

# A REVIEW PAPER ON CATALYTIC CONVERTER FOR AUTOMOTIVE EXHAUST EMISSION

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**ABSTRACT** - The purpose of this paper is to present Air pollution generated from mobile sources is a problem of general interest. Vehicle population is projected to grow close to 1300 million by the year 2030. Due to incomplete combustion in the engine, there are a number of incomplete combustion products CO, HC, NO<sub>x</sub>, particulate matters etc. These pollutants have negative impact on air quality, environment and human health that leads in stringent norms of pollutant emission. Numbers of alternative technologies like improvement in engine design, fuel pre-treatment, use of alternative fuels, fuel additives, exhaust treatment or better tuning of the combustion process etc. are being considered to reduce the emission levels of the engine. Among all the types of technologies developed so far, use of catalytic converters based on platinum (noble) group metal is the best way to control automotive exhaust emissions. This review paper discusses automotive exhaust emissions and its impact, automotive exhaust emission control by platinum (noble) group metal based catalyst in catalytic converter, history of catalytic convertor, types of catalytic convertor, limitation of catalytic convertor and also achievements of catalytic convertor.

**Keywords:** Catalytic converter, Exhaust emission, Conversion

## I. Introduction

Issue always been debated among the environmentalists over the decades and recent years is air pollution. As the technology keep on evolving and emerging, it carries along undesirable effects apart from its broad application and use. One of the main contributors is said to be the emission of harmful gases produced by vehicle exhaust lines. The number of vehicles miles travels per year continues to increase as a result of higher demand and needs. Consequently, an increase in the number led to the increase of the content of pollutants in air. The need to control engine emissions was recognized as early as 1909. Due to the more stringent rules and emission standards, automotive manufacturers begun to develop a treatment device for exhaust gases known as catalytic converter for their vehicle models. pollution generated from mobile sources such as automobiles contributes major air quality problems in rural as well as urban and industrialized areas in both developed and developing countries. About 50 million cars are produced every year and over 700 million cars are used worldwide. Vehicle population is projected to grow close to 1300 million by the year 2030. Most vehicular transportation relies on combustion of gasoline, diesel and jet fuels with large amount of emission of carbon monoxide (CO), unburned hydrocarbons (HC), nitrogen oxides (NO<sub>x</sub>) and particulates matter (PM) are especially concern. HC and CO occur because the combustion efficiency is less than 100%. The NO<sub>x</sub> is formed during the very high temperatures (>1500 °C) of the combustion process resulting in thermal fixation of the nitrogen in the air which forms NO<sub>x</sub>.

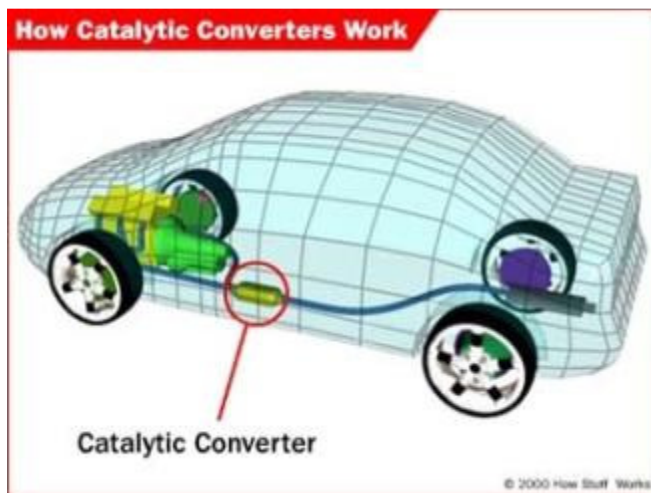
Typical exhaust gas composition at the normal engine operating conditions are: carbon monoxide (CO, 0.5 vol.%), unburned hydrocarbons (HC, 350 vppm), nitrogen oxides (NO<sub>x</sub>, 900 ppm) hydrogen (H<sub>2</sub>, 0.17 vol.%), water (H<sub>2</sub>O, 10 vol.%), carbon dioxide (CO<sub>2</sub>, 10 vol.%), oxygen (O<sub>2</sub>, 0.5 vol.%). Carbon monoxide is a noted poison that has an affinity for haemoglobin in the blood 210 times greater than the As the emission standards were tightened, more advanced control strategies were applied that included modifications in engine design and fuel system, control of engine parameters and use of sophisticated exhaust after treatment devices. Reduction of toxic substances emission from combustion engines can be achieved by primary (inside engine) measure and secondary (outside engine) measures. As primary measures many different possibilities and technical methods of reducing exhaust gas emission are used e.g. combustion of lean air fuel mixture, multistage injection fuel, exhaust gas recirculation, fuel gas after burning, loading of additional water into cylinder volume .

Nowadays secondary measures, in automotive exhaust after treatment processes a range of advanced technology is applied based on oxidation and three-way catalyst adsorption storage and filtration process. This enables reduction of the carbon monoxide (CO), hydrocarbons (HC), nitrogen oxide (NO<sub>x</sub>) and particulate emissions from a gasoline or diesel engine to meet the demands of current and future exhaust emission regulations. This review paper discusses automotive exhaust emissions and its impact, automotive exhaust emission control by

platinum (noble) group metal based catalyst in catalytic converter, history of catalytic converter, types of catalytic converter, limitation of catalytic converter and also achievements of catalytic converter.

## **II. Catalytic Converter**

The pollutants have negative impact on air quality, environment and human health that leads in stringent norms of pollutant emission. Numbers of alternative technologies like improvement in engine design, fuel pre-treatment, use of alternative fuels, fuel additives, exhaust treatment or better tuning of the combustion process etc. are being considered to reduce the emission levels of the engine. Out of various technologies available for automobile exhaust emission control a catalytic converter is found to best option to control CO, HC and NO<sub>x</sub> emissions from petrol driven vehicles while diesel particulate filter and oxidation catalysts converter ordiesel oxidation catalyst have so far been the most potential option to control particulates emissions from diesel driven vehicle. A catalytic converter (CC) is placed inside the tailpipe through which deadly exhaust gases containing unburnt fuel, CO, NO<sub>x</sub> are emitted. The function of the catalytic converter is to convert these gases into CO<sub>2</sub>, water, N<sub>2</sub> and O<sub>2</sub> and currently, it is compulsory for all automobiles plying on roads in US and Japan to have catalytic converters as they use unleaded petrol. In India the government has made catalytic converters mandatory for registration of new cars.



**Fig. 1. Catalytic Converter Position in a Vehicle**

### **History**

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 - an idea ahead of its time for which he attained a patent (US2742437). But, until the extremely effective anti-knock agent tetra-ethyl lead was eliminated from most gasoline over environmental concerns, it would "poison" the converter by forming a coating on the catalyst's surface, effectively disabling it. 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. Beginning in 1979, a mandated reduction in NO<sub>x</sub> required the development and use of a three way catalyst for CO, HC and NO<sub>x</sub> abatement.

Catalytic converter has gone through many processes and remarkable evolution for the past 30 years. It is said to be one of the most effective tool to fight against the overwhelming pollutant contents in our environment, as it reduces almost 80% of the harmful gases resulting from the incomplete combustion of the engine. Catalytic converter is a stainless steel container mounted somewhere along the exhaust pipe of the engine and inside the container is a porous ceramic structure through which the exhaust gas flows (V.GANESAN). 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. Early converters used loose granular ceramic with the gas passing between the packed spheres. Since it is difficult to keep the spheres in place, many converter developers opted for ceramic monolith which offers various advantages. Among these advantages are smaller volumes, lower mass and greater ease of packaging.

### III. Types Of Catalytic Converter

1)

#### 2) The oxidization catalytic converter

An oxidation catalyst is a device placed on the tailpipe of a car. The oxidation catalyst is the second stage of the catalytic converter. It reduces the unburned hydrocarbons and carbon monoxide by burning (oxidizing) them over a platinum and palladium catalyst. This catalyst aids the reaction of the CO and hydrocarbons with the remaining oxygen in the exhaust gas.

#### 3) The reduction catalytic converter

A reduction catalyst to control NO<sub>x</sub> can be used as a separate system in addition to the oxidation catalytic converter. The reduction catalyst is fitted upstream of the oxidation system. The reduction catalyst is the first stage of the catalytic converter. It uses platinum and rhodium to reduce the nitrogen oxide emissions. When such molecules come in contact with the catalyst, the catalyst rips the nitrogen atom out of the molecule and holds on to it, freeing the oxygen in the form of O<sub>2</sub>. The nitrogen atoms bond with other nitrogen atoms that are also stuck to the catalyst forming N<sub>2</sub>.  $2NO = N_2 + O_2$  (1)

#### 4) The three-way catalytic converter (TWC)

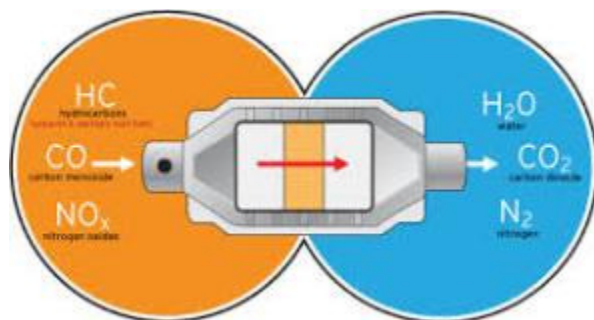
TWCs have the advantage of performing the oxidation of carbon monoxide (CO), hydrocarbons (HC) and the reduction of nitrogen oxides (NO<sub>x</sub>) simultaneously. Noble metals are usually used as the active phase in TWCs. Pd catalysts are especially attractive since Pd is by far the cheapest noble metal in the market and has better selectivity and activity for hydrocarbons. Rhodium the other essential constituent of three-way catalysts is widely recognized as the most efficient catalyst for promoting the reduction of NO to N<sub>2</sub>. The TWCs performance in the emission control can be affected by operating the catalyst at elevated temperatures (> 600°C). Reactions occurring on the automotive exhaust catalysts are very complex as listed below. The major reactions are the oxidation of CO and HC and the reduction of NO<sub>x</sub>. Concept is based on incorporation of a Also, water gas shift and steam reforming reaction occur. Intermediate products such as N<sub>2</sub>O and NO<sub>2</sub> are also found. The NO<sub>x</sub> storage storage component into the three-way catalyst (TWCs) to store NO<sub>x</sub> during lean conditions for a time period of minutes. Reactions in Catalytic Converter:- Oxidation :  $2CO + O_2 \rightarrow 2CO_2$   $HC + O_2 \rightarrow CO_2 + H_2O$  Reduction/3-way:  $2CO + 2NO \rightarrow 2CO_2 + N_2$   $HC + NO \rightarrow CO_2 + H_2O + N_2$   $2H_2 + 2NO \rightarrow 2H_2O + N_2$

Water Gas Shift:  $CO + H_2O \rightarrow CO_2 + H_2$

Steam reforming:  $HC + H_2O \rightarrow CO_2 + H_2$

#### Modern Three way catalytic converter

A typical design of a modern three-way catalytic converter is a stainless steel container that incorporates a honeycomb monolith made of ceramic or metal. The monolith acts as the inert substrate coating with washcoat and active catalysts. Washcoat is a layer of mixture (mainly aluminum) which gives a further irregular and larger surface area also contains oxygen storage promoters and stabilizers. To prepare the active monolith, a layer of washcoat is first deposited on the substrate and the catalysts are then deposited on the washcoat or dipping the monolith into a slurry containing washcoat components and platinum group metals. The excess of the deposited material (washcoat) is removed using high-pressure air or by applying a vacuum. Then the monolith is calcined to obtain the finished catalyst. The monolith's geometrical characteristics play a key role in effecting the distributions of temperature and species throughout the device and then determining the efficiency of the converter. It combines the requirements of compactness, high volumetric flow rates and low back pressure.



**Fig 2. Catalytic Converter**

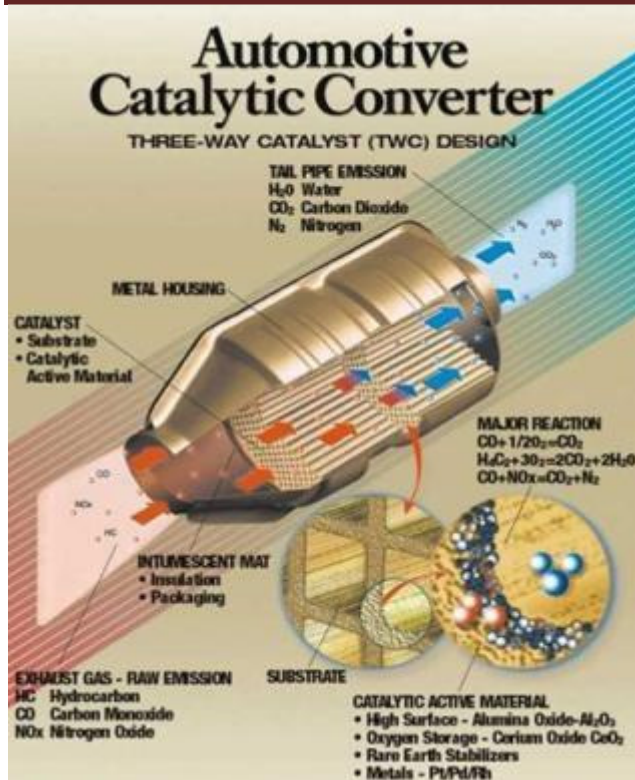


Fig.3. Schematic diagram of Catalytic Converter Catalyst

#### IV. Catalyst

These include oxides of base metals e.g. copper, chromium, nickel, cobalt etc. and the noble metals platinum (Pt), palladium (Pd) and rhodium (Rh). Base metal oxides although found to be effective at higher temperature but they sinter and deactivate when subjected to high-end exhaust gas temperature of conventional SI (Spark-Ignition) engine operation. Also, their conversion efficiency is severely inhibited by sulphur dioxide resulting from sulphur in fuel. The base metal catalysts are required in a relatively large volume and consequently due to high thermal inertia they took longer to heat up to operating temperature. Therefore in practice only the noble metals are used as they have high specific activity high resistance to thermal degradation, Superior cold start performance and low deactivation caused by fuel sulphur. The noble metal are more expensive but the amount required for an automotive catalytic converter is small about 1 to 2 gm only. The noble metal loading typically varies from about 1.0 to 1.8 g/l (30 to 50 g/ft<sup>3</sup>) of catalytic converter volume.

A mixture of platinum and palladium in 2:1 mass ratio is usually employed as oxidation catalyst. Palladium has higher specific activity than Pt for oxidation of CO, olefins and methane. For the oxidation of aromatics, Pd and Pt have similar activity while for the oxidation of paraffin hydrocarbon (higher than propane) Pt is more active than Pd. Palladium has a lower sintering tendency than platinum at high temperatures of about 980 °C in the oxidizing atmosphere. Rhodium is primarily a NO reduction catalyst. The NO reduction activity of noble metals is in the order Rh>Pd>Pt. when simultaneous conversion of CO, HC and NO<sub>x</sub> is desired in the 3-way catalytic converters, mixture of Pt + Pd is used with Rh in a ratio of 5:1 to 10:1. The active metal in the automotive catalysts Pt, Pd and/or Rh is very small (0.1 to 0.15 % by weight of monolith) and it is highly dispersed on the surface of the catalyst support. The particle size of the noble metal particles when fresh is around 50 nm or smaller. At high temperature the noble metals sinter and particles may grow to a size of around 100 nm.

#### Substrate /Support

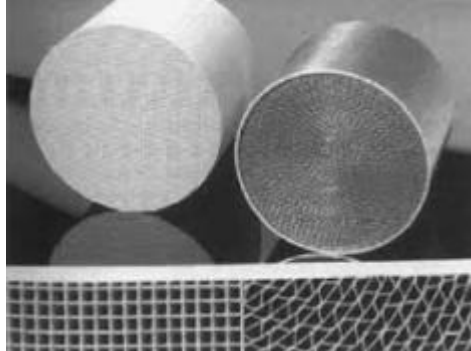
##### Pellets:

The first catalytic converters of passenger cars in early 1970s used a bed of spherical ceramic pellets. These are also known as packed bed catalytic converter. The spherical pellets made of  $\gamma$ -alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) of 3-6 mm diameter were used. The material of pellets is selected to have a high mechanical strength against crush and abrasion even after exposure to high temperature of around 1000°C on the porous surface of pellets that provides a large surface area, the noble metal salts are impregnated to a depth of about 250  $\mu$ m. The pellets are then dried

at about 120<sup>0</sup>C and claimed to a temperature of about 500<sup>0</sup>C. The pellets catalysts were loaded with approximately 0.05 % by weight of noble metals composed of Pt : Pd in 2.5 : 1

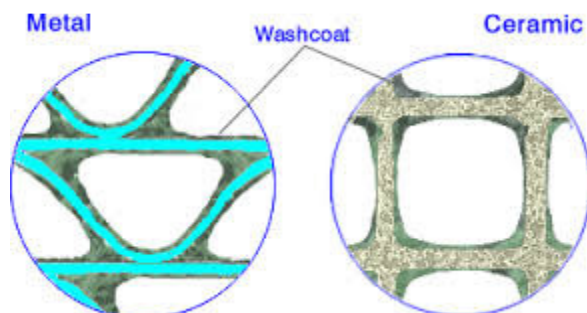
### Monoliths

A monolith is a ceramic block consisting of a large number of small straight and parallel channels. The monoliths are made by extrusion. A special mixture of clay binders and additives is pushed through a sophisticated dye to create the monolith structure. The material is dried cut to the required length and fired at high temperatures. The monolithic structure has a diameter of about 15 cm and can have different shapes. The diameter of the channels ranges from 0.5 to 10 mm and the length of the monolith can be up to 1 meter long. On the walls of the channels a catalytic active layer can be applied in which chemical reactions can take place. Because of the large number of channels the contact area between the catalytic layer and the fluid that travels inside the channels is very large. Further the channels are straight and parallel so that the flow is not obstructed.



**Figure 4: ceramic and metallic exhaust monolith**

The ceramic and metallic monolithic allows high conversion efficiencies at high gaseous throughput, provides a high geometric surface area with lower pressure drop, excellent high temperature and thermal shock resistance and can be conveniently oriented in the exhaust train in any number of directions. The monolithic catalyst is mounted in a stainless-steel container with a matting material wrapped around it to ensure resistance to vibration.



**Fig.5. Internal structure of Ceramic and Metallic monolith.**

The size and shape of the final catalyst configuration varies with each automobile company but typically, they are about 10-12 cm in diameter and 7-10 cm in long with multiple honeycomb catalysts.

### Air to fuel ratio

There is a narrow range of air- fuel ratio near stoichiometry in which high conversion efficiencies for all three pollutants are achieved. The width of this window is narrow about 0.1 air fuel ratio for catalyst with high mileage use and depends on catalyst formulation and engine operating conditions. Conversion efficiency of NO, CO and HC as a function of the air-fuel in a three way catalytic converter. Fig.5 shows the conversion efficiency of NO, CO and HC as function of the air - fuel ratio.

#### 1) When the A/F ratio is leaner than stoichiometry

The oxygen content of the exhaust stream rises and the carbon monoxide content falls. This provides a high efficiency operating environment for the oxidizing catalysts (platinum and palladium). During this lean cycle the catalyst (by using cerium) also stores excess oxygen which will be released to promote better oxidation during the rich cycle.

#### 2) When the A/F ratio is richer than stoichiometry

The carbon monoxide content of the exhaust rises and the oxygen content falls. This provided a high efficiency operating environment for the reducing catalyst (rhodium). The oxidizing catalyst maintains its efficiency as stored oxygen is released [27], [28]. A closed loop feedback fuel management system with an oxygen sensor in the exhaust is used for precise control of air-fuel ration. To obtain an efficient control of the A/F ratio the amount of air is measured and the fuel injection is controlled by a computerized system which uses an oxygen ( $\lambda$ ) sensor located at the inlet of the catalytic converter. The signal from this  $\lambda$  sensor is used as a feedback for the fuel and air injection control loop. A second  $\lambda$  sensor is mounted at the outlet of the catalytic converter (Fig. 4). This configuration constitutes the basis of the so-called engine onboard diagnostics (OBD). By comparing the oxygen concentration before and after the catalyst, A/F fluctuations are detected. Extensive fluctuations of A/F at the outlet signal system failure. Effect of A/F ratio on the conversion efficiency of three-way catalysts narrow A/F window at the stoichiometric point is the fingerprint of an effective TWC system. A simple closed loop feedback engine fuel management system is shown schematically in fig. 5.

## **V. Limitation**

In the exhaust stream with temperatures up to 1000 °C the metal in the catalyst is prone to deactivation by sintering, leading to a reduction in surface area and hence catalytic activity. The conventional means to meet tightening legislative emissions control targets is simply to increase the amount of PGM in the auto catalyst. The need to guarantee catalyst performance over the typical vehicle lifetime of 80,000 km also means that excess metal must be added, since the performance of the catalyst drops off over time. In addition rising PGM demand and costs are incentives towards achieving lower metal loadings and higher activity. The catalytic converters in the exhaust system become deteriorated by several mechanisms e.g. thermal deterioration and poisoning. Thermal deterioration occurs as a result of exposure of the catalyst to high temperature conditions. This cause sintering of the PGM, loss of support surface area and phase transformation. Poison also cause loss of activity mainly by blocking the pores leading to active sites or even by direct blockage of the active sites themselves.

## **Conclusion**

Today's automobiles are meeting emission standards that require reductions of up to 99 percent for HC, CO and NO<sub>x</sub> compared to the uncontrolled levels of automobiles sold in the 1960s. Environmental, ecological and health concern result in increasingly stringent emissions regulations of pollutant emissions from vehicle engines. Among all the types of technologies developed so far, use of Metal Monolith type catalytic converters is the best way to control auto exhaust emission. Three-way catalyst with stoichiometric engine control systems remain the state of art method for simultaneously controlling hydrocarbon, CO and NO<sub>x</sub> emissions from vehicle. The economical reasons, limited resources of platinum group (noble) metal and some operating limitations of platinum group metal based catalytic converters have motivated the investigation of alternative catalyst materials. This type of Catalytic converters have also been developed for use on trucks, buses and motorcycles as well as on construction equipment lawn and garden equipment marine engines and other non-road engines. Catalytic converters are also used to reduce emissions from alternative fuel vehicles powered by natural gas, methanol, ethanol and propane. To date more than 500 million vehicles equipped with catalytic converters have been sold worldwide. In 2005, 100 percent of new cars sold in the U.S. were equipped with a catalytic converter, and worldwide over 90 percent of new cars sold had a of metal monolith type catalyst.

## **Acronyms**

CO Carbon monoxide

HC Hydrocarbons

NO<sub>x</sub> Nitrogen oxides

PM Particulates matter

A/F Air to fuel ratio

TWC Three way catalytic convertor

Rh Rhodium

Pt Platinum

Pd Palladium

## **References**

- [1] Ganesan, V., 2004, "Internal Combustion Engines,"
- [2] Second Edition, McGraw Hill.

- [3] Heck, R.M. and Farrauto, R.J., 1995, “.Catalytic Air Pollution Control,,” New York: Van Nostrand Reinhold.
- [4] Braun, J., Hauber, T., et al., 2002, “Three Dimensional Simulation of the Transient Behavior of a Three-Way Catalytic Converter,” SAE Paper 2002-01- 0065.
- [5] Marsh, P., Acke, F., et al., 2001, “Application Guideline to Define Catalyst Layout for Maximum Catalytic Efficiency”, SAE Paper 2001-01-0929.
- [6] [http://www.cleanairnet.org/baq2004/1527/articles- 59196\\_Kisku.doc](http://www.cleanairnet.org/baq2004/1527/articles- 59196_Kisku.doc)
- [7] R. Heck, and R. Farrauto, Automobile exhaust catalysts, Applied Catalysis A: General, vol. 221, pp.443-457, 2001.
- [8] P. Pundir, Engine emissions pollutant Formation and Advances in Control Technology, Narosa Publishing house, New Delhi, Chapter 1, pp. 1-10.
- [9] K. Wark, G. Warner, and W. Davis, Air Pollution and its control, 3rd edition, Wesley Longmann., Chapter 10, pp. 489.
- [10] Roy M. Harrison, Pollution causes, effects & control, 2<sup>nd</sup> edition, The Royal Society of Chemistry, pp. 221.