DIESEL CATALYTIC CONVERTERS AS EMISSION CONTROL DEVICES

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1. INTRODUCTION:

Internal combustion engines are devices that generate work from combustion reactions. Combustion products under high pressure produce work by expansion through a turbine or piston. The combustion reactions inside these engines are not necessarily neutralizing or complete and air pollutants are produced.

There are three major types of internal combustion engine[(1)] in use today: 1) the spark ignition engine, which is used primarily in automobiles; 2) the diesel engine, which is used in large vehicles and industrial systems where cycle efficiency offers advantages over the more compact and lighter-weight spark ignition engine and; 3) the gas turbine, which is used in aircraft due to its high power/weight ratio and is also used for stationary power generation.

Each of these types of engine is an important source of atmospheric pollutants. Automobiles are the one of the major source of carbon monoxide, unburned hydrocarbons, and nitrogen oxides. Probably more than any other combustion system, the design of automobile engines is now being guided by requirements to reduce emissions of these pollutants. While substantial progress has been made in emission reduction, automobiles remain important sources of air pollutants.

In order to reduce emissions, modern cars have been designed to carefully control the amount of fuel they burn. The goal is to keep the air-to-fuel ratio very close to the "stoichiometric" point, which is the calculated ideal ratio of air to fuel. Theoretically, at this ratio, all of the fuel will be burned using all of the oxygen in the air. [The stoichiometric ratio is about 14.7 to 1, meaning that for each Kilogram of fuel, 14.7 Kilogram of air will be burned. The fuel mixture actually varies from the ideal ratio quite a bit during driving. Sometimes the mixture can be "lean" (an air-to-fuel ratio higher than 14.7); and other times the mixture can be "rich" (an air-to-fuel ratio lower than 14.7).]

2. THE EMISSIONS OF A VEHICLE ENGINE ARE:

- **2.1. Nitrogen gas:** Air is 78 percent nitrogen gas, and most of this passes right through the car engine.
- **2.2. Carbon Dioxide:** This is one product of combustion. The carbon in the fuel bonds with the oxygen in the air.
- **2.3. Water vapor:** This is another product of combustion. The hydrogen in the fuel bonds with the oxygen in the air.

These emissions are mostly benign (although carbon dioxide emissions are believed to contribute to global warming), however because the combustion process is never perfect, some smaller amounts of more **harmful emissions** are also produced in car engines:

- **2.4. Carbon monoxide:** A poisonous gas that is colorless and odorless.
- **2.5. Hydrocarbons or volatile organic compounds (VOC's):** Produced mostly from unburned fuel that evaporates. Sunlight breaks these down to form oxidants, which react with oxides of nitrogen to cause ground level ozone, a major component of pollution.
- **2.6. Oxides of nitrogen:** Contributes to smog and acid rain, and also causes irritation to human mucus membranes.

3. CONTROLLING DIESEL VEHICLES EMISSIONS:

Five approaches([2]) have been used in the world to control emissions from diesel vehicles.

3.1. Clean Engine: The most widely used one is the so-called "clean" engine which uses exhaust gas recirculation (EGR), precise control of diesel to air ratio, turbo charging and other modifications. But changing an engine is an expensive option for an old vehicle.

3.2. Engine Coating: The second option is to coat the internal walls of the old cylinders with a catalytic material so that HC and CO are oxidized (or minimized). But the cost of this treatment is also high and it requires that the sulfur level of diesel be less than 100 ppm.

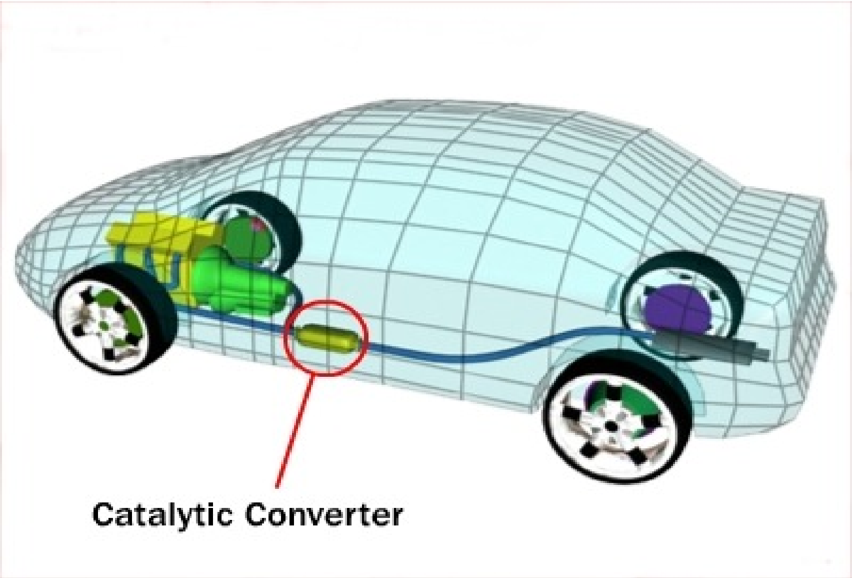
3.3. Catalytic Converters: Two-way catalytic converters have been used. For most such converters the sulfur level has to be less than 100 ppm. In some European countries, 3-way catalytic converters are used. The cost of these systems is roughly 4 times that of a 2-way converter([2]). These require that the sulfur level of diesel be less than 50 ppm.

3.4. Diesel Particulate Filter (DPF): Catalytic converters in combination with DPFs have also been used. The DPF is made of fiberglass or ceramic. The PM is burned off either on line or off line using electric heaters or by running the engine. Again, all of the DPF suppliers require that the sulfur level be less than 100 ppm.

3.5. CNG Engine: Converting the old diesel engine bus to use a new CNG engine seems to be the option of choice in some countries.

4. THE CATALYTIC CONVERTER:

From the chemical point of view, a catalyst is any substance able to accelerate a chemical reaction while maintaining its own structure. In the case of automobiles, the catalyst is a box, located between the gas collector of the motor and the muffler of exhaust tube. Exhaust gases are passed through the converter where an almost total degradation of exhaust smoke can be achieved by catalytic reactions over a hyperactive area made of platinum and rhodium. In spite of its modest volume, the active surface area inside a catalytic converter would cover two football fields ([3]).



Inside the motor, a piston pushes residual hot gases from the combustion chamber to the exhaust valve, and when these gases pass through the active areas inside the ceramic cells of the converter, two opposite chemical processes take place simultaneously: an oxidation reaction which converts hydrocarbons and carbon monoxide into carbon dioxide and water; and a reduction reaction of nitrogen oxides to produce pure nitrogen.

A catalytic converter[(4)] is a device that uses a catalyst to convert three harmful compounds in car exhaust into harmless compounds. The three harmful compounds are:

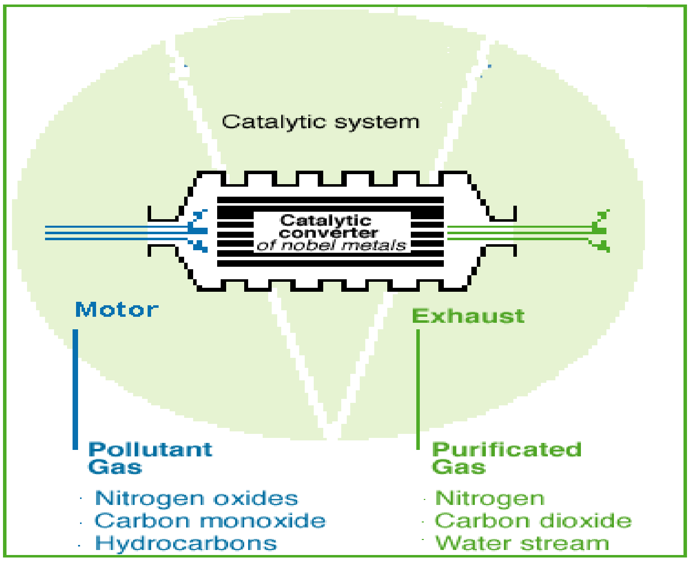
-Hydrocarbons - Carbon monoxide -Nitrogen oxides

Carbon monoxide is a poison for any air-breathing animal. Nitrogen oxides lead to smog and acid rain, and hydrocarbons produce smog.

In a catalytic converter, the *catalyst* (in the form of platinum and palladium) is coated onto a ceramic honeycomb or ceramic beads that are housed in a muffler-like package attached to the exhaust pipe. The catalyst helps to convert carbon monoxide into carbon dioxide. It converts the hydrocarbons into carbon dioxide and water. It also converts the nitrogen oxides back into nitrogen and oxygen.

5. <u>THE CATALYTIC CONVERTER SYSTEMS</u>: [(5)]

As the internal combustion engine utilizes the exhaust stroke to expel the 'spent' gases via the exhaust system, the harmful emissions are passed through a special muffler type looking device called a catalytic Converter. After the emissions have passed through the Converter they are passed through the rest of the exhaust system in the conventional manner and finally to atmosphere. The catalytic converter's purpose is to reduce the original harmful emissions to negligible levels by means of catalyst controlled chemical reactions. Within the structure of the catalytic Converter is a form utilizing a catalyst.



5.1.Catalytic conversion is a *three stage process:* ([6])

1. **The Reduction Catalyst:**

   This stage consist of reducing the emissions of nitrogen oxides by using platinum and rhodium.

2. **The Oxidation Catalyst:**

   The second stage of the process reduces the unburned hydrocarbons and carbon monoxide by burning them over a platinum and palladium catalyst.

3. **The Control System:**

   The control system basically monitors the exhaust stream and takes this information to control the fuel injection system. To do this, the catalytic converter is equipped with an oxygen sensor that tells the engine's computer how much oxygen is in the exhaust. This allows the engine's computer to make sure that there is enough oxygen in the exhaust to allow the oxidization catalyst to burn the unburned hydrocarbons and CO.

6. COMPONENTS OF THE CATALYTIC CONVERTER([7]):

There are three main components of the Catalytic Converter:

- The Monolith (also known as the substrate), a ceramic or metal structure constructed like a honeycomb, through which exhaust gases pass.
- Washcoat, porous ceramic sponge-like coatings applied in a thin layer to the monolith that multiplies the surface area to that of approximately two football pitches, over which the catalytic metals can be deposited.
- The Catalyst, normally consisting of a mixture of Platinum and Rhodium although Palladium is also used. They carry out the chemical reactions that purify the exhaust.

7. THE CATALYTIC CONVERTER OPERATES UNDER THE FOLLOWING CONDITIONS ([7]):

7.a. Working Temperature:

The catalyst starts operating once the monolith has attained a temperature of 250-270 ºC, the temperature (commonly known as light-off) which a car will normally reach from cold start within a few seconds. Under normal operating conditions the catalyst maintains a temperature of between 400-600 ^{o}C. To work most effectively, a catalytic converter needs to reach an optimum temperature. It may not reach this in a short journey. Devises to pre-warm the catalyst are being developed which improve the overall performance of catalytic converters.

7.b. Stoichiometric Ratio:

And for the catalyst to function properly, the engine must burn an ideal mixture of air and fuel (about 14.7:1 depending on the quality of the fuel).
There is a control system mounted upstream of the catalytic converter, meaning it is closer to the engine than the converter. It monitors the exhaust stream. It has a sensor that tells the engine computer how much oxygen is in the exhaust. The engine computer can increase or decrease the amount of oxygen in the exhaust by adjusting the air to fuel ratio. This control scheme allows the engine computer to make sure that the engine is running at close to the *stoichiometric point (14.7:1),* and also to make sure that there is enough oxygen in the exhaust to allow the oxidization catalyst to burn the unburned hydrocarbons and CO.

7.c. Amount of catalysts used:

Platinum or Palladium accelerate the oxidation of hydrocarbons and carbon monoxide, while Rhodium reduces the oxides of nitrogen. As a general rule there are only between 1-2 grams of precious metals in every catalytic converter. The idea is to create a structure that exposes the maximum surface area of catalyst to the exhaust stream, while also minimizing the amount of catalyst required (they are very expensive).

7.d. Reactions in a Catalytic Converter:

It is not precisely understood how platinum and rhodium work as catalysts but technically, the catalytic converter's action involves two types of reactions: - Oxidation Reaction. - Reduction Reaction.

1.Oxidation Reaction: In a Catalytic Converter unburned hydrocarbons are oxidized to water and carbon dioxide.

2.Reduction Reaction: nitrogen oxides are reduced back into nitrogen, the major component of air. The catalyst in this chamber makes this possible. The converter uses two different types of catalysts, a reduction catalyst and an oxidation catalyst.

The Reduction Catalyst:

The reduction catalyst uses Platinum and Rhodium to help reduce the NOx emissions. When an NO or NO2 molecule contacts the catalyst, the catalyst rips the nitrogen atom out of the molecule and holds on to it, freeing the oxygen in the form of O2. The nitrogen atoms bond with other nitrogen atoms that are also stuck to the catalyst, forming N2.

For example: $2NO \Rightarrow N_2 + O_2$ or $2NO_2 \Rightarrow N_2 + 2O_2$

The Oxidation Catalyst:

The oxidation catalyst uses Platinum and Palladium to reduce the unburned hydrocarbons and carbon monoxide by burning (oxidizing) them over a catalyst. This catalyst aids the reaction of the CO and hydrocarbons with the remaining oxygen in the exhaust gas.

For example: $2CO + O_2 \Rightarrow 2CO_2$

8. THE CATALYTIC CONVERTERS TYPES ([8]):

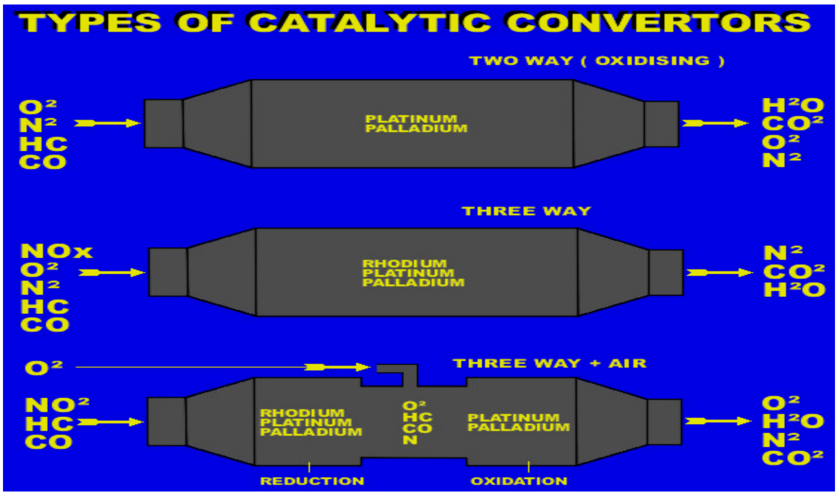
There are three basic types of automotive catalytic converters;

-Two-Way

-Three-Way

and

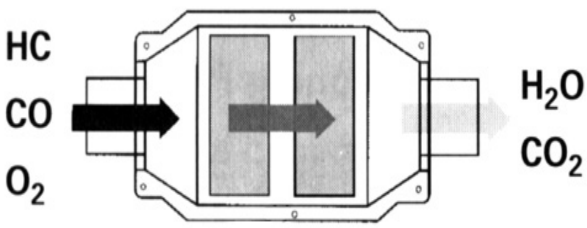
- Three-Way + Air.



Each type uses a slightly different method and chemistry to reduce the harmful elements in exhaust emissions. Early model converters used a palletized catalyst, but most modern converters are now designed with a free-flowing honeycomb ceramic catalyst. The type of converter required on a particular vehicle varies with model year, engine size and vehicle weight. Some vehicles even make use of more than one type of converter or a pre-converter to meet emission reduction standards.

8.1. Two-Way Oxidation Converter([9]):

A Two-Way converter, used on cars between 1975 - 1980, oxidizes unburned harmful hydrocarbons and carbon monoxide into water and carbon dioxide.

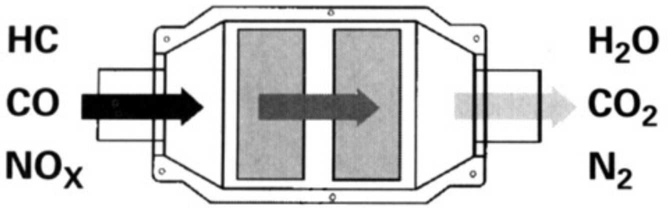


HC, CO oxidizes to H_20 and CO_2

The first vehicles with catalytic converters had Two-Way Oxidation capabilities only.

8.2. Three-Way Reduction/Oxidation Converter(9):

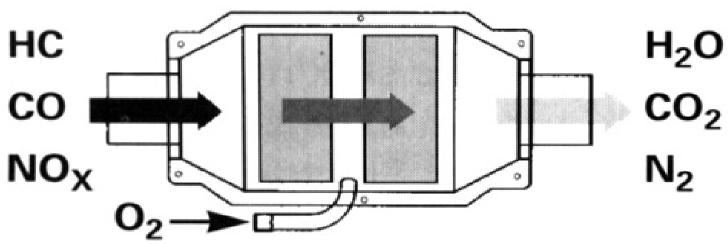
A Three-Way converter is a triple purpose converter. It reduces nitrous oxides into nitrogen and oxygen. And, like the two-way converter, it also oxidizes unburned harmful hydrocarbons and carbon monoxide into water and carbon dioxide. "Three-way" refers to the three regulated emissions it helps to reduce carbon monoxide, VOCs and NOx molecules.



CO oxidizes to H_20 and CO_2
NO_X reduces to N_2

8. 3. Three-Way + Air Reduction/Oxidation Converter(9):

A Three-Way + Air converter performs the same functions as the Three-Way converter. It oxidizes and reduces. The difference is the addition of secondary air between the two internal catalyst substrates that improves the oxidation capabilities of the converter. The secondary air is pumped into the middle of the converter between two separate catalyst coated ceramic substrates. The front ceramic performs the reduction and the back ceramic performs the oxidation.



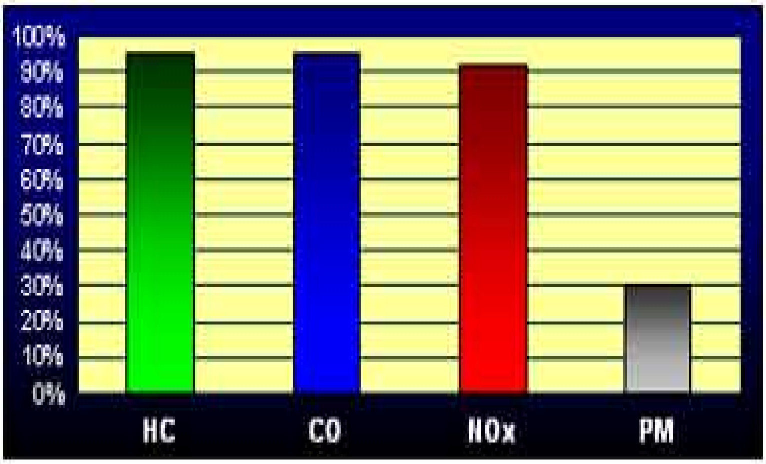
HC, CO oxidizes to H_20 and CO_2
NO_X reduces to N_2

8.4.Pre-Converter and Main Converter(9):

Each of the three types of converters mentioned above have a common need in order to function properly. Each needs to reach a minimum operating temperature before any emissions reduction or oxidation takes place. This warm-up period immediately after a vehicle is started is when the catalytic converter is least efficient and the vehicle expels the most pollutants. Some vehicles employ a pre-converter in the exhaust system immediately after the manifold to help during this warm-up period. The pre-converter's small size and proximity to the engine allow it to heat up and start functioning in less time than the main converter. It also preheats the exhaust gasses and helps the main converter reach operating temperature sooner.

9. EMISSIONS REDUCTION DUE TO USING DIESEL CATALYTIC CONVERTER:

The purpose of catalytic converters is to convert harmful hydrocarbons, carbon monoxide, and nitrogen oxides into harmless compounds. The average efficiency for some chemical reactions under ideal conditions can be read from the following table [10]:

Chemical reactions	Average reduction of polluting emissions at 450^o(C)	
$HC + O_2 \xrightarrow{Oxidation} H_2O + CO_2$	up to 95%	
$CO + O_2 \xrightarrow{Oxidation} CO_2$	up to 95%	
$NO_x \xrightarrow{Reduction} N_2 + O_2$	up to 92%	
$SO_x \xrightarrow{Reduction} S + O_2$	N.A.	
$C(PM) + O_2 \xrightarrow{Oxidation} CO_2$	up to 30%	

ref. Shanghai Chuangyi Environmental Technology Co., Ltd

10. DIESEL CATALYTIC CONVERTER EFFICIENCY TEST RESULTS ([11]):

The following table illustrates the results obtained in Misr petroleum search center from testing Nasr 190 diesel motor, with capacity 9572 cm3 , six cylinders (v) type, direct injection

distance Km	CO % before catalytic	CO % after converter	HC (ppm) before catalytic	HC (ppm) after converter	Catalytic converter efficiency[1] before catalytic	Catalytic converter efficiency[1] after converter
1000	3.86	0.25	550	41	93.5%	92.5%
2000	3.64	0.23	518	38	93.7%	92.7%
3000	3.91	0.26	580	45	93.4%	92.2%
4000	4.15	0.31	610	52	92.5%	91.5%
5000	4.4	0.33	590	52	92.5%	91.2%
6000	4.38	0.33	670	58	92.5%	91.3%
7000	4.51	0.37	700	63	91.8%	91.0%
8000	4.63	0.38	720	66	91.8%	90.8%
9000	4.6	0.39	780	70	91.5%	91.0%
10000	4.62	0.39	780	72	91.6%	90.8%

(1) at 700 rpm after distance from 1000 to 10000 km
ref. technical report about testing diesel catalytic converter, Misr Petroleum Company, research center

11. REASONS FOR A CONVERTER FAILURE ([12]):

Catalytic Converters should not fail under normal vehicle operating conditions. There are no moving parts and the catalyst is never Used Up. The converter should last the life of the vehicle. However, several other components in the emission control system can fail or deteriorate with time and use. These failing components are often the cause of a catalytic converter failure. Early detection of these components will reduce the risk of a failure.

11.1. Engine Tune-Up Required:

A number of problems could occur to the catalytic converter as the result of an engine that is out of tune. Any time an engine is operating outside proper specifications, unnecessary wear and damage may be caused to the catalytic converter as well as the engine itself. The damage is often the result of an incorrect air/fuel mixture, incorrect timing, or misfiring spark plugs. Any of these conditions could lead to a catalytic converter failure or worse.

11.2. Excess Fuel Entering Exhaust:

The fuel that powers your vehicle is meant to burn in the combustion chamber only. Any fuel that leaves the combustion chamber unburned will enter the exhaust system and light-off when it reaches the catalytic converter. This can super-heat the converter far above normal operating conditions and cause a Melt Down. Possible causes are an incorrect fuel mixture, incorrect timing, corroded spark plugs, a faulty oxygen sensor, sticking float, faulty fuel injector or a malfunctioning check valve.

11.3. Deteriorated Spark Plug or Spark Plug Wires:

Spark plugs that don't fire or misfire cause unburned fuel to enter the exhaust system. The unburned fuel ignites inside the converter and could result in a partial or complete melt down of the ceramic catalyst. Spark plugs and spark plug wires should be checked regularly and replaced if damaged or if wires are worn or cracked.

11.4. Oxygen Sensor Not Functioning Properly:

An oxygen sensor failure can lead to incorrect readings of exhaust gasses. The faulty sensor can cause a too rich or too lean condition. Too rich and the catalyst can melt down. Too lean and the converter is unable to convert the hydrocarbons into safe elements and may not pass a state inspection.

11.5. Road Damage or Broken Hangers:

The ceramic catalyst inside a catalytic converter is made from a lightweight, thin-walled, fragile material. It is protected by a dense, insulating mat. This mat holds the catalyst in place and provides moderate protection against damage. However, rock or road debris s striking the converter or improper or broken exhaust system support can cause a Catalyst Fracture. Once the ceramic catalyst is fractured, the broken pieces become loose and rattle around and break up into smaller pieces. Flow is interrupted and backpressure in the exhaust system increases. This leads to heat build up and loss of power. Possible causes of a catalyst fracture are road debris striking the converter, loose or broken hangers, potholes or off-road driving.

12. WHY DIESEL CATALYTIC CONVERTERS IN EGYPT:

The total number of vehicles registered in Egypt has reached 3.3 million in mid 2003, of which about 1.52 million (46%) are running in the Governorates of Cairo, Kalyoubia and Giza, which together constitute the Cairo Metropolitan area.([13]).

The main features of the Egyptian vehicle population are outlined as follows:

- There are essentially no diesel-powered passenger cars , this is because they were prohibited for the public by law.
- Almost all trucks and buses are diesel powered.
- In order to satisfy the requirements for development process, it is expected that the number of trucks and buses powered by diesel will increase with higher growth rate in the near future.

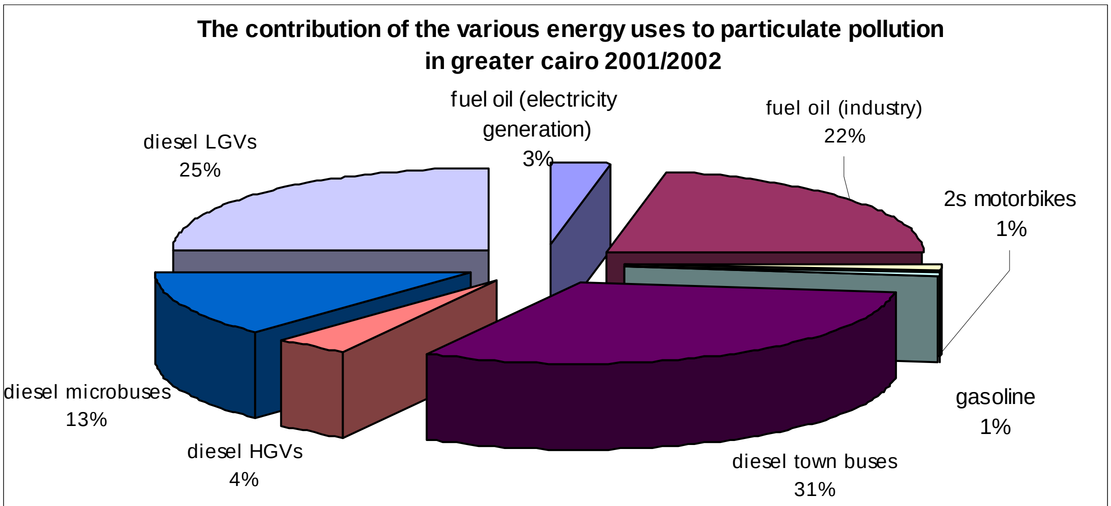
Most of diesel fuel consumption at Egypt is in the transportation sector. In 2003/2004, the gas oil & diesel consumed in the transportation sector represented about 58.7% of the total fuel consumed in that sector, while gasoline represented only about 20%

Emissions([14]) from transport in Greater Cairo (Tones/year)

Vehicles Type	PM10		SO2		Nox	
Diesel LGVs	7637	28%	6742	45%	3338	12%
Diesel HGVs	2996	11%	923	6%	2849	10%
Diesel Town Buses	10561	39%	3685	25%	2995	10%
Diesel Micro-Buses	4188	16%	1559	10%	1830	6%
All Gasoline	467	2%	2006	13%	17963	62%
2s motorbikes	572	2%				
Non-fuel transport	410	2%				
Total transport emissions	26831	100%	14915	100%	28975	100%

ref. Ambient air quality status report, Egyptian environmental policy program, chemonics international, march 2004

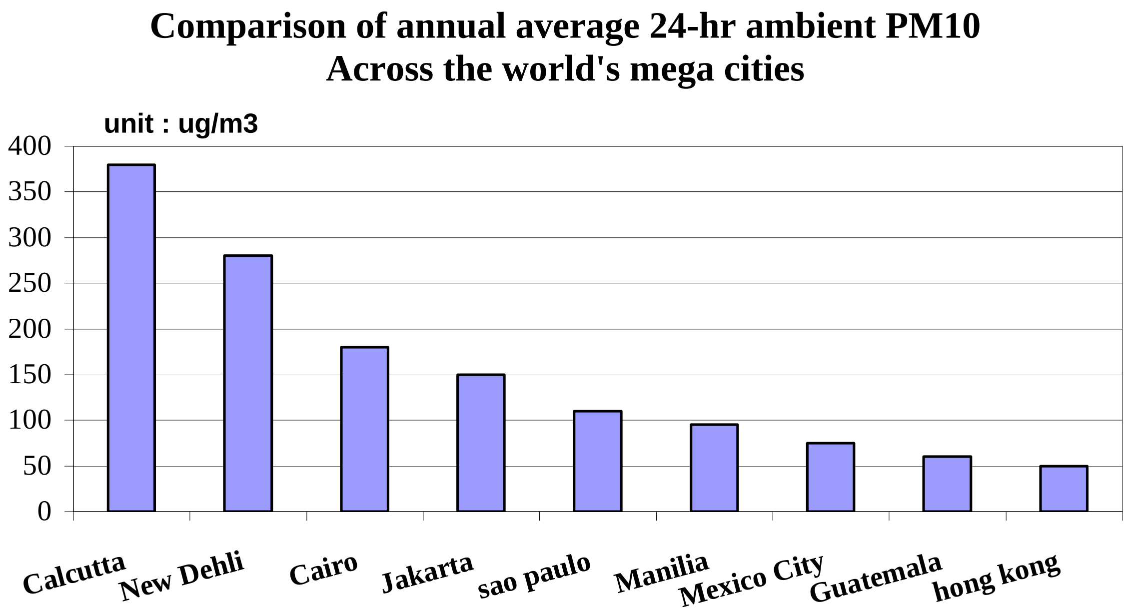
The combustion of diesel, often in old and poorly maintained vehicles, produces high PM_{10}emissions (carbon).



ref. :proposed components for the national air quality strategy framework, Egyptian environmental policy program, Chemonics, Egypt, march 2004.

Emissions from diesel fuel combustion contributes to approximately 22% of the particulate pollution load suffered by Greater Cairo([15]); approximately half of which comes from light goods vehicles and microbuses.

Geographical comparison of air pollution is always difficult to make; individual city results depend on the positioning of the monitoring stations, the quality control exercised and treatment of the data sets. All these extenuating circumstances need to be borne in mind when such a comparison is made. On the other hand comparing cities allow at least some "reality check" on the situation being considered.



The chart ([14]) indicates that the situation in Greater Cairo is very serious, annual average particulate values are greater than cities such as Jakarta, San Paulo, and Mexico city which are 'renown' for their air pollution problems.

13. <u>CONCLUSION</u>:

Emissions from diesel vehicles contribute to the low visibility over many parts of Egypt caused by particulates and by photochemical smog, the 'black smoke' incidents above Cairo in the autumn months provide a vivid illustration of the air pollution problem.

Air pollution causes damage, principally to human health. The number of cases of respiratory diseases such as bronchitis and asthma increase as air pollution levels increase; the populations' resistance to other diseases falls. Diseases reduce both the quality of life of the population and the productivity of the economy.

In order to solve air pollution problem, Egypt has had a number of major recent successes in reducing environmental impacts, including the widespread introduction of natural gas, the introduction of lead free gasoline to 95% of customers. There is no doubt that the introduction of using catalytic converters in diesel vehicles will aim to build on these successes.

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