CHAPTER III

THEORY

The multitude of internal combustion engines has introduced environmental problems. Since they occur at ground level and cannot be vented through high chimneys as with waste gases or stationary sources such as power stations.

The main pollutants released by internal combustion engines are as follows (Paker, 1978) :

1. carbon monoxide
2. unburnt hydrocarbon
3. nitrogen oxides
4. sulfur oxides
5. lead compounds
6. smoke
7. particles

The internal combustion engine can be divided into two major types.

1. Otto Cycle (gasoline engine).
2. Diesel engine.

In this research the otto cycle was emphasized . Before considering the various methods of exhaust emission control, the chemical mechanisms which cause the pollutant compound will be described.

3.1 Mechanism of pollution formation in the petrol engine(Parker and Haslett, 1978).

Exhaust : The compounds released by the petrol engine which are termed pollutants are carbon monoxide, unburnt hydrocarbons, nitrogen

oxides, and particulates, and a small amount of sulfur oxides, carbon monoxide and unburnt hydrocarbons are the result of incomplete combustion of the fuel in the engine. Nitrogen oxides are formed during combustion, due to the high gas temperature. Lead compounds and sulfur oxides are also formed during combustion due to the inclusion of lead and sulfur in the fuel. Following the path of the air and petrol through an engine to see how these contaminants arrive in the exhaust. Air, composed mainly of oxygen and nitrogen, is drawn into the engine through the carburettor and throttle. The amount of air inhaled is controlled by the position of the throttle. There is a pressure drop across the throttle, being ambient on the carburettor side and some lower pressure, termed intake manifold pressure, in the pipes to each cylinder of the engine. The function of the carburettor is to add petrol to the air, such that the mass ratio of air inhaled to fuel is roughly constant. This content is about 14, though the ratio can fluctuate between 10 and 17 under some conditions. Petrol is compounded of a number of different hydrocarbons derived from hydrogen and carbon in various arrangements. This mixture of hydrocarbons is often simplified in description to the equivalent of a single average component, octene C_8H_{16}. During refining, various additives are mixed with the petrol, the principal one being tetraethyl lead(TEL). This is an anti-detonating compound which prevents the fuel from spontaneously exploding before it is ignited by the spark plug. It is an important additive as it allows a petrol engine to run at a higher compression ; ratio is raised, engine efficiency improves and the vehicle travels further on a litre of petrol. Additional additives are the scavengers, ethylene dibromide and dichloride. Sulfur and phosphorus compounds are other components of the fuel. These are not additives but occur naturally in

crude oil and are not completely removed during oil refining. The quantity of sulfur in petrol depends partly of the particular source of the crude oil and partly on the refining processes. The mixture of air and petrol passing the engine throttle contains the following components of importance in relation to air pollution; oxygen, nitrogen, hydrocarbons, TEL, scavengers and sulfur compounds.

Table 3.1 The composition of exhaust gas emitted on the mixture in the vicinity of stoichiometrical air/ fuel ratio is burnt.

Name of material	Volume rate (% or ppm)
N_2	83.5 (%)
O_2 (including argon)	2.22 (%)
CO_2	13.0 (%)
H_2	0.23 (%)
CO	0.97 (%)
HC	205 (ppm)
NO	2900 (ppm)
NO_2	18 (ppm)

Remark : 1. Fuel : gasoline 2. All values have been measured without regard to water content and (1 %) = 10,000 ppm

The low pressure on the intake manifold side of the throttle causes some of the fuel to vaporize and mix with the air. However, vaporization is not complete and some of the fuel remains in liquid form, running towards the engine cylinder along the bottom of the intake tracts. As the piston descends, the air-fuel mixture and the liquid fuel enter the cylinder through the inlet valve ,as shown in figure.3.1. Since the cylinder is hot, the liquid fuel quickly vaporizes and a homogeneous air and and fuel mixture forms after the intake valve closes.
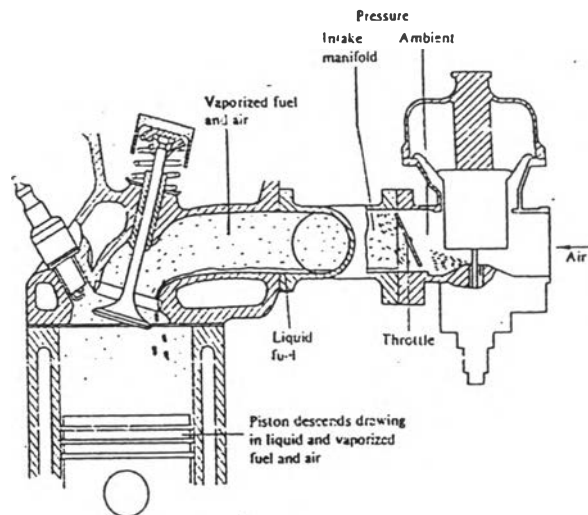

Figure 3.1 Petrol engine induction stroke. (Paker, 1978)

During the compression stroke, the pressure and density of the mixture increase and the gas is forced into the crevices, such as between the piston and cylinder above the top piston ring. At the conclusion of the compression stroke the mixture is ignited by the spark plug and combustion proceeds. Most of the exhaust pollutants are formed during this combustion period. The amount of carbon monoxide is related to the ratio of air and fuel in the cylinder. If the petrol-air mixture is chemically correct, that is the

mass ratio of air to fuel is about 14.5:1, then the products of combustion are mainly carbon dioxide and water:

$$C_8H_{16} + 12(O_2 + 3.79N_2) \longrightarrow 8CO_2 + 8H_2O + 45.5N_2 \quad (1)$$

If the mixture is lean, i.e., there is an excess of air then the products of combustion also contain oxygen:

$$C_8H_{16} + 13(O_2 + 3.79N_2) \longrightarrow 8CO_2 + 49.3N_2 + O_2 + 8H_2O \quad (2)$$

If the mixture is rich ,i.e., there is an excess of fuel, then the products of combustion also contain carbon monoxide , since there is insufficient oxygen to form carbon dioxide from all the carbon. The amount of carbon monoxide measured in the exhaust of an engine at various mixture strengths is shown in Figure 3.2.
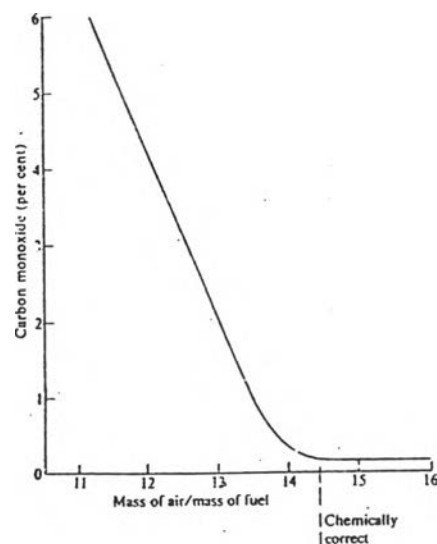

Figure 3.2 Volume concentration of carbon monoxide in exhaust of spark ignition engine as air-fuel ratio is changed.(Paker,1978)

The mixture does not burn spontaneously but an ignition at the spark plug causes a flame to sweep across the combustion chamber. In front of the flame the mixture is unburnt, while within the flame combustion is intense (figure 3.3) and the temperature is high -in the region of 2500° C- so some unusual reactions occur.
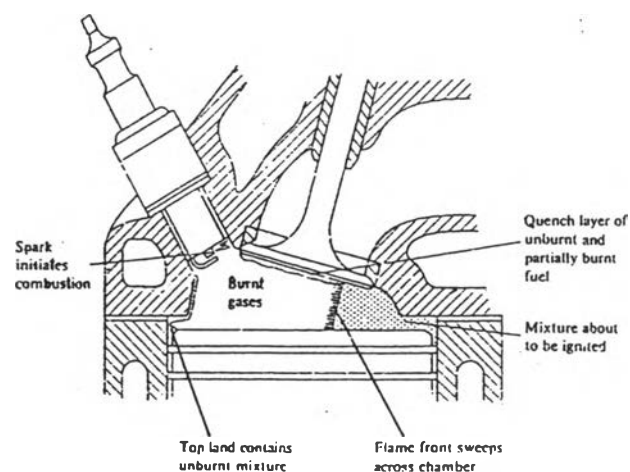

Figure 3.3 Combustion in spark ignition engine. (Paker,1978)

A small amount of oxygen and nitrogen combine to form nitrogen oxides. The sulfur compounds in the fuel are changed to sulfur oxides. The TEL burns to lead oxide with the air and to lead chloride and bromides with the scavenger. A portion of the lead compounds is deposited in the combustion chamber. Some of the lead deposits are removed, due to the chemical action of lead chlorides and bromides. A small proportion of the lead enters the lubrication oil and the remainder is carried by the waste gases into the exhaust system in which a small proportion is deposited. The result is that on average from, two- thirds to three-quarters of the lead

originally in the TEL is discharged in the gases leaving the exhaust system to enter the atmosphere.The flame sweeps across the combustion chamber initiating all these reactions, but the flame can never quite touch the walls of the chamber. The flame is very hot and as it approaches the walls, it loses heat by radiation to the cooler metal surface and is eventually doused. As a result, a layer of unburnt mixture of air and fuel, less than 0.24 mm thick remains on the wall of the combustion chamber. In addition, there is a transition layer between this unburnt region and the fully reacted products in the combustion zone , which contains partially oxidized hydrocarbons. Another region to which the combustion does not propagate is the top land, between piston and cylinder, above the top piston ring. Here again a mixture of fuel and air remains. A proportion of the gas in the region is forced into the crankcase due to combustion pressure, but a significant amount still remains. After combustion, the piston descends and work is extracted from the crankshaft. The exhaust valve opens and gases in the cylinder expand into the exhaust. Then the piston ascends and the remaining gases are displaced into the exhaust pipe. The unburnt fuel and air mixture of the combustion chamber walls is forced into the exhaust and the mixture in the top land, which was compressed during combustion, expands into the main body of the cylinder. The exhaust gases contain mainly nitrogen, carbon dioxide and water vapour , with carbon monoxide if the intake mixture is rich. In addition , there are small proportions of nitrogen oxides, unburnt hydrocarbons ,sulfur oxides, lead compounds and particulates. The relative concentrations of these compounds are illustrated in Figure.3.4.
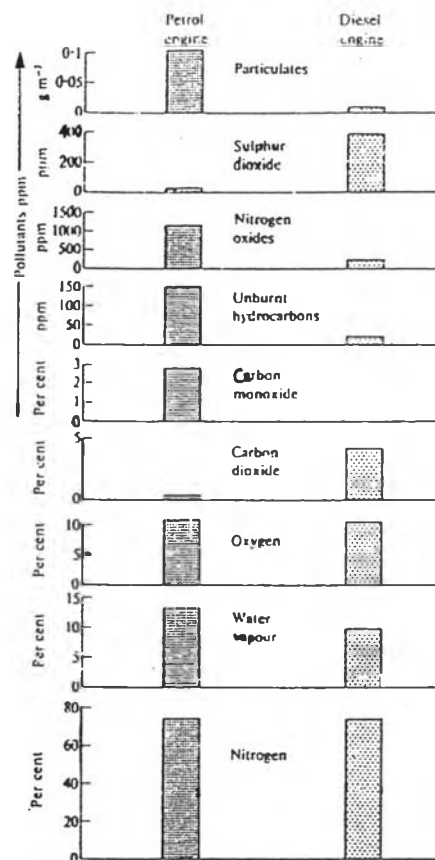
Figure 3.4 Comparison of exhaust constituents of petrol and diesel engines. (Paker,1978)

This description of engine operation becomes slightly more complex during vehicle transients, that is when the throttle is suddenly opened or closed. Consider throttle opening. The fuel flowing along the inlet manifold is partially in liquid form and partially evaporated due to the low pressure. When the throttle is snapped fully open, the pressure rises to ambient conditions and the ratio of evaporated to liquid fuel changes. There is now more liquid fuel in the pipes and less is evaporated. The air and evaporated fuel reach the cylinder before the liquid fuel and the engine will operate very weakly for a few revolutions, until the liquid fuel reaches the cylinder. The car driver would feel this as a slight hesitation before the car accelerated.

To overcome this, an accelerator pump is incorporated in the carburettor to inject fuel into the induction system as the throttle opens. Therefore, the inlet mixture becomes very rich for a few seconds to prevent vehicle hesitation and this causes a high percentage of carbon monoxide to be emitted from the exhaust. A different effect takes place as the throttle is snapped shut. The liquid fuel in the manifold evaporates almost completely and the intake mixture to the engine becomes very rich. In addition, the intake manifold pressure is low , since the engine is acting like a vacuum pump. These two effects may prevent the mixture being ignited by the spark plug. If this happens, then raw fuel is released to the exhaust and hydrocarbon emissions may instantaneously rise to levels of 8000 ppm (part per million) in comparison with values of about 200 ppm when the engine is running at a constant throttle position. These vehicle transient effects which cause high emissions are very important.

Exhaust emission control by catalytic converter is the most effective emission reducing technology in Japan and America. There are 2 types of catalyst, for instance.

1. The oxidation catalyst to purify HC and CO in an oxidizing atmosphere.

2. The three-way catalyst which causes both oxidation of HC and CO and reduction of NO_x simultaneously by controlling the air/fuel ratio to a narrow range near the stoichiometric air / fuel ratio, which is shown figure 3.5.
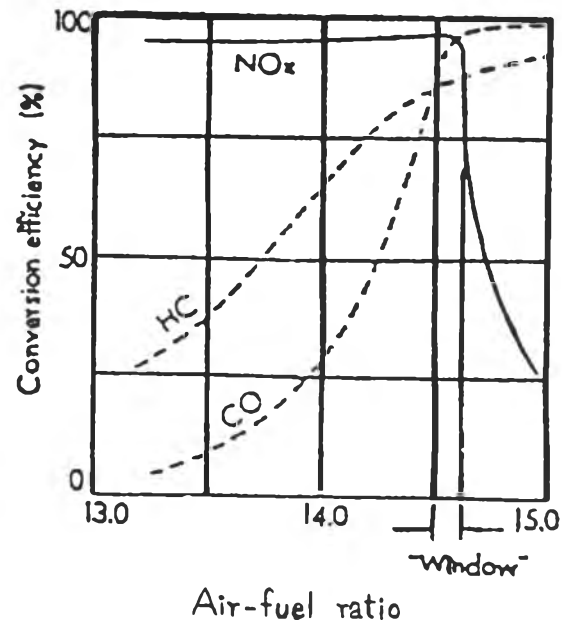
Figure 3.5 HC, CO and NO_x conversion efficiencies of three-way catalyst.

(Toyota Emission Control Systems for Japanese ,1978)

3.2 The concept of three-way catalyst system.

In nearly of the stiochiometric air/fuel ratios, the gas which is emitted from the engine contains small quantities of NO_x, CO, HC, H_2 and O_2. A technique for feeding this gas through a catalyst, in order to reduce NO_x and to oxidized CO and HC, thereby decreasing the three components simultaneously by means of a single catalytic converter, has been employed in passenger cars.

The catalyst used for this purpose is termed a three-way catalyst (shows in figure 3.6).
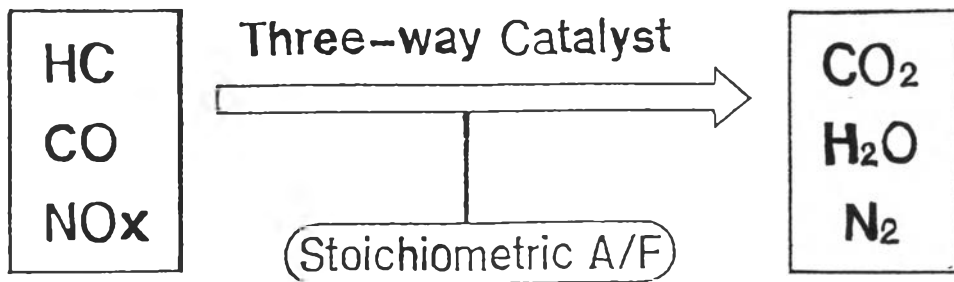
Figure 3.6 Concept of emission control by three-way catalyst.

(Toyota motor corp.,1991)

Such a simultaneous treatment of the three gas components requires that the concentrations of the respective constituents be maintained within a certain range, and that the reducing gases of CO, H_2 and HC(for NO_x) and the oxidizing gas of O_2 (for CO and HC) exist in the quantities appropriate to their respective reactions. And thus, the range of air/fuel ratios satisfying these conditions is a very narrow $\pm$ 0.25, When the air/fuel ratio deviates toward the rich side, the exhaust gas passing out of the converter contains more CO and HC and when the ratio deviates toward the lean side, NO_x increase. In an improved carburettor, the range of air/fuel ratios may be controlled to with in a deviation of $\pm$ 0.5,but such a range does not permit use of a three-way catalyst because more accurate control of the air/fuel ratio is required. To better cope with this situation, a technique has been developed which detects the presence of O_2 concentration in exhaust gas by means of a sensing device (O_2 concentration detector), that uses the electric out put obtained in order for a feed back type carburator. Precious metals such as platinum, palladium, rhodium and ruthenium are used as the catalyst, to generate low levels of NH_3. A sufficiently durable O_2 sensor,

which is exposed to high temperature exhaust gases for a longtime, has not been deviced. However, its durability has been improved considerably. And the O_2 sensor is provided in some passenger cars. The three-way catalyst system of passenger cars employs EFI (Electronic Fuel Injection) or a feed back carburator to control air/fuel precisely, and the complication of the catalysts system is unavoidable.

3.2.1 O_2 Sensor.

The O_2 sensor is designed to monitor O_2 concentration in the exhaust gas and provide an electrical signal to the control unit.

A cross-section of an O_2 sensor is shown in Fig 3.7. The O_2 sensor is composed of a test-tube-like Zirconia element with platinum eletrodes attached to both its surfaces. The surface of the outer platinum electrode is coated with porous alumina to protect it physically. The Zirconia element is a kind of solid electrolyte, and generates an electrical potential according to the difference in O_2 concentrations between both electrodes, when it becomesheated. In short, the O_2 sensor is an oxygen concentration cell with the inside exposed to the ambient air and the outside to the exhaust gas.

The O_2 sensor must be kept in the appropriate temperature range to ensure its effective operation and durability because the temperature of the element has a great influence on the characteristics of the O_2 sensor such as sensor voltage, response time and internal resistance. In addition to these considerations, the location of the O_2 sensor must be determined carefully so that cylinder to cylinder deviation of the air-fuel ratio may be alleviated as much as possible. It is usually located on the converged room of the exhaust manifold. In the case of the liquefied petroleum gas (LPG) fueled engine,
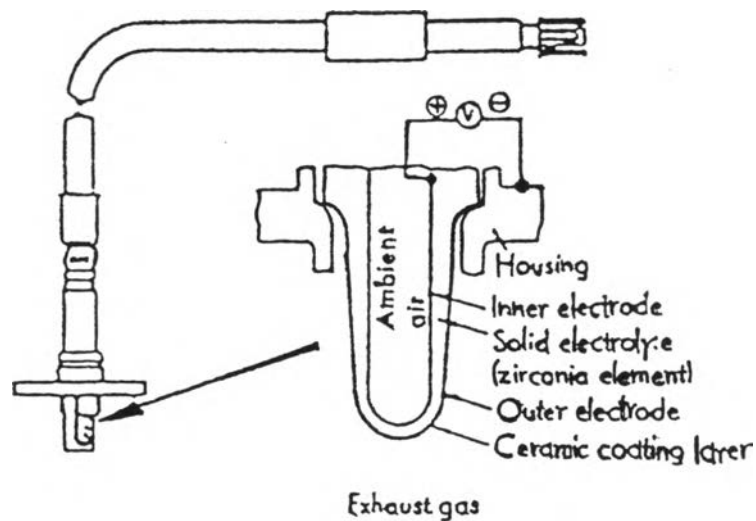
Figure 3.7 Shows the oxygen sensor.

(Toyota Emission Control Systems for Japanese ,1978)

however, it must be attached close to the exhaust port to compensate for the lower exhaust gas temperature.

3.2.2 Air - to - fuel control system.

Simultaneous oxidation and reduction can take place in a single catalytic bed, provided that the air to fuel ratio is adjusted precisely at the stoichiometric 14.7 ± 0.1. This precise metering is required for the three-way catalyst. A narrow " window " exists for some catalysts where more than 80 % conversion efficiency can be obtained on all three pollutants (Zechnall, Baumann and Eiele,1973). This precise metering cannot be attained by more than ± 0.1 from the set point ; a charge of fuel type, a change in atmosphere humidity, and a chance in altitude will also affect this ratio. A feed back control mechanism , equipped with an oxygen sensor to measure the oxygen pressure in the exhaust gas has been developed that can achieve this

precision in the air/fuel ratio. This strategy also leads to good fuel economy and derivability. Thus, EFI system was proposed. EFI system has the highest potential for precise air-fuel ratio control. The concept of this operation is O_2 sensor monitoring the concentration of oxygen in the exhaust gas. Then the O_2 sensor sends the signal through a circuit of operation. The controller determines the amount of injected fuel to be corrected.
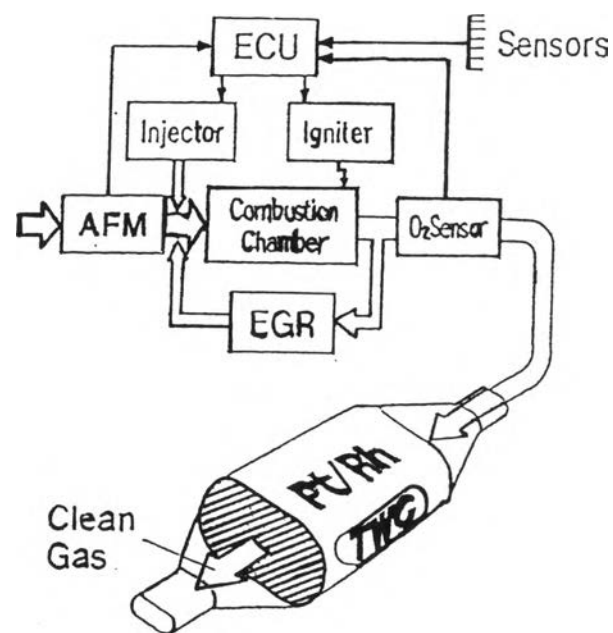

Figure 3.8 Three-way catalyst System. (Toyota motor corp.,1991)

3.2.3 Operating in the four window.

There are many constraints on the design of a catalytic converter for an automobile volume : shape and location of converters suitable for automotive design. Another constraints is the pressure drop across the catalytic bed, which must be kept to a minimum to avoid a loss in engine power and performance, in order to achieve an automotive catalytic converter which operates well. There are four narrow operating ranges (or "window")

in each and every one of four variables : temperature , gas   composition ,

gas flow rate and poison concentration (shows in figure3.9).

air-to-fuel ratio

rich.reducing   13   14.7   16.0   lean, oxidizing

suitable for
NO_x reduction

suitable for
oxidation of CO
and HC

(a)

Temperature °F

600   1100   1400   1600

Catalyst too cold

best operation

Catalyst thermal
ageing and destruction

(b)

gas hourly space velocity $hr.^{-1}$

0   100,000   200,000   300,000

best operation

insufficient residence
time, channelling

(c)

low   high
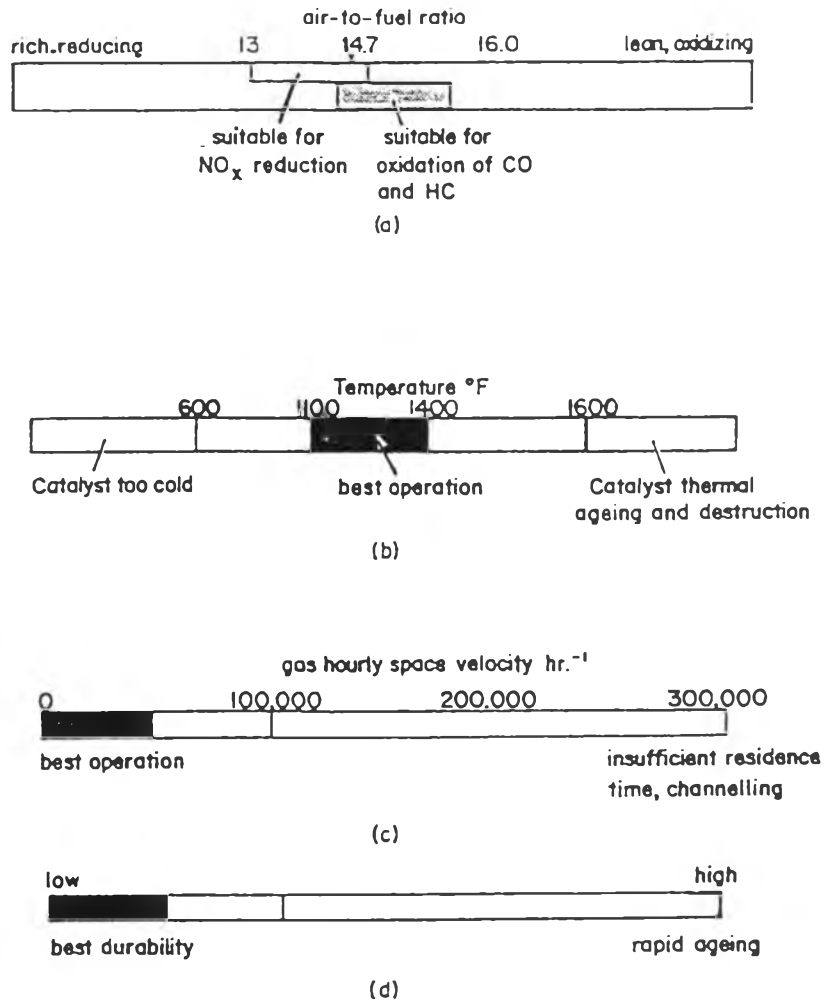
best durability   rapid ageing

(d)

Figure 3.9 Four window of operation. (Wei, 1975)

In actually practice, an automobile is always in transient conditions:

the catalyst is too cold during start-up and too hot during a long downhill

cruise; the air/fuel ratio is too rich on idle and too lean while cruising; the

exhaust gas flow is slow during idle, and fast during an upgrade cruise. The

catalysts are also exposed to repeated cycles of heating and cooling

evaporation and condensation of water , pulsating flow from exhaust gases ,

vigorous shaking on the road, and a variety of poisons including lead and

sulfur. The variations in the operating conditions cause the catalysts in automobiles to deteriorate prematurely.

3.3 Temperature Programmed Reduction : (TPR) (Hurst, 1982).

Temperature programmed reduction (TPR) is a relatively new technique which is highly sensitive and which does not depend on any specific property of the catalyst other than that the species under study be in a reducible condition. Over the last few years TPR has been applied to the study of many supported and unsupported catalyst systems, and we feel that it is timely to review the subject.

3.3.1 Thermodynamic of reduction.

Although TPR is in no way restricted to studies of the reductions of oxides, much of the work to date has been concerned with these systems. We therefore restrict the content of this section to refer to oxides only.

The reaction between metal oxide (MO) and hydrogen to form metal M and water vapor can represented by the general equation (3)

$$MO \, (s) \; + \; H_2 \, (g) \; \longrightarrow \; M \, (s) \; + \; H_2O \, (g) \qquad (3)$$

The standard free energy change for the reduction ΔG° is negative for a number of oxides (see Fig 3.10.) and thus for these oxides the reductions are thermodynamically feasible.

$$\Delta G = \Delta G^\circ + RT \log (P_{H2O} / P_{H2}) \qquad (4)$$

However, since it may still be possible for the reduction to proceed even when ΔG° is positive. The TPR experimental method is such that the water

vapor is constantly swept from the reaction zone as it is formed. Thus if P_{H2O} is lowered sufficiently at elevated temperatures, it is possible that the term RT log (P_{H2O} / P_{H2}) could be sufficiently negative to nullify a positive ΔG^{o}. Thus it has been possible to obtain TPR profiles for oxides of vanadium, tin, and chromium which, at the reduction temperatures, have approximate positive ΔG^{o} values (kJ / mol) of 45,50 and 100 , respectively.
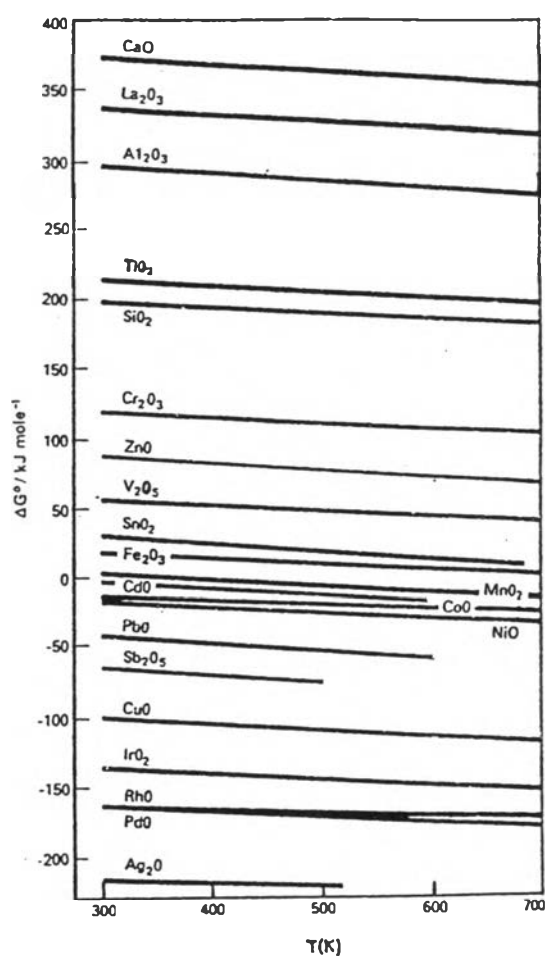

Figure 3.10 Standard free energy change (ΔG^{o}) as a function of temperature for the process:Metal oxide + H_2 ------> Metal + H_2O. (Hurst, 1982)