the reducing nature of H_2, where the hydrogen may react with the aromatic compounds and convert them to saturated hydrocarbons, which in turn are more readily oxidised.

8.1.4 Determination of carbonyl species with 2,4-Dinitrophenyl-hydrzine method from HCCI/SI Gasoline Engine, Equipped with Prototype Catalyst

The air/fuel ratio (λ) has a higher impact on unsaturated carbonyl. The formation of unsaturated aldehydes (e.g. acrolein, crotonaldehyde) were more significant in HCCI lean operation mode (low combustion temperature), compared to other engine conditions. On the other hand aromatic aldehydes were mainly observed in SI mode and high load HCCI engine operation. Benzaldehyde concentrations were found to be higher in the SI mode, while saturated species such as acetaldehyde was mainly found in the exhaust in both engine modes. Analysis showed that the hydrocarbon concentration of HCCI lean exhaust contained more of the heavier species (e.g. m-tolualdhyde, benzaldehyde) compared to HCCI stoichiometric operation.

A prototype catalytic converter showed more efficient conversion on aromatic and unsaturated aldehyde for both engine modes. During lean operation, regardless of the low exhaust temperature, most of the carbonyl emissions downstream of the catalyst was eliminated except for the acetaldehyde. High catalytic conversion of benzaldehyde was achieved in all engine conditions. Aromatic aldehyde emissions such as benzaldehyde should arouse public attention because of the potential health and environmental effects. Hydrogen addition during HCCI lean operation did not have any beneficial effects on catalytic HC conversion. Instead, the conversion of formaldehyde reduced from 80% to 65%.

8.2 Future Work Recommendations

- An important study of HCCI/SI combustion technology could be essential to gain more understanding of the emissions reduction possibility via different combustion conditions such as changing the compression ratio or ignition timing etc. Emissions of some potentially important pollutants such as carbonyls (especially carbonyls other than formaldehyde and acetaldehyde) have not been thoroughly investigated for pure fuels such as ethanol, methanol or other fuels.
- In terms of end-use properties and exhaust emissions, gasoline fuels to be used for HCCI combustion are not problem-free. For instance their use reportedly results in the increase of aromatic hydrocarbons and carbonyls

(aldehydes and ketons), and so more investigation needs to be done for different HCCI fuel components.

- Diesel and gasoline could be mixed to form different fuel blend which could be analysed from HCCI engine-out emissions and downstream the converter.
- Further speciation of the HCCI exhaust hydrocarbons is needed, by using a new set of known polycyclic aromatic hydrocarbons to study the relationship between amount, type, and carcinogenic potency of polycyclic aromatic hydrocarbons in HCCI engine emission and the fuel composition.
- The investigation of carbonyls in the exhaust of HCCI combustion should be extended to oxygenate and alcohols fuel, to bring a clear picture and gather comprehensive data about oxygenated hydrocarbons produced in HCCI engine mode.
- One of the major drawbacks with HCCI engine operation is controlling the ignition timing over a wide load and speed range. Load level, auto ignition timing, exhaust emission and efficiency can change significantly with injection timing, so it will be beneficial to investigate the impact of injection timing on the hydrocarbons speciation generated from the HCCI engine mode.
- Particulate matter (PM) emissions from HCCI combustion should not be neglected. More studies should be carried out in order to understand PM emissions and chemical composition and would also aid in the clarification of unidentified chemical species formation.
- Deterioration of the three way catalytic converter under HCCI/SI stoichiometric and lean engine operation conditions could be investigated via monitoring the catalyst performance by an on board method.

- Investigating of the impact of changing monolith geometric parameters on the catalyst performance in reducing the exhaust gas emissions needs to be carried out.
- Cold-start HC emissions produced from the spark ignition engine could be investigated over the prototype catalyst.
- Improvement of conversion performance in reducing NOx emissions under HCCI/SI variable engine conditions could be achieved by improving zone 1 in the catalyst to be more sensitive to NOx reduction.
- Further investigation on the performance of the catalytic converter using different fuels under HCCI/SI engine operation would be beneficial.

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