A COMPARATIVE EVALUATION ON THE PERFORMANCE AND EMISSION CHARACTERISTICS OF AN INTERNAL COMBUSTION ENGINE USING CERAMIC AND METALLIC CATALYTIC CONVERTER

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For my beloved mother and father

For my beloved husband
ACKNOWLEDGEMENT

Alhamdulillah, I am so grateful to Allah S.W.T for giving me strength and guidance throughout my studies and to complete this thesis. First of all, I would like to express my gratitude to my supervisor, Assoc. Prof. Dr. Engr. Abdul Mutalib bin Leman for becoming my motivator, inspirer through all the stages during my Master journey. Without his supervision and invaluable time spent with me, this thesis would not been completed successfully.

I would like to thank to Mr Supa’at Zakaria and Mr Dafit Feriyanto for their ideas and assistance throughout this thesis.

I would like to extend my gratitude to my beloved parents and my husband who always provided me a moral support and guidance in the completion of this thesis. I am so grateful for the love, support and educational opportunities that they have provided for me throughout the years.
Automobile exhaust emission control is one of trending issues in automotive research field. Ceramic and metallic catalytic converters are the most common types of catalytic converters. Most current researches focus on the modeling and characterization of catalytic converter and there is a lack of exhaust gas conversion data of different catalyst types that correspond to real engine operating condition. This project focuses on comparing and analyzing the performance of ceramic and metallic catalytic converter on its conversion efficiency. Mitsubishi 4G93 1800cc gasoline engine was attached with a dynamometer and Kane Auto 5-1 series exhaust gas analyzer were used for emission measurements of carbon monoxide (CO), hydrocarbon (HC) and nitrogen oxide (NO$_x$) in different speed and constant load. The experimental results of the engine performance and exhaust emission were used to compare the performance of ceramic and metallic catalytic converters in reducing the concentration of the exhaust emission without affecting the engine performance. Based on the result, metallic catalytic converter showed a higher 97.9% reduction of CO concentration reduction emission as compared to the ceramic catalytic converter. The ceramic catalytic converters on the other hands showed better reduction of NOx and HC concentration of 87.2% and 85.4% percentage of reduction. It can be concluded that metallic catalytic converters performs a better exhaust gas conversion on high temperature condition at reducing CO emission while ceramic catalytic converters reduced HC and NO$_x$ emission more effectively due to its lower thermal conductivity.
ABSTRAK

Kawalan pelepasan ekzos automobil adalah salah satu daripada isu yang mendapat perhatian dalam bidang penyelidikan automotif. Penukar pemangkin seramik dan logam adalah jenis penukar pemangkin yang biasa digunakan. Kebanyakan kajian semasa memberi tumpuan kepada model dan pencirian penukar pemangkin, di mana terdapat kekurangan data berkaitan penukaran gas ekzos bagi mengkaji prestasi pemangkin yang berbeza dan sepadan dengan keadaan operasi enjin sebenar. Projek ini memberi tumpuan kepada perbandingan dan menganalisis prestasi penukar pemangkin seramik dan logam dalam kecekapan penukaran. Enjin petrol jenis Mitsubishi 4G93 1800 cc yang disambungkan dengan dinamometer dan penganalisis gas jenis Kane Auto 5-1 digunakan untuk pengukuran pelepasan gas karbon monoksida (CO), hidrokarbon (HC) dan nitrogen oksida (NO\textsubscript{x}) dengan perubahan kelaju dan beban yang tetap. Keputusan eksperimen prestasi enjin dan pelepasan ekzos penukar pemangkin seramik telah dibandingkan dengan penukar pemangkin logam dari segi kecekapan mengurangkan pelepasan ekzos tanpa menjejaskan prestasi enjin. Berdasarkan keputusan yang diperolehi, penukar pemangkin logam menunjukkan pengurangan pengurangan CO yang lebih tinggi iaitu sebanyak 97.9% berbanding penukar pemangkin seramik. Penukar pemangkin seramik pula menunjukkan pengurangan yang ketara bagi kandungan NO\textsubscript{x} dan HC iaitu 87.2% dan 85.4% kecekapan penukaran. Analisis kedua-dua penukar pemangkin seramik dan logam menunjukkan prestasi yang berbeza dalam mengurangkan pelepasan ekzos. Kesimpulannya, penukar pemangkin menunjukkan penukaran gas ekzos yang lebih baik pada keadaan suhu yang tinggi untuk mengurangkan pelepasan CO manakala penukar pemangkin seramik mengurangkan pelepasan HC dan NO\textsubscript{x} yang lebih berkesan akibat kekonduksian terma yang lebih rendah.
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<th>Description</th>
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<tr>
<td>2WCC</td>
<td>Two-Way Catalytic Converter</td>
</tr>
<tr>
<td>$\gamma$-Al$_2$O$_3$</td>
<td>Gamma Alumina</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>Alumina</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>Ceria</td>
</tr>
<tr>
<td>Cu(NO$_3$)$_2$</td>
<td>Copper nitrate</td>
</tr>
<tr>
<td>CO</td>
<td>Carbon Monoxide</td>
</tr>
<tr>
<td>CuO</td>
<td>Copper oxide</td>
</tr>
<tr>
<td>CrO$_2$</td>
<td>Cerium oxide</td>
</tr>
<tr>
<td>DOE</td>
<td>Department of Environment</td>
</tr>
<tr>
<td>EGR</td>
<td>Exhaust Gas Recirculation</td>
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<tr>
<td>EHC</td>
<td>Electrical Catalytic Converter</td>
</tr>
<tr>
<td>EICHC</td>
<td>Electrically Initiated Chemically Heated Catalytic Converter</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>E.U</td>
<td>European Union</td>
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<tr>
<td>FeCrAl</td>
<td>Ferum Chromium Aluminium</td>
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<tr>
<td>FTP</td>
<td>Federal Test Procedure</td>
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<tr>
<td>H$_2$</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>HC</td>
<td>Hydrocarbon</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric Acid</td>
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<tr>
<td>H$_2$O</td>
<td>Hydrogen Dioxide</td>
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<tr>
<td>ICE</td>
<td>Internal Combustion Engine</td>
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<tr>
<td>kHz</td>
<td>Kilo Hertz</td>
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<td>LDV</td>
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LEV - Low Emission Vehicle
NaOH - Sodium Hydroxide
NEDC - New European Drive Cycle
NiO - Nickel Oxide
NO\textsubscript{x} - Nitrogen Oxides
O\textsubscript{2} - Oxygen
OEM - Original Engine Manufacture
PC - Personal Computer
Pd - Palladium
PGEs - Platinum Group Elements
PM - Particulate Matter
PPM - Parts Per Million
Pt - Platinum
Rh - Rhodium
rpm - Rotation Per Minute
SCR - selective catalytic reduction
SI - Spark Ignition
SO\textsubscript{2} - Sulphur Dioxide
TLEV - Transitional Low Emission Vehicle
TWC - Three Way Catalyst
ULEV - Ultra Low Emission Vehicle
ZEV - Zero Emission Vehicle
ZrO\textsubscript{2} - Zirconia
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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Air pollution has been known to be a major risk to health and environment. Outdoor air pollution is estimated to cause 1.3 million annual deaths worldwide (WHO, 2011). All over the world, mobile sources stand out as the largest contributors of a number of air pollutants which produced about 70 to 75% of the total air pollutions.

One automobile exhaust can release gas that contains nearly 200 different components into the atmosphere (Mishakov, 2011). The emission potential of gasoline-powered vehicles are carbon monoxide (CO, 0.5 vol.%), unburned hydrocarbons (HC, 350 ppm), nitrogen oxide (NO\textsubscript{x}, 900 ppm), hydrogen (H\textsubscript{2}, 0.17 vol.%), water (H\textsubscript{2}O, 10 vol.%), carbon dioxide (CO\textsubscript{2}, 10 vol.%), and oxygen (O\textsubscript{2}, 0.5 vol.%). Table 1.1 shows the estimated average contributions of vehicle emissions of major air pollutants.
Table 1.1: Estimated average contributions of vehicle emissions to ambient levels of major air pollutants in developed countries (Greenbaum, 2013)

<table>
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<th>Pollutant</th>
<th>Contribution (%)</th>
<th>Reference</th>
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<td>Carbon monoxide</td>
<td>~90</td>
<td>EPA (2000)</td>
</tr>
<tr>
<td>PM$_{2.5}$</td>
<td>~25–30</td>
<td>DEFRA (2012)</td>
</tr>
<tr>
<td>Nitrogen oxides</td>
<td>~40</td>
<td>EPA (2000)</td>
</tr>
<tr>
<td>Volatile organic compounds</td>
<td>~35</td>
<td>EPA (2000)</td>
</tr>
<tr>
<td>Average air toxics</td>
<td>~21</td>
<td>EPA (1999)</td>
</tr>
<tr>
<td>Urban air toxics</td>
<td>~42</td>
<td>EPA (1999)</td>
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Over the recent years, exhaust after treatment for automobile presents a range of advanced technologies based on oxidation and three-way catalyst, adsorption, storage and filtration processes. This enables the reduction of CO, HC, NO$_x$ and particulate emissions (PM) from any gasoline or diesel engine in order to meet the demands of current and future of exhaust emission regulations. Catalytic converters were first introduced in the market of the United States in the mid-1970s in order to comply with the strict Environmental Protection Agency (EPA) on automobile exhaust emissions (Pankaj and Manish, 2012). Catalytic converter has been known as a built-in device in the exhaust system of an automobile to reduce the amount of CO, NO$_x$ and unreacted HC in automotive emissions (Sebayang et al., 2007). These gases are eliminated by the basic reactions occur inside a catalytic converter through oxidation of CO, HC and reduction for NO$_x$. This catalytic converter is mounted along the exhaust pipe of the engine and has a base mesh or substrate to enable the exhaust gas to flow inside the container (Mansha, 2012).

The act of simultaneous reaction of oxidation and reduction is referred as Three Way Catalyst (TWC) and it has become the most common type of catalytic converter (Sebayang et al., 2007 and Heck et al., 2009). Catalytic converters come in many concepts, structures and even the materials; nevertheless, it continues to evolve depending on different vehicle requirements. Catalytic converter is consisted of three basic components such as substrate, washcoat and catalyst (Sebayang et al., 2006). The active catalyst layer is applied on the surface of the monolith walls. The coating, called ‘washcoat’, is composed of porous, high surface area inorganic oxides such as $\gamma$-Al$_2$O$_3$ (gamma alumina), CeO$_2$ (Ceria) and ZrO$_2$ (Zirconia). Noble metal catalysts,
such as Platinum (Pt), Palladium (Pd) and Rhodium (Rh), are deposited on the surface and within the pores of the washcoat (Pontikakis, 2003).

In the last few years, the monolith or honeycomb structure catalyst has been the most dominant catalyst used for gasoline engine. This type of catalyst is a mixture of alkaline earth-metals, oxides and platinum group elements (PGEs) such as Pt, Pd and Rh in which are all coated with highly porous washcoat of 90% $\gamma$-Al$_2$O$_3$ (Paraskevas, 2012). Ceramic and metallic substrates are the most common catalytic converter used in regard to the catalyst type (Kaspar et al., 2003). In spite of extruded ceramic monoliths being the most widely used substrate material, mainly because of its relatively low manufacturing costs, foil metallic monolith substrates has become more advanced in after-treatment market. It is selected as the substrate due to its high thermal conductivity, lower heat capacity, greater thermal and mechanical shock resistant, thinner wall lower pressure drop (Wu et al., 2005), higher coefficient of thermal expansion (CTE) (Zhao et al., 2003) high temperature oxidation resistance and is able to achieve larger specific surface area as shown in Figure 1.1.

![Catalytic converter monolith of (1) ceramic and (2) metallic material](Putrasari et al., 2010).

As many researchers have been focused on the modeling and characterization of the catalytic converter, there is a need for experimental testing on both ceramic and metallic converters. In this project, the experimental measurement of exhaust emission of both ceramic and metallic catalytic converter were compared in order to examine the conversion efficiency of the exhaust gases in respond to the real engine operating conditions such as engine speed and load.
1.2 Problem Statement

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 (Hasan, 2011). The most common type of after treatment used for the petrol engine is the ‘three-way catalyst’ (TWC) which caters for a simultaneous oxidation and reduction of exhaust gas components. Ceramic and metallic catalytic converters are the most commonly used products available in the exhaust after treatment market (Bode, 2002). There have been a vastly increased interest in experimental studies that investigated the performance of the catalytic converters. Martin et al. (1998) has experimentally investigated the effects of flow distribution, space velocity and light-off temperature on the performance of catalytic converters. Buchner et al. (2001) have gathered an experimental data base from test bench and dynamometer in order to determine the heat transfer coefficients in catalytic converters. Silva et al. (2006) evaluated the conversion efficiency of a catalytic converter under steady operating condition. The inlet and outlet chemical species concentration, temperature and air fuel ratio (A/F) were measured as a function of the brake mean effective pressure (BMEP) and engine speed (rpm). Pannone and Mueller (2001) and Santos and Costa (2008) have compared catalyst system using ceramic and metallic substrates in order to assess the influence of various substrate parameters on the exhaust gas conversion efficiencies. Despite that, there is still lack of literature on the exhaust gas conversion data for different catalyst types for two different gasoline fuels (RON 95 and RON 97).

Thus, the present study attempts to analyze the performance of the ceramic and metallic catalytic converter on its conversion efficiency. Ceramic and metallic three way catalytic converter have been compared to assess the influence of physical parameters and fuel properties on the engine parameters and exhaust gas conversion for several different operating conditions. The inlet and outlet chemical species concentration and temperature were measured as a function of the engine speed (rpm).
1.3 Objectives of Study

The objectives of this study are:

   i. To examine the conversion efficiency of the substrate materials in reducing CO, HC and NO\textsubscript{x} of gasoline engine through experimental measurement.
   
   ii. To analyze the influence of ceramics and metallic substrate properties towards the engine performance and emission of a gasoline
   
   iii. To investigate experimentally the performance of engine and the characteristics of emission using RON 95 and RON 97.

1.4 Scopes of Study

Several points are listed here to elucidate the scopes of the study as follows:

   i. Experimental study is conducted to measure the emission and engine performance data from the tested engine.
   
   ii. Mitsubishi 4G93 gasoline engine with eddy current dynamometer used as test engine.
   
   iii. Two type of catalytic converter which is ceramic and metallic catalytic converter.
   
   iv. Two type of petrol fuel were used which is RON 95 and RON 97.
   
   v. The emission testing was conducted at different engine speeds from 1000 rpm to 4000 rpm at constant engine loads of 25%.
   
   vi. The exhaust emission of carbon monoxide (CO), nitrogen oxide (NO\textsubscript{x}) and hydrocarbon (HC) are measured during the engine test.
1.5 Significant of Study

The significant of this research are:

i. The outcome of this research is expected to contribute in the development of ceramic and metallic substrate.

ii. The intent is to further clarify the performance of metallic and ceramic substrates under different engine conditions.

1.6 Thesis Organization

This thesis consists of several chapters which contain different discussion as follows:

**Chapter 1:** Consists of the background of the study, problem statement, research objectives, significant research, expected results and scope or limitation of the project.

**Chapter 2:** Review about the terminology of catalytic converter, the development material and method for developing catalytic converter and the experimental studies from the past research.

**Chapter 3:** Described the current method and material used in this research and also the analysis and equipment used to achieve the research objectives.

**Chapter 4:** Discuss a result of the experimental result of exhaust emission testing in order for determining the effectiveness of the new catalyst and technique approach applied in this project.

**Chapter 5:** Consist of conclusions of this research which answer the objectives and also recommendation to continue this research for the next researcher.
CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter presents an overview of regulation of vehicle emission standard and the theoretical background and previous research related to the component of catalytic converter and its development in after treatment application. It discusses on the development of ceramics and metallic substrate and its properties in which affect the overall performance of the catalytic converter in reducing the vehicle exhaust emission.

2.2 Regulation of Vehicles Emission

Automobile emission has always been a major source of atmospheric pollution. Kaspar et al., (2003) suggested that automobile exhaust composition is depended on a variety of factors such as type of engine, driving conditions and vehicle speed. The creation of pollutants may result from a number of chemical changes that take place from the mixture of hydrocarbons or gasoline and air which is ignited through combustion process (Kaleli, 2003). In the 20th century, the pollutants released from internal combustion engines had raised serious health and environmental issues (Seinfeld, 2004). In response to this concern, a stringent legislation regulating emissions has been developed in many countries. Table 2.1 shows the current
summary of the California emission standard for passenger cars which involve Transitional Low Emission Vehicle (TLEV), Low Emission Vehicle (LEV), Ultra Low Emission Vehicle (ULEV) and Zero Emission Vehicle (ZEV).

Table 2.1: California emission standard for passenger cars (EPA, 2000)

<table>
<thead>
<tr>
<th>Category</th>
<th>Durability Basis (miles)</th>
<th>NMOG (g/mile)</th>
<th>CO (g/mile)</th>
<th>NOx (g/mile)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TLEV</td>
<td>50,000 120,000</td>
<td>0.125 0.156</td>
<td>3.4 4.2</td>
<td>0.4 0.6</td>
</tr>
<tr>
<td>LEV</td>
<td>50,000 120,000</td>
<td>0.075 0.09</td>
<td>3.4 4.2</td>
<td>0.05 0.07</td>
</tr>
<tr>
<td>ULEV</td>
<td>50,000 120,000</td>
<td>0.04 0.055</td>
<td>1.7 2.1</td>
<td>0.05 0.07</td>
</tr>
<tr>
<td>ZEV</td>
<td>-0-</td>
<td>-0-</td>
<td>-0-</td>
<td>-0-</td>
</tr>
</tbody>
</table>

The Environmental Protection Agency (EPA) has established a vehicle test procedure namely the Federal Test Procedure (FTP) which stimulates the average of the driving conditions of vehicles in the United State where the pollutant emission gases such as CO, NOx and unburned HC are measured and analysed. The FTP cycle is conducted by attaching a dynamometer to a vehicle. The FTP test also measure gases emitted from vehicle exhaust during conditions such as cold start conditions, hot start and combination of urban and highway driving conditions (Heck and Farrauto, 2009). The United State (U.S) and the European Union (E.U) have different specification for vehicle emission control in terms of test cycle conducted to the vehicles, fuel quality and type of pollutants as shown in Table 2.2.
Table 2.2: Comparison between vehicle emission control legislation United State and European Union (EU) (EPA, 2000)

<table>
<thead>
<tr>
<th>Test Cycle</th>
<th>United State (U.S)</th>
<th>European Union (E.U)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Federal Test Procedures + Supplemental Cycles:</td>
<td>• FTP-75 (city cycle, includes cold start)</td>
<td>• NEDC (city and extra urban, cold start)</td>
</tr>
<tr>
<td></td>
<td>• US06 (high speed)</td>
<td>World-Harmonized Light-Duty Vehicle Test Procedure:</td>
</tr>
<tr>
<td></td>
<td>• SC03 (air conditioning)</td>
<td>• WLTP (cold start, low, medium, high and aggressive driving in a single cycle)</td>
</tr>
<tr>
<td></td>
<td>• HWFET (highway cycle, fuel economy only)</td>
<td>• Expected implementation in 2017</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fuel Quality</th>
<th>United State (U.S)</th>
<th>European Union (E.U)</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Gasoline: 30 ppm sulphur average / 80 max (2006); 10 ppm average / 80 max (2017)</td>
<td>• Gasoline &amp; diesel: 50 ppm sulphur max (2005)</td>
<td></td>
</tr>
<tr>
<td>• Diesel: 15 ppm sulphur max (2007)</td>
<td>• Gasoline &amp; diesel: 10 ppm sulphur max (2009)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pollutants</th>
<th>United State (U.S)</th>
<th>European Union (E.U)</th>
</tr>
</thead>
<tbody>
<tr>
<td>• NOx + NMOG and CO (bin certification, fleet averaging)</td>
<td>Emissions:</td>
<td></td>
</tr>
<tr>
<td>• HCHO (limit value)</td>
<td>• NOx, HC, NOx+HC (diesels), PM and PN (limit values per vehicle category)</td>
<td></td>
</tr>
<tr>
<td>• PM mass (limit values, phased in)</td>
<td>CO₂:</td>
<td></td>
</tr>
<tr>
<td>GHG:</td>
<td>• CO₂ (fleet average)</td>
<td></td>
</tr>
<tr>
<td>• CO₂ (fleet average)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• CH₄, N₂O (limit values)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.3 Performance and Emission with RON 95 and RON 97 Gasoline

Gasoline is the most widely used fuel for on-road vehicles worldwide and therefore the main power source for this energy user. Demand for gasoline is continually expanding with the increasing number of on-road vehicles supported by the development of fuel efficient direct gasoline injection and hybrid engines. Table 2.3 shows the parameter for gasoline RON 95 and RON 97.
Table 2.3: Gasoline properties for RON 95 and RON 97 (Owen and Tao, 2015)

<table>
<thead>
<tr>
<th>Description</th>
<th>RON 95</th>
<th>RON 97</th>
</tr>
</thead>
<tbody>
<tr>
<td>Research octane number</td>
<td>95</td>
<td>97</td>
</tr>
<tr>
<td>Initial Boiling Point (°C)</td>
<td>35.7</td>
<td>35.7</td>
</tr>
<tr>
<td>Final Boiling Point (°C)</td>
<td>197.2</td>
<td>200.5</td>
</tr>
<tr>
<td>Density @ 15°C (kg/L)</td>
<td>0.764</td>
<td>0.7639</td>
</tr>
<tr>
<td>Reid vapor pressure</td>
<td>66</td>
<td>65.5</td>
</tr>
</tbody>
</table>

Gasoline engine formulation is mainly indexed with respect to octane numbers; RON or MON. Rating of the octane numbers is considered to be one of the important parameters in deciding the quality of the fuel as it influences the vehicles engine performance and emission (Nagai, 2000). Octane number is also an impartment parameter for vehicle combustion. Farayedhi (2002) showed decreases in CO and HC emissions along with but higher NOx emission with increasing octane number of the fuel. The combustion duration becomes prolonged as octane number increases; longer combustion duration may result in low thermal efficiency and increased fuel consumption Shen et al. (2008).

Many studies have been conducted to investigate the effects of RON number to engine performance and emissions. Sayin (2005) has found that the use of RON which is higher than the engine requirement not only reduces brake thermal efficiency but also increased brake specific fuel consumption, CO and HC emission but can be reduced with a more advanced spark timing. However, recent study by Mohamad and Geok (2014) has found that RON95 produced higher engine performance for all part-load conditions within the speed range. RON95 produced an average of 4.4% higher brake torque, brake power, and brake mean effective pressure as compared to RON97. The difference in engine performance was more significant at higher engine speed and loads. Cylinder pressure and ROHR were evaluated and correlated with engine output. With RON95, the engine produced 2.3% higher fuel conversion efficiency on average but RON97 was advantageous with 2.3% lower brake specific fuel consumption throughout all load condition. In terms of exhaust emissions, RON95 produced 7.7% lower NOx emission but higher CO2, CO and HC emissions by 7.9%, 36.9% and 20.3% respectively. Higher octane rating of gasoline may not necessarily be beneficial on engine power, fuel economy and emissions of
polluting gases. Even though RON97 proves to be beneficial in terms of emission reduction of CO₂, CO and HC, the price is 38% higher and higher NOₓ emission is more expensive in the long run.

2.4 Emission of Gasoline Engine

Emission of gasoline engine has been known as a major source of air pollution along urban traffic routes in developed countries. In Malaysia, it was estimated that nearly 51% from 12 millions of registered vehicles used gasoline engine (Kalam, 2011). Generally, gasoline engines are referred to as internal combustion engine (ICE) where initiation of the combustion process of air–fuel mixture is ignited within the combustion chamber which is done either by spark ignition (SI) or compression ignition (CI) (Bera, 2010). Emission from gasoline engine can be reduced through improvement of engine design, combustion conditions and catalytic after treatment devices (Faiz, 2006). Table 2.4 listed the common gasoline exhaust gas composition at different operating condition.

Table 2.4: Typical exhaust gas compositions at the common gasoline engine operating conditions (GM Research& Development, 2006)

<table>
<thead>
<tr>
<th>Gas</th>
<th>Cold-Start</th>
<th>Warm-up</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>0.2 to 6% (~1.5 % avg.)</td>
<td>~0.8 % avg.</td>
</tr>
<tr>
<td>HC</td>
<td>400 to 1200 ppm (C3) (~650 ppm avg.)</td>
<td>~450 ppm (C 3) avg.</td>
</tr>
<tr>
<td>H₂</td>
<td>1/3 CO</td>
<td>1/3 CO</td>
</tr>
<tr>
<td>NO</td>
<td>100 to 1200 ppm (~500 ppm avg.)</td>
<td>~500 ppm avg.</td>
</tr>
<tr>
<td>O₂</td>
<td>0.5~2.5% (~1.2 % avg.)</td>
<td>~0.7% avg.</td>
</tr>
<tr>
<td>SO₂</td>
<td>20 ppm or lower</td>
<td>20 ppm or lower</td>
</tr>
</tbody>
</table>

2.4.1 Emission of Nitrogen Oxides (NOₓ)

Motor vehicles are usually the major sources of nitrogen oxides in urban areas. NOₓ primarily is a mixture of nitric oxide (NO) and lesser quantities of nitrogen dioxide (NO₂). The NOₓ gases are formed by oxidation of nitrogen in air at high combustion temperatures. When oxidised to NO₂ in ambient air, NO plays a major role of the
formation of photochemical oxidants (such as ozone) and particles (such as nitrates). Zhao et al., (2004) referred the reduction of NO\textsubscript{x} to nitrogen and oxygen caused by temperature as thermal mechanism which derived the NO reaction under reducing conditions as Eq. 2.1.

\[ 2\text{NO}_x \rightarrow x\text{O}_2 + \text{N}_2 \] (2.1)

Nitrogen dioxide appears to exert its effects directly on the lung, leading to an inflammatory reaction on the surfaces of the lung (Streeton, 1997).

### 2.4.2 Emission of Carbon Monoxide (CO)

CO is a product of incomplete combustion, which simply means that there was a lack of oxygen for burning when the combustion process took place (Kaleli, 2003). The conversion of CO is as Eq. 2.2 (Kaspar et al., 2003):

\[ 2\text{CO} + \text{O}_2 \leftrightarrow 2\text{CO}_2 \] (2.2)

CO is a highly toxic, colourless, odourless gas that is dangerous to those who inhale it. This is because CO has a high affinity to blood, and when inhaled, it combines with the haemoglobin in blood to produce carboxyl haemoglobin, which is an extremely toxic substance (Narendran, 2013).

### 2.4.3 Emission of Hydrocarbon (HC)

Hydrocarbons react in the presence of nitrogen oxides and sunlight to form ground-level ozone, a major component of smog. It is our most widespread and intractable urban air pollution problem. A number of exhausts HC are also toxic, with the potential to affect human health. HC includes many toxic compounds that cause cancer and other adverse health effects (WHO, 2003). The conversion of HC gas is shown as in Eq. 2.3:

\[ C_x\text{H}_{4x} + 2x\text{O}_2 \rightarrow x\text{CO}_2 + 2x\text{H}_2\text{O} \] (2.3)
2.5 Emission Standard of Gasoline Engine

Every country has its own strict regulation for vehicle emissions which are varied significantly. In 2005, the first major reductions in all emitted pollutants are gained by electronic optimization of the combustion process when gasoline-powered vehicle is restricted to emitting between 1% to 3% CO of a comparable size unit in 1970 (Martyr and Plint, 2012). The United States (US) and European Union (EU) regulation standards have been recognized and used worldwide. Table 2.5 presented the comparison of EU Vehicle Emission Standard in ASEAN countries while Figure 2.1 illustrates the EU emission standard for exhaust emission gases of HC and CO for gasoline powered vehicles.

Table 2.5: Light Duty Vehicles (LDVs) Emission Standard in ASEAN countries (Silitonga et al., 2012)

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<tbody>
<tr>
<td>Australia</td>
<td>Euro 2</td>
<td>Euro 3</td>
<td>Euro 1</td>
<td>Euro 4</td>
<td>Euro 5</td>
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<tr>
<td>Bangladesh</td>
<td>Euro 1</td>
<td>Euro 2</td>
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<tr>
<td>Bhutan</td>
<td>Euro 1</td>
<td>Euro 2</td>
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<tr>
<td>China</td>
<td>Euro 1</td>
<td>Euro 2</td>
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<tr>
<td>Hong Kong</td>
<td>Euro 2</td>
<td>Euro 3</td>
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<tr>
<td>India</td>
<td>Euro 1</td>
<td>Euro 2</td>
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<tr>
<td>Indonesia</td>
<td>Euro 1</td>
<td>Euro 2</td>
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<tr>
<td>Japan</td>
<td>Japan 98</td>
<td>Japan 00/02</td>
<td>Japan 02/04</td>
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<tr>
<td>Malaysia</td>
<td>Euro 1</td>
<td>Euro 2</td>
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<tr>
<td>Nepal</td>
<td>Euro 1</td>
<td>Euro 2</td>
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<tr>
<td>New Zealand</td>
<td>Euro 2</td>
<td>Euro 3</td>
<td>Euro 4</td>
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<tr>
<td>Pakistan</td>
<td>Euro 2</td>
<td>Euro 1</td>
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<tr>
<td>Philippines</td>
<td>Euro 2</td>
<td>Euro 1</td>
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<tr>
<td>Singapore</td>
<td>Euro 2</td>
<td>Euro 4</td>
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<tr>
<td>South Korea</td>
<td>Euro 4</td>
<td>Euro 5</td>
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<tr>
<td>Sri Lanka</td>
<td>Euro 2</td>
<td>Euro 1</td>
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<tr>
<td>Taiwan</td>
<td>Euro 2</td>
<td>Euro 3</td>
<td>Euro 4</td>
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<tr>
<td>Thailand</td>
<td>Euro 1</td>
<td>Euro 2</td>
<td>Euro 3</td>
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<tr>
<td>Vietnam</td>
<td>Euro 2</td>
<td>Euro 1</td>
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</table>
Since Euro 1, vehicles have to be tested for emission not only to gain type approvals new vehicles, but also after a number of miles in service. EU recently state that the original equipment manufacturer (OEM) is responsible for assuring that vehicles meet emission standard for 80,000 kilometers, in the US which the rules use 160,000 km.

2.6 Factors Affecting Exhaust Emission

Consideration of several variables and parameters can control exhaust emission. A complete combustion in engine cylinder is needed in order for the engine to work efficiently. Barry (2006) stated that in order to ensure a complete combustion in an engine, several matters such as the accurate amount of air and fuel must be mixed with the correct amount of heat at the correct time. These two factors, air-to fuel ratio and cold-start seems to be the most important factors that could affect exhaust emission.
2.6.1 Air-To-Fuel Ratio

The air-fuel ratio is known as the mass ratio of air to gasoline, which is required to ensure the operation of injection system of an engine (Halderman, 2012). The emission of pollutant can be caused by improper ratio of air to fuel during the combustion process. Thus, it is important to ensure a correct air-fuel ratio in order to control the exhaust emission, good drivability and prevention internal damage of engine parts (Barry, 2006). All three pollutants can be converted (essentially equilibrated to CO$_2$, H$_2$O and N$_2$) with high efficiency over a single catalyst if the air–fuel ratio can be controlled sufficiently close to the stoichiometric value. Figure 2.2 shows the illustration of the total effect of the air-fuel ratio on engine emission. Table 2.6 list the relationship between the air-fuel-ratio condition and its effect on the emission gases.

![Figure 2.2: Air-fuel-ratio for exhaust SI gasoline emission (Heywood, 1998)](image-url)
Table 2.6: Air fuel mixture and emission relationship (Barry, 2006)

<table>
<thead>
<tr>
<th>Air-Fuel Mixture</th>
<th>Effect on Vehicle</th>
</tr>
</thead>
</table>
| Too Lean         | Increase NOx emissions  
                  | Poor Engine Power   
                  | Misfiring at cruising speed  
                  | Burned valves          
                  | Burned pistons         |
| Slightly Lean    | Low exhaust emissions  
                  | High gas mileage    
                  | Reduced engine power  
                  | Slight tendency to knock or ping |
| Stoichiometric   | Best all-around performance and emission levels |
| Slightly Rich    | Increased CO emissions  
                  | Increased HC emissions  
                  | Maximum engine power    
                  | Higher fuel consumption  
                  | Less tendency to knock or ping |
| Too Rich         | Increased CO emissions  
                  | Increased HC emission  
                  | Poor fuel mileage       
                  | Misfiring              
                  | Oil contamination      
                  | Black exhaust          |

SI engines operate normally at stoichiometric conditions ($\lambda = 1$). This is to ensure that the TWC operation is satisfactory. If the mixture is too lean, NOx will not be converted to nitrogen and oxygen and if the mixture is too rich, the CO and unburned HC will not be converted to carbon dioxide and water (Mansha et al., 2013). Ferguson (2004) and Stone Richard (1999) state that the allowable air-fuel-ratio for efficient catalytic operation is ±0.25% to ±1% of stoichiometric. This occurs when the air-fuel-ratio is between 14.6 and 14.8 for gasoline. Within this window, the conversion of all three polluting emissions is almost complete, although outside this window the efficiency decreases rapidly. Only at stoichiometric conditions are appropriate amounts of reducing and oxidizing agents present in the exhaust to carry out the catalytic reactions by using oxygen sensor as shown in Figure 2.3.
2.6.2 Cold-Start Condition

Cold start condition in engine plays an important role in producing exhaust emission. Cold start or unstable engine running period is the time period required for the catalyst to reach its light-off temperature (Raja and Arasu, 2015). Favez et al., (2009) define cold start as emission in SI engine that begin after a minimum halt time of 12 hours or more. During cold start condition, CO and HC are emitted in large quantities in the first few minutes after the spark ignition (SI) of the engine due to less active or inactive catalytic converter (Iliyas et al., 2007). It has been found that the conversion efficiency in catalytic converter is more effective only after the catalyst reaches above 150°C, which is the light-off temperature (Singer et al., 1999).
Recently, automobile manufacturers and researchers were forced to undertake extensive investigation on reducing the cold start emission. Andrianov et al., (2012) has presented a methodology for minimizing emissions constrained for cold start emissions. This study has developed an Integrated Model for the optimization of spark ignition engine control strategies. The Integrated Model is a warm-up model in which describes a thermodynamics processes in a gasoline fuel spark ignition engine. Using the dynamometer control system model, Integrated Model provides an alternative way for calculation of instantaneous fuel consumption, as well as the mass flow rates of the legislated CO, NOx and HC tailpipe emissions under transient driving conditions, specified by engine torque and speed trajectories by using the dynamometer control system model as shown in Figure 2.4.

Chang et al., (2014) has developed a new technology of gasoline Cold Start Concept (gCSC™) for cold start or low temperature emission control. This new concept uses the novel of mixed oxide Al2O3/CeO2/ZrO2 in which has a higher oxygen storage capacity especially at low temperatures in which reduced the light-off temperature of catalyst. It also combines low temperature TWC with extruded zeolite substrates to further reduce the cold start emissions.
2.6.3 Exhaust Temperature

Exhaust gas temperature is the indication of the combustion quality in the combustion chamber (Sureshkumar et al., 2008). The exhaust of vehicles gas temperature may vary from 300°C to 400°C from idling to around 900°C at full load condition in internal combustion engine. However, the common temperature of exhaust gas lies between 400°C to 600°C. It requires lower temperature for unburned HC to be oxidizing compare for the oxidation of CO in which normally oxidizes at a specific residence time (Mansha et al., 2012). Without having a catalyst for the conversion of pollutant gases, the temperature in the exhaust pipeline will exceed 600°C and the residence time to oxidize HC is greater than 50ms while the temperature that are required to oxidize CO is more than 700°C (Heywood, 1988).

Temperature in the catalytic warm-up also plays a vital role for the oxidation of the gases. In reference to the previous research, Ferguson (2004) states that the conversion will be efficient at fully warmed up catalytic conditions about 98% to 99% for CO and 95% for unburned HC depending on HC components. Willard (2003) state that at temperature of 400°C or higher, the catalytic converter is fully warmed up and will eliminate about 98-99% of CO, 95% of NOx and more than 95% of unburned HC from the engine out exhaust. Conversion process in the catalytic does not occur at NOx, CO and unburned HC is not observed. The rate of oxidation of CO and HC increases and NOx decreases as exhaust gasses increases. 50% conversion efficiency is referred as light off of catalyst (Mansha et al., 2013).

2.7 Catalytic Converter

Catalytic converter is a stainless steel container mounted along the exhaust pipe of the engine that incorporates a honeycomb monolith made of ceramic or metal (Ganesan, 2004). Today, most vehicles with gasoline-fuelled engines achieve the emissions limits by using the three-way catalysts, which are installed a part of the exhaust system. These devices are designed to convert CO, NOx and HC engine-out emissions to much less harmful CO2, H2O and N2 as shown in Figure 2.5.
Catalytic Converters are important post combustion after treatment devices mounted in the exhaust system of engines to reduce the engine exhaust emissions and are classified as either Two-Way or Three-Way. Two-Way Catalytic Converter (2WCC) works on two gases, CO and unburned HC while the NO\textsubscript{x} is controlled though exhaust gas recirculation (EGR) by retarding the ignition timing (Mansha et al., 2013). A catalytic converter is consists of three basic components, which are substrate, washcoat and catalyst (Sebayang et al., 2009).

The Three-Way Catalytic Converter (TWCC) will convert all the three gaseous pollutant that are mainly CO, unburned HC and NO\textsubscript{x}. TWCC typically contains active catalytic materials of Pt, Rh and Pd, which promote the oxidation of CO and unburned HC and reduction of NO\textsubscript{x}. Pt and Pd are functioning as an oxidation catalyst while Rh (Rhodium) act as a reducing catalyst for NO\textsubscript{x} reduction (Kamble et al., 2008).

The efficient conversion of CO, unburned HC and NO\textsubscript{x} are simultaneously carried out on the same catalyst bed. The maximum conversion efficiency can be achieved by operating the engine near stoichiometric condition through precise control of A/F ratio mixture. The TWCC is at most efficient when the exhaust gas composition from the engine is cycling around stoichiometric conditions. A ceramic or metallic honeycomb monolithic substrate, particularly cylindrical or oval shaped) is the common option for most environmental applications that requires high flow rates and low pressure drop (Santos, 2007).
2.7.1 Substrate

Monolithic substrate supports are uni-body structures composed of interconnected repeating cells or channels. They are most commonly composed of ceramic or metal materials but some can also be made of plastic (Heck et al., 2002) as shown in Figure 2.6. The monolith parts itself can be produced in a number of sizes and shapes, typically round or oval cross-sectional areas for automotive applications, or square for stationary emission uses. Cross-sectional part diameters for single pieces up to 35 cm have been produced commercially for heavy duty vehicle uses.

![Figure 2.6: Ceramic and metallic monolith (Heck et al., 2002)](image)

The honeycomb or also called “catalyst support” are capable to support the catalyst as it can increase the amount of surface area (Mizanuzzaman et al., 2013). In mid 1970s, the United States has been the first country to use ceramic substrates (Heck and Farrauto, 1995). Each ceramic monolith is coated with a washcoat and a catalyst coating made from precious metal.

In the automotive and stationary emission control area, monolith substrate is a common component that is used for selective catalytic reduction (SCR) of nitrogen oxides. Thus, the usage of the monolith substrates is increasingly used under
development and for evaluation in new reactor application such as ozone abatement, chemical process system, refining industries and other types of industries usage as (Jimme, 2001). The manufacturing of monolith substrate consists of several steps that need to be followed by referring the flow in Figure 2.7.

Figure 2.7: Fabrication of monolith honeycomb substrates (Jimme, 2001)

For the first steps, the raw materials need to undergo mixing process where the materials are mixed in the binder. The result of the mixing process is continued with the second steps, the plasticizing steps where the raw materials are plasticized with solvent, which is usually water. The plasticizing step requires the materials to undergo extrusion process (Jimme, 2001). The extrusion processes usually use unique dies to fabricate monolith structure. After extrusion process, the monolith substrate will be dried at elevated temperature in order to ensure that moisture elimination is done without cracking the monolith substrates. In the final steps, the component will undergo firing steps; the monolith is placed at elevated temperature to complete the solid-state reactions and to obtain the desired physical condition of the complete monolith substrates. The monolith type substrate has been widely used due to the catalyst coating method, flexibility in reactor design, low pressure drop and high heat and mass transfer (Nijhuis, 2001).

2.7.2 Washcoat

The washcoat is a type of ceramic layer (oxide layer) with specific surface area and acts as a support for catalyst materials. The waschoat also acts as a barrier from high temperature corrosion (Cueff et al., 2004). Alumina (Al₂O₃) is one of the most
applied washcoat materials (Heck, et al., 2009). The washcoat is a thin layer of alumina (Al₂O₃) coating, typically 20-150 μm thick with a high surface area on the top of substrate. Cross section image of the coating, called ‘washcoat’ is composed of porous, high surface area inorganic oxides such as γ-Al₂O₃ (gamma alumina), CeO₂ (Ceria) and ZrO₂ (Zirconia). Alumina is chosen due to its high surface area and relatively good thermal stability under the hydrothermal conditions of the exhausts (Kaspar et al., 2003).

2.7.3 Catalyst

In the last few years, the most dominant catalyst for gasoline vehicles has been the monolith or honeycomb structure catalyst. This catalyst is consisted of a skeleton coated with highly porous washcoat of about 90% γ-Al₂O₃ and a mixture of alkaline-earth metals, oxides and noble metals such as Pt, Pd and Rh which are fixed in the washcoat surface as shown in Figure 2.8. Noble metal catalysts are deposited on the surface and within the pores of the washcoat (Pontikakis, 2003).

![Figure 2.8: Washcoat and catalyst development focused area in catalytic converter (Twigg, 2007).](image)

2.8 Ceramic Catalytic Converter

Ceramics materials are mainly processed from clay products such as sewer tiles, bricks for building usage, and sewer pipes. According to Keane (2003) ceramic is a
combination between non-metallic and metallic elements such as Alumina Oxide (Al₂O₃) Calcium Oxide (CaO) and Silicon Nitride (Si₃N₄). Advanced ceramic production includes structural materials used for engine components, machining cutting tools and bio-ceramics for hospitality usage such as tooth and bone replacements. Ceramic has wide range of application areas and catalysis of catalytic converter is one of it (Hart et al., 1989).

Ceramic has high potential in withstanding high temperatures, exhibit chemical durability and wear resistance in which is suitable for catalytic use for various operating conditions. The applications of ceramic can be divided into catalysts usage and materials support such as substrates to diffuse a variety of active metals. The investigation had been made on direct synthesis and stabilization of nano-crystalline ceramic materials for automobiles catalytic usage. Nano powders fabrication from ceramic improved the properties of the materials, resulting in production of advanced nanophase materials which may conduct heat, electrons and ions more efficient compared to conventional materials.

The application of ceramic materials in ceramic substrates for automobiles exhaust component possesses a large surface area for gas conversion process that improves the efficiency of pollutant gases filtering and also acts as good thermal shock resistance. It is one of the important components in conversion process in term of performance balancing, pressure drop and maintaining strength of catalytic materials. Ceramic substrates in commonly manufactured with honeycomb structures which has high mechanical strength with low thermal expansion coefficient shown in Figure 2.9.

![Honeycomb structure of ceramic substrates in three dimensional](image)

**Figure 2.9:** Honeycomb structure of ceramic substrates in three dimensional (Keane, 2003)
REFERENCES


Greenbaum, D.S. (2013). Diesel and gasoline engine exhausts and some nitroarenes. IARC Monogr Eval Carcinog Risks Hum, 105, pp. 49–62


