# CHAPTER 18

# AUTOMOBILE AIR POLLUTANT EMISSIONS AND CONTROL

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## ABSTRACT

One major problem the populace, and indeed the people in the urban cities, are facing today is environmental pollution. This paper analyses various sources of pollutant emissions from the internal combustion engines. For proper determination of emission levels, the detailed chemical processes of pollutant formation with the methods of obtaining the specific emission and emission index were analysed. The paper also discusses how emission of pollutants from automobile can be controlled by incorporating catalytic converter and particulate traps in the exhaust system.

## 1.0 INTRODUCTION

Unrestrained human activities all over the world have contributed to environmental destruction and ecological crisis. These activities are not bad as they are bound to occur if there must be development and progress. The living environment is a cornerstone for good health, and as such very appropriate investment to the environment should bring about improvement to people's health (Abegunde and Omisore, 2003).

Technology advancement is important, desirable and a necessary ingredient of economic and social growth. It has made it possible for a large number of persons to enjoy the goods of life. The introduction and the use of inappropriate technologies often destroy the productive potential of ecosystems. Moreover, the expansion of technology has been at the expense of other form of life. Energy is directly implicated in the atmospheric pollution caused by the burning of fossil fuels for transportation, industry and domestic uses-leading to the problem of acid rain and the emission of carbon dioxide which is of concern as a global warming threat. The procurement of energy is also responsible in varying degrees for much of the on-going deforestation, desertification and loss vegetation and soil (Okonkwo, 2001; Walter, 1995). The recent increase in the number of vehicles on the road is a welcome development as the movement of people and goods are greatly enhanced thus boosting economic activities through improved transportation of people, goods and services, social interactions have also increased. Nevertheless, according to Adegoke (2002), the negative effects of all these on the environment include:

(i) increased air pollution through the exhaust fumes – the products of combustion from vehicles; and
(ii) increased cases of accidents.

The spark ignition and diesel engines, both internal combustion engines, are the only engines in wide spread use in the world's automobile transportation systems. And they are the major source of urban air pollution (John, 1998). Clouds of smoke are a common sight in cities, especially in the Ikeja, Oshodi, Ijora and Apapa areas of Lagos metropolis in Nigeria. These pollutants directly or indirectly find their ways into human beings causing sickness and diseases some of which are difficult to cure if not incurable.

The automobile engine exhaust gases contain oxides of nitrogen, $NO_x$, (nitric oxide and small amounts of nitrogen dioxide), carbon monoxide (CO). And organic compounds which are unburned or partially burned hydrocarbons ($H_xC_y$). The relative amounts depend on the engine design and operating conditions but are of order: $NO_x$, 20 g/kg fuel; CO, 200 g/kg fuel; and HC, 25 g/kg fuel (Browman, 1975).

## 2.0 POLLUTANT FORMATION PROCESSES AND EMISSIONS IN INTERNAL COMBUSTION ENGINES

The detailed chemical processes of pollutant formation are important in determining emission levels. For some pollutant species e.g., carbon mono oxide, organic compounds and particulate, the formation and destruction reactions are intimately coupled with the primary fuel combustion process. Therefore, an understanding of the formation of these species requires knowledge of the combustion chemistry. For Nitrogen oxides and sulphur oxides, the formation and destruction process 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.

The processes of pollutants' formation within the cylinder of a conventional spark-ignition engine are illustrated quantitatively in Fig. 1. The schematic drawings show the combustion chamber during four different phases of the engine cycle: Compression, combustion expansion and exhaust. Nitric oxide (NO) forms through the high-temperature burned gases behind the flame through chemical reactions involving nitrogen and oxygen atoms and molecules, which do not attain chemical equilibrium. The higher the burned gas temperature, the higher the rate of formation of NO. As the burned gases cool during expansion stroke (Fig. 1c) the reactions involving NO freeze, and leave NO concentrations far in excess of levels corresponding to equilibrium at exhaust conditions (Patterson and Henein, 1992).

Carbon monoxide (CO) also forms during the combustion process. With rich fuel-air mixtures, there is insufficient oxygen to burn fully all the carbon in fuel to carbon dioxide, $CO_2$, also, in the temperature products,

even with weak mixture, dissociation occurs and there are significant CO levels which also freezes during expansion stroke (Fig. 1c) as the burned gas temperature falls. (Lahaye and Prado, 1991). The unburned hydrocarbon emissions have several different sources. During compression and combustion, the increasing cylinder pressure forces some of the gas in the cylinder into crevices, or narrow volumes, connected to the combustion chamber: the volumes between the piston, rings and cylinder wall are the largest of these. Most of this gas is unburned fuel-air mixture; much of it escapes the primary combustion process (Fig. 1b) because the entrance to these crevices is too narrow for the flame to enter. This gas which leaves these crevices later in the expansion and exhaust processes is one of the sources of unburned hydrocarbon emissions (Lavoie and Blumberg, 1980).

Another possible source of hydrocarbon ($H_xC_y$) emissions is the combustion chamber walls. According to John (1998), partially burned fuel-air mixture is left at the flame is extinguished as approaches the wall. He further showed that the unburned $H_xC_y$ in these thin layers burn up rapidly when the combustion chamber walls is clean. He also showed that the porous deposits on the walls of engines in actual operation do increase engine $H_xC_y$ emissions. A third source of unburned hydrocarbons is believed to be any engine oil left in a thin film on the cylinder wall, piston and perhaps on the cylinder head. These oil layers can absorb fuel hydrocarbon components before and after combustion, respectively, thus permitting a fraction of the fuel to escape the primary combustion process unburned (John, 1981). The fourth source of ($H_xC_y$) in engines is incomplete combustion due to bulk quenching of the flame in the fraction of the engine cycles where combustion is especially slow. Such conditions are most likely to occur during transient engine operation when the air/fuel ratio and spark timing may not be properly matched (Lavoie and Blumberg, 1980).

The unburned hydrocarbons exist the cylinder being entrained in the bulk-gas flow during blow-down and at the end of the exhaust stroke as the piston pushes gas escape of the wall out of the exhaust valve. Substantial oxidation of the hydrocarbons which escape the primary combustion process by any of the above processes can occur during expansion and exhaust (Figs. 1c and Figs. 1d).
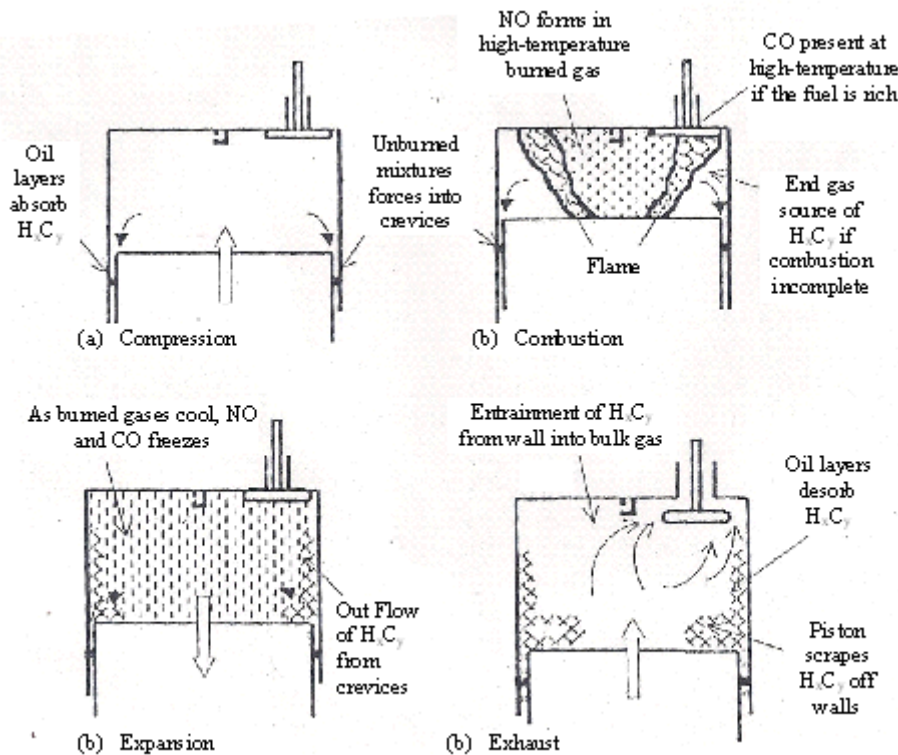


Fig. 1. Processes of pollutants' formation within the cylinder of a conventional spark-ignition engine.

## 2.1 Nitric Oxide (NO) Formation and Emissions

Nitric oxide and nitrogen dioxide ($NO_2$) are usually grouped together as nitrogen oxides ($NO_x$) emissions. Nitric oxide is the predominant oxide of nitrogen produced inside the engine cylinder. The principal source of NO is the oxidation of atmospheric (molecular) nitrogen. However, if the fuel contains significant nitrogen, the oxidation of the fuel nitrogen-containing compounds is an additional source of NO

In the combustion of near-stoichiometric fuel-air mixtures, the principal reactions governing the formation of NO from molecular nitrogen are:

$$O_2 + 2N_2 \rightarrow 2NO + N_2 \tag{1}$$
$$N_2 + 2O_2 \rightarrow 2NO + O_2 \tag{2}$$
$$N_2 + 2OH^- \rightarrow 2NO + H_2 \tag{3}$$
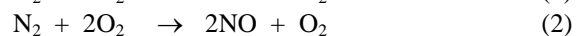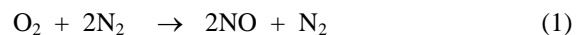
The rate of 'NO" formation is given by John (1998) as:

$$\frac{d[NO]}{dt} = \frac{60 \times 10^{16}}{T^{\frac{1}{2}}} \exp(-69090/T)[O_2]_e^{\frac{1}{2}}[N_2]_e \quad mol/cm^3.s \tag{4}$$

Where: [ ]$_e$ denotes equilibrium concentration.

High temperatures and high oxygen concentrations result in high NO formation rates. A characteristic time for the NO formation process $t_{NO}$, is defined by (Aoyagi *et al.*, 1980):

$$t_{NO}^{-1} = \frac{1}{[NO]_e} \cdot \frac{d[NO]}{dt} \qquad (5)$$

$[NO]_e$ can be obtained from the equilibrium m constant $K_{NO} = 20.3 \times \exp(-21650/T)$ for the reaction:

$$O_2 + N_2 \rightarrow 2NO$$
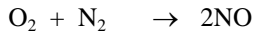
as $[NO]_e = \{K_{NO} [O_2]_e [N_2]_e\}^{1/2}$. Eqns 4 and 5 can be combined to give:

$$t_{NO} = \frac{18 \times 10^{-15} T \exp(58300/T)}{T^{\frac{1}{2}}} \qquad (6)$$

or $t_{NO} = 8 \times 10\text{-}15 T^{1/2} \exp(58300/T)$

Where: $t_{NO}$ is in seconds and T in Kelvin.

## 2.2 Nitrogen Dioxide (NO$_2$) Emissions

Hilliard and Wheeler (1979) worked on chemical equilibrium of burned gases at typical flame temperatures, their studies revealed that NO$_2$/NO ratio is negligibly small for spark ignition engines. While in diesel engines, NO$_2$ can be 10 to 30 % of the total exhaust oxides of nitrogen emissions. NO formed in the flame zone can be rapidly converted to NO$_2$.

$$NO + O_2 \rightarrow NO_2 + \tfrac{1}{2}O_2 \qquad (7)$$
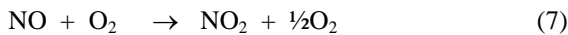
It is customary to measure total oxides of nitrogen emissions. NO plus NO$_2$, with a chemiluminescence's analyser and call the combination NO$_x$ (Lavoie and Blumberg, 1980). It is always important to check carefully whether specific emissions data for NO$_x$ are given in terms of mass of NO$_2$, which have molecular weights of 30 and 46 respectively.

## 2.3 Carbon Monoxide (CO) Emissions

Carbon monoxide (CO) emissions from internal combustion engines are controlled primarily by air/fuel equivalence ratio. For rich air/fuel mixtures, CO concentration in the exhaust is high, since the amount of excess fuel (unburned fuel) will be high. While for weak air/fuel mixtures, CO emissions are very low, therefore, they are not considered as important. According to John (1998), the levels of CO observed in spark ignition engine exhaust gases are lower than the value measure within the combustion chamber. Hence, some of the CO that formed in the combustion process are oxidised to CO$_2$ before they are discharged into atmosphere. The principal CO oxidation reaction in hydrocarbon-air flame is (Bowman, 1975):

$$2CO + 2OH^- \rightarrow 2CO_2 + H_2 \qquad (8)$$

The rate constant for this reaction is:
$$K^+_{CO} = 6.76 \times 10^{10} \exp(T/1102) \ cm^3/gmol \qquad (9)$$

## 2.4 Unburned Hydrocarbon (H$_x$C$_y$) Emissions

Hydrocarbons, or more appropriately organic emissions, are the consequences of incomplete combustion of the hydrocarbon fuel. The level of unburned hydrocarbons in the exhaust gases is generally specified in terms of the total hydrocarbon concentration expressed in parts per million of carbon atoms. The hydrocarbons emission is a useful measure of combustion inefficiency. Some of these hydrocarbons are nearly inert physiologically and are virtually unreactive from standpoint of photochemical smog. Others are highly reactive in the smog-producing chemistry. Hydrocarbon compounds are divided into non-reactive and reactive based on their potential for oxidant formation in the photochemical smog chemistry. Some hydrocarbons are known carcinogens (Patterson and Henein, 1992).

Fuel composition can significantly influence the composition and magnitude of the organic emissions. Fuels containing high proportions of aromatics and olefins produce relatively higher concentrations of reactive hydrocarbons. Oxygenates are present in engine exhaust and are known to participate in the formation of photochemical smog. Some oxygenates are also irritants and odorants. The oxygenates are generally categorised as carbonyls, phenols and other non-carbonyls. The carbonyls of interest are low molecular weight aldehydes and aliphatic ketones. The volatile aldehydes are eye and respiratory tract irritants. Carbonyls account for about 10 % of the H$_x$C$_y$ emissions from diesel passenger car engines, but in spark ignition engine H$_x$C$_y$ emissions are very low. Phenols are odorants and irritants but their levels are much lower than aldehyde levels (Adamczyk *et al.*, 1981, 1983; Kaiser *et al.*, 1981, 1982).

## 3.0 PARTICULATE EMISSIONS

There are three classes of automobile engine particulate emissions: lead, organic particulate (including soot) and sulphates. Significant sulphate emission can occur with oxidation-catalyst equipped engines. Unleaded gasoline contains sulphur, which is oxidised within the engine cylinder to sulphur dioxide, SO$_2$. This SO$_2$ can be oxidised by the exhaust catalyst to SO$_3$ which combines with water at ambient temperatures to form a sulphuric acid aerosol. Levels of sulphate emissions depend on the fuel/sulphur content, the operating conditions of the engine and the details of the catalyst system used (Kummer, 1981).

The particulate emission rates of automobile engines operated with regular and premium leaded gasolines are very high. This particulate is dominated by lead compounds and the emission rates are considerably higher when the engine is cold, following start-up. Most of these particles are presumed to form and ground in the exhaust system due to vapour phase condensation enhanced by coagulation. Some of the particulates are emitted directly without settling. Some of the particles either form or are deposited on the walls where agglomeration may occur. Many of these are removed when the exhaust flow rate is suddenly increased and these particles together with rust and scale account for the increase in mass and size of particles emitted during acceleration.

Diesel particulates consist principally of combustion generated carbonaceous materials (soot) on which some organic compounds have become absorbed. Most particulate material results from incomplete combustion of hydrocarbon fuels and some are contributed by the lubricating oil.

## 3.1 Specific Emission and Emission Index

### 3.1.1 Specific Emission

The concentrations of gaseous emissions in the engine exhaust gases are usually measured with normalised indicators in parts per million or percentage by volume. Specific emission is the mass flow rate of pollutant per power output (g/kW.h).

$$sNO_x = \frac{m_{NO_x}}{P} \qquad (10)$$

Similarly,

$$sCO = \frac{m_{CO}}{P}$$

$$sH_xC_YO = \frac{m_{C_X O_Y}}{P} \qquad \text{and}$$

$$sPart = \frac{m_{Part}}{P}$$

Where; P is the power output and $m_{NOx}$, $m_{CO}$, $m_{HxCy}$ and $m_{Part}$ are mass flow rate of oxides of nitrogen, carbon-monoxide, hydrocarbons and particulate respectively.

### 3.1.2 Emission Index

When emission rates can be normalised by the fuel flow rate, the rating is measured in terms of emission index (EI):
For oxides of nitrogen ($NO_x$),

$$EI_{NO_x} = \frac{m_{NO_x}\,(g/s)}{m_f\,(kg/s)} \qquad (11)$$

Similarly, expressions can be obtained for CO, $H_xC_y$ and particulate.

## 4.0 AUTOMOBILE POLLUTANT CONTROL

The emission of pollutants from automobile can be controlled by incorporating devices that will remove pollutants from the exhaust gases in the engine exhaust system. These devices are catalytic converters and particulate traps or filters.
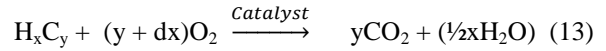
## 4.1 Catalytic Converters

Metal casing can be specially designed to contain an active catalytic material which will directs the exhaust gas flow through the catalyst bed. Oxidising catalysts can be employed to remove CO and $H_xC_y$ from exhaust gases, while reducing catalysts can be employed to remove nitric oxide (NO). The active materials that can be used for oxidation or reduction are noble metals or base metals' oxides. This must be distributed over a large surface area so that the mass transfer characteristic between the gas phase and the active catalyst surface will be sufficient to allow close to 100 % conversion with high catalyst activity.

### 4.1.1 Oxidation Catalysts

The function of oxidation catalyst is to oxidise CO and hydrocarbons ($H_xC_y$) to $CO_2$ and water in an exhaust gas stream (Eqns. 12 and 13). The saturated hydrocarbons are the most difficult to oxidise. The ease of oxidation increases with increasing molecular weight. Sufficient oxygen must be present to oxidise the CO and $H_xC_y$. This may be supplied by the engine itself running with weak air/fuel mixture (excess air) or with a pump that introduces air into the exhaust parts just downstream of the valve. Venturi air addition into the exhaust port using the pressure pulsation generated by the exhaust process can also be used to add the required air.

$$CO + \tfrac{1}{2}O_2 \xrightarrow{Catalyst} CO_2 \qquad (12)$$

$$H_xC_y + (y + dx)O_2 \xrightarrow{Catalyst} yCO_2 + (\tfrac{1}{2}xH_2O) \quad (13)$$

For $H_xC_y$ oxidation, noble metals are most suitable as the catalytic material, they are more thermally resistant to loss of low-temperature activity and are much less deactivated by the sulphur in the fuel than base metal oxides. Mixtures of platinum (Pt) and palladium (Pd) are the most noble metals that are commonly used. The conversion efficiency of a catalyst is the ratio of the rate of mass removal in the catalyst of the particular constituent of interest to the mass flow rate of that constituent into the catalyst.
For $H_xC_y$,

$$\frac{m_{H_xC_y,in} - m_{H_xC_y,out}}{m_{H_xC_y,in}} = 1 - \frac{m_{H_xC_y,out}}{m_{H_xC_y,in}} \qquad (14)$$

### 4.1.2 Reduction Catalysts

Nitric oxide (NO) is removed by reduction using the CO, hydrocarbons, and $H_z$ in the exhaust. The possible NO reactions under reducing conditions are:

(i) $NO + CO \rightarrow \tfrac{1}{2}N_2 + CO_2$

(ii) $2NO + 5CO + 3H_2O \rightarrow 2NH_3 + 5CO_2$

(iii) $2NO + CO \rightarrow N_2O + CO_2$

(iv) $NO + H_2 \rightarrow \tfrac{1}{2}N_2 + H_2O$

(v) $2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O$

(v) $2NO + H_2 \rightarrow N_2O + H_2O$

The catalyst used under these conditions is referred to as NO reduction catalyst. Reduction of NO by CO or $H_2$ can be accomplished by base metal catalysts e.g., CuO and NiO.

### 4.1.3 Three-Way Catalysts

If an engine is operated at all times with an air/fuel ratio at or close to stoichiometric, then both NO reduction, and CO and $H_xC_y$ oxidation can be done in a single catalyst bed. The catalyst effectively brings the exhaust gas composition to a near-equilibrium state at these exhaust conditions; that is, a composition of $CO_2$, $H_2O$ and $N_2$. Enough reducing gases will be present to reduce NO and enough $O_2$ to oxidise the CO and hydrocarbons. Such a catalyst is called a three-way catalyst since it removes all three pollutants simultaneously.

### 4.2 Particulate Traps

An exhaust treatment technology that substantially reduces automobile engine particulate emissions is the trap oxidiser. The filter of trap first removes the particulate materials from the exhaust gas and then the filter is cleaned off by oxidising the accumulated particulate. Types of particulate filters that can be used include ceramic monoliths, alumina-coated wire mesh, ceramic foam, ceramic fibre mat and woven silica-fibre rope wound on a porous tube.

Each of these filters has different inherent pressure loss and filtering efficiency. Regeneration of the trap by burning up the filtered particulate material can be accomplished by raising its temperature to the ignition point while providing oxygen-containing exhaust gas to support combustion and carry away the heat released. The particulate oxidation rate depends on the trap temperature. With suitable trap location and design, the regeneration process can be self-regulating and the particulate emissions from the engine can be reduced by 70 % or more.

### 5.0 CONCLUSION

The living environment is a cornerstone for good health, and as such every appropriate investment to the environment should bring about improvement to people's health. The major problem that the people in the urban cities are facing today is environmental pollution due to gaseous emittance from automobile engines. The automobile exhaust gases contain oxides of nitrogen, carbon monoxide, unburned or partially burned hydrocarbons and particulate. For proper determination of emission levels, the detailed chemical processes of pollutant formation with the methods of obtaining the specific emission and emission index were analysed in this paper. The emission of air pollutants from automobile engine is controlled by incorporating catalytic converter device in the engine exhaust system. Oxidising catalysts remove carbon monoxide and hydrocarbons from exhaust gases, reducing catalysts remove nitric oxide while the three-way catalysts remove all the common pollutants except the particulate materials. The various particulate emissions from automobile engine such as lead, organic particulate (soot) and sulphates are removed from the exhaust gas by filtering through particulate filter or traps oxidiser in the engine exhaust system.

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