# Gasoline Engine Emissions and TWC Modeling in Axisuite

## Master Thesis

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# Summary

Automobiles are an important part of life in today's world. These machines are the main escorts for our daily travels. Automobiles are also one of the source of air pollution. So, reducing engine out emission is a great challenge for OEM's and all of them work to continuously improve their control strategies to reduce pollutants as much as possible from the engine out emissions. Three way catalyst is a efficient element of the exhaust system for gasoline engine because it removes the pollutants (NOx, CO, HC)[1] significantly from the combustion residues before they are released into the environment.

Toyota is one of the world's leading car manufacturers. Toyota takes serious responsibilities to help protect the environment that means creating the vehicles which have a little impact as possible on the natural world around us. Toyota's research and technology roadmap brings together a broad range of environmental technologies for cleaner, more efficient future mobility.

This thesis mainly deals with the development of aged TWC[2] models because Toyota wants to ensure the clean mobility of Toyota cars along their entire life period .Usually, the ageing of the catalyst are done on specific test benches. This is time consuming and have high cost for testing and prototyping.

Model Based Design (MBD) team of R&D Powertrain in Toyota Motor Europe is responsible for developing the TWC predictive models for Toyota cars. Previously, MBD team was calibrating each aged TWC model individually. To improve the process of TWC modeling, I took the responsibility to develop TWC ageing laws in order to reduce prototype, testing cost and model calibration time. Therefore, I proposed a methodology by extracting an ageing law from the existing models. As an outcome, two ageing laws were proposed, one for full catalyst, the other one depending on the washcoat properties. Final accuracy is similar as the existing models.

As a next step , the ageing law was applied on the new generation fresh TWC to validate the ageing law. Detailed investigation indicates that ageing law prediction is accurate. Even the improvement of fresh model OSC[3] reactions and thermal behaviour could improve the final accuracy.

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[1] NOx, CO, HC – Nitrogen oxides, Carbon Monoxide, Hydrocarbons
[2] TWC – Three-way catalyst
[3] OSC – Oxygen storage capacity

# Preface

This thesis report is the final requirement to complete the Master's program, European Master in Automotive Engineering (EMAE), a program organized by Czech Technical University, Prague (Czech Republic).The enrolled student works on an automotive engineering project, provided by companies and Research centres.

In EMAE, after three semesters of theoretical study, the fourth semester is dedicated to practical learning and based on the implementation of built up theoretical concepts. Upon successful completion of the project along internship, students will be awarded 30 ECTS credits. This project is conducted with the collaboration of Toyota Motor Europe and Czech Technical University.

# Acknowledgements

Foremost, I want to offer this endeavour to our **God Almighty** for the wisdom he bestowed upon me ,the strength, peace of mind and good health in order to achieve every important things in my life.

I would like to express my sincere gratitude to my mentor **Dr. Julie Le Louvetel-Poilly** from Toyota Motor Europe for her continuous support and motivation during my internship and thesis study. She consistently allowed this project to be my own work, but steered me in the right direction whenever she thought I needed it.

I would specially like to thank **Ing. Vojtěch Klír, Ph.D.** my supervisor from Czech Technical University for the guidance, patience, passionate participation and input throughout my thesis work. I extend my heartfelt gratitude to **doc. Dr. Ing Achtenová,** who stood as a well-wisher along my way to make me achieve great.

My hearty thanks also goes to **Mr. François-Alexandre Lafossas** and **Mr. Kotaro Maeda** who provided me an opportunity to join their Model Based Design team in Toyota Motor Europe as an intern, and who kindly gave access to the research facilities. I would like to extend my thanks to **Mr. Martin Guingouain** who assisted me with his immense knowledge throughout the learning process of my project.

I must express my very profound gratitude to my respected parents and to my beloved one Pavithra for providing me with unfailing support, prayers and continuous encouragement throughout my years of study and through the process of researching and writing this thesis. This accomplishment would not have been possible without them.

In the end, thanks to one of my good friend Sindhiya ,my seniors and friends - Arun Asokan, Nagendran, Rishi, Arun, Ashrith, Balaji, Gokul, Guhan, Santhosh, Sanjal, Surya, Praveen, Yuva, Vishwas, Shashank for their support and encouragement during this whole journey which was worth more than I can express on paper. I would like to thank Rohan, Giuseppe, Dario and Michele for many memorable refreshing lunch and breaks at Toyota.

This thesis becomes a reality with the kind support and help of many individuals, I would like to extend my sincere thanks to all of them.

I dedicate this thesis to my parents who made sure that “No matter how far apart we live, but their love and constant support would always be there.”

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# Toyota Way

***"Natural resources are limited. We must be friendly to the planet. We have to hand it to our future children."***

- Akio Toyoda, President Toyota Motor Corporation

## Toyota in the World

The history Toyota began in 1937 with the founding of the Toyota Motor Co. Ltd. Today Toyota have grown to become one of the world's largest and best-known automobile manufacturing businesses. Toyota employ more than 340,000 people and make vehicles in factories on every continent. Toyota cars and trucks are sold in more than 160 countries and territories.

Toyota aim is to help build a more prosperous society with a business that values respect and fairness and which grows in harmony with the global community. Toyota strive to enhance the quality of people's lives by using our skills and advanced technologies to create great new products and services.

## Toyota Global Vision

Toyota will lead the way to the future of mobility, enriching lives around the world with the safest and most responsible ways of moving people. Through our commitment to quality, constant innovation and respect for the planet, we aim to exceed expectations and be rewarded with a smile.

## Toyota Environmental Challenge 2050

1) New Vehicle Zero CO2 Emissions
2) Life Cycle Zero CO2 Emissions
3) Plant Zero CO2 Emissions
4) Minimizing and Optimizing Water Usage
5) Establishing a Recycling-based Society and Systems
6) Establishing a Future Society in Harmony with Nature

*Figure 1 Toyota environmental challenge 2050 logo*

The Toyota environmental challenge 2050 logo is shown in Figure 1.

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Source : https://www.toyota-europe.com/

# Toyota’s Cleaner Mobility

Around the world, people use different types of vehicles to suit their lifestyle and their local environment. Concern about the environment and cutting carbon emissions cuts across these differences, which is why Toyota believe there is no single solution when it comes to creating the ultimate eco-car.

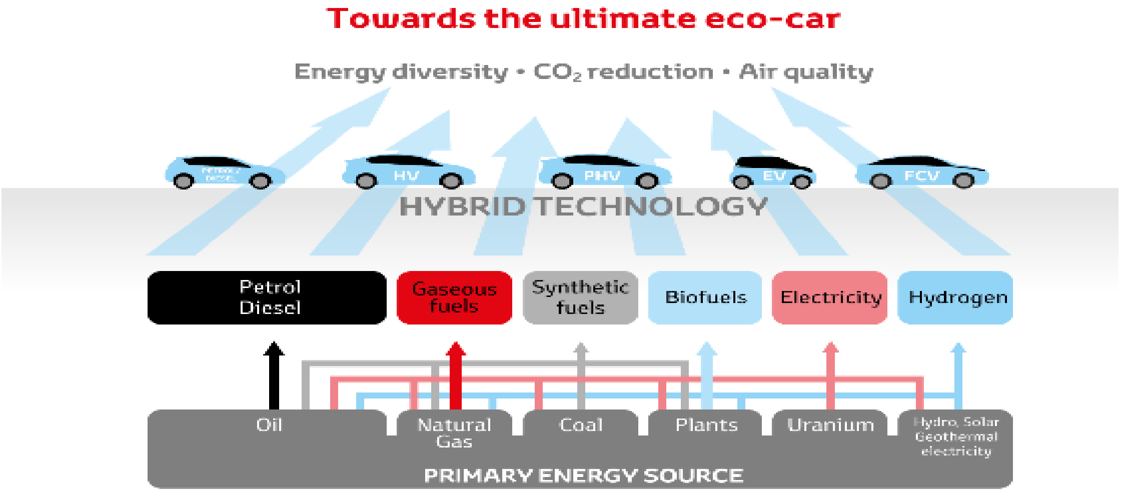

*Figure 2 Toyota towards ultimate eco car*

Toyota’s research and technology roadmap brings together a broad range of environmental technologies for cleaner, more efficient future mobility, including hybrid, plug-in hybrid, and electric battery power and fuel cell systems. Each technology moves us closer to our goal of creating the ultimate eco-car and it’s clearly represented in Figure 2.

# Sustainable Society and Environmental Governance

Toyota sees itself as more than a company providing all-round mobility solutions. We are citizens of the world, and therefore have a responsibility towards the planet - to leave things better than we find them.

Toyota are committed in protecting and improving the environment, so it’s a need to be sure that all aspects of the business understand what is required of them and that Toyota work together successfully to achieve its environmental goals. As well as Toyota’s own environmental plans, and of course also have to make sure we comply with environmental laws and regulations and have the right measures in place to recognize and deal with all environmental risks.

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Source : https://www.toyota-europe.com/

# Toyota Motor Europe

Toyota Motor Europe (TME) is the regional headquarters of Toyota in Europe. TME began selling cars in Europe under an official distributor agreement in 1963.TME Head Office is located in Brussels, Belgium and houses key activities for Toyota and Lexus in Europe. It also acts as the nerve centre for all European operations including the principal areas of manufacturing, engineering and marketing and sales activities.

TME Technical centre in Zaventem, Belgium is home to Toyota Motor Europe's Research & Development (R&D), Purchasing and Production Engineering activities. The internship and thesis work has been carried out in this technical centre.

I was a part of the Model Based Design team of the R&D Powertrain Engineering division as an intern. The MBD team has been classified into two system:

1) Engine and Emission system
2) Powertrain system

The engine and emission system carry out projects with the research and development of engines and the full exhaust system for the present and future European automotive market. The powertrain system deals with projects based on research and development of thermal management systems, transmissions and mainly they concentrate on the hybrid system of the Toyota cars.

During this internship in MBD team, I was able to obtain a deep knowledge about the research and development approach for the gasoline engine exhaust system and got an insight about the overall European automotive market and the future requirements. I would really thank this opportunity to be a part of MBD team.

# Chapter 1. INTRODUCTION

## 1.1. Project Background

This thesis is conducted with the collaboration of Toyota Motor Europe and Czech Technical University. Toyota takes its responsibility and interest to keep the environment green and safe.

So, Model Based Design team of R&D powertrain engineering division does research and development on TWC predictive models which contributes a lot in the emission prediction.

To attain these outcomes, the project revolves around the case study and research on gasoline emissions, three way catalyst functions, behaviour and the modeling to predict the emission levels.

## 1.2. Problem Definition

The main aim is to develop a TWC ageing model using Axisuite[2] by formulating an ageing law correlation, by which it will help to predict any ageing level in future from the fresh TWC model.

**Why?**

I. Aged TWC are used to ensure the clean mobility of Toyota cars along their entire life period.

**Challenges:**

TME previously had developed TWC models for fresh and three aged conditions independently.

- (i) TWC models had no correlation between each ageing level.
- (ii) No possibilities to predict aged TWC performances based on fresh TWC model.

**Why MBD and predictive model base approach?**

I. In the engine test bench, the three way catalyst ageing process is valid only for one exhaust line design and one vehicle engine.
II. The ageing process has to be redone for any geometrical changes or vehicle application each and every time.
III. These validations done in the engine test bench for every test requires a lot of time, resources, skilled technicians, financial investments etc.

## 1.3. Objective of my internship

I. To learn, investigate and obtain broad knowledge on gasoline emissions, European emission norms, three way Catalyst and its ageing phenomena.

II. To do research and develop a predictive ageing model with similar accuracy as existing TME aged TWC model using Axisuite.

III. The ageing model should predict any level of ageing in TWC with only fresh model provided in the future.

## 1.4. Deliverable in this report

I. Case study based on literature research of the background of gasoline emissions, European emission norms, description and construction of the TWC and its ageing phenomena.

II. Ageing model of TWC based on chemical kinetics with similar accuracy provided by previous TME models.

III. Validation of the ageing law on the aging TWC model for the driving cycles.

**-There might be a possibility that the proper strategies are not published due to confidentiality reasons.**

## 1.5. Report Structure

The report is structured as follows:

Chapter 2, 3, 4 and 5 covers the case study done from the literature research based on many journals, books and automotive society research papers and their references are quoted and attached along the report.

**Chapter 2:** The gasoline pollution and pollutants are elaborately discussed with its formation and its effects.

**Chapter 3:** Discussions of emission standards, testing procedure and driving cycles.

**Chapter 4:** History of three way catalyst, its construction and performance.

**Chapter 5:** Detailed information on ageing phenomena and its effects on three way catalyst.

Chapter 6, 7 and 8 covers the technical assignment of the research work done in Toyota Motor Europe R&D in the Model Based Design team in powertrain engineering division. The research work is considered as a highly confidential job, so all the technical details and detailed strategies will not be published in the thesis. The examiner will be explained during the Master thesis defence with the confidentiality agreement with Toyota Motor Europe.

**Chapter 6:** Calibration and formulation of ageing law with creation of predictive ageing TWC model using Axisuite.

**Chapter 7:** Validation results on the driving cycles by the predictive ageing model and discussion of the outcomes.

**Chapter 8:** Conclusion from the validation results and review on the work done.

# Chapter 2. GASOLINE EMISSIONS

## 2.1. History of Gasoline engines

Gasoline (spark-ignition) combustion engines was invented by German engineer N.A. Otto in 1878. In 19th century the door towards automobiles was opened for quick means of transportation by which the mass production of automobiles started to bloom. During the 20th century, the number of gasoline-driven cars increased from a few thousand to several hundred million on the planet.

The gasoline used in the modern automobile is a complex blend of both straight and branched chain hydrocarbons .The fictitious molecule C8H17 is used to approximate the blend of different hydrocarbon compounds found in gasoline. Gasoline is a very complex blend of several different molecules. C8H17 is used to represent the average “gasoline molecule”.

## 2.2. Gasoline engine emissions

When gasoline mixes with air along the ignition in the combustion chamber it leads to spontaneous reaction which burns the molecule, and it reorganizes the carbon, hydrogen, and oxygen atoms. So these atoms have the tendency to form carbon monoxide, oxides of nitrogen and organic compounds which are unburned or partially burned hydrocarbons.

Optimum combustion occurs at an A/F ratio of about 14.6:1. Perfect combustion would result in the formation of nothing CO2, H2O.

$$C_xH_y + (x+y/4)O_2 \rightarrow xCO_2 + y/2\ H2O + \text{energy} \qquad (2.1)$$

In reality, the combustion is never complete, since the air-to-fuel mixture is not entirely homogenous. So, they form additional compounds which can be stated as pollutants (NOx, CO, THC).

The formation and destruction reactions of carbon monoxide, organic compounds, and particulates are intimately coupled with the primary fuel combustion process. For nitrogen oxides and sulphur oxides, the formation and destruction processes are not part of the fuel combustion process. However, the reactions which produce these species take place in an environment created by the combustion reactions, so the two processes are still intimately linked [1].Each combustion process is a source of different types of pollutants. The chemical equilibrium with detailed chemical mechanism and the kinetics of these processes are treated to determine the concentrations of these pollutants in the exhaust.

Pollutant formation in the compression, combustion, expansion and exhaust stroke of a gasoline engine is shown in the Figure 3.

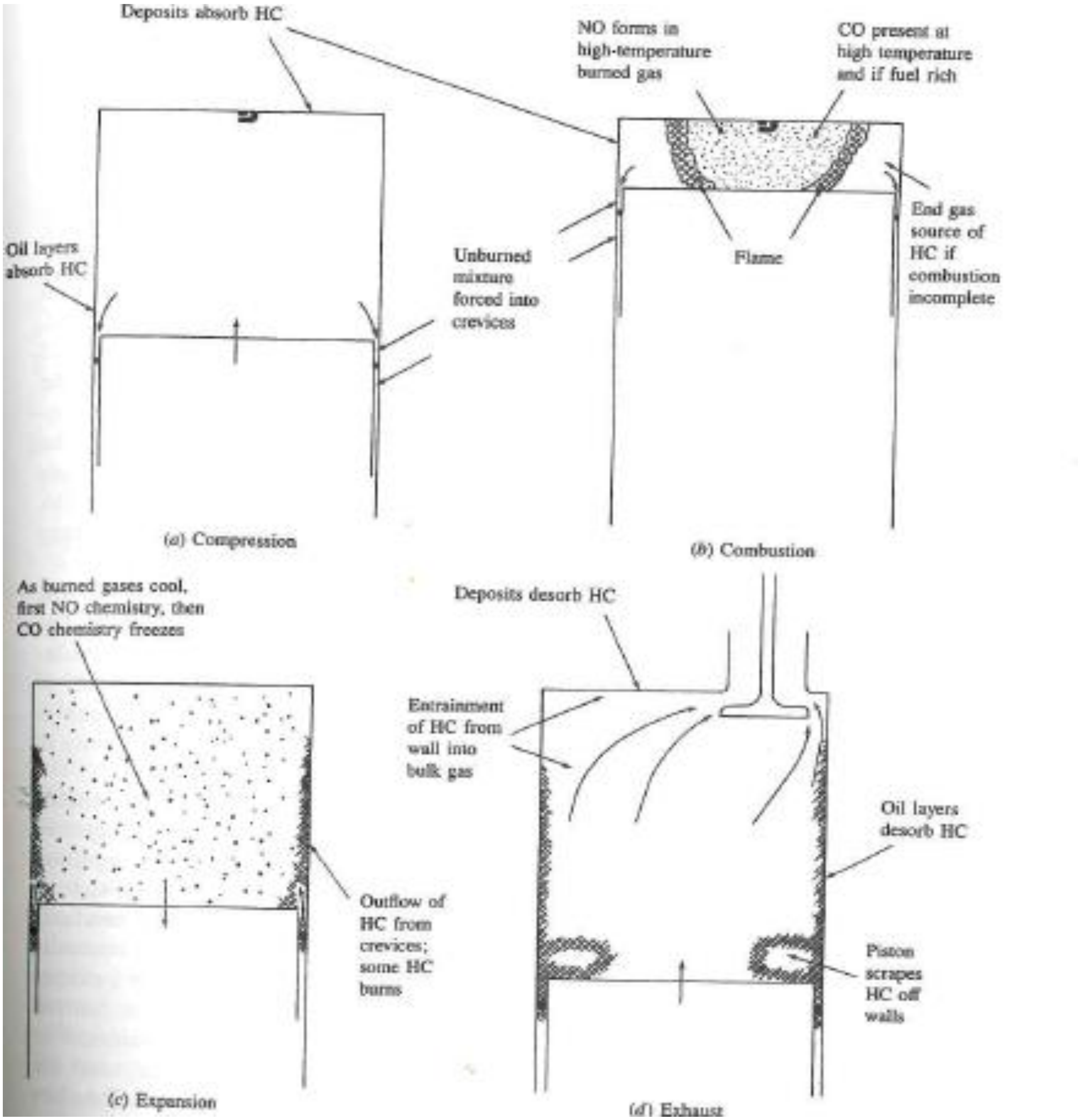


*Figure 3 Summary of HC,CO,NO pollutant formation mechanism in gasoline engine*

## 2.2.1.Carbon Monoxide

### Description

Carbon monoxide is a colourless and odourless gas. Carbon monoxide is a product of a partial combustion of hydrocarbons in fuel. CO is always present when there is a lack of oxygen during combustion which has a dependency on the applied engine air/fuel ratio. The CO concentrations in the exhaust increase steadily with increasing equivalence ratio[2] as the amount of excess fuel increases during engine transients like acceleration, deceleration, gear shifting. Sometimes the mixture is intentionally made richer for torque demand or during the cold start to assure smooth combustion.

Poor mixing, local rich regions and incomplete combustion will also be the source for CO emission. A well designed S.I engine for fuel lean mixtures will have an exhaust mole fraction of CO concentrations as low as 0.001.

CO is a fuel that can be combusted to supply additional thermal energy

$$CO+1/2\ O2 \rightarrow CO2 + heat \quad [3] \qquad (2.2)$$

### CO Formation

CO formation is one of the principal reaction steps in the hydrocarbon combustion mechanism, which may be summarized by

$$RH \rightarrow R \rightarrow R02 \rightarrow RCHO \rightarrow RCO \rightarrow C0 \quad [1] \qquad (2.3)$$

Where, R stands for the hydrocarbon radical. The CO formed in the combustion process via this path is then oxidized to CO, at a slower rate.

### Effects of CO

CO exhibits a higher affinity to haemoglobin than oxygen. It blocks the supply of oxygen to the body tissue, thus leading to suffocation and cause dizziness and headaches. Since the local level of CO is more dangerous than the global level, the most dangerous areas are where the traffic is dense or engines are running in poorly ventilated or confined spaces.

## 2.2.2.Nitrogen Oxides

### Description

NO is odourless and colourless, $NO_2$ is reddish-brown, pungent and very toxic. NOx is formed during combustion in the engine when oxygen reacts with nitrogen because of a high combustion temperature with an air-fuel ratio (λ )of about 1.05. The amount of NOx produced in the exhaust gas is very dependent on the combustion temperature.

### NO Formation

The extensive literature on the subject gives the information about three mechanisms of the formation of this compound in thermal processes. They are:

a. Zeldovich mechanism
b. Fuel mechanism
c. Fenimore prompt mechanism

In the report we see mainly the NO formation by thermal Zeldovich mechanism.

#### a. Zeldovich mechanism [4]

The formation of NO from molecular nitrogen is formed during the combustion of near stoichiometric fuel- air mixture and it's known as Zeldovich mechanism .The strong dependence of the Zeldovich kinetics on temperature provides the major tool used in the control of NO formation in combustion systems.

$$\mathrm{O+N2} \rightarrow \mathrm{NO+N} \tag{2.4}$$

$$\mathrm{N+02} \rightarrow \mathrm{NO+0} \tag{2.5}$$

$$\mathrm{N+OH} \rightarrow \mathrm{NO+H} \tag{2.6}$$

The factors affecting the production of NO are:

1. The effect of air fuel ratio which is shown in the Figure 4[5]
2. Advanced spark timing

The emissions data for Nitrous oxides are given in terms of mass of NO or mass of NO2, which have molecular weights of 30 and 46 respectively.

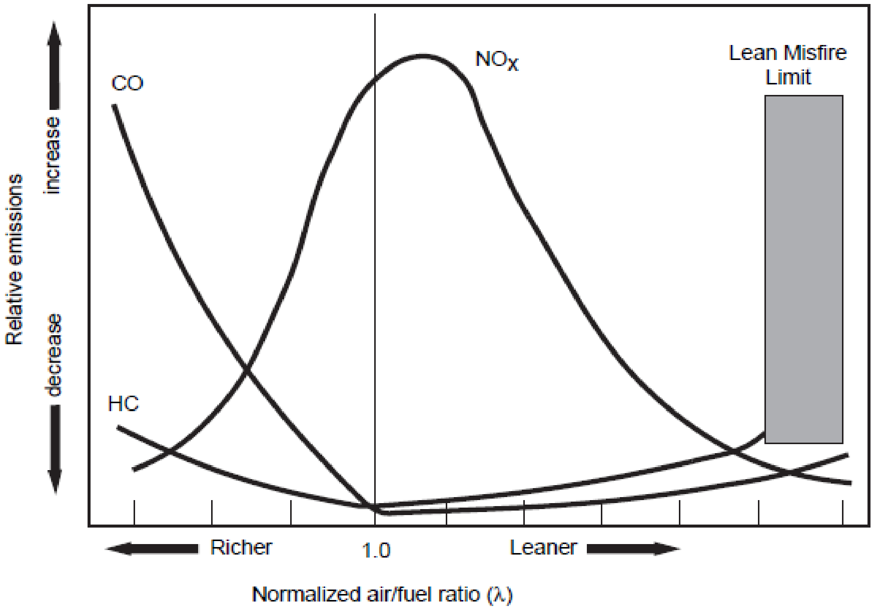


*Figure 4 Effect of Air-Fuel ratio on spark-ignition*

Smog is formed by the photochemical reaction of automobile exhaust and atmospheric air in the presence of sunlight.

$$NO_2 + \text{energy from sunlight} \rightarrow NO + O + \text{smog}$$

Monoatomic oxygen is highly reactive and initiates a number of different reactions, one of which is the formation of ozone

$$O + O_2 \rightarrow O_3$$ [3]

## EFFECTS OF NO

Oxides of nitrogen affects respiratory tract, damages lung tissue and increases airway resistance. It may also interfere with oxygen transport in blood via reaction with haemoglobin, provoke coughing, running noses, bronchitis, etc. Nitrous oxide is an important greenhouse gas. Usually, the fraction of NO in the NOx emissions of a gasoline engine is well above 98%. NOx is also involved in secondary pollution (smog, depletion of the ozone layer). $NO_2$ together with sulphur oxides, responsible for acid rains.

## 2.2.3.Hydrocarbons

### Description

The term ’hydrocarbons (HC)’ in the exhaust emission stands for the unburned organic compounds that contain hydrogen and carbon. A larger definition can be ’Volatile Organic Compounds (VOC)’ that would include all carbon containing compounds present in the gaseous state at ambient temperatures. However, due to the largest presence of hydrocarbons in the exhaust only the term HC is usually applied.

### HC Formation

HC is evident that it is a strong function of air fuel ratio. In rich mixture there is not enough oxygen to react with all the carbon resulting in high levels of HC and CO in the exhaust products. When combustion quality deteriorates example with very lean mixtures, HC emission can rise due to incomplete combustion or misfire in a fraction of the engine’s operating cycles.

The causes for hydrocarbon emission in SI engine are: [6, 3]

I. Flame quenching at the combustion chamber walls and deposits.
II. Filling of crevice volumes and flow in crevices
III. Incomplete combustion
IV. Leakage past the exhaust valve
V. Oil on combustion chamber walls.

### Effects of HC

Hydrocarbons irritate mucous membranes, leading to coughing, sneezing and drowsiness. Some have a narcotic effect. Benzene, for example, is very toxic and carcinogenic, while 80% of benzene in atmosphere stems from the automotive exhaust. Especially alkenes also react with NOx to create secondary pollution such as tropospheric ozone and photochemical smog.

### 2.2.4.Particulate emissions

#### Description

There are three classes of gasoline engine particulate emissions: lead, organic particulates (including soot), and sulphates.

#### Particulates Formation

The particulate emission rates are considerably higher when the engine is cold, following start-up. The exhaust temperature has a significant effect on emission levels. The particle size distribution with leaded fuel is about 80 percent by mass below 2 pm diameter and about 40 percent below 0.2 pm diameter [1]. Particles with diameter between about 0.05 to 2.5µm contained in the so-called accumulation mode, are mainly formed by coagulation and generated from condensation processes. Soot emissions (black smoke) can result from combustion of overly rich mixtures.

#### Effects of Particulates

The major conduit for the translocation of particulates into body has been linked to a number of different health outcomes, including lung inflammatory reactions, reduction in lung function, adverse effects on the cardiovascular [7]

## 2.3. Greenhouse gases :

The greenhouse effect is also experienced on a large-scale on earth. The surface of the earth, which warms up during the day as a result of the absorption of solar energy, cools down at night by radiating part of its energy into deep space as infrared radiation. Carbon dioxide (CO2), water vapour, and trace amounts of some other gases such as methane and nitrogen oxides act like a blanket and keep the earthworm at night by blocking the heat radiated from the earth. Therefore, they are called “greenhouse gases,”

Motor vehicles, which are powered by fossil-fuel burning engines that emit carbon dioxide and nitrous oxide, contribute significantly to the production of potentially climate altering greenhouse gases. Carbon dioxide is currently the most significant greenhouse gas, responsible for about half of current increases in the greenhouse effect

Each litre of gasoline burned produces about2.5 kg of $CO_2$. An average car is driven about 12,000 miles year, and it consumes about 600 gallons of gasoline. Therefore, a car emits about 5,600 kg of $CO_2$ to the atmosphere a year, which is about four times the weight of a typical car. [8]

## 2.4. Consequences of Gasoline emissions

Since almost every vehicle is driven by an internal combustion engine, the above mentioned exhaust components affects both the environment and the human health in many unpleasant ways. So, it became clear during the second half of the 20th century that measures had to be taken to reduce the levels of the emissions to tolerable limits.

Reducing engine out emission is a great challenge for OEM, who continuously improve their control strategies to reduce as much as possible engine out emissions. It is apparent that the improvement of the combustion in gasoline engines alone is not sufficient. This has led to the introduction of pollution control and significant advances in this field over the last three decades.
On another hand, legislation with standard norms were set to bring the emission level within limits to ensure the air standard quality.

# Chapter 3. EMISSION STANDARDS

## 3.1. Birth of Emission standards

1970 is considered to be the beginning of the U.S. motor vehicle emission control programmer with the Clean Air Act Amendments .At the time these requirements were too stringent but were setting the pace for new technology development, needed to meet such standards. After that, California took the lead in emission control legislation and worked in a way as a "proving ground" for very stringent exhaust gas limits.

The initial EU legislation on emissions from vehicles dates from 1970. While EU action was a response to growing concerns on air quality, and to the adoption of Member State measures aimed at improving emissions standards.

The essentiality of legislation is to reduce the environmental impacts, concern on human health, and latterly the impacts on climate change, of vehicle emissions.

The emissions of regulated air pollutants have been decreasing in the European Union (EU) over the past two decades. Nevertheless, 20% of Europe's urban population is still living in areas where pollutant concentrations (most prominently NOx and PM) exceed established air quality standards.

## 3.2. European emission norms

The new emission standards of the EU demand more sophisticated optimisation of all the compounds that contribute to the performance of the emission control system. In order to control the vehicle's emissions, several test procedures have been developed and standardized. Efforts to reduce $CO_2$ from passenger cars in the aftermath of the conclusion of the Kyoto Protocol in the EU date back to 1998 when a voluntary agreement was reached between the European Commission and the Association of European Automobile Manufacturers (ACEA) and developed an earlier focus on CO2 emissions from vehicles; and EU fleet average targets for CO2 emissions are currently more ambitious than those adopted for emissions in the USA [10].In 2005, the European Commission adopted Thematic Strategy on air pollution to reduce transportation emissions as part of an overall air-quality improvement policy.

The European emission standards limits for gasoline vehicles are very much demanding relative to earlier standards and is clearly explained in Table.1. The Euro 6 for gasoline cars has NOx standards are 60% lower than those for Euro 1 but remains same as the Euro 5. The particular improvement in Euro 6 is the limits introduced on particle number emissions of GDI engines

In terms of in-service requirements under Euro 6, Regulation 715/2007 requires manufacturers to check in-service conformity for all vehicles it certifies to the Euro 6 emission standards for a period of up to five years or 100,000 km, whichever comes first. Durability testing of pollution control devices undertaken for type approval shall cover 160,000 km, the mileage over which these devices are expected to perform. **[9]**

Adaptation of Euro 6 vehicle emission standards can achieve up to a 99 percent reduction in the emission of pollutants like fine particulate matter (PM2.5), reducing the risk of ischemic heart disease, lung, cancer, stroke, asthma and further ill effects on humans and plants

*Table 1 EU emission standards for passenger cars (gasoline)[11]*

| **Stage** | **Date** | **CO** | **HC** | **HC +NOx** | **NOx** | **PM** | **PN** |
|---|---|---|---|---|---|---|---|
| Gasoline | g/km | | | | | | #/km |
| Euro 1 | Jul-92 | 2.2 | - | 0.97(1.13) | - | - | |
| Euro 2 | Jan-96 | 2.3 | 0.2 | 0.5 | - | - | |
| Euro 3 | Jan-00 | 1 | 0.1 | - | 0.15 | - | |
| Euro 4 | Jan-05 | 1 | 0.10 | - | 0.08 | - | |
| Euro 5 | Sep-09 | 1 | 0.10 | - | 0.06 | 0.005 | |
| Euro 6 | Sep-14 | 1 | 0.10 | - | 0.06 | 0.005 | $6*10^{11}$ |

## 3.3. Testing regime

Vehicle exhaust emissions are inherently rather variable, and so the best way to ensure that an emission test is reproducible is to perform it under standardised laboratory conditions. The procedure for the collection an analysis of pollutants are specified in legislation.

For emission measurements, special driving cycles have been developed, where the vehicle speed and load, the gear shift events, the braking, idle, and standstill phases as well as the ambient conditions, such as the temperature, pressure, and humidity are exactly defined. The sampling of exhaust emissions is then performed as the vehicle progresses through a pre-defined driving cycle which is designed to represent a particular type of real world operation.

To ensure the requirement of emission legislation emissions are sampled during the cycle by a constant volume sampler (CVS) and the emission factor is usually stated in grams per vehicle kilometre (g/km).

To ensure consistent performance across all tests, trained driver is employed to follow the driving cycle on the chassis dynamometer and a driver aid is provided to ensure that the driven cycle is as close as possible.

As it is not practical to test every single vehicle made, for example for exhaust emissions, one production vehicle is tested as being representative of the 'type', that may encompass a number of different variants with similar characteristics such as engine size and type.[10]

For gasoline vehicles the regulated gaseous emissions (HC, CO and NOx) were measured using the bags as prescribed by the legislation. The CVS sample of the exhaust is collected in "Tedlar" bags during the test then the concentration of each pollutant will be measured inside these bags at the end of the test. The background level is determined by analysing a sample of the dilution air collected in other bags [12] as shown in the Figure 5.

For the diesel vehicle, in agreement with the legislative procedure, the HC emissions were measured using an on-line heated FID analyzer sampling directly from the dilution tunnel.IR analyser for CO and CO2 and chemiluminescence analyzer for NOx [12].

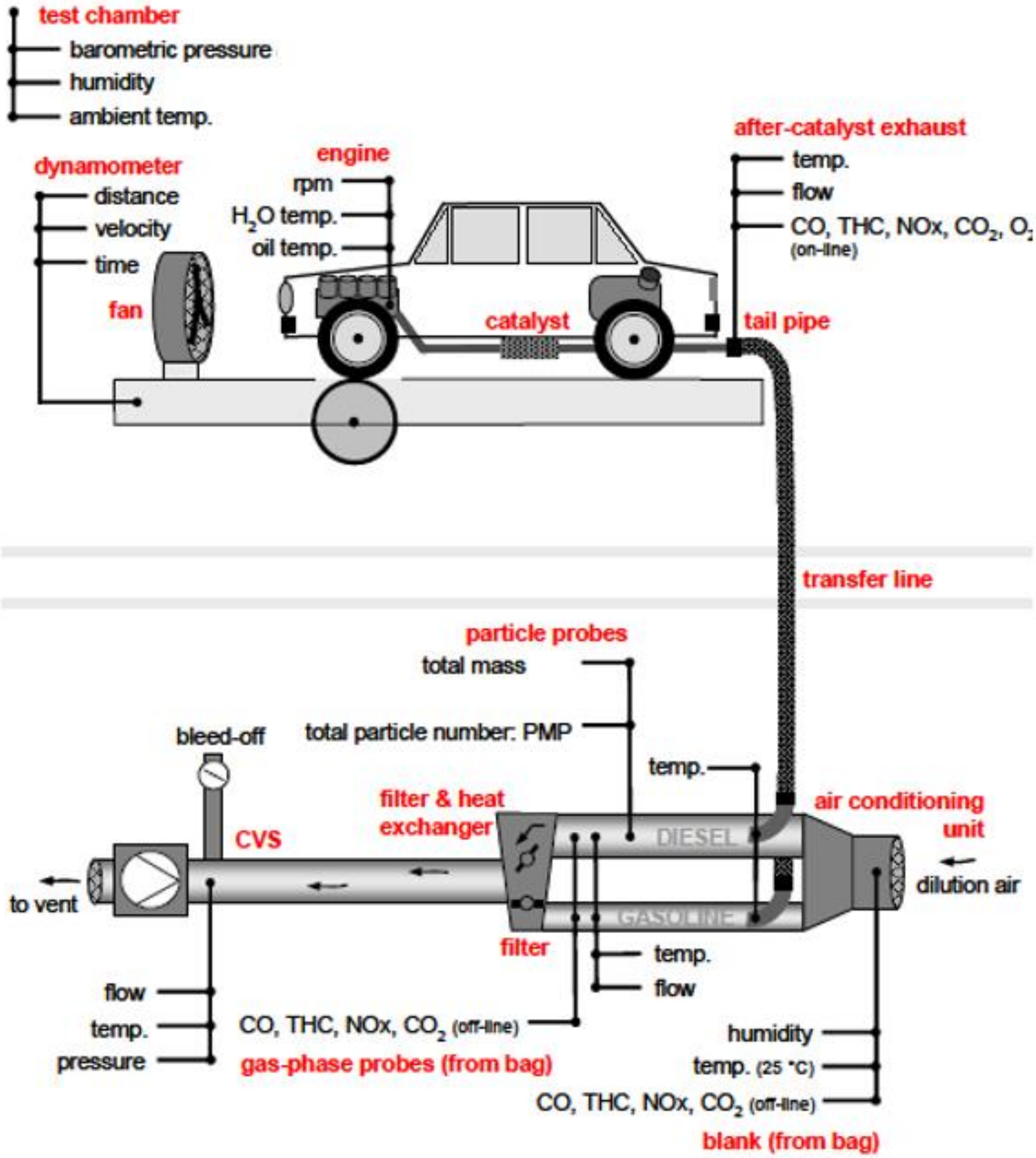


*Figure 5 General layout emission facility [12]*

## Driving Cycles

A driving cycle is a pre-determined and fixed schedule of vehicle operation which allows an emission test to be conducted under reproducible conditions. Driving cycles are usually defined in terms of vehicle speed and gear selection as a function of time.

Depending on the character of speed and engine load changes, cycles can be broadly divided into steady state cycles and transient cycles. A steady state cycle is a sequence of constant engine speed and load modes.

Prior to the Euro 3 standards, vehicles were allowed to run for 40 seconds from cold before emissions were measured, permitting the catalyst on gasoline vehicles to heat up and become effective. From Euro 3 onward this allowance was removed to better reflect the effects of cold start emissions, and so measurements are now made from the beginning of the drive cycle.

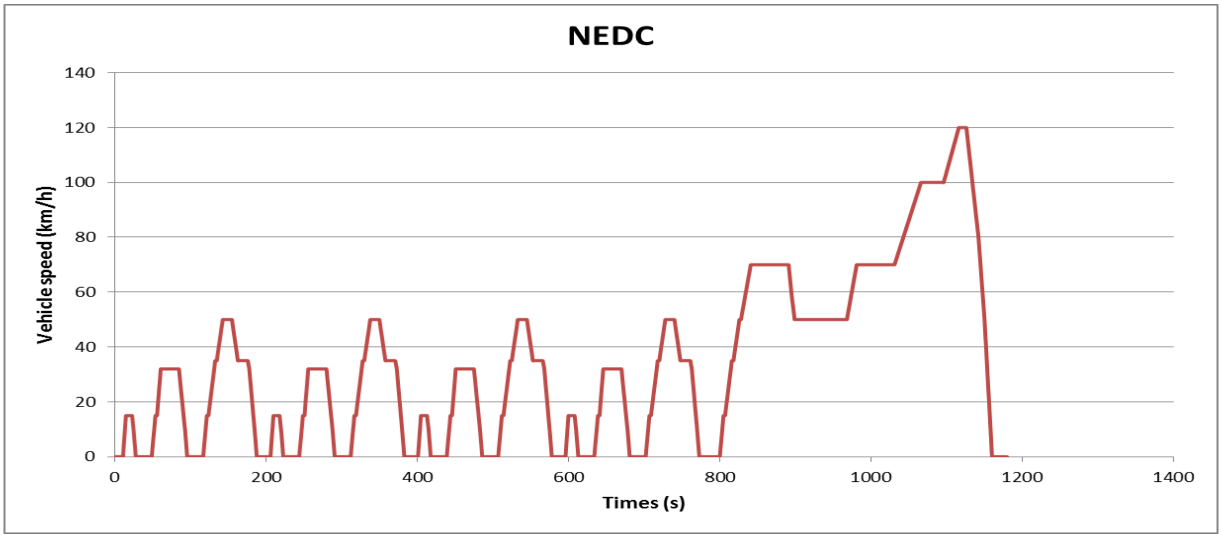


*Figure 6 Representation of NEDC driving cycle*

Since the agreement of Regulation 715/2007, research has shown the NEDC (New European Driving Cycle) to be a poor representation of real-world driving as shown in Figure 6, with serious implications for emissions, particularly those of $NO_X$ from diesel cars, and for the ambient air quality in Europe. The more recently developed Worldwide Harmonized Light Vehicles Test Cycle (WLTC) is represented in Figure 7 contains more dynamic driving conditions than the NEDC, such as higher maximum velocity and less idling time, as it was designed using a large number of real-world drives to better reflect real-world driving conditions[12].

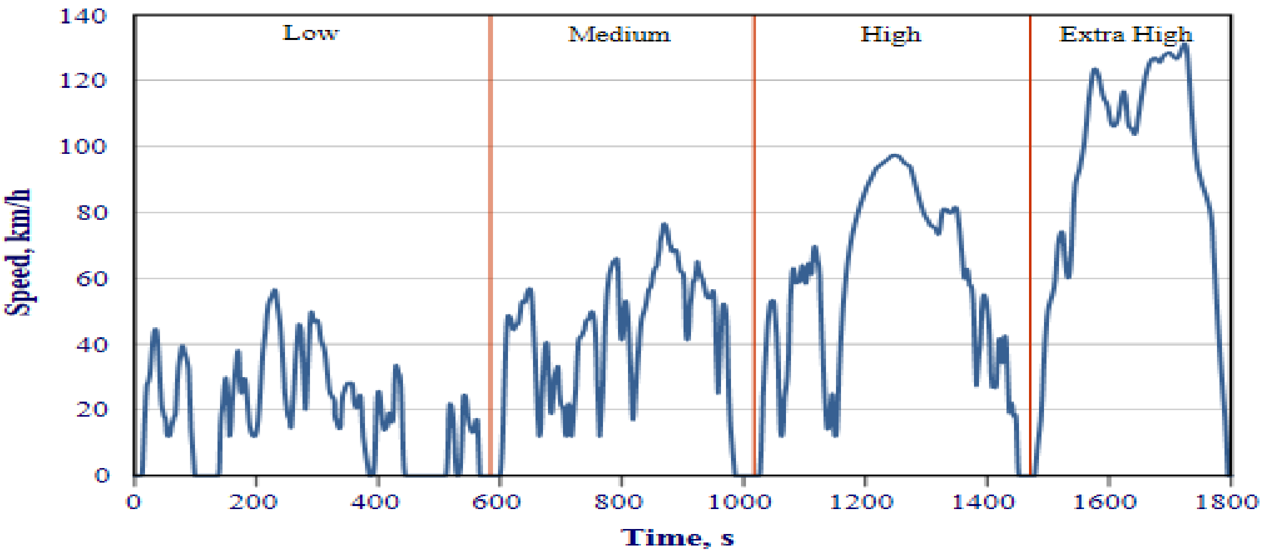
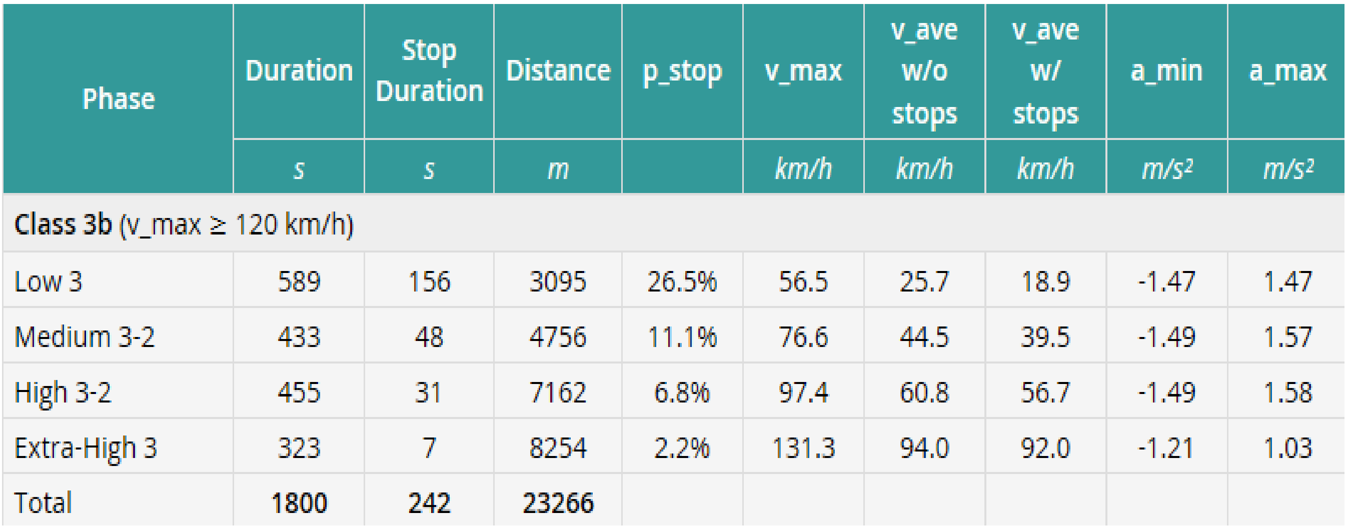


*Figure 7 Representation of WLTC driving cycle [11]*

*Table 2 WLTC driving cycle phase by phase classification [11]*



| Phase | Duration | Stop Duration | Distance | p_stop | v_max | v_ave w/o stops | v_ave w/ stops | a_min | a_max |
|---|---|---|---|---|---|---|---|---|---|
| | *s* | *s* | *m* | | *km/h* | *km/h* | *km/h* | *m/s²* | *m/s²* |
| **Class 3b** (v_max ≥ 120 km/h) | | | | | | | | | |
| Low 3 | 589 | 156 | 3095 | 26.5% | 56.5 | 25.7 | 18.9 | -1.47 | 1.47 |
| Medium 3-2 | 433 | 48 | 4756 | 11.1% | 76.6 | 44.5 | 39.5 | -1.49 | 1.57 |
| High 3-2 | 455 | 31 | 7162 | 6.8% | 97.4 | 60.8 | 56.7 | -1.49 | 1.58 |
| Extra-High 3 | 323 | 7 | 8254 | 2.2% | 131.3 | 94.0 | 92.0 | -1.21 | 1.03 |
| Total | **1800** | **242** | **23266** | | | | | | |

A shift to WLTC for certification of new vehicles would lead to improved emission limits in the real world, although by reducing the importance of cold start emissions, a shift to the WLTC may also reduce the stringency of gasoline emissions limits [9]. The Table 2 and Table 3 illustrates the clear picture of the improvement in WLTC cycle.

*Table 3 Difference between NEDC and WLTC test cycle*

| **Parameters** | **Unit** | **NEDC** | **WLTC** |
|---|---|---|---|
| Duration of cycle | (sec) | 1180 | 1800 |
| Length of cycle | (km) | 11.03 | 23.27 |
| Average speed | (km/h) | 33.6 | 46.5 |
| Maximum speed | (km/h) | 120 | 131.3 |
| Neutral share | (%) | 23.7 | 12.6 |
| Constant drive share | (%) | 40.3 | 3.7 |
| Acceleration share | (%) | 20.9 | 43.8 |
| Deceleration share | (%) | 15.1 | 39.9 |

Pollutant emissions of road vehicles depend on many parameters including vehicle weight, engine capacity, fuel type, exhaust after treatment technology, driving pattern, environmental conditions, road gradient and the level of maintenance of the vehicle.

Real Driving Emissions (RDE), a requirement that adds a road test to laboratory-based certification of vehicle engines, with the goal of further reducing the gap between certification and real-world emissions. This may go even further toward improving real-world compliance with emission standards.

The tests are likely to be carried out using PEMS in real-world drives, although random drive cycles on a chassis dynamometer are a likely alternative for the measurement of particle number (PN) emissions. A large share of diesel cars will not meet the Euro 6 standards during the initial application period for real-drive testing, so in October 2015 the committee approved a second package of measures setting a “conformity factor” that defines agreed that a conformity factor of 2.1 will apply to all new vehicle types beginning in September 2017, and extending to all vehicle types beginning in September 2019. The committee also agreed to lower the conformity factor to 1.5 beginning in January 2020 for all new vehicle types, extending to all vehicle types by January 2021. **[9]**

## 3.4. Outcome of the Emission Standards

The increasing stringency of emissions standards for cars has gradually is a challenge for vehicle manufacturers. They develop more sophisticated engine control systems and calibration strategies, and to introduce highly efficient after treatment technologies both in gasoline and diesel vehicles.

From the outset, the Euro 1 emission standard had the effect and the intention of requiring spark ignition cars to be fitted with three-way catalytic converters.

A fundamental prerequisite for the efficient operation of exhaust after treatment devices for both light- and heavy-duty vehicles is having fuel with a very low sulphur content. The sulphur content of gasoline and diesel fuels in Europe has therefore been regulated to meet very stringent fuel-quality standards.

For light-duty gasoline vehicles, the standards for Euro 6 are largely unchanged from Euro 5, with the exception of a new particle number standard for gasoline direct injection (GDI) vehicles. Gasoline direct injection engines produce higher particle emissions than the older port fuel injection gasoline engines, hence the introduction of a PN limit to prevent an increase in particle emissions from the gasoline fleet. This new limit may require the use of particulate filters on GDI engines, in addition to improved fuel-injection techniques. **[9]**

For diesel vehicles manufacturers will utilize new after treatment technologies to reduce NOX emissions

- Exhaust gas recirculation (EGR)
- Lean NOX traps (LNT) or
- Selective catalytic reduction (SCR)

Technologies already adopted to meet CO, HC, and PM limits, including diesel oxidation catalysts (DOC) and diesel particulate filters (DPF).To improve the fuel economy of cars sold on the European market, targets were reinforced at the end of 2013, and the European Parliament and the Council of the European Union reached an agreement regarding two regulatory proposals for mandatory 2020 $CO_2$ emission targets. Passenger car standards are set at 95 g/km of CO2, phasing in for 95% of vehicles in 2020 with 100% compliance in 2021. Light-commercial vehicle standards are 147 g/km of CO2 for 2020. The 95 g/km target implies a fuel consumption of around 4.1 l/100 km of petrol or 3.6 l/100 km of diesel. **[10]**

# Chapter 4. THREE WAY CATALYST DESCRIPTION

## 4.1. History of TWC

The catalytic converter was invented by Eugene Houdry, a French mechanical engineer who lived in the United States. In 1950, when the results of early studies of smog in Los Angeles were published, Houdry became concerned about the role of automobile exhaust in air pollution and founded a special company, Oxy-Catalyst, to develop catalytic converters for gasoline engines - In 1952, Eugene Houdry filed and was eventually awarded a patent for the initial catalytic converter (US2742437) **[13]**. The catalytic converter was later on further developed by John J. Mooney and Carl D. Keith at the Engelhard Corporation creating the first production catalytic converter in 1973. In the start, it was only simple oxidizing converters aiming to convert CO and HC. With help of net oxidizing inlet feed and sufficient high temperature. Beginning in 1979, a mandated reduction in NOx required the development and use of a three way catalyst for CO, HC and NOx abatement.

## 4.2. Need of TWC

Poor air quality has been shown to have seriously adverse effects on public health. The World Health Organization estimated that 650,000 people died prematurely from urban air pollution in developing countries in 2000. The European Environmental Agency (2007) has claimed that about 9% of the EU-27 population live within 200 m of a road carrying more than 3 million vehicles per year, and 25% within 500 m resulting in 4 million life-years are lost each year due to pollution. Pollutants are still emitted into the air during hydrocarbon fuel burning in an engine despite legal controls and regulations **[14].**

Even improving combustion strategies the engine out emissions are not enough reduced, thus automobile manufactures introduced exhaust after treatment systems. To always improve air quality, a lot of investment is made in the research and development of catalytic converter and it is one of the most effective tools to fight against the overwhelming pollutant contents in our environment. To maximize catalytic convertor efficiency, high focus is done on combustion control and on board diagnostics.

# 4.3. TWC – Construction

## 4.3.1. Catalytic Converters – Basic Terms

Catalytic converter is a stainless steel container mounted somewhere along the exhaust pipe of the engine Many vehicles have a close-coupled catalytic converter which is located near the engine’s exhaust manifold. The exhaust gases are led through the exhaust train of the catalytic converters at a high speed and high temperature. The structure of the substrate and the surface enlarging washcoat ensures that a large reactive surface of the catalyst is available to convert the exhaust gases into less toxic ones [15]. Geometrical surface area of the catalyst plays a major role in determining the catalyst efficiency. The catalytic converter is composed of a substrate, washcoat and a mix of precious metals placed inside a steel shell as shown in Fig.8. Thus it is composed of three major parts,

1. Catalyst support/ substrate
2. Washcoat
3. PGM materials

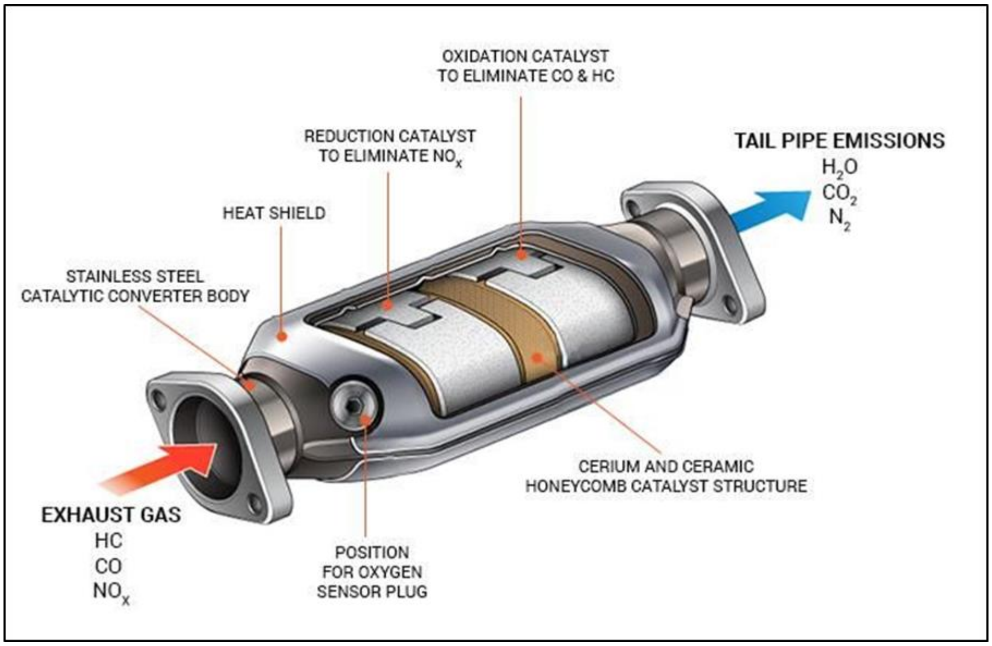


*Figure 8 Representation of the three way catalyst*

## 1. Catalyst support/ substrate

The catalytic substrate core is made up of metallic foil or ceramic monolith. Metal foil monoliths are usually thin when compared to the ceramic substrate. The substrate usually consists of a honeycomb ceramic block through which the exhaust gas flows. In most converters, the ceramic is a single honeycomb structure with many flow passages.

The passages comprise of many shapes, including square, triangular, hexagonal and sinusoidal. The ceramic monolith which offers various advantages. Among these advantages are smaller volumes, lower mass and greater ease of packaging. **[16]**

Metal foil monoliths are made up of ferritic iron- chromium- aluminium alloys of high thermal durability and can be used in the case where high heat resistance is required **[15].** These foils are corrugated to have a continuous honeycomb structure with parallel square channels of elliptical cross section and welded together to provide good durability and resistance to thermal shock.

## 2. Washcoat (WC)

Washcoat is typically made of oxides of Al, Ce, Zr, etc. High wash coat surface enables a high conversion despite low residence times. i.e. The catalytic materials are suspended in the washcoat before they are applied to the core. This component produces a high porosity coat and a suitable surface for PGM with increase in surface area available to react with the engine exhaust **[17].**

## 3. Catalyst material

The catalyst material used in the automobile converters is a mixture of precious metals including platinum, palladium and rhodium. The PGMs have the capacity to convert toxic pollutants into less toxic ones due to their catalytic activity. Platinum is the most active catalyst, but unwanted additional reactions and high cost of PGMs limits their wide application. Platinum and palladium helps in the oxidation of CO, and hydrocarbons and reduce its toxicity by means of catalytic activity, whereas rhodium is used as a reduction catalyst and it reduces the NOx gas [18]. The PGM particles are uniformly dispersed in the external layer of alumina washcoat [19].

## 4.3.2. Three-way Catalyst (TWC) activity on PGM

The combination of the oxidation and reduction converters leads to the formation of TWC's and are known for their simultaneous redox reactions based on the catalytic activity of PGMs in the converter. Because of these cyclic variations in exhaust gas composition about a set point close to stoichiometric, it is desirable that the catalyst be able to reduce NO when a slight excess of oxygen is present (on the lean side) and remove CO and HC when there is a slight deficiency of oxygen (on the rich side). Hence, TWC's have two honey comb units each containing different composition of PGM catalysts. The reactions occurring in the three-way converter are summarized as follows.

Oxidation of carbon-monoxide to carbon-dioxide:

$$2CO + O2\ (g) \rightarrow 2CO2\ (g) \qquad (4.4)$$

Oxidation of Hydrocarbons to yield carbon-dioxide and water as products

$$HC + O2 \rightarrow CO2 + H2O \qquad (4.5)$$

Reduction of carbon-monoxide and nitrogen-oxide to form carbon-dioxide and nitrogen product

$$2CO + 2NO \rightarrow 2CO2 + N2 \qquad (4.6)$$

Water gas shift reaction

$$CO + H2O \rightarrow CO2 + H2 \qquad (4.7)$$

Steam reforming reaction

$$HC + H2O \rightarrow CO2 + H2 \qquad (4.8)$$

The necessary condition for an optimal conversion is that the engine runs with stoichiometric mixture and is shown in Figure 9. When the feed is net oxidizing the conversion of CO and HC is promoted, while the conversion of NO is very low, whereas the opposite happens when the feed becomes rich.

$$A/F = \frac{\dot{m}_a}{\dot{m}_f} \tag{4.9}$$

$$\lambda = \frac{A/F}{A/F_{stoichiometry}} \tag{4.10}$$

For the stoichiometric mixture holds that λ = 1, for a lean mixture λ > 1 and for a rich mixture λ < 1. Stoichiometric A/F is around 14.6, depending on the applied fuel.

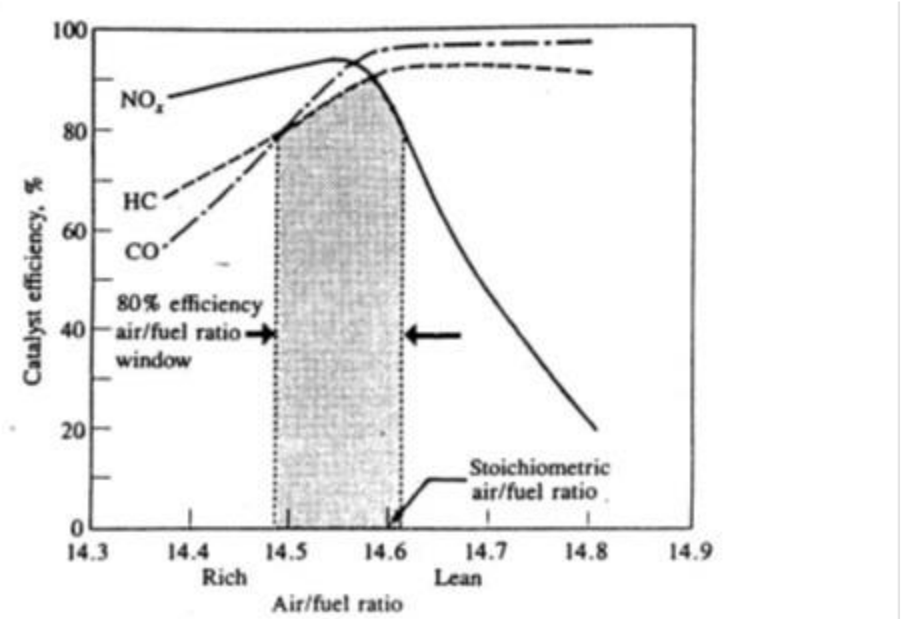


*Figure 9 Conversion efficiency of TWC window*

## 4.3.3. OSC activity of the TWC

In the field of three-way catalysis (TWC), oxygen storage is a crucial point. As a result, lots of studies have been devoted to oxygen storage capacity (OSC) measurements. Although large quantity of chemical processes are occurring in the TWC, the dynamic behaviour of the converter is dominated by the oxygen storage capability of the cerium washcoat. This catalyst property is exploited as an oxygen buffer, which compensates for air–fuel ratio deviations from stoichiometry ($\lambda$ = 1) to maximize pollutant conversion efficiency.

The preparation of catalysts that are able to store and release oxygen very efficiently has been the subject of extensive catalyst research [22].

When the engine is running lean ($\lambda$ > 1), HC and CO are completely oxidized because of the excess oxygen in the exhaust gas. Oxygen is stored in the cerium until the oxygen storage capacity of the converter is saturated. However, once the oxygen storage capacity is saturated, $NOx$ reduction ceases. On the other hand, when the engine is running rich ($\lambda$ < 1), there is inadequate exhaust gas oxygen to oxidize all the CO and HC. Therefore, the oxygen previously stored in the cerium reacts to compensate for such a deficiency.

Temperature not only influences the TWC steady state conversion efficiency, but it also affects its oxygen storage dynamics. In fact, catalyst temperature affects the reaction rates occurring in the TWC and consequently the oxygen storage capacity.

## 4.4. Advancements in TWC

The performance of TWCs today is astonishing compared with that of catalysts introduced three and a half decades ago. Activity is high (99% efficiency in hot condition) and thermal stability is so good catalyst is now placed on the exhaust manifold where it heats up rapidly when the engine is started, and in this hot location less PGM is needed than in a cooler downstream location **[20].** Information about catalyst temperature can be useful to design a closed-loop control strategy focused on TWC warm up to minimize pollutant emissions and the fuel consumption during a cold start.

Development of more accurate fuel injectors, that were able to accurately control the amount of the injected fuel, was the system able to obtain the necessary high performance.

Thus performance is very high with use of less costly materials than previously was the case. A drawback of three-way catalytic converters at the time of their introduction was that a very accurate engine air/fuel control (i.e. fuel metering) was necessary to maintain the exhaust mixture at stoichiometry. With the development of exhaust gas oxygen (EGO) sensors, popularly called λ sensors, it was possible to develop a control system that keeps the engine air/fuel ratio at stoichiometry.

Performance is routinely monitored by on-board diagnostics (OBD) via two oxygen sensors (one upstream and one downstream of the TWC) via computer algorithms that periodically change the exhaust oxygen content and thereby determine the level of active oxygen Storage capacity of the catalyst [21].

Major developments in converter's durability, decreased susceptibility to poisoning, thermal stability, etc. Light-off temperature (the temperature where the conversion reaches 50%) of converter is constantly decreasing, together with improvements in catalyst's oxygen storage capability. As a result a new generation of catalysts has now been developed with substantially improved thermal stability.

Together with the advances in the converter performance, the last decade has also witnessed great improvements in the engine electronic control system. The engine exhaust after treatment system is thus becoming one of the most advanced collaborations between chemistry and electronics.

## 4.5. Conclusion on TWC efficiency

Between 1990 and 2005, emissions of acidifying substances decreased by 36%, ozone precursors by 45% and particulates by 33% **[23]** largely due to advances in exhaust gas after-treatment devices, including advanced three-way catalytic converters and particulate filters and improved fuel quality.

With a warmed up catalyst and at steady state and stoichiometric conditions conversions of more than 99% are reached for the three pollutants CO, NO and HC but this conversion decreases eventually on its usage due to ageing of the catalyst.

# Chapter 5. AGEING OF THE THREE WAY CATALYST

## 5.1. What is ageing?

The quality of catalytic converters can perform well for hundreds of thousands of kilometres. The ability of TWC's conversion efficiency of the exhaust gas emissions degrades over time due to converter ageing. Catalysts may lose their activity as a result of a number of unwanted chemical and physical changes. This reduction in conversion efficiency must be accounted for to ensure full useful life compliance.

## 5.2. Effects of Ageing

The ageing of converters has a lot of adverse effect on depleting the quality of the environment. The ageing of catalyst delay the warm up period of the catalyst which has a decrease in the emission conversion efficiency. It also decreases the OSC efficiency. This leads to the final effect of increase in the tail pipe emission. The emission of the pollutants upsurge in volume causing global warming, acid rain and harming the environment and human health.

Toyota actively focus TWC development based on aged TWC in order to ensure that tailpipe emission of any Toyota vehicle will be as low as possible along its entire life.

## 5.3. Types of Ageing

The converters ageing are majorly affected by three important mechanisms: Thermal, chemical and mechanical. TWC ageing is a function of time and magnitude of exposure to elevated temperatures and chemical poisoning and inhibition.

## 5.4. Thermal Ageing

The biggest share of the emissions are formed during cold start, and during the low temperature operation of the catalyst. So, the pre-converter or starter catalyst is installed near the engine to uphold the efficient reduction of pollutant. Exhaust gas out of gasoline engine has very high temperature (more than 500degC) moreover, oxidation reactions leads to an exotherm of about 100 to 200degC. Therefor catalytic materials have to work at very high temperature.

Thermal deactivation occurs at high temperatures and is strongly aggravated by exhaust gas which have a negative effect on the activity of the catalyst.

Temperature at which the solid phase becomes mobile depends on several factors such as texture, size and morphology. One cause of this is the sintering which is dependent on several other factors, such as precious metal loading and wash coat composition. The high temperature ageing may result in deep encapsulation of sintered precious metal particles which decrease of the number of active sites, and therefore a decrease in catalytic efficiency [24]. The sintering, or agglomeration, can be described through two mechanisms. The difference between sintering and melting is that sintering occurs below the material melting temperature. Sintering is generally accelerated.

Among the active PGM's, rhodium the most sensitive metal towards sintering at high temperatures under the exhaust gas conditions. This leads to poor activity, especially in the reduction of NOx [40].The use of a bimetallic catalyst, such as Pd-Rh or Pt-Rh, gives a better catalytic activity at high temperatures. The rich and lean operation conditions also affect the sintering of active metals. Rare earth metal oxides are used to stabilize the precious metals against sintering [25]

Another effect of the high temperature is the phase-transition of the support washcoat material. One of the most common support materials is $\gamma$-Al2O3, which changes phase according to the following order [24]:

$$\gamma\text{–}\ (500\text{–}850{\circ}\mathrm{C}) \rightarrow \delta\text{–}\ (850\text{–}1050{\circ}\mathrm{C}) \rightarrow \theta\text{–}\ (1050\text{–}1150{\circ}\mathrm{C}) \rightarrow \alpha\text{–}\ (> 1150{\circ}\mathrm{C}) \qquad (5.1)$$

For instance, highly porous $\gamma$-alumina is much more sensitive to sintering than non-porous $\alpha$-alumina.

## 5.5. Chemical Ageing

Chemical ageing generally occurs due to the unwanted, harmful components of fuels and lubricants or other impurities, are accumulated on the catalyst's surface and slowly poison the catalyst. For gasoline engine three-way applications, the main chemical aging effect is caused by oil additives. Common poisons, such as S(sulphur), Pb(Lead), Ca(Calcium), Mg(Manganese), Zn(Zinc) and P(Phosphorous)[26].Poisons contaminate the washcoat and precious metals and reduce the catalytically active surface by blocking active sites through chemisorption. Phosphorus and sulphur are present in aged catalytic converters in higher concentrations than other poisons, which increases the probability of their interaction with catalyst components such as aluminium oxide (Al2O3) and cerium oxide (CeO2).

Driving conditions also affect the catalyst's chemical deactivation. Especially in cold countries, due to the cold weather and urban driving which keeps the catalyst temperature low for a the whole trip. This easily accelerates the catalyst's chemical ageing, because the unburned soot and particles which adsorb on the active material. The stability against thermal and chemical deactivation can be improved by a proper choice of the catalyst material and active material can be placed in separate washcoat layers improves the durability [27].

## 5.5.1.Poisoning

Usually, a distinction is made between poisons and inhibitors. Poisons are substances whose interaction with active sites is strong and often irreversible whereas the adsorption of inhibitors on the catalyst surface is weak and reversible. This means that if the catalyst is subjected to certain conditions, the poison will detach, resulting in a regained activity. This can be used effectively for automotive catalysts in the case of sulphur. **[24, 28]**

Catalyst poisons can also be classified as selective or non-selective, depending on whether the poisoning is universal or takes place only at certain sites or crystal faces or affects only certain adsorbed species. In such a case, the poison is selective in one reaction, but non-selective in another. Even the low levels of impurities are enough to cover the active sites and decrease the performance of a catalytic converter.

However, the poisoned three-way catalyst can hardly be regenerated and, therefore, the best method to reduce poisoning is to decrease the amount of poisons in the fuel and lubrication oils to more acceptable levels**[29,28]**.Earlier the catalytic converters were known to loose already their effectiveness after 10 refills with leaded gasoline. In present, role of lead as a catalyst poison is far less significant than in the past because due to the use of unleaded or low Pb concentrations in gasoline.

### Sulphur

Sulphur poisoning is a complex phenomenon that can involve significant changes in the structural, morphological, and electronic properties of a catalyst. In the case of TWCs, fast poisoning by sulphur can be to some extent reversible and the poisoned catalyst can be regenerated.

During the combustion processes in the engine, fuel sulphur oxidizes to $SO_2$ and $SO_3$. These compounds adsorb on the precious metal sites on the catalyst's surface at low temperatures (below 300°C) and react with alumina to form aluminium sulphates that reduce the active surface of washcoat and deactivate the catalyst.

Sulphur clearly affects the efficiency and oxygen storage capacity (OSC) of the catalyst. Sulphur poisoning can lead to the formation of new inactive compounds on the catalyst's surface and also to the morphological changes in the catalyst [30]

## Phosphates:

Zinc dialkyldithiophosphate (ZDDP) is an antiwear, antioxidant, and corrosion inhibiting additive that is used in engine lubricating oils, hydraulic oils, and other lubricants. ZDDP is produced by first letting an alkyl or aryl alcohol react with phosphorous pentasulphide (P2S5), and then neutralizing the resultant acid with zinc oxide. [31]

The phosphorus composition depends on many factors, such as the chemical composition of oil and oil additives, the age of the oil used, and conditions in the motor [32].Phosphorus contamination can be observed on the surface of catalytic converters as several different compounds

Secondly, phosphate compounds can also be formed directly with washcoat components. In that case, the resulting compounds are, for instance, aluminium and cerium phosphates

## Poisoning by other compounds

Automotive catalysts can also be deactivated by compounds commonly used in the structure of an engine. The, iron (Fe) is a poison for platinum group metals [33] .Iron detected on the catalytic surface is often assumed to originate from the corrosion of metal components in the engine. Other similar impurities may be copper (Cu), nickel (Ni), and chromium (Cr). Chromium and nickel are added to the construction materials in order to improve the thermal stability of engines.

### 5.5.2. Effects on PGM

Precious metals have different types of resistance against poisoning. Palladium is more sensitive than platinum and rhodium to chemical deactivation, in particular to poisoning by sulphur and lead [34, 35].

Pd is easily oxidized at room temperature to PdO and it reduces to metallic Pd in the temperature range of 500°– 1200°C. At normal operation temperatures of the catalytic converter, Rh is in the form of $Rh_2O_3$, if the oxidation of Rh is kinetically favoured. The oxygen content in the exhaust gas strongly affects the formation of Rh oxides; the higher the amount of oxygen, the higher the transition temperature is.

## 5.6. Mechanical Ageing

A catalytic converter can be damaged by a strong mechanical impact. In such a case, the monolith is crushed or crumbled and as a result, the back pressure of the exhaust gas is increased. If the damage is not noticed in time, local overheating can cause thermal deactivation and finally melting of the honeycomb can occur. Metallic catalysts can endure mechanical deactivation better than ceramic ones.

There is a chance that the ceramic material cracks because of large temperature oscillation or thermal shocks, resulting in loss of active substances or decreased active area [36].

Two types of factors can cause high catalyst temperatures.

1. The engine operating conditions.
2. The misfiring, non-combusted fuel-air mixtures undergo catalytic combustion, which can produce very strong exothermic reactions within the catalyst.

At about 1200°C, the metallic foil starts to soften and probably shrink. If the catalyst temperature exceeds 1400°C, the foil will melt, after which it is destroyed. At high temperatures, catalysts may suffer from the loss of active phase through volatilization. Metal loss through direct volatilization is generally an insignificant route of the catalyst deactivation.

## 5.7. Further Causes of ageing

The wash coat on an automotive catalyst has a very high effective area per volume of material. This type of structure makes them sensitive to fouling. Fouling covers all phenomena where the surface is covered with a deposit, e.g. with combustion residues such as soot Substances such as Mg, Zn and P as well as metal flakes and particles from the engine and exhaust pipe can clog pores and block active sites, reducing the efficiency of the catalyst. Coke formation is the most widely known form of fouling. Coke might be so large that carbon deposits block the internal pores in the catalyst. In many cases, hydrocarbons and aromatic materials are primarily responsible for coke formation. Pore blocking is probably one of the most important mechanisms. Pore blocking is often connected to coke formation, and when the amount of coke is high on the catalyst's surface, it may be possible for the coke itself to block off the pore structure **[24, 37]** .This effect can be reduced by decreasing the amount of problematic substances in the engine oils and by using more resilient materials in the engine and exhaust pipe.

The thermal ageing and chemical ageing impacts are considered in this thesis.

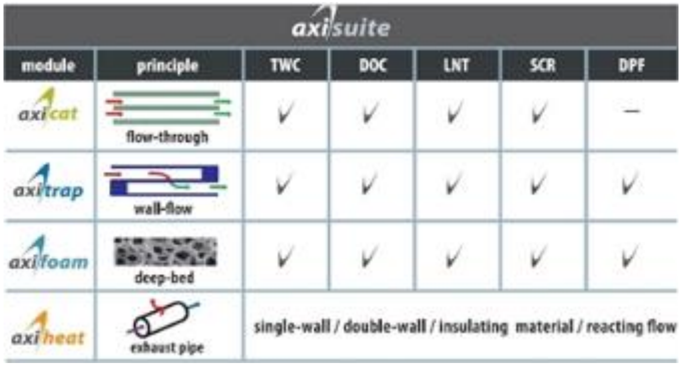
# Chapter 6. CALIBRATION AND DEVELOPMENT OF AGEING TWC MODELS

## 6.1. Introduction to Axisuite

The technical work of this thesis is performed with the Axisuite software to build , calibrate and develop TWC models.

Axisuite is a software package for the simulation of exhaust systems which was developed by Exothermia SA. It consists of different modules:

- Axitrap
- Axicat
- Axifoam
- Axiheat



axisuite

| module | principle | TWC | DOC | LNT | SCR | DPF |
|---|---|---|---|---|---|---|
| axicat | flow-through | ✓ | ✓ | ✓ | ✓ | – |
| axitrap | wall-flow | ✓ | ✓ | ✓ | ✓ | ✓ |
| axifoam | deep-bed | ✓ | ✓ | ✓ | ✓ | ✓ |
| axiheat | exhaust pipe | single-wall / double-wall / insulating material / reacting flow | | | | |

*Figure 10. Application of Axicat modules*

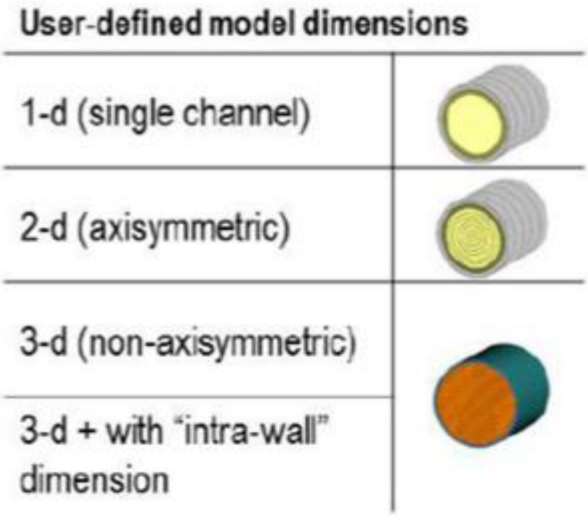
The above modules can be used independently, to simulate a single device, or in combination, to simulate covering the complete range of exhaust line components as shown in Figure 10.The high level of model detail provides accurate predictive simulations of the physical and chemical processes in exhaust after treatment systems with fast computation time, user friendly interface and integration with third party software.

In this thesis, TWC modeling and calibration have been performed with the support of Axicat module.

## Application of Axicat

Axicat is a solver module of the Axisuite software, aimed at the simulation of flow-through, honeycomb catalytic converters and modeling of three way catalysts is supported by this module.

The TWC monolith geometry can be discretized in 1D, 2D or 3D meshes as shown in Figure 11. In the 1D case all the channels are assumed to behave identically. In the 2D case the frontal area of the converter is divided in sectors shaped as rings. To obtain more accurate prediction of results 2D mesh calculations are used in this thesis.



| User-defined model dimensions |
|---|
| 1-d (single channel) |
| 2-d (axisymmetric) |
| 3-d (non-axisymmetric) |
| 3-d + with "intra-wall" dimension |

*Figure 11. Channel geometry*

As shown in Figure 12 Axicat model contains chemical, thermal and flow calculation. My work was focussing on calibration of chemical model. Axicat calculates reaction using apparent reaction rate expressions, based on Langmuir Hinshelwood rate expressions. The reaction scheme is flexible and the user may easily change the rate parameters.

The system configuration is shown in Figure 13 and it gives an overview on the configuration options available in the Axicat module. These configuration tabs have many sub- options by which the model is used to calibrate. By assigning all the required parameters in the system configuration the model can be proceeded further for the simulation process and the post processing are done from the results obtained.

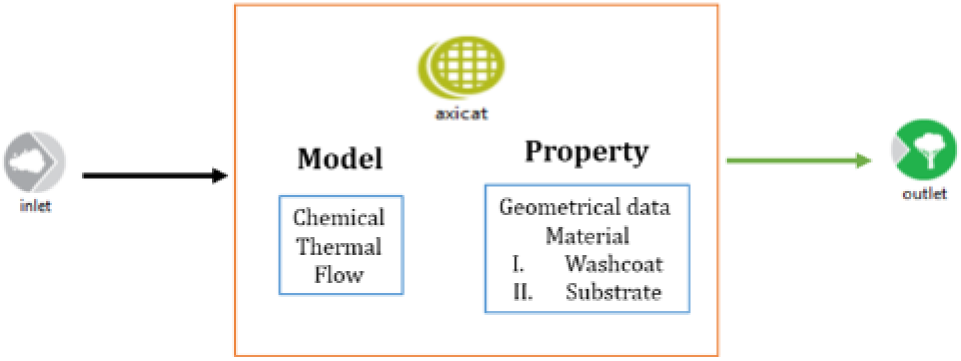


*Figure 12 Axisuite TWC System Layout*

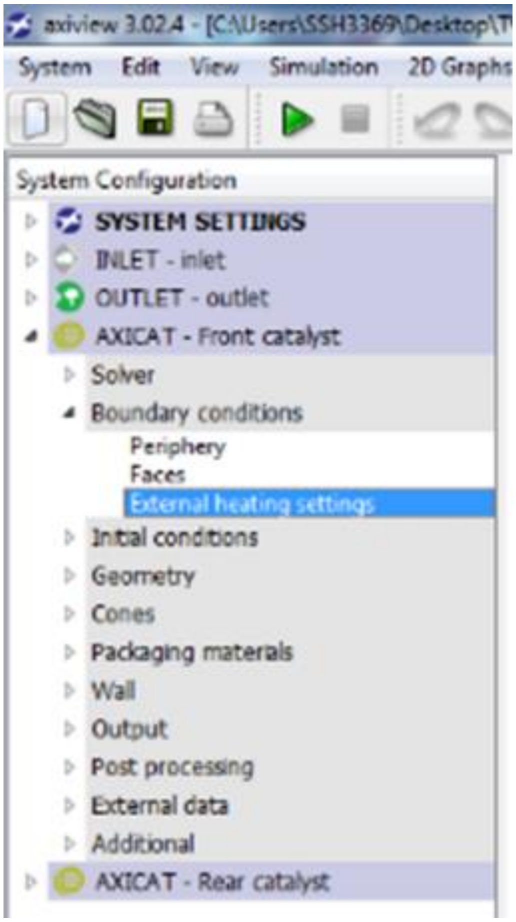


*Figure 13 System configuration*

## 6.2. TME Three Way Catalyst description

TME uses two three way catalyst with one in the front position (starter) and another one in the rear position (underfloor).The both catalyst are different in properties like geometrical data, washcoat and substrate properties according to their function. Sectors are made up of materials which are impermeable to flow, such as cement, skin, insulation and canning sectors. For the purpose of this report, I will present front (starter) catalyst investigation.

The scheme of front catalyst in Figure 14 illustrates the presence of 3 zones in the catalyst.

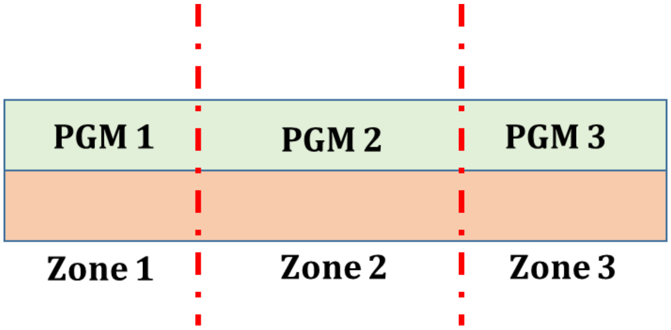


*Figure 14. Schematic representation of front TWC*

For each zone we have 6 reaction groups and in total 24 individual reactions as mentioned in the Table 4.

*Table 4 Representation of the available reaction groups and number of reactions in the TWC*

| Group No. | Reaction Group | No. of reactions | Example |
|---|---|---|---|
| I | PGM O2 | 3 | $CO+½O_2 \rightarrow CO_2$ |
| II | PGM NO | 6 | $CO + 2NO \rightarrow CO_2 + N_2O$ |
| III | NH3 & N2O | 2 | $N_2O + H_2 \rightarrow N_2 + H_2O$ |
| IV | Fast cerium | 6 | $fCe_2O_3 + ½ O_2 \rightarrow 2fCeO_2$ |
| V | Cerium | 6 | $Ce_2O_3 + ½O_2 \rightarrow 2CeO_2$ |
| VI | Water storage | 1 | $H_2O$ < -- > $H_2O$ (l) |

## 6.3. TWC modeling methodology

Based models were developed by TME following the bellow methodology. In my project, I worked with validated model.

The TWC modeling consists of two main phases

1. Calibration of the models
2. Validation of the models

The base TWC models are calibrated by identifying the governing phenomena of TWC functionality, based on synthetic gas bench (SGB) experiments. A synthetic gas bench is used to examine and analyze catalyst samples independently from the engine. The operation principle of SGB is the generation of synthetic gas mixtures. The mass flow controllers are used switch between lean and rich conditions and to dose exhaust gas composition to the catalyst sample. These are used for lambda scan, light off and oxygen storage capacity tests. Some of the gaseous components used in SGB are NO, CO2, N2, air, CO, HC.

For more detailed model, each zone has been studied and calibrated separately. Therefore, the experiments were performed for reaction model usually for each zone. Combination of these individual zone models formulated the 100% length of the catalyst which was intermediately validated against SGB measurements with the full length sample.

Final model validations were done in engine bench tests by simulating driving cycles. To calibrate and to have an in depth study of the chemical kinetics behaviour, the tests were performed by placing both the front and rear catalyst in the underfloor position. The front catalyst and rear catalyst are validated separately and by acquiring accurate results they are used to validate the full exhaust line.

The prime work of this thesis deals with the validation of the model using the full length (front) catalyst in engine test bench data.

## 6.4. Ageing law development methodology

TME had 4 existing TWC models consisting of one fresh TWC model and three aged models. The aged TWC's were defined based on different ageing time at high temperature. The aged models were developed and calibrated by considering the same reactions scheme as the fresh TWC, only reaction rates were calibrated for each aging.

As there are many individual reactions in each reaction groups it is difficult to calibrate each reaction which is long way process. Moreover, the provided aged models doesn't have any correlation as the models were separately calibrated based on the experimental results.

The objective of my internship was to find an ageing law providing emission level with similar accuracy as TME existing aged models. From now, this report describes calibration and validation of this law.

The ageing level is caused by thermal and chemical ageing factors which may strongly affect the TWC reactivity and the catalyst diffusivity as well. So, the elements that should be taken in account are:

I. The reactivity of the PGM reactions is expected to be affected and therefore all PGM reactions needed to be re-calibrated.

II. The ageing process leads to decrease of the surface area of the CeO2 phase as well as to the decreased contact between PGMs and CeO2, due to sintering effect. Therefore, the reactivity of ceria reactions is expected to be affected by thermal ageing process, due to the synergistic effect between PGM and ceria sites.

As discussed before the models have the same reactions and rate expression as the fresh TWC and the kinetics are formulated from Arrhenius equation.

$$\boldsymbol{R = Ae^{-E_a/RT}} \tag{6.1}$$

Where,

A – Pre-exponential factor (inhibitors, cross-interaction factor, active site dispersion)

$E_a$ – activation energy (depends on the nature of PGM, reactions, environment, substrate)

As, ageing process is expected to reduce the number of active sites, which are physically related to the pre exponential factors. Therefore no modifications are expected for the activation energy values. With the TME base model for each time 72 ageing parameters are needed to be calibrated because as discussed in the Table 4 each zone has 24 reactions so totally 3 zones will have 72 reactions.

Hence the developed ageing law is calibrated for the pre-exponential factor A for all the reactions.

An ageing parameter is defined as:

**Ageing Parameter (X) = A aged / A fresh** (6.2)

According to this equation, ageing parameter is 1 in Fresh condition and are decreasing with the ageing level increase. The idea of the development of the ageing model is shown in Figure 15.The goal of this project is to develop ageing model which predicts any ageing level from the fresh model calibration as explained in equation (6.3) (6.4) (6.5).In equation (6.3) and (6.4) it is evident that only the ageing parameter "X" are varied instead the pre-exponential factor "A" remains the same as the fresh model.

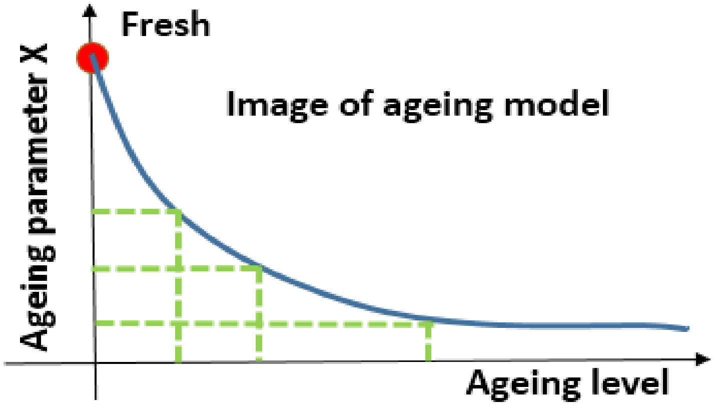


*Figure 15 Image of ageing model*

$$Fresh\ model = X_{fresh} * A_{fresh} e^{-Ea/_{RT}} \tag{6.3}$$

$$Aged\ model\ 1 = X_{aged\ 1} * A_{fresh} e^{-Ea/_{RT}} \tag{6.4}$$

$$Aged\ model\ n = X_{aged\ n} * A_{fresh} e^{-Ea/_{RT}} \tag{6.5}$$

The development methodology of the ageing law is explained with the front catalyst configuration.

### 6.4.1. Zone model

Toyota TWC has 3 zones and each zone has 6 group of reactions. The impact of the ageing process is different for each zone due to different PGM, different loading and different location in TWC.

Firstly, I developed an ageing law based on zone and reaction groups. This model is referred as “Zone Model” in the following.

The methodology I used to develop for each zone is:

- The ageing parameters of each reaction were attained by using equation 6.2.
- For each reaction group and each ageing level, I average the ageing parameters of reactions included in the group. Figure 16 shows as example Zone model development using PGM NO reaction group for zone 1.

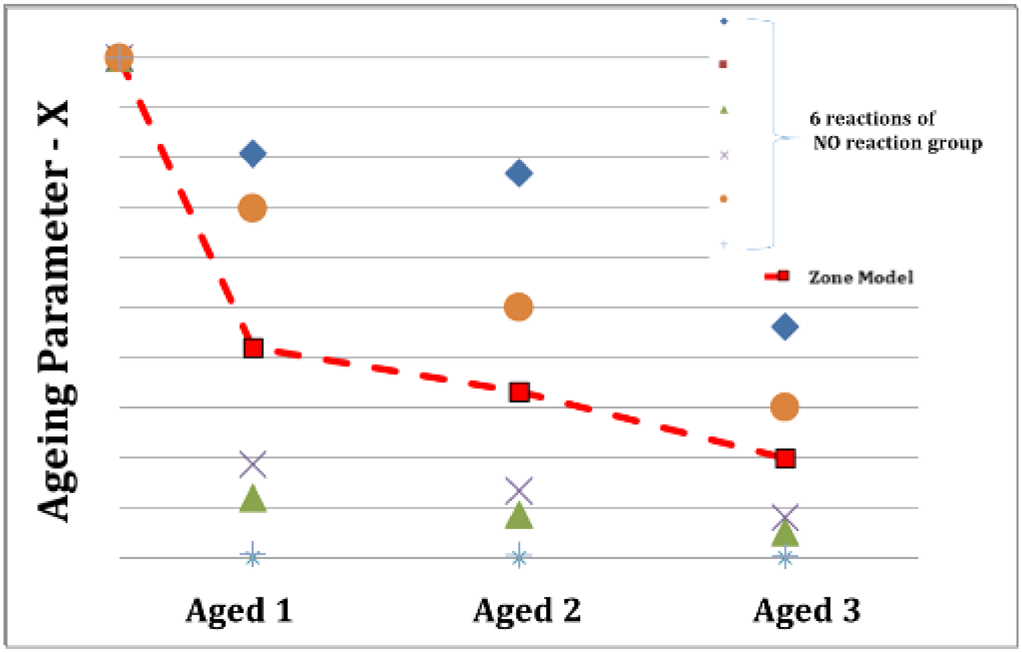


*Figure 16 Example of ageing law of PGM NO reaction group (zone 1)*

So, finally with the Zone model, the number of ageing parameters needed to be calibrate has been drastically reduced to 18 parameters from 72 parameters (TME based model).

The extraction of 18 parameters are clearly pictured in the Table 5.

*Table 5 Number of ageing parameters in Zone model*

| ZONE | ZONE 1 | | | | | | ZONE 2 | | | | | | ZONE 3 | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Reaction group | I | II | III | IV | V | VI | I | II | III | IV | V | VI | I | II | III | IV | V | VI |
| No. of ageing law | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| No.of ageing laws/ zone | 6 | | | | | | 6 | | | | | | 6 | | | | | |
| Total | 18 | | | | | | | | | | | | | | | | | |

## 6.4.2. Full length model

The ageing law for reaction groups of each separate zones are grouped together as shown in the Figure 17. It's apparent that the ageing level of each zones tend to follow the same trend (with low difference). Full length model is obtained by averaging the ageing level for the zones. The dotted line in the Figure 17 gives an example of Full Length model parameter for PGM NO reaction group for full length.

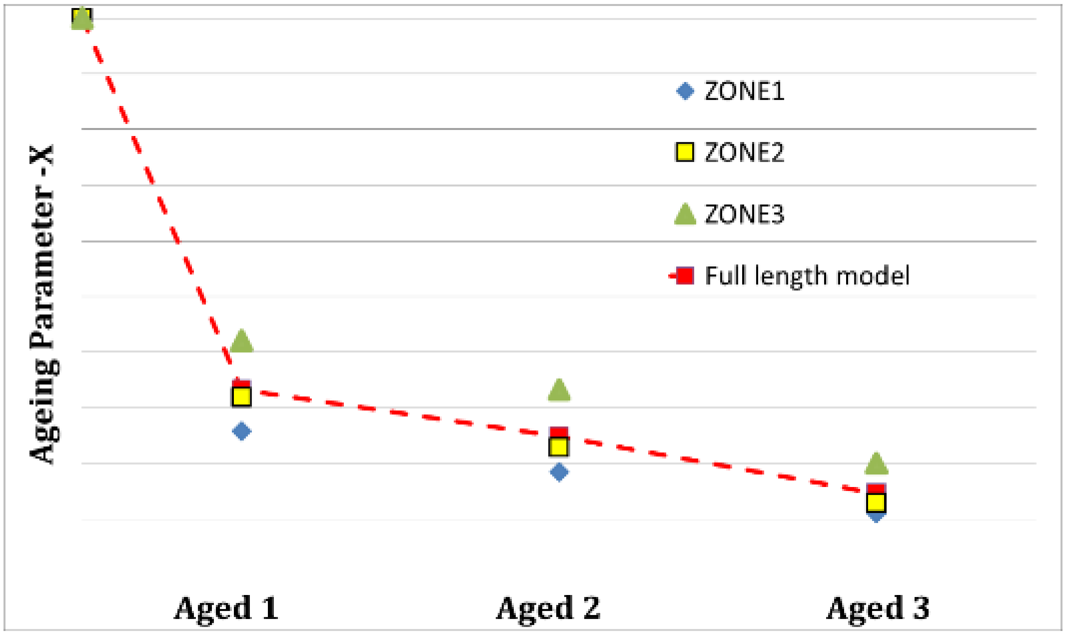


*Figure 17 Ageing law of PGM NO reaction group (full length)*

*Table 6 Number of ageing parameters in Zone model*

| Full length catalyst | | | | | | |
|---|---|---|---|---|---|---|
| Reaction group | I<br>Zone(1,2,3) | II<br>Zone(1,2,3) | III<br>Zone(1,2,3) | IV<br>Zone(1,2,3) | V<br>Zone(1,2,3) | VI<br>Zone(1,2,3) |
| No. of ageing law | 1 | 1 | 1 | 1 | 1 | 1 |
| Total | 6 | | | | | |

To summarize with the Full length model, the ageing parameter needed to calibrate has been reduced to 6 parameters from 72 parameters of TME base model. The extraction of ageing parameters for the full length catalyst is pictured in the Table 6.

The representation of developed ageing model's ageing parameter numbers compared to the TME based model has been pictured in the Figure 18

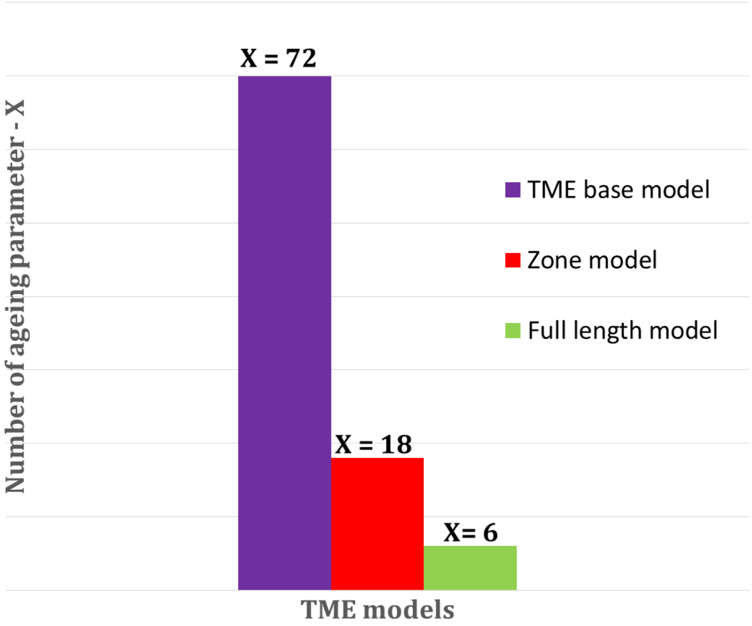


*Figure 18 Number of ageing parameters of TME models*

### 6.4.3. Next step

The next step is to check the accuracy of the two developed models compared to the TME base model and the experimental results. The target accuracy has been fixed for each part of the driving cycle and the behaviour of the developed models are examined.

The deviations with the experimental results can be caused due to the error in the existing model. So, to check the behaviour of developed ageing model a target accuracy with the TME based models prediction is defined, on top of the accuracy target compared to experimental values.

The emissions are separated into two parts namely cold start and hot part. Cold start is where the emissions are emitted before the particular warm-up phase of the catalyst which is around 400 deg C. The hot part is the region were emissions are taken in account after the warmed up phase of the catalyst. Both in addition yields the final total cumulative emissions.

The target accuracies are defined below:

*Table 7 Target accuracy table*

| Emission Part | Experimental results | TME base model |
|---|---|---|
| Cold start | +/- 20% | +/- 10 % |
| Hot part | +/- 20% | +/- 10% |
| Total Cumulative | +/- 10% | +/- 5% |

In the bar graphs for pollutant comparison the target accuracies are plotted as error bars in the experimental and TME base model results.

A summary of WLTC results using developed ageing laws is presented below in section 6.5.

## 6.5. Front catalyst WLTC results (aged 1, aged 2, and aged 3)

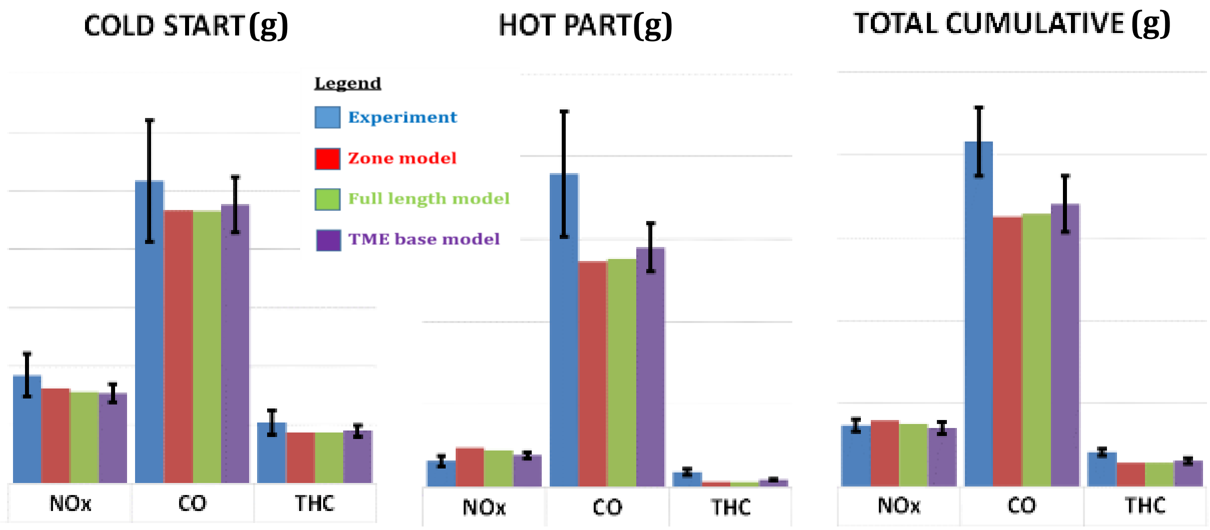


*Figure 20 Bar graphs for Pollutant comparison (Aged 1)*

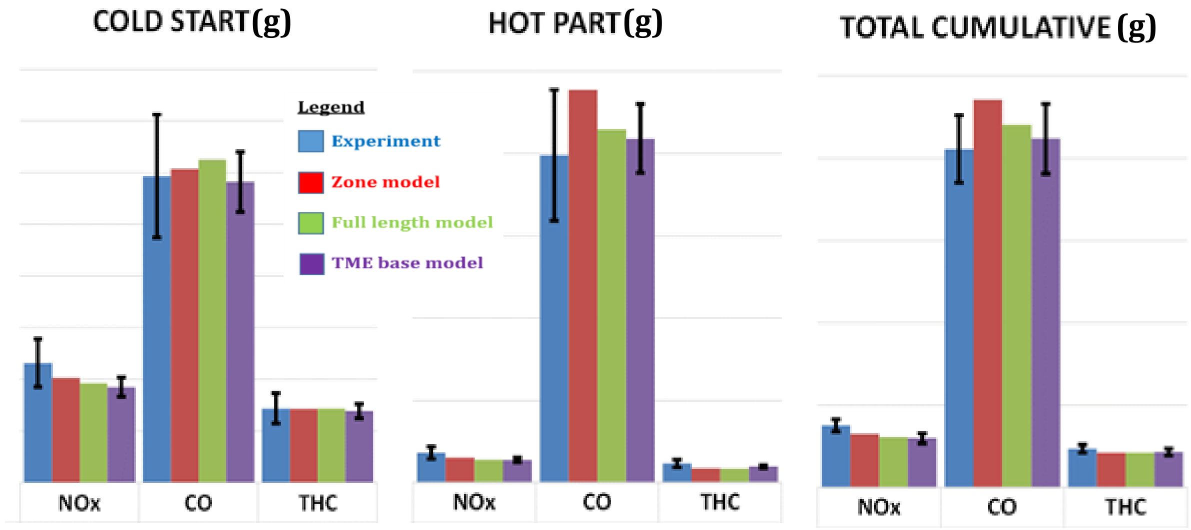


*Figure 19 Bar graphs for Pollutant comparison (Aged 2)*

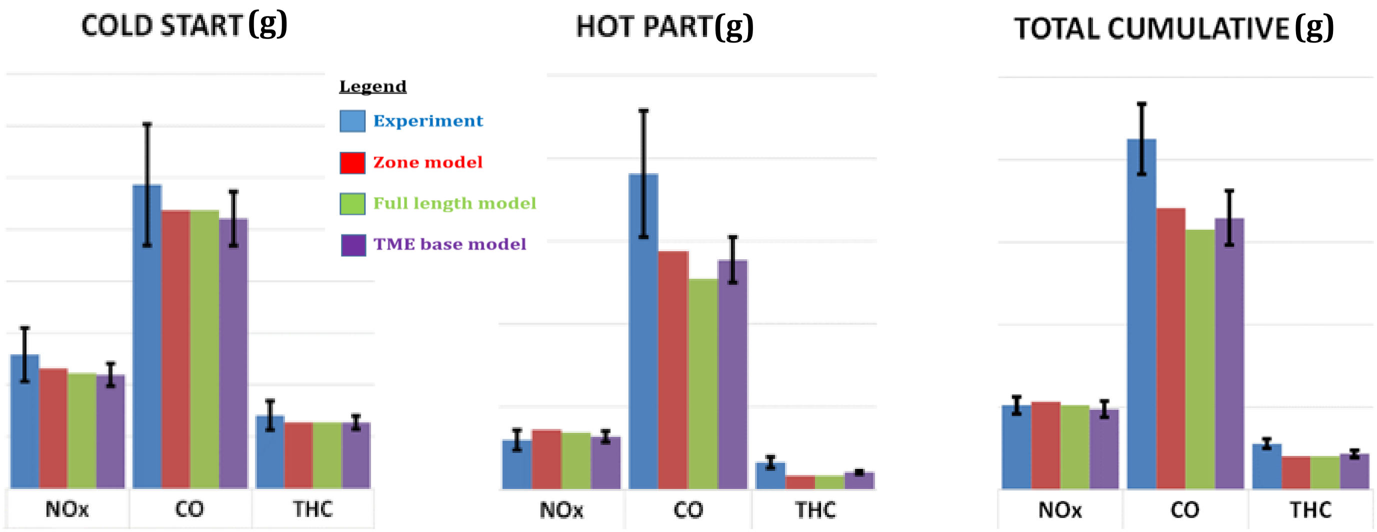


*Figure 21 Bar graphs for Pollutant comparison (Aged 3)*

The bar graphs for the pollutant comparisons are shown in the Figure 20 Figure 19 Figure 21 according to their aged level and classified according to the cold start, hot part and total cumulative. The bar corresponds to emissions in gram (g).The vertical axis have been removed for the confidentiality reasons. The blue colour bar corresponds to the experimental results, red colour for the zone model emission results, green colour for the full length model emission results, and violet colour for the TME base model results. The error bars corresponds to the accuracy targets.

More detailed graphs (WLTC driving cycle) are presented in Annex.

## Observation from section 6.5.

This pollutant comparison graphs provides a clear insight about the emission level estimation in each part of the driving cycle. So, the discussions can be separated into cold start, hot part and total cumulative emissions.

## Cold start:

- The cold start is the region is the warm up phase until it reaches 100 % efficiency. From the Figure 20 Figure 19 Figure 21 it is clearly seen that the 2 developed ageing models (zone model & full length model) seems to have good emission results within the experimental and TME base model's target accuracy levels for the aged 1 , aged 2 , aged 3 models.

- This signifies that the ageing law developed has a very good chemical model behaviour.

## Hot part:

- The hot part shows inaccuracies for all the pollutants (NOx, CO, THC) in all the 3 aged models as shown in Figure 20 Figure 19 Figure 21 compared to the experimental results except CO in aged 2 and NOx in aged 3.

- In hot part the 2 developed aged models predicts the emission levels as similar as TME base model results for all the 3 pollutants(NOx, CO, THC). The inaccuracy in the developed aged models occur due to the error from the TME base models.

- No deep investigations are done because the objective is to develop the ageing law on chemical kinetics with similar accuracy as the provided TME base models.
- As, the developed 2 models (zone model & full length model) are within the target accuracy of the TME base model results it can be considered to have the accurate chemical kinetics.

## Total cumulative:

- The total cumulative is always considered to represent the final emission results and they are represented in the Figure 20 Figure 19 Figure 21.
- The NOx emissions are within the target accuracy of the experimental results and TME base model for aged 1 and aged 3 condition. There is a very slight underestimation visible in the aged 2 condition due to the small inaccuracy in the cold start and hot part but are within target accuracy of the TME base model.

- The CO emissions are under estimated for aged 1 and aged 3 condition compared to the experimental results and overestimated for the aged 2 condition but all the aged models are within the target accuracy of the TME base model. This under estimation and over estimation of pollutants are developed from the error of the model itself both in cold start and hot part correspondingly.

- The THC emissions are slightly under estimated in total cumulative due to the inaccuracy in the hot part of the cycle but found to be within the target accuracy of the TME base model for all the 3 aged models.

From these observations, the developed zone model and full length model predict emission levels with similar accuracy as the TME base models. So, the ageing law seems to provide the similar results by reducing the number of ageing parameters to be calibrated. Now, a correlation is also built for the ageing level of the TWC.

# Chapter 7. VALIDATION ON NEW GENERATION TWC

## 7.1. Validation process

- This chapter deals with the validation part of the developed ageing law in the new generation TWC.
- TME provided fresh model of new generation TWC which was built with a different technology compared to the TME base model.
- The experimental tests were carried out for the aged 1 level of the new generation TWC and the results were collected from the engine test bench.
- Therefore due to the availability of aged 1 TWC results, the validation was planned to be done for the aged 1 level of the model.
- From the developed 2 models, zone model has been preferred for the validation purpose because of its detailed development methodology based on zone and PGM type.
- The next step was to adapt the ageing law developed for the new generation TWC.
- The target accuracy has been set for the results compared with experimental results as discussed in the Table 7.
- The WLTC results for the front catalyst is presented in the next section. To add with, the investigation and observation on the results are also presented in this chapter.

## 7.2. New generation front catalyst WLTC results – Aged 1

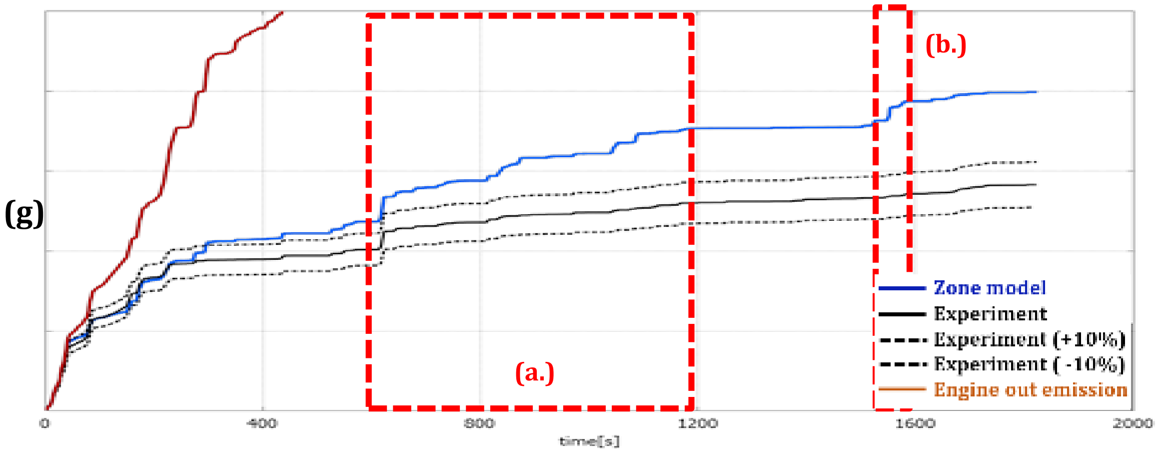


*Figure 22 Cumulative NOx emissions*

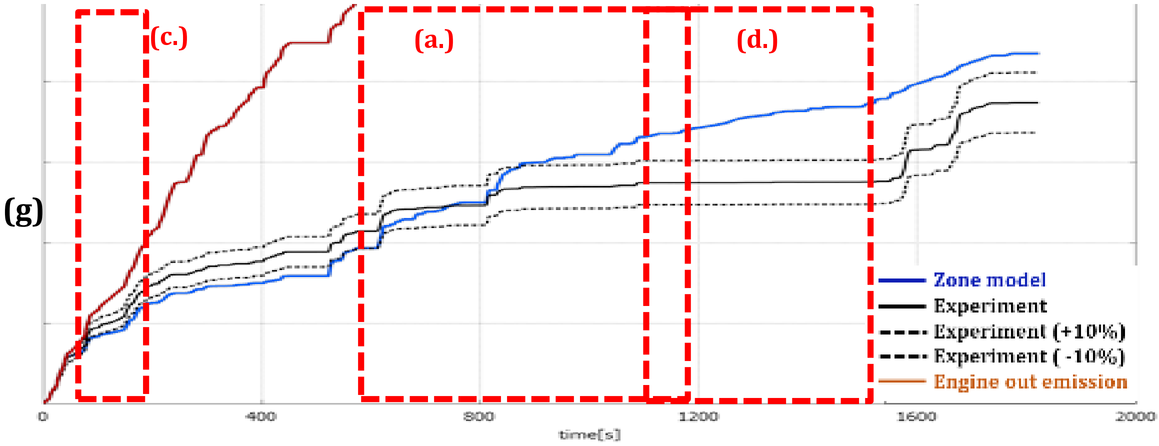


*Figure 23 Cumulative CO emissions*

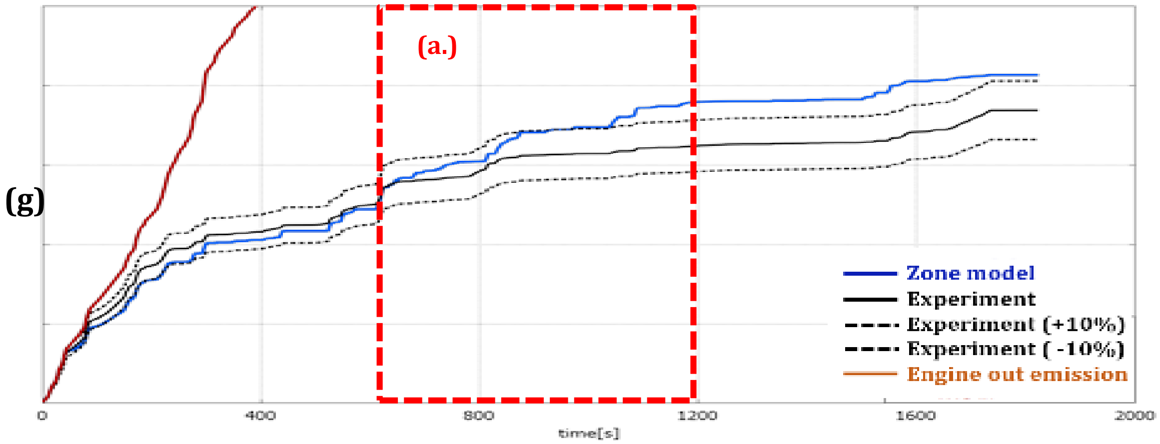


*Figure 24 Cumulative THC emissions*

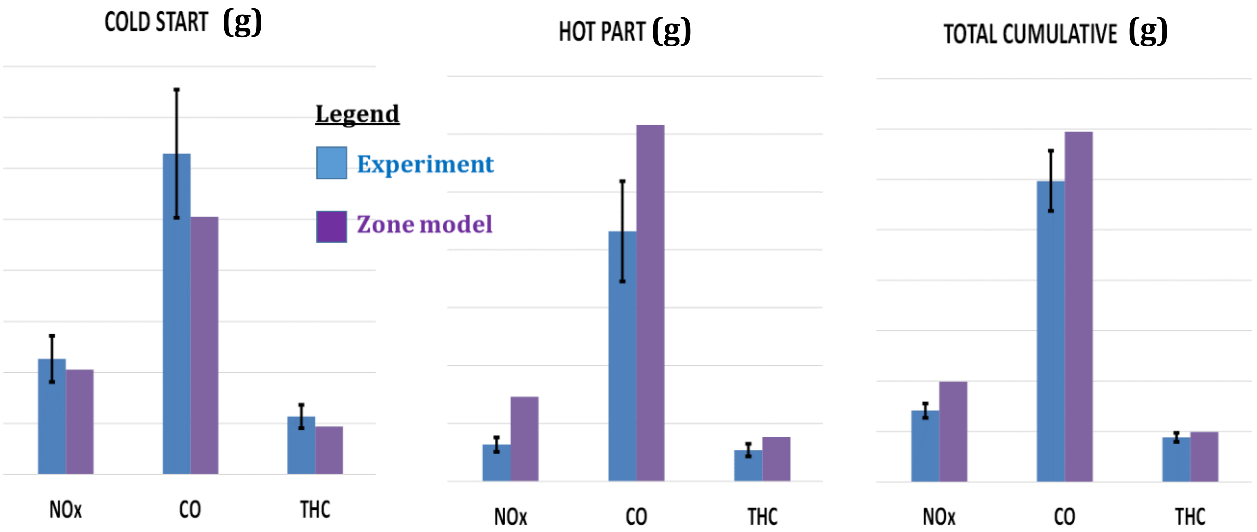


*Figure 25 Bar graphs for Pollutant comparison (Aged 1)*

The cumulative emission results for the WLTC driving cycle are shown in the Figure 22 Figure 23 Figure 24 . The graph compare the result of the zone model and the experimental results. The blue line represents the zone model cumulative emission results and the black line represents the experimental results. The dotted black lines covers the target accuracy of (+/- 10%) for the total cumulative results as mentioned already in the Table 7. The brown line shows the engine out emissions but due to the zoomed view of the graph only a smaller part is visible.

The figure 25 illustrates the bar graphs for pollutants classified according to the cold start, hot part and total cumulative. The bars correspond to emissions in gram. The error bar is placed in the experimental result bar (blue colour) as mentioned in Table 7. The zone model results are presented in violet colour.

## Observation from section 7.2.

The discussions are separated into cold start, hot part and total cumulative emissions for better understanding of the emission results as shown in the Figure 25.

### Cold start:

- From Figure 25 it's visible that the emissions in the cold start are to be within target accuracy for NOx and THC whereas CO seems to be slightly underestimated. The under estimated region is marked with red dotted lines in the Figure 23 and named as section (c).

### Hot part:

- From Figure 25 it's evident that the overestimation of the emission is spotted in the hot part of the driving cycle for all the three pollutants (NOx, CO, THC).
- One of the major part which affects this over estimation seems to lie within 600-1200 seconds of the driving cycle and they are marked as section (a) in the Figure 22 Figure 23 Figure 24.
- The sudden peaks were observed in the NOx emissions and a part of it is highlighted as section (b) in the Figure 22 which also influences the over estimation in the total cumulative emissions.
- In Figure 23 , section (d) is noted to have a continuous rise of CO compared with the experimental results which adds up the emission level in the total cumulative.

### Total cumulative:

- The inaccuracy in the hot part contributes for the over estimation in the total cumulative of all the three pollutants (NOx, CO, THC) as pictured in Figure 25.

All the highlighted sections shown in Figure 22 Figure 23 Figure 24 are investigated and observations are delivered below.

### 7.2.1.Reason for over estimation of the pollutants in region (a)

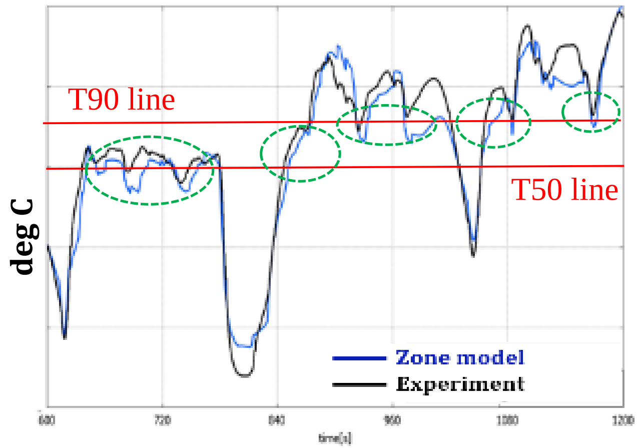


*Figure 26 Temperature Tgas centre (600-1200) s*

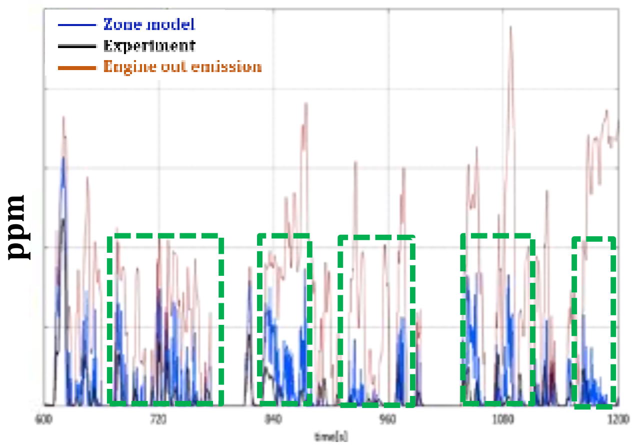


*Figure 27 Instantaneous NOx emissions (600 -1200) s*

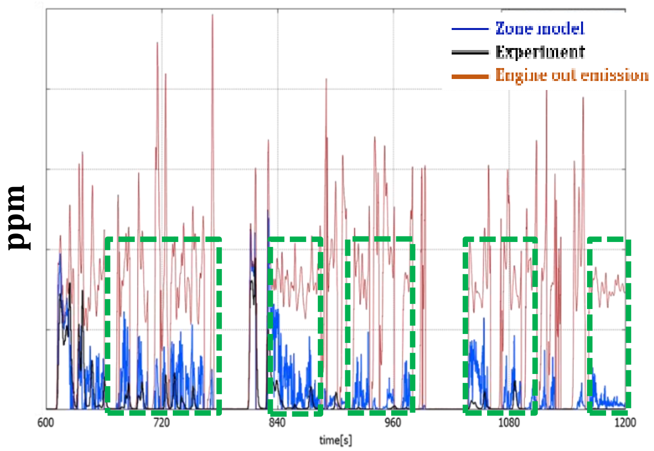


*Figure 28 Instantaneous CO emissions (600-1200) s*

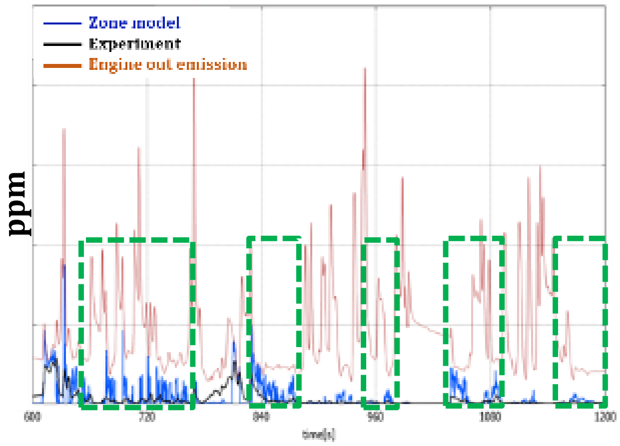


Figure 29 Instantaneous THC emissions (600-1200) s

## Observation from section 7.2.1.

- The instantaneous emissions for all the pollutants between 600 -1200 seconds are displayed in the *Figure 27* Figure 28 *Figure 29* to have a detailed view how the emissions are over predicted.

- To have a picture how the temperature affects the pollution conversion, the temperature prediction for 600 -1200 seconds are also shown in *Figure 26* and the T 50 & T 90 conversion efficiency line is also highlighted to compare the variations between the simulation and experimental results. The temperature affected parts are highlighted in the green box.

- T50 line corresponds to the 50% emission conversion efficiency of the catalyst and T90 line is for the 90 % emission conversion efficiency of the catalyst.

- It is undoubtedly visualized that how the instantaneous emissions are over predicted when the simulation temperature drops down below T50 and T90 line which reduces the conversion efficiency of the model.

- This misprediction is due to the thermal behavior of the model.

- The experimental temperature can be imposed in the model to check the behavior of the chemical kinetics. These results are discussed in the section 7.3.

## 7.2.2. Reason for higher peaks of NOx in region (b)

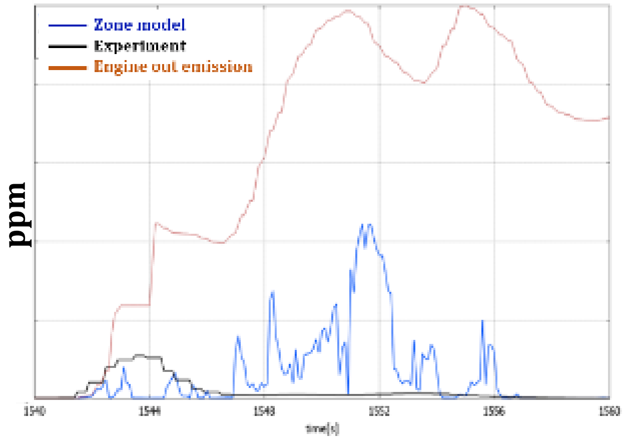


*Figure 30 Instantaneous NOx emissions (1540 -1560) s*

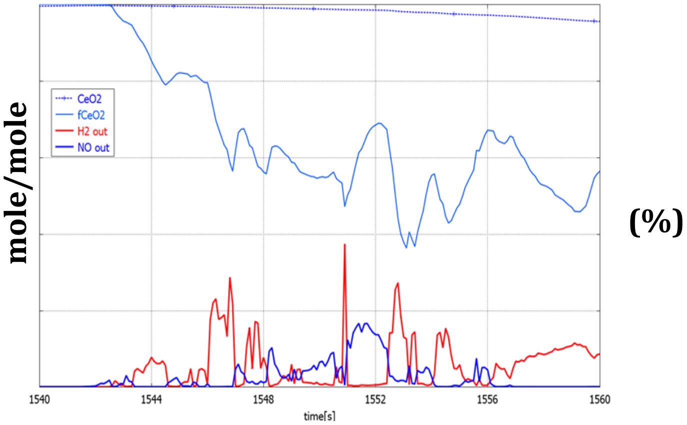


*Figure 31 OSC vs H2 out and NO out (1540 – 1560) s*

*Figure 32 Lambda (1540 -1560) s*

## Observation from section 7.2.2.

- The *Figure 30* shows the instantaneous NO emissions between 1540 -1560 seconds. It is readily seen that there is a sudden rise in the emission level compared to the experimental results.

- By careful examination, it's been noticed that the huge rise of NO occurs in the slightly lean lambda conditions as seen in the *Figure 32* where there is almost no $H_2$ which plays a major role in the reduction of NO as shown in Figure 31.

- However, this should be the same behaviour in the experimental tests, the inaccuracy in the model is due to the OSC behaviour which is not well calibrated because between the time (1548-1552) s it seen that the lambda in is same as the lambda out in Figure 32.

- The stored oxygen helps in water gas shift reaction to produce H2 which supports NO reduction. So, the oxygen is not stored enough in the fast ceria sites between the same as seen in Figure 31.

- So, it's clear that this OSC model miscalibration leads to the higher peaks of NOx in section (b).

### 7.2.3. Reason for under estimation of CO in region (c)

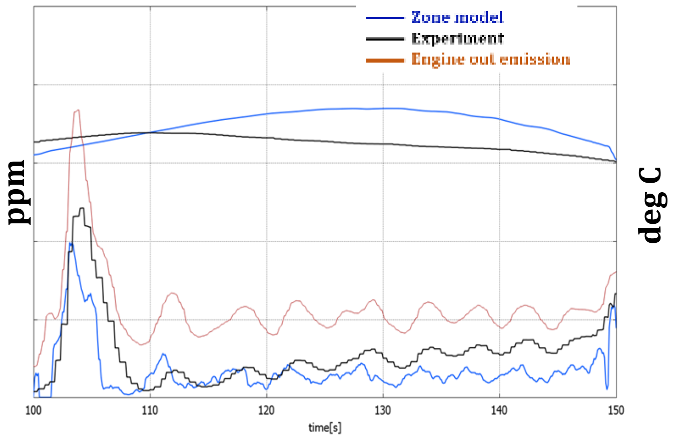


*Figure 33 Instantaneous CO emissions (100 – 150) s*

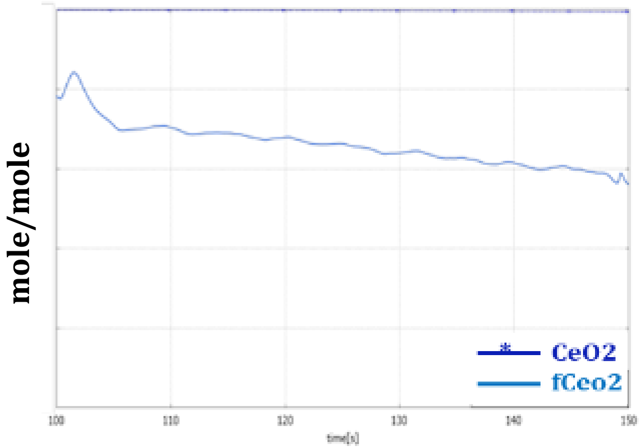


*Figure 34 OSC (100 -150) s*

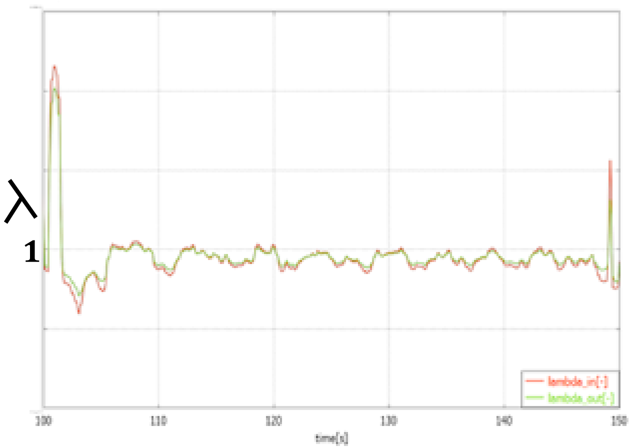


*Figure 35 Lambda (100 -150) s*

## Observation from section 7.2.3.

- As discussed earlier in Figure 25 , there is an under estimation of CO in the cold start region. So, to examine the inaccuracy the investigation has done in this section.

- The instantaneous CO emissions and the temperature profile between 100-150 seconds are shown in the Figure 33 and it is noticed that the simulation model converts the CO with higher efficiency compared to the experimental results.

- The oxygen storage capacity (OSC) is used to react with the CO during the rich lambda condition by providing the oxygen stored during the lean lambda condition because of the insufficient amount of oxygen present to convert the pollutants.

- There are fast ceria sites (fCeO2) and bulk ceria sites (CeO2) in OSC model and they are responsible for the storage and reaction of the oxygen with the pollutants. Fast ceria sites reacts firstly in the situation of insufficient oxygen.

- In the Figure 35 when the lambda is in slightly rich condition and the fast ceria sites helps to convert the CO but in the *Figure 34* it is visible that the storage amount of fast ceria sites are decreasing continuously and a very small difference is seen in the temperature profile.

- This is because of the CO consumption on the fast ceria sites seems to be over consumed than the expected amount. So, obviously the conversion of CO is higher than the experimental results.

- This inaccuracy is due to the miscalibration of OSC fresh model behaviour in the lower temperature as this region lies before the warm up phase.

### 7.2.4. Reason for over estimation of CO in region (d)

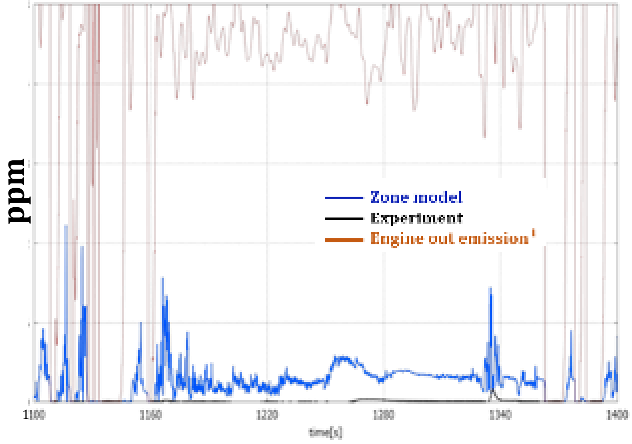


*Figure 36 Instantaneous CO emissions (1100-1400) s*

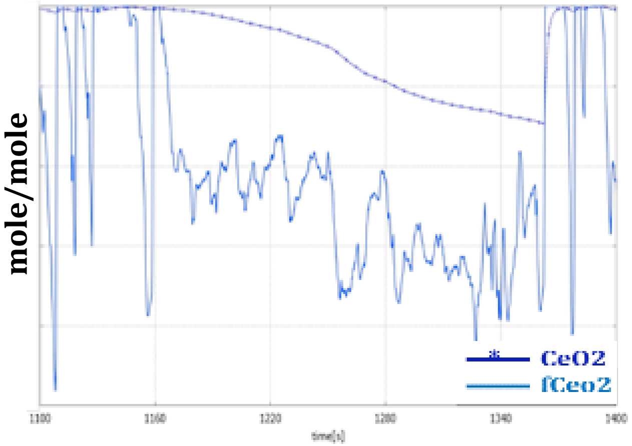


*Figure 37 OSC (1100 -1400) s*

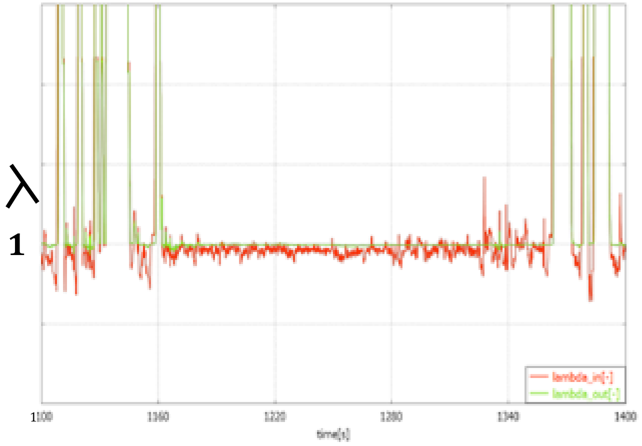


*Figure 38 Lambda (1100 -1400) s*

## Observation from section 7.2.4.

- The Figure 36 visualize clearly how the CO emissions are not converted the same as the experimental results.

- This CO over estimation takes place in the continuously rich lambda phase of the cycle as seen in the Figure 38.

- The continuous slightly rich lambda condition remains to hold for a long period of time and it is witnessed in the *Figure 37* that the stored bulk ceria sites start to reduce.

- Due to this partial reduction of bulk ceria sites the oxygen is not sufficient enough for the CO conversion which causes the CO slip during this region.

- From these observations it’s noticed that the OSC model is not well predicted. Thus it opens up the inaccuracy in the emission levels.

## 7.3. New generation front catalyst WLTC results (axial temperature imposed)

- In the previous section 7.2.1. it has been discussed that the deviations in the simulated temperature profile causes the over estimation of the emissions.
- So, to validate the chemical behaviour of the model the experimental temperature has been imposed in the zone model and the outcomes of this implementation is shown in the Figure 39 .
- When the axial temperature is imposed the internal and external heat transfer including the reaction enthalpies are ignored during the simulation time.
- The axial temperature imposed model is named as Zone model (A.T).
- From the Figure 39 the deviations between the zone model and zone model (A.T) temperatures are very apparent.
- The emission results are displayed in the Figure 40 Figure 41 Figure 42 for all the three pollutants and the behaviour of the chemical model is well seen with the axial temperature imposed models.
- The observations of the attained results are discussed below with the individual phase of the emission which is illustrated in the Figure 43.

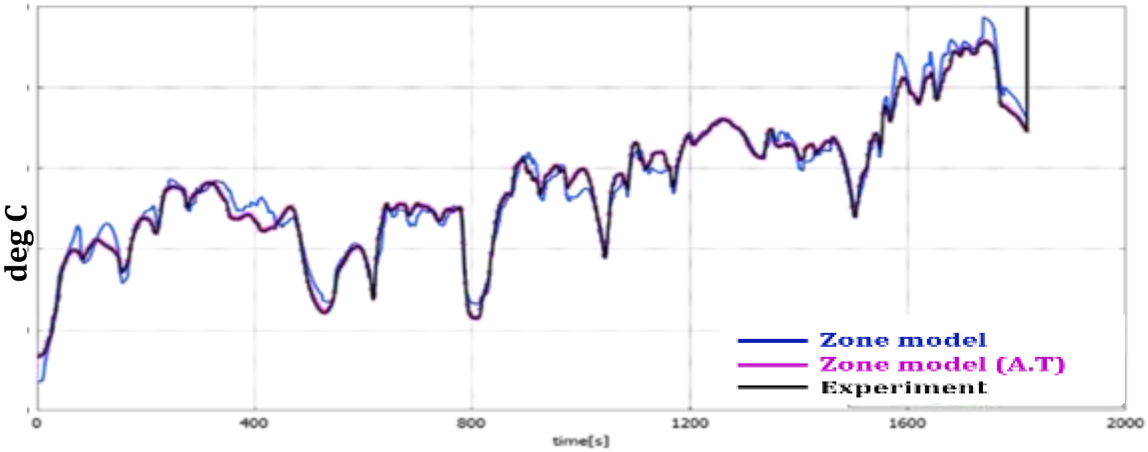


*Figure 39 Temperature Tgas centre*

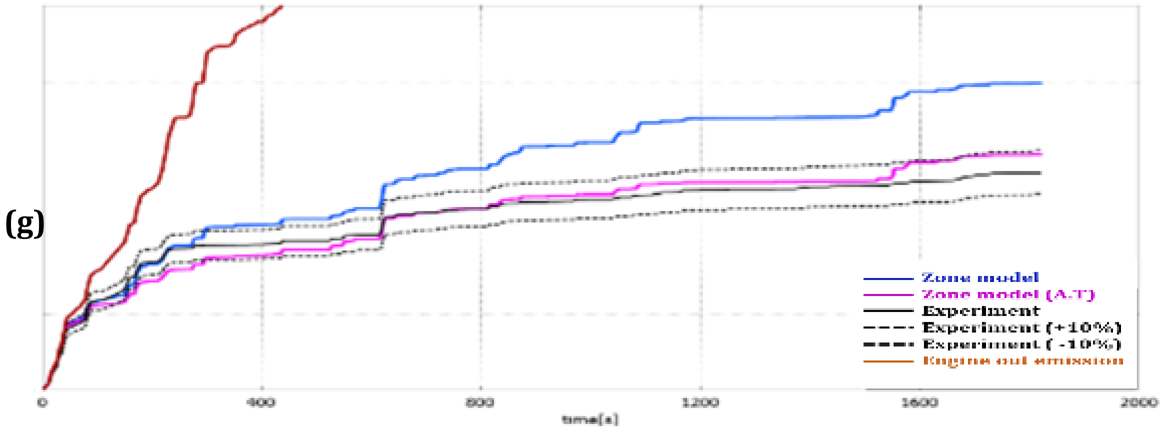


*Figure 40 Cumulative NOx emissions*

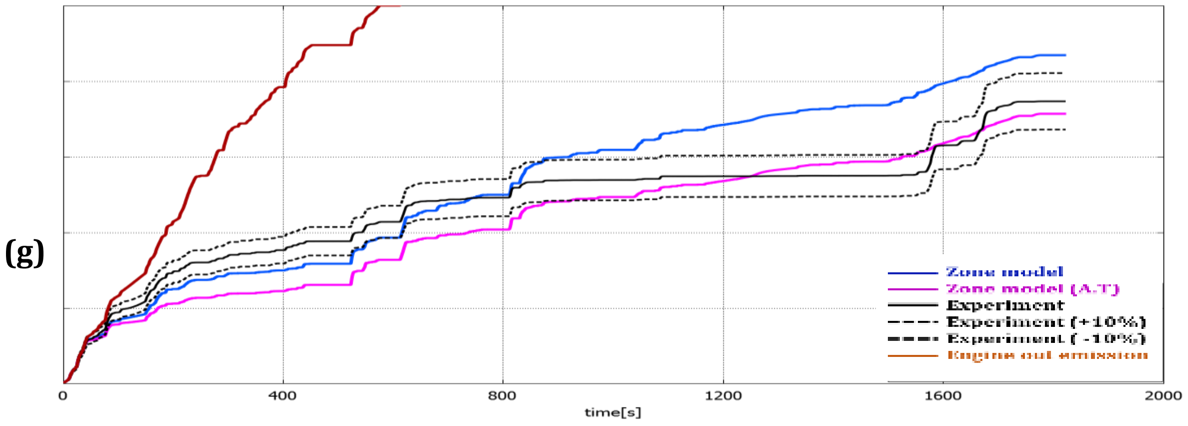


*Figure 41 Cumulative CO emissions*

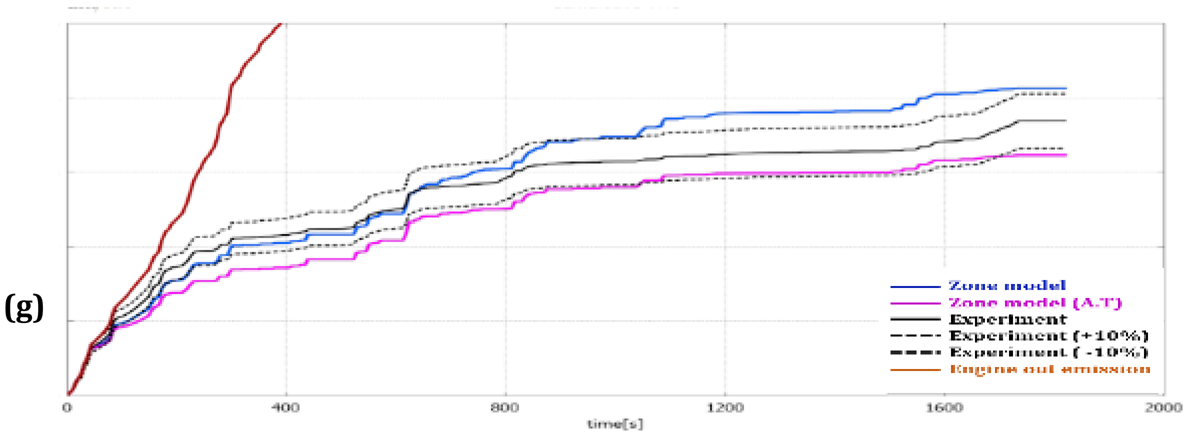


*Figure 42 Cumulative THC emissions*

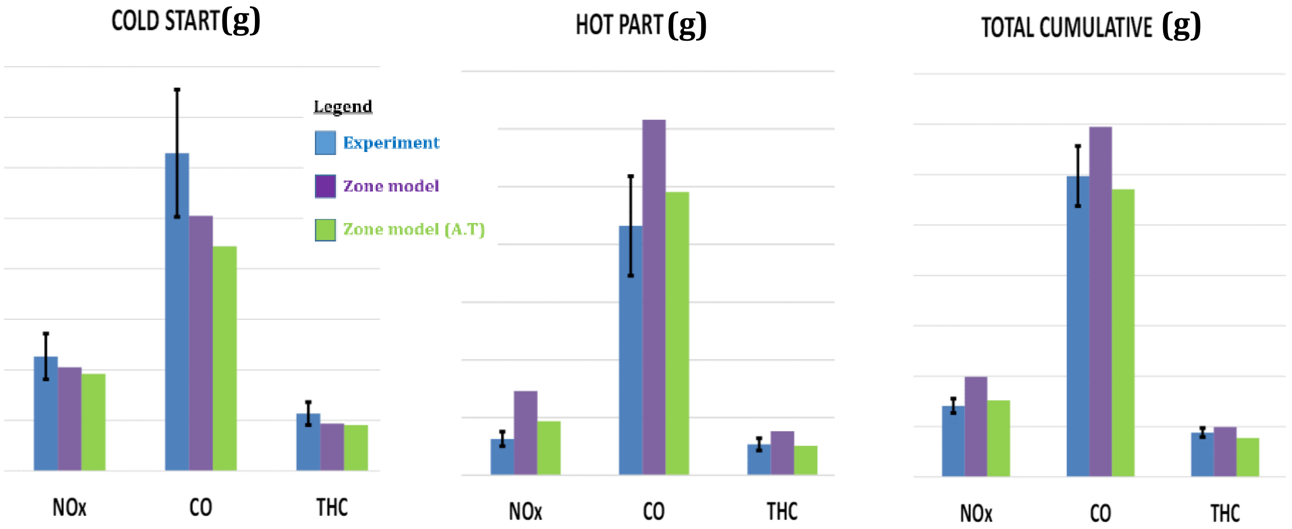


Figure 43 Bar graphs for Pollutant comparison (Aged 1)

The cumulative emission results of the front catalyst WLTC driving cycle for the axial temperature imposed are shown in the Figure 40 Figure 41 Figure 42. The graph has the results comparing the zone model, zone model (A.T) and the experimental results. The blue line represents the zone model cumulative emission results, the pink line represents the zone model (A.T) cumulative emission results and the black line represents the experimental results. The dotted black lines covers the target accuracy of (+/- 10%) for the total cumulative results as mentioned already in the Table 7. The brown line shows the engine out emissions but due to the zoomed view of the graph only a smaller part is visible.

The Figure 43 illustrates the bar graphs for pollutants classified according to the cold start, hot part and total cumulative. The bars correspond to emissions in gram. The error bar is placed in the experimental result bar (blue colour) as mentioned in Table 7. The zone model results are presented in violet colour and zone model (A.T) results are presented in green colour

## Observation from 7.3.

The discussions are separated into cold start, hot part and total cumulative emissions for better understanding of the emission results as shown in the Figure 43.

### Cold start:

- The cold start for the CO zone (A.T) model is reduced further due to the consumption of fast ceria sites with accurate temperature profile which clearly shows the error of the OSC model calibration.
- A very slight under estimation of THC in cold start is seen because the availability of fast ceria oxide is also critical a critical reason for THC consumption.

### Hot part:

- It's very easily seen that the emissions in the hot part are reduced in zone model (A.T) compared with the zone model because of the improvement in the temperature profile which cuts down the inaccuracy which was discussed in the section 7.2.1.
- The zone model (A.T) results are within the target accuracy of the experimental results.
- The slight over estimation in zone model (A.T) for NOx and CO are due to the OSC model miscalibration as discussed in section 7.2.2 & 7.2.4.

### Total cumulative:

- From Figure 40 Figure 41 Figure 42 it is understood that the test attempt done with axial temperature imposed in the model has an effect in the emission level reductions which is seen in all the three pollutants (NOx, CO, THC). This indicates that the thermal model should be improved. This can be done by enhancing the physical properties like washcoat properties and substrate properties of the model.
- The total cumulative of zone model (A.T) for NOx and CO are within the target accuracy of the experimental results and THC is very slightly under estimated ( inaccuracy in the cold start)

Through all these investigations and observations the behaviour of the chemical kinetics of the ageing model turnout to have good results. Hence, the validation of the ageing model has reached its objective by providing good prediction as same as the experimental results. So, zone model can be used for any ageing level of the TWC with only the fresh model calibration.

# Chapter 8. CONCLUSION

The outcomes from the previous seven chapters and my internship work experience at Toyota Motor Europe are discussed in this chapter.

The case study on the gasoline engine emissions, European emission norms, and Three-way catalyst gave me a clear insight on these topics which made me easy to understand the fundamental background of this thesis work and they are presented in chapter 2, 3, and 4.

The focus of the thesis and internship project was to develop a predictive ageing model using Axisuite software. So, the study on ageing of the TWC supported me to grasp about the different types of ageing phenomena that affects the TWC and they are summarized in the chapter 5.This thesis work mainly concern on the thermal and chemical ageing on the TWC.

The necessity to develop the ageing model is to reduce the prototype, testing cost and time. So, I worked in developing an ageing law from the existing aged models and finally two models were developed (zone model, full length model). The target was to attain the emission results with similar accuracy (+/- 10%) to the TME base model. The developed ageing model achieved the target successfully by reducing the number ageing parameters to be calibrated.

From the developed ageing law it was clear that only fresh model calibration is enough to predict any ageing level. Therefore, I applied the ageing law in the new generation fresh TWC model to validate and predict the aged 1 level behaviour of the model and compared it to the experimental results. After the investigation and observation from the obtained results it was apparent to conclude that the ageing model achieved the objective by having good prediction of emission results based on the chemical kinetics.

So, the next steps are to improve the OSC calibration and thermal model behaviour of the TWC models to acquire accurate emission predictions. MBD team is working on the continuous improvement for developing TWC models and also for the other powertrain functionalities to deliver technologies for cleaner and more efficient future mobility.

During this internship at Toyota Motor Europe, I was able to see myself progressing every day in the technical field especially in the gasoline emissions area and TWC development. To add with, myself attained a lot of basic awareness in the present and future powertrain functionalities and Toyota's direction towards future.

As everyone knows Toyota are committed in protecting and improving the environment, I'm very much happy and proud to be a part of Toyota by which I also contributed a small part in developing an eco-friendly environment. Moreover, I personally gained a lot of pleasant experience by working in the multicultural environment and could able to see people respecting everyone and appreciating teamwork and progression towards continuous improvement.

# Chapter 9. ANNEX

## 9.1. Front catalyst WLTC results – Aged 1

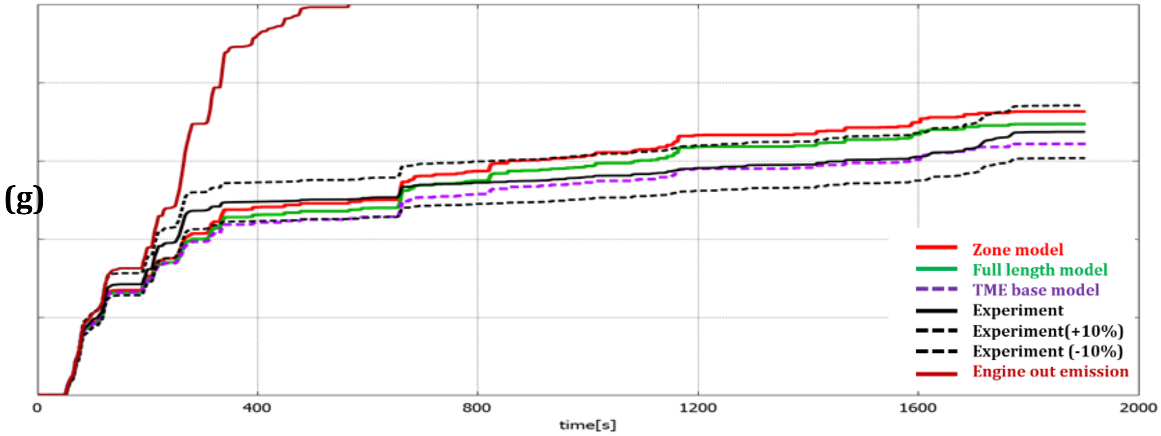


*Figure 44 Cumulative NOx emissions*

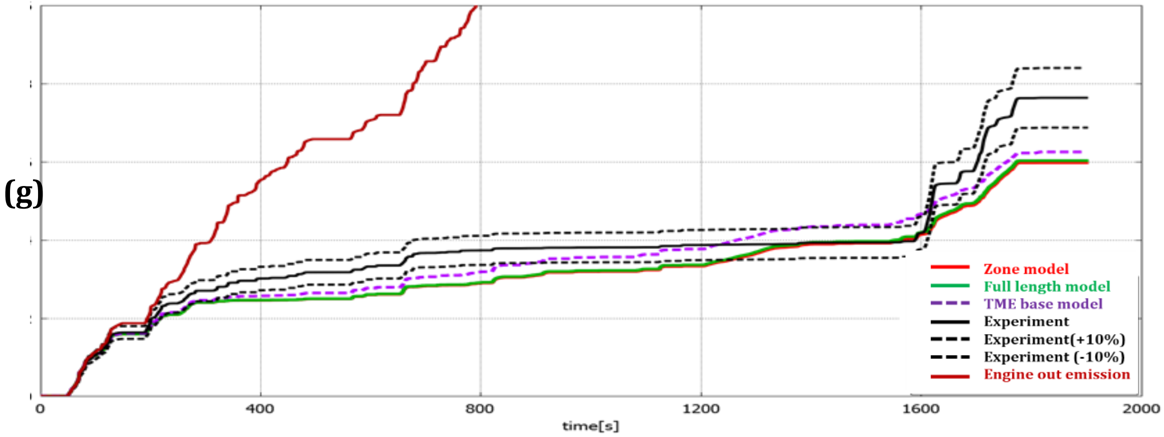


*Figure 46 Cumulative CO emissions*

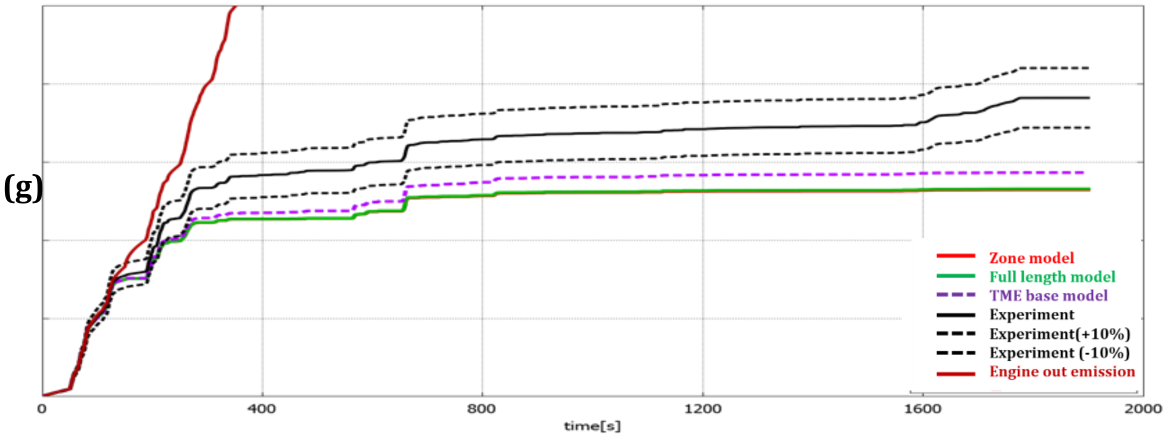


*Figure 45 Cumulative CO emissions*

## 9.2. Front catalyst WLTC results – Aged 2

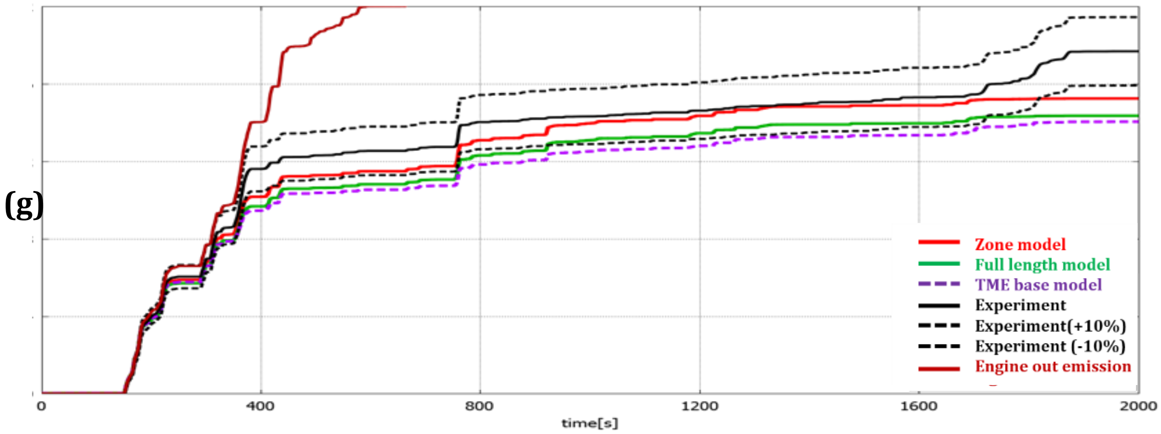


*Figure 47 Cumulative NOx emissions*

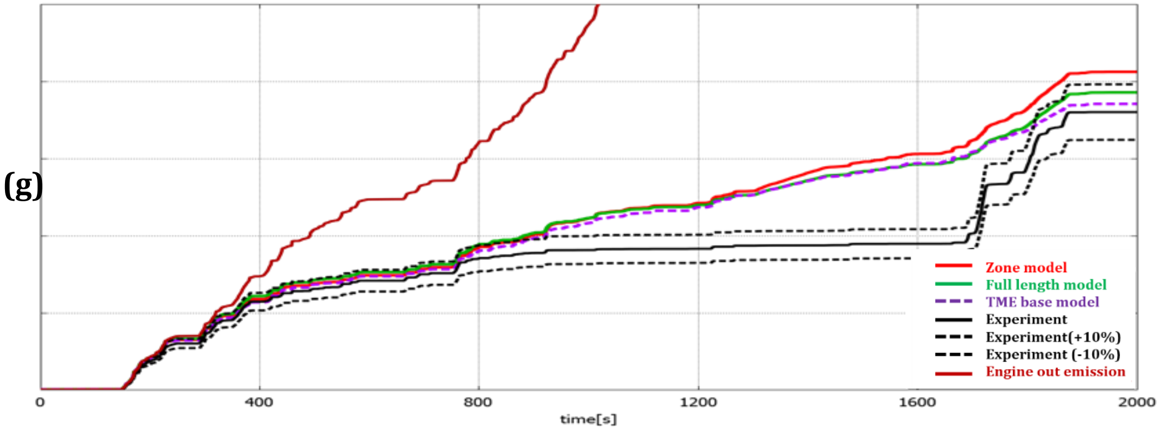


*Figure 49 Cumulative CO emissions*

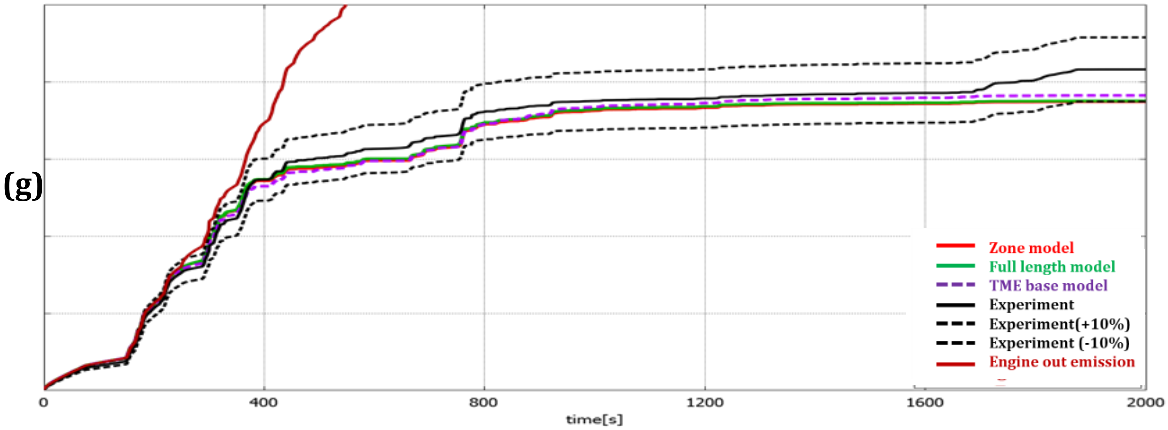


*Figure 48 Cumulative THC emissions*

## 9.3. Front catalyst WLTC results – Aged 3

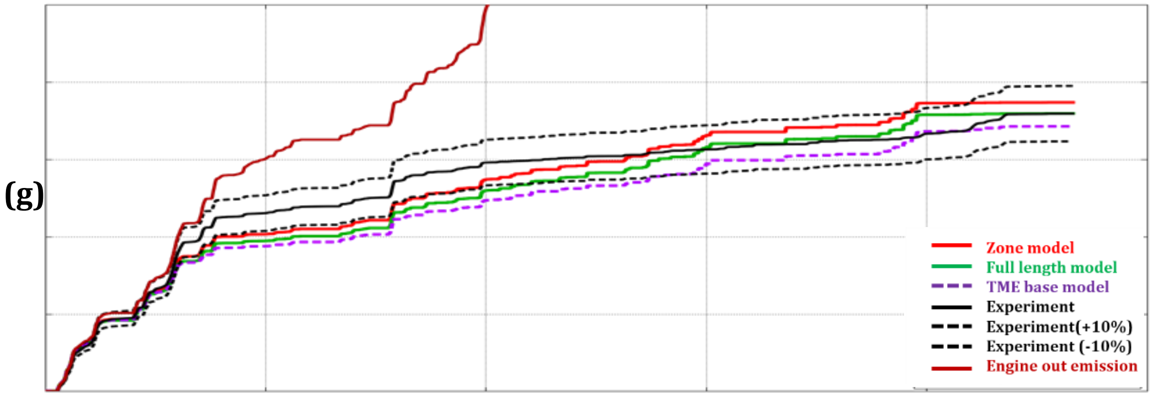


*Figure 50 Cumulative NOx emissions*

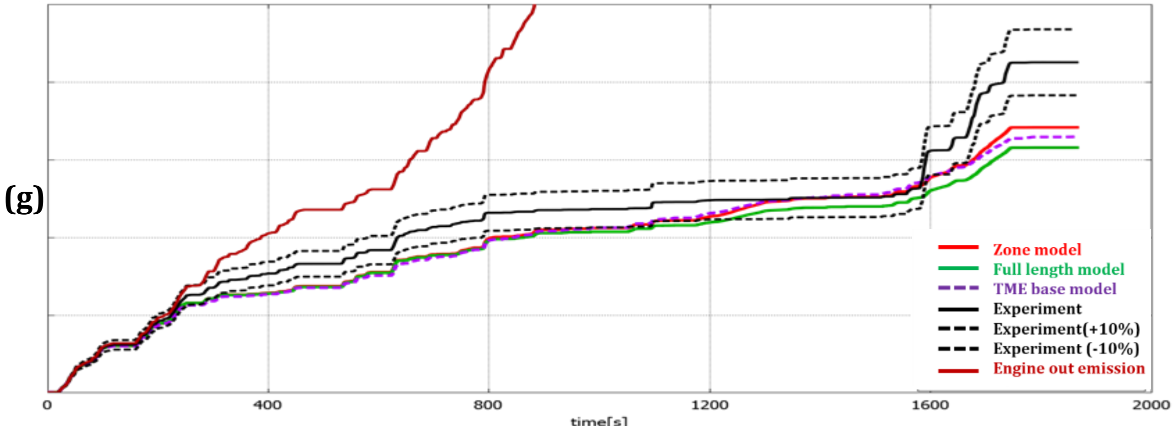


*Figure 51 Cumulative CO emissions*

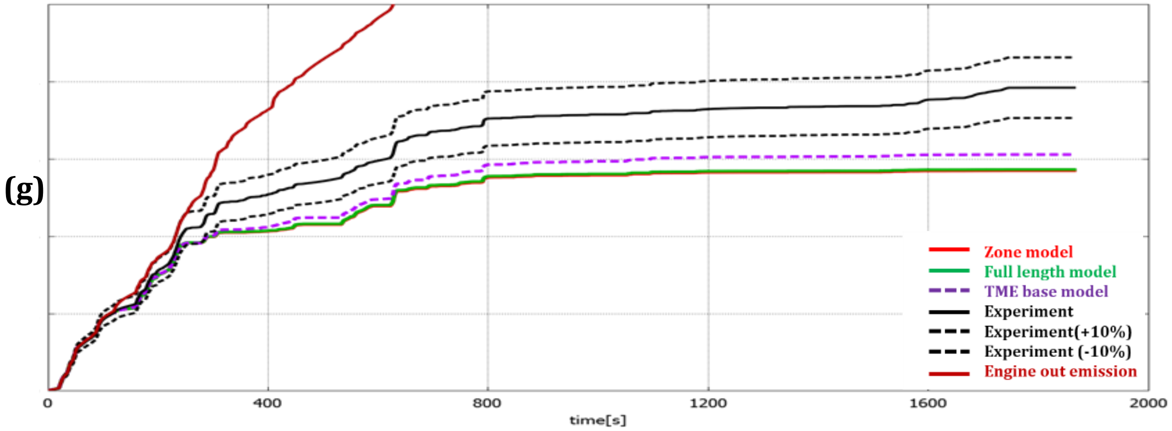


*Figure 52 Cumulative THC emissions*

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# ABBREVIATIONS

- CO - Carbon monoxide
- deg C - degree C
- g – gram
- HC - Hydrocarbon
- NEDC - New European Driving Cycle
- NOx – Nitrous oxides
- OSC – Oxygen storage capacity
- pm – picometre
- PM - Particulate Matter
- PN – Particulate Number
- ppm – parts per million
- S.I – Spark ignition
- THC - Total hydrocarbons
- Tgas – gas temperature
- TWC - Three way catalyst
- WLTC - Worldwide Harmonized Light Vehicles Test Cycle