Module 5:Emission Control for SI Engines

Lecture 22:Oxidation and Three Way Catalytic Converters

The Lecture Contains:

- OXIDATION AND 3-WAY CATALYTIC CONVERTERS
- Oxidation Catalytic Converters
- Reduction and 3-Way Catalytic Converters
- 3 -Way Catalytic Converters
- Oxygen Sensor

Previous Next

OXIDATION AND 3-WAY CATALYTIC CONVERTERS

Since 1975, in the production gasoline vehicles two main types of catalytic converters have been used:

- Oxidation catalytic converters
- 3-Way catalytic converters.

The catalytic converters for the first time were used to reduce only HC and CO emissions from the US gasoline passenger cars in 1975. As these converters reduced HC and CO by oxidation, they were called as 'oxidation' catalytic converters. NO_x emission standards were met by use of EGR at that time. The engines were operated on rich mixtures and with application of EGR engine out NO_x emissions were reduced. Secondary air was injected in the exhaust system upstream of the converter to provide sufficient oxygen for oxidation of CO and HC on the catalyst. Later, when the NO_x standards were made stringent from 1981, reduction catalysts were also developed. An exhaust gas oxygen sensor developed in the early 1980s facilitated engine operation at near stoichiometric mixtures that made it possible to simultaneously oxidize CO and HC to CO_2 and H_2O and reduce NO_x to N_2 . As all the three pollutants were converted simultaneously in the same reactor these were termed as 3-way catalytic converters. T he three-way catalytic converter is presently a standard fitment on most gasoline passenger cars.
During mid-1990s, gasoline direct injection (GDI) engines with charge stratification were introduced in the market by two Japanese car manufacturers. During part load city operation, these GDI engines work as stratified-charge engines with overall very lean air/fuel mixtures. For NO_x control in these engines, lean de-NO_xcatalytic converters have been developed. The de-NO_x x catalysts and other advanced catalyst systems such as for cold start HC control are discussed later.

Previous Next

contd...

Oxidation Catalytic Converters

The oxidation catalyst converts CO and HC to $CO_2$and H_2O at substantially low temperatures and at higher conversion efficiency tan the thermal reactors. The required oxygen for oxidation reactions is made available either by operating engine lean or by injecting secondary air ahead of the catalytic converter when engine is operated rich. Vehicles employing the oxidation catalysts were generally tuned rich for better NO_xcontrol and secondary air injection was employed

The conversion efficiency of a catalytic converter is defined as:

$$n_{out} = \frac{\dot{m}_{CO,in} - \dot{m}_{CO,out}}{\dot{m}_{CO,in}} = 1 - \frac{\dot{m}_{CO,out}}{\dot{m}_{CO,in}}$$

Light-Off Tempersature

The catalytic conversion efficiency depends upon the exhaust temperature and its relationship with temperature is shown on Fig 5. 13. The temperature at which 50% CO or HC conversion is obtained is defined as the light off temperature. The catalyst light off temperature is desired to be as low as possible for good emission reduction during actual vehicle operation. . The light off temperature for a new catalyst varies from about 220° C for CO to 260 - 270° C for HC. With ageing, the catalyst light off temperature increases. For the first generation catalytic converters, t he temperature of operation was in the range of 250 – 600 ºC and the typical gas space velocity during vehicle operation varied from 3 to 30 s -1 .

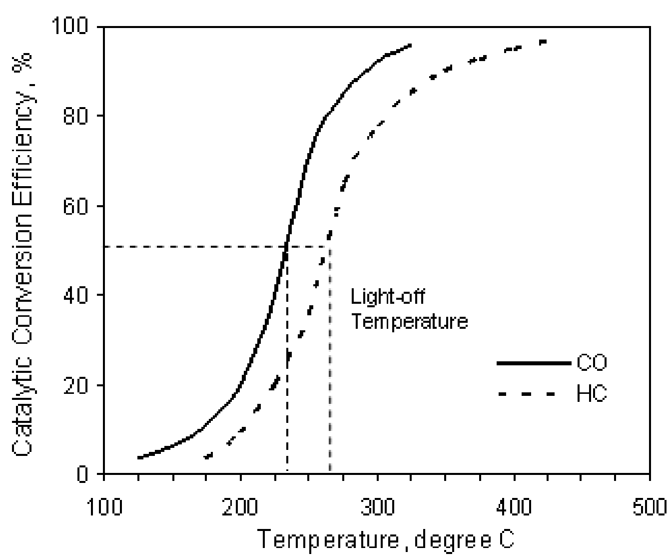

Figure 5.13	Conversion efficiency dependence on temperature for an oxidation catalyst

Previous Next

Reduction and 3-Way Catalytic Converters

For reduction of NO_x, the CO, HC and H_2which are present in the exhaust during rich engine operation are made to react with NO_x over a catalyst when NO_x is converted to N_2 . Possible reactions under reducing conditions are given in Table 5.3.

Table 5.3

Possible Reactions for Reduction of NO_x

1.	$NO + CO \rightarrow \frac{1}{2} N_2 + CO_2$
2.	$NO + 5CO + 3H_2O \rightarrow 2NH_3 + 5CO_2$
3.	$2NO + CO \rightarrow N_2O + CO_2$
4.	$NO + H_2 \rightarrow \frac{1}{2} N_2 + H_2O$
5.	$2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O$
6.	$2NO + H_2 \rightarrow N_2O + H_2O$

A number of catalysts like CuO, NiO, monel etc., were studied for NO_x reduction However, their NOx conversion efficiency being just 25 to 35 % only, they did not find acceptance. Rhodium (Rh) from the noble metal group has been found to be the most successful reduction catalyst so far and is being used in actual systems. .

The concentration of NO_x being relatively small, only small fractions of CO, HC present in exhaust is utilized in the reduction reactions. Most of HC and CO is required to oxidized simultaneously or in a separate reactor.. Initially, separate reduction and oxidation catalyst systems were considered but their operation was complex, the engine had to be operated rich. Also, some ammonia is generated during reduction reactions, which is oxidized again to NO in the downstream oxidation reactor. Due to these reasons, the dual-bed catalysts did not find much acceptance and the 3-Way catalyst was developed and used on cars around 1980.

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3 -Way Catalytic Converters

The essential condition to simultaneously oxidize CO and HC and reduce NO_x on the same catalyst bed is to operate engine at very close to stoichiometric air-fuel ratio. Under stoichiometric engine operation, enough reducing gases CO and HC are present in the exhaust to reduce NO_x to N_2 and at the same time enough oxygen to oxidize CO and HC. Thus, all the three pollutants are removed simultaneously in a 3-way catalyst. . Dependence of conversion efficiency for the three pollutants on fuel-air equivalence ratio in a 3-way catalyst is shown in Fig. 5.14 . High conversion rates of over 80% of all the three pollutants are obtained in a small window of about 0.12 A/F unit width (0.997 < f < 1.005) around the stoichiometric air-fuel ratio.

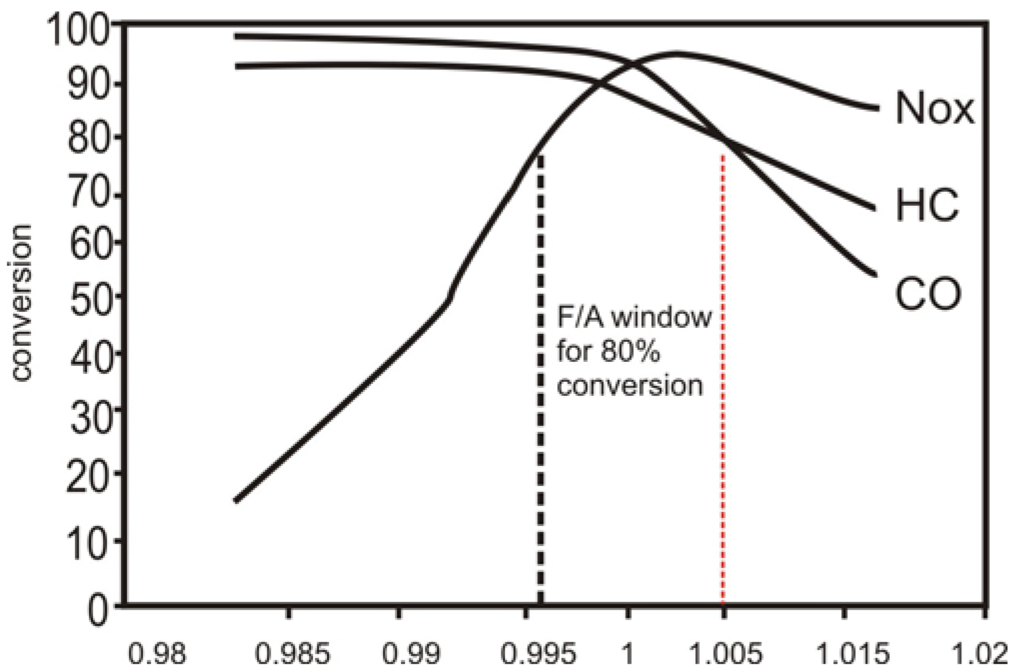

Figure 5.14	Conversion efficiency of a 3-way catalytic converter as a function of air-fuel ratio.

Previous Next

contd...

- A closed loop feedback controlled fuel management system is used for precise control of air-fuel ratio. A simple closed-loop feed back engine fuel management system is shown schematically in Fig. 5.15.
- An oxygen sensor installed in the exhaust system detects presence of free oxygen in the exhaust gas which determines whether the fuel-air mixture is leaner or richer than stoichiometric.
- The signal from the oxygen sensor is fed to a microprocessor controlled fuel management system to adjust fuel injection rate so that the engine operates in a narrow window around the stoichiometric set point.
- Fuel-air ratio oscillates around the set point at a frequency of 0.5 to 1 Hz as the fuel flow is varied.

Signals of air mass flow rate, engine load, speed, spark timing temperatures and several other parameters are also fed to the engine electronic control unit for management of engine operation. Carburetors were found to be incompatible with such control systems although initially electronically controlled carburetors were developed and used. Now, multipoint port fuel injection system is a standard feature of engines using 3-way catalytic converters.

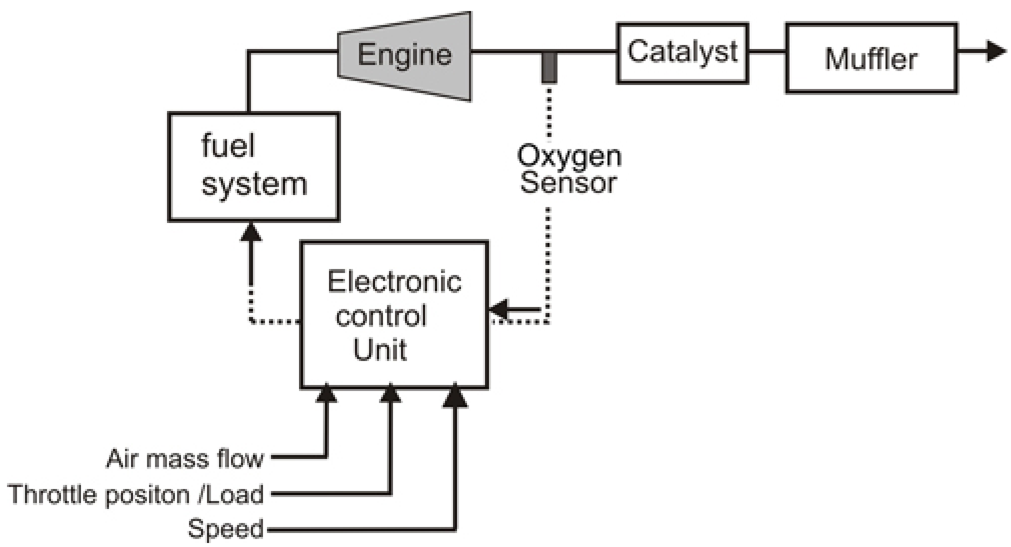

Figure 5.15	A simple closed-loop feedback control system for air/fuel ratio control

Previous Next

contd....

Modulation of F/A Window

Oscillations in fuel flow rate around the set point widen considerably the F/A window, thereby adversely affecting the conversion efficiency. To maintain high conversion efficiency for all the three pollutants, the adverse effect of these oscillations in F/A ratio is countered by use of an oxygen storage/release system in the catalyst wash coat. Components like cerium oxide (CeO_2) and zirconium oxide (ZrO_2) are added to the washcoat. CeO_2 acts as oxygen storage system and widens the air-fuel ratio window when high conversion rates of all the three pollutants are possible. CeO_2 undergoes the following chemical changes as the mixture transits from rich to lean and back due to variations in fuel-flow rate.

Rich Operation:

$$2CeO_2 + CO \rightarrow Ce_2O_3 + CO_2 \qquad (5.4)$$

Lean operation:

$$Ce_2O_3 + {}^{1}/_{2}\,O_2 \rightarrow 2CeO_2 \qquad (5.5)$$

During fuel rich operation, CeO_2releases oxygen for oxidation of CO and HC and in the process gets itself reduced to Ce_2O_3When the engine operation becomes lean as a result of control of fuel flow by engine fuel management system, Ce_2O_3 gets oxidized back to $CeO_2$by reacting with excess O_2 or NO. These reduction-oxidation (Redox) reactions in cerium oxide continue and effectively even in a wider F/A (nearly 0.06 F/A ratio) widow high conversion efficiency of all the three pollutants is obtained.

Previous Next

Oxygen Sensor

The exhaust gas oxygen sensor (EGO) also called, as 'λ-sensor' or 'lambda sensor' is used to control air-fuel ratio within about 1% of stoichiometric value for operation of 3-way catalysts. The sensor is fitted in the exhaust pipe just upstream of the catalytic converter. EGO operates on the principle of electro-chemical cell. Lambda-sensor is used to detect the presence or absence of free oxygen in the exhaust gas. Typical construction of an EGO is shown in Fig 5.16. Solid zirconium oxide (ZrO_2) stabilized with yttrium oxide (Y_2O_3) is used as electrolyte. The outer and inner surfaces of the hollow cylindrical are coated with porous platinum to form inner and outer electrodes. The outer electrode is exposed to the exhaust gas while the inner electrode to air having a fixed oxygen concentration. Due to catalytic effect of platinum electrode the exhaust gas reaches equilibrium composition very rapidly.. The electrochemical reactions at the electrodes produce oxygen ions that carry current through solid electrolyte producing a voltage signal. The e.m.f. voltage, e_0 produced is a function of the ratio of partial pressures of oxygen at the two electrodes and is given by Nernst equation (Eq 5.6) :

$$e_0 = \frac{RT}{4F} ln\left(\frac{P_{O_2r}}{P_{O_2s}}\right)$$

where R is the universal gas constant, T is sensor temperature in K, F is Faraday constant equal to 9.649 x 10 7 C/kmol, $P_{O_{2r}}$ and $P_{O_{2s}}$ are partial pressures of oxygen in the reference gas and the sample, respectively.

The partial pressure of oxygen in the exhaust gas increases by many orders of magnitude (from about 10^{-20} to 10^{3} P a at 500 ºC) as the fuel equivalence ratio varies from 1.01 to 0.99 . The effect of fuel – air equivalence ratio on sensor output signal is shown on Fig. 5.17. The sensor output voltage increases rapidly during transition from lean to rich mixture. For rich conditions a voltage of about 800 mV is produced and for lean mixtures about 50 mV is generated. The stoichiometric point is set at about 0.5 V. Voltage signal lower than the set point is taken by the engine control unit as lean mixture and higher voltage signal as the rich operation.

Previous Next

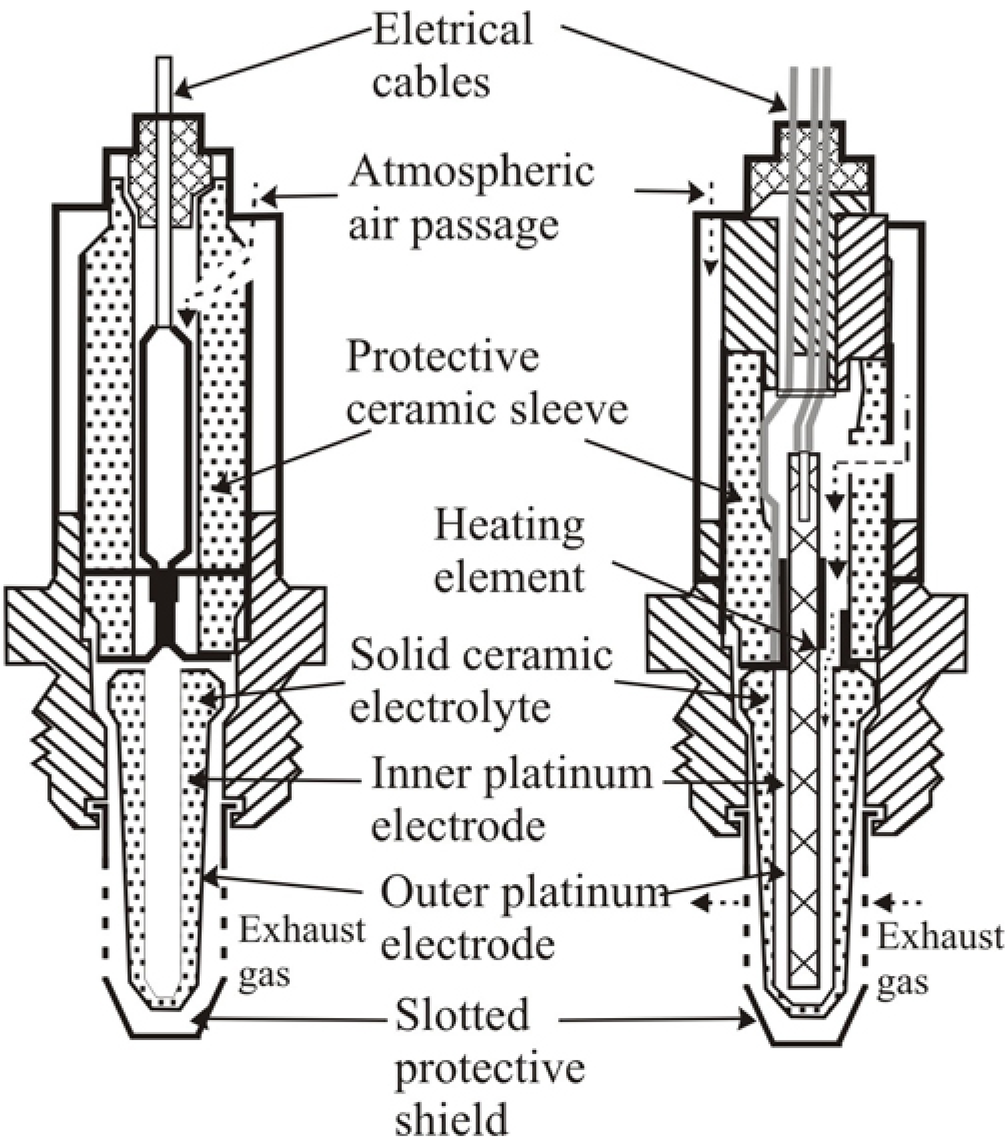

Figure 5.16	(a) an unheated oxygen sensor (b) heated oxygen sensor (HEGO)

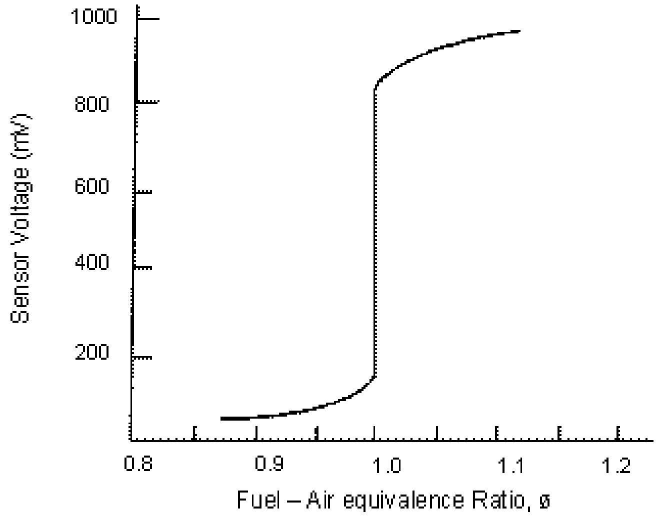

Figure 5.17	Oxygen sensor output voltage as a function of fuel-air equivalence ratio

Previous Next

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The temperature of sensor electrolyte affects its conductivity and hence the output voltage. The optimum operation temperature for the oxygen sensor is between 300 and 600º C. During engine warm-up the unheated EGO sensor is not operative. Electrically heated exhaust gas oxygen (HEGO) sensors are therefore used.

For meeting ULEV emission requirements, the performance of 3-way catalyst is to be further improved and oscillations in air-fuel ratio are to be minimized. For this, a new sensor which measures actual oxygen content in the exhaust and the engine control unit responds gradually to the changes in air-fuel ratio is used. This sensor is known as universal exhaust gas oxygen (UGEO). With the use UEGO, a better control of air-fuel ratio is obtained and 3-Way catalyst operates in a very narrow window of high conversion efficiency (Fig 5.18).

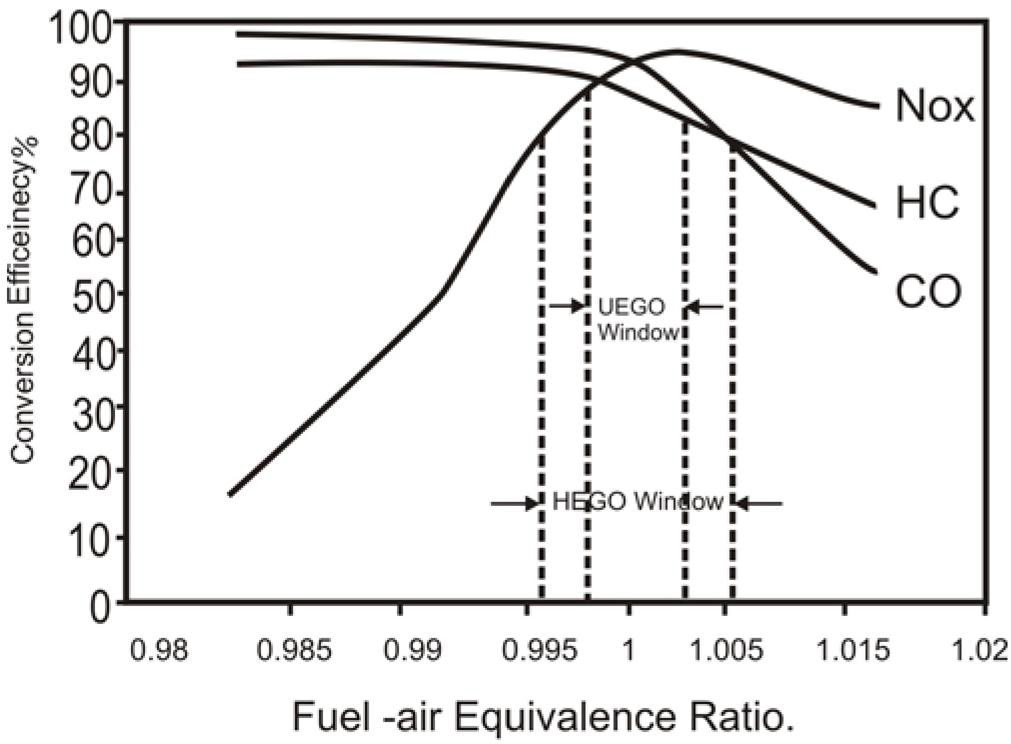

Figure 5.18	Comparison of fuel- air ratio window of operation for UEGO and HEGO

Previous Next