

## CHAPTER I



## INTRODUCTION

Presently, the environmental problems are widely discussed by the people of many nationality. One of the most serious problems of their discussion, is the air pollution. The main sources of air pollutants are industrial factories and vehicles engines. In a big city, as Bangkok, the main environmental pollution is the pollutants emitted from car engines in use. These pollutants are the toxics which cause of the sickness, thus the concern organizations should find the means to control these pollutions.

Many countries, such as the United States, Canada, Germany, Switzerland and Sweden, have tackled this problem through the enforcement of various laws to control the level of pollutants as carbon monoxide (CO), hydrocarbons (HC) and nitrogen oxides (NO<sub>x</sub>) which vehicles can legally emit.

An uncontrolled gasoline-powered vehicle (i.e., one not equipped with an anti-pollution device) operated in a city area releases, on average, 55.0 g/km of carbon monoxide, 10.0 g/km of hydrocarbons and 2.5 g/km of nitrogen oxides. Compared with the amount of pollutants from other sources, CO in vehicle emissions is found to be 90% higher, HC 60-80% higher and NO<sub>x</sub> 60-75% higher (1).

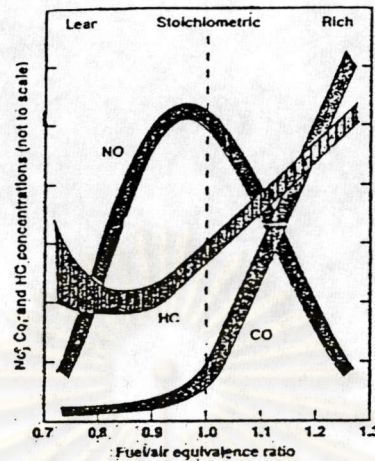


Carbon monoxide and hydrocarbons produced during the combustion process are exhausted in varying amounts depending on the air-fuel ratios of combustible mixture supplies.

The hydrocarbon level is found to be lowest when the air-fuel ratio (A/F ratio) is closest to the Stoichiometric A/F ratio, which is theoretically the best for attaining complete combustion. The HC level increases when the A/F ratio is below the Stoichiometric A/F ratio (which means the mixture is "rich" or has a high fuel proportion). The CO level is lowest when the A/F ratio is higher than the Stoichiometric A/F ratio (i.e., the mixture is "lean" or has a lower fuel proportion). The CO level increases when the A/F ratio is below the Stoichiometric A/F ratio. The chemical reaction between nitrogen and oxygen which produces  $\text{NO}_x$  occurs only when the temperature during combustion rises above  $1650^\circ\text{C}$ . The higher the temperature, the greater the production of nitrogen oxides. The amount of nitrogen oxides can be reduced by lowering the peak temperature during combustion, but this would have a negative effect on the engine's thermal efficiency.

The amount of CO, HC and  $\text{NO}_x$  exhausted by an average gasoline engine at different fuel-air equivalence ratios are shown in Figure 1.1.





**Figure 1.1 Relationship between the amount of CO, HC and NO<sub>x</sub> at different fuel-air equivalence ratios.**

**(The fuel-air equivalence ratio compares the Stoichiometric A/F ratio with the actual A/F ratio. A fuel-air equivalence ratio of less than 1 indicates a lean unburned mixture.)**

The most pressing problem faced by the automobile industry is how to keep pollutant exhaust gas levels below legal limits while also ensuring the lowest-possible rate of fuel consumption. There are three principal methods currently used in meeting the legal restrictions on pollutants in emissions: (1) developing a better combustion system; (2) choosing suitable operating parameters ; and (3) installing an anti-pollution device in the exhaust system.

An anti-pollution device installed in the exhaust system is commonly known as a "catalytic converter". Details of the device's design and instructions on its use are given below.



## Catalytic Converter

The catalytic converter is a metal box installed between the exhaust manifold and the muffler. The converter contains one or a mixture of catalytic substances such as platinum, palladium and rhodium known collectively as "Platinum Group Metal" (PGM).

A thin PGM coating is applied to a substance which served as a substrate. This substrate and the interior surface of the converter are both porous. As exhaust gases pass through the converter, the PGM substance causes a chemical activity which quickens the oxidation and reduction processes. These convert carbon monoxide (CO) and hydrocarbons (HC) into carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O) (respectively). Nitrogen oxides (NO<sub>x</sub>), meanwhile, react with CO and change into CO<sub>2</sub> and N<sub>2</sub> (or nitrogen with twin-atom molecules). NO<sub>x</sub> also react with HC to produce CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>O.

Catalytic converters are divided into the "pellet" (Figure 1.2) and "monolith" (Figure 1.3) types, which differ in their internal structures. The pellet type consists of a stainless steel box containing a large number of ceramic pellets, each of which has a diameter of about 3 mm and is coated with PGM about 0.25 mm thick. To increase the efficiency of this type of converter, the pellets can be coated with a porous substance such as alumina before the PGM is applied. These pellets are highly resistant to friction and high temperatures (up to about 1000 °C).



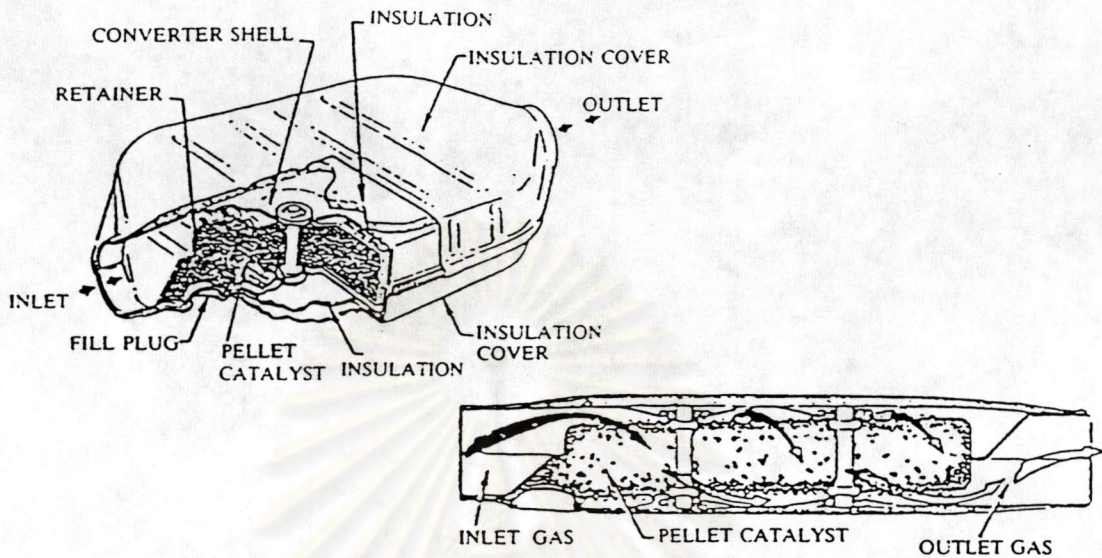


Figure 1.2 Pellet catalytic converter

CERAMIC MONOLITH CATALYTIC CONVERTER

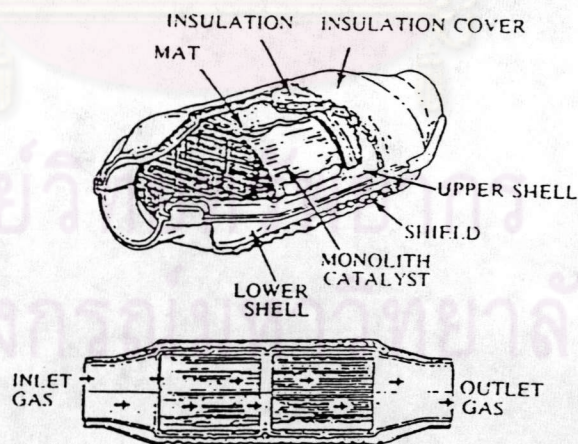


Figure 1.3 Monolith catalytic converter



The monolith type, on the other hand, is a stainless steel box whose inside surface is a ceramic honeycomb with about 30-60 tiny openings per square centimetre. These openings, which allow exhaust gases to pass through, are coated first with porous alumina and topped with PGM.

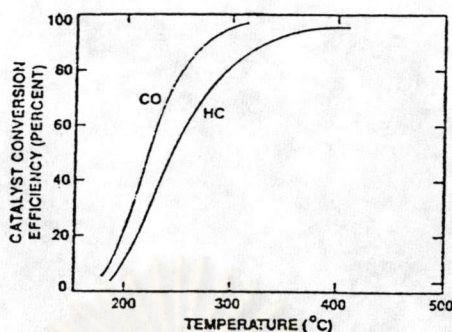
The monolith type is currently most popular in the United States, Europe and Japan. The pellet type of converter is no longer used in new cars manufactured in Europe, but can still be found in the United States and Japan.

### **Oxidation Catalyst Converter**

The oxidation catalyst converter relies on the oxidation process to convert CO and HC in exhaust fumes into CO<sub>2</sub> and H<sub>2</sub>O and so involves some O<sub>2</sub> (oxygen with twin-atom molecules). The necessary amount of O<sub>2</sub> can be obtained by controlling the engine so it operates using a lean fuel mixture, or by pumping air into the exhaust system above the converter using an air pump powered by the engine itself.

PGM substances used in the oxidation catalyst converter are usually a mixture of platinum and palladium. These catalytic substances work best at high temperatures (Figure 1.4). It has been discovered that a converter's efficiency is more than halved if its temperature remains below 230-235 °C. To achieve maximum levels of conversion efficiency without seriously affecting the device's life span, its working temperature should range from 400-800 °C, but should not exceed 850 °C. A rise to 950 °C is also acceptable, but must be for a brief period.





**Figure 1.4 Shows the correlation between the conversion efficiency and temperature**

As one of the first types of converter introduced in the early 1970s, the oxidation catalyst converter is not designed to handle  $\text{NO}_x$  in emissions as the controls at the time on nitrogen oxides were less severe than today. The method then employed to reduce  $\text{NO}_x$  was to lower temperatures during combustion by a process known as exhaust gas recirculation or EGR, which was quiet effective in controlling the level of  $\text{NO}_x$  in emissions.

### **Reduction and Oxidation Catalyst Converter**

As restrictions on pollutant exhaust gases, especially  $\text{NO}_x$ , grew more severe, it became harder and harder to continue using the usual method of combining the oxidation catalyst converter with the EGR system. (In the United States, for example, it was decided in 1982 to limit the level of  $\text{NO}_x$  in emissions at no more than 1.0 gramme/mile). Attempts to increase the quantity of recirculated exhaust gas in unburned mixtures to meet this requirement proved unsuccessful as they caused serious engine vibrations and increased the rate of fuel consumption. This led to serious efforts to develop a new type of



converter which could handle all three pollutant exhaust gases, and thus the dual-bed catalyst and the three-way catalyst converters.

### Conditions for Effective Use

Catalytic converters work well at temperatures above 250 °C. The ideal range is from 400-800 °C for the device to work most effectively without too much self-damage. Temperatures of between 800-1000 °C will cause the PGM and alumina coatings to suffer from thermal degradation, so high temperatures will seriously affect the device's usability. Engine malfunctions, such as misfiring when the spark plug fails to ignite the fuel mixture at the proper time and causes an explosion in the exhaust system, can also cause exhaust gas temperatures to rise above 1400 °C, which will destroy the converter by melting its substrate. It is therefore very important that vehicles equipped with catalytic converters have high-precision and durable ignition systems such as the electronic ignition type.

Another thing which shortens the converter's life is "poisoning". This occurs when octane-raising additives in gasoline such as tetraethyl lead or TEL are burnt and produce lead bromide or lead chloride which accumulates and clogs up the converter's porous surface. This prevents the PGM coating from coming into contact with CO, HC and NO<sub>x</sub> in emissions and so affects the device's ability to convert them through the reduction and oxidation processes. That is why vehicles equipped with catalytic converters should use unleaded gasoline only. Sulphur in gasoline and phosphorus in lubricants can also "poison" the converter.

Finally, the converter's efficiency will decrease gradually with use, with the rate of deterioration depending largely on the user. Precautions must be taken to ensure the converters is not used in conjunction with leaded gasoline.



Even when only unleaded gasoline is used, the converter's efficiency can still be affected by phosphorus and sulphur, though less seriously and at a slower rate than by lead compounds. (US regulations fix the converter's average life span at above five years or 80,000 kilometres.)

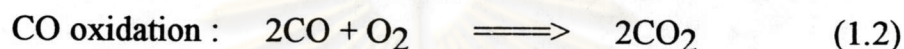
Efforts continue to improve catalytic converter technology since environmental issues have become global concerns of much greater gravity than in the past. Many countries, which to date still lack the legislation to control levels of pollutant gases in emissions, are following the examples of the United States, Japan and some European countries in tackling the problem. Manufacturers are also working hard to develop more efficient devices to meet the most demanding restrictions on pollutants in emissions.

### **Advantages and Disadvantages of PGM**

The activity of the catalysts used for automotive pollution control is based on that of the noble metals Pt, Rh and Pd (2). These noble metal catalysts are very active and fairly resistant to the sulphur present in the exhaust gas. There are, however, also some obvious disadvantages in the use of noble metal catalysts; they are relatively scarce and therefore expensive, they require a strict air/fuel ratio control, and because of the low amounts of metal present they are relatively sensitive to impurities. Mainly because of these disadvantages, so we should focus on the development of non-noble metal alternatives. In the early years of exhaust gas catalysis research, base metals were recognized as promising active components for catalysts, especially, combinations of Cu and Cr were found to be very active (3,4,5). Forced by the pace of the evolution of the legislation, the attention was focussed on the noble metals, leaving the base metal catalysts underdeveloped. The last decade shows a renewed interest in the possibilities of base metal catalysts (6,7,8). Previous



research at our laboratory on carbon-supported catalysts showed that catalysts based on the combination Cu and Cr have an activity comparable to that of noble metal catalysts. Both for the oxidation and the reduction reactions required (6). The performance of alumina-supported catalysts has been tested in two, for the catalytic purification of exhaust gases, important reactions:



These reactions have been carried out both separately and simultaneously. A range of catalysts with varying Cu/Cr-ratio has also been tested in the reaction system containing NO, CO, and O<sub>2</sub>. Special attention has been given to the thermal stability of differently pretreated catalysts.

On the basis of the results with alumina-supported catalysts, also a monolith-supported catalyst has been prepared. These monoliths contained a Zr-stabilized alumina washcoat and were loaded with active phase resulting in a 10 wt% loading of the washcoat. These monoliths have also been tested on "bench-scale" at the research laboratory of P.S.A. France for simultaneous NO reduction, CO and HC oxidation, both under stationary and oscillating feed conditions (9).

Gerald J. Barnes (10) studied about comparison of platinum and base metal oxidation catalysts thus: The activities of fresh, supported platinum and base metal oxidation catalysts are evaluated in vehicle tests. Two catalysts of each type were tested by the 1975 FTP in four 600 - 4300 cm<sup>3</sup> catalytic converters installed on a vehicle equipped with exhaust manifold air injection. As converter size decreased, base metal conversions of HC and CO decreased



monotonically. In contrast, the platinum catalysts maintained very high 1975 FTP CO conversions (>90% ) at all converter size; HC conversions remained constant (70%) at volumes down to 1300 cm<sup>3</sup>. Performance of the base metal catalysts with the 4300 cm<sup>3</sup> converter nearly equalled that of the platinum catalysts. However, platinum catalysts have a reserve activity with very high conversions attained at the smallest converter volumes, which makes them more tolerant of thermal and contaminant degradation. It shows that leading other metals replace platinum in the oxidation reaction. And the result is nearly equalled that of the platinum catalyst.

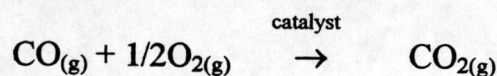
## Objective and Scope of the Research

### 1. Objective

The principle objective of this research was to compare the catalytic activity of transition metal oxides catalysts, tricobalt tetraoxide (Co<sub>3</sub>O<sub>4</sub>), ferric oxide (Fe<sub>2</sub>O<sub>3</sub>), trimanganese tetraoxide (Mn<sub>3</sub>O<sub>4</sub>) and chromic oxide (Cr<sub>2</sub>O<sub>3</sub>), in the oxidation reaction of carbon monoxide (CO) that is oxidized to carbon dioxide (CO<sub>2</sub>) with oxygen (O<sub>2</sub>) and nitrous oxide (N<sub>2</sub>O).

### 2. Scope of the Research

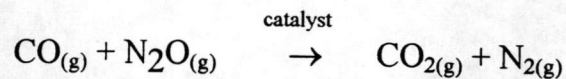
1. To study the catalytic activity of the transition metal oxide catalysts in the oxidation reaction of CO with O<sub>2</sub>.



The catalysts used in this reaction are Co<sub>3</sub>O<sub>4</sub>, Mn<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>, and Cr<sub>2</sub>O<sub>3</sub>.



2. To study the catalytic activity of the oxide catalysts in the oxidation reaction of CO with N<sub>2</sub>O.



The catalysts used in this reaction are Co<sub>3</sub>O<sub>4</sub>, Mn<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>, and Cr<sub>2</sub>O<sub>3</sub>.

3. To compare the catalytic activity between the oxidation reactions of CO and O<sub>2</sub>, and CO and N<sub>2</sub>O.



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