EMISSION CONTROL, AUTOMOTIVE

1. Introduction

There are over 210 million U.S. automobiles and trucks on the road, consuming large amounts of gasoline and producing commensurately large amounts of gaseous exhaust. The exhaust consists primarily of carbon dioxide [124-38-9] (qv), water, unburned hydrocarbons (qv), carbon monoxide [630-08-0] (qv), oxides of nitrogen (NO_x), remaining oxygen, and nitrogen (see GASOLINE AND OTHER MOTOR FUELS). The latter three atmospheric pollutants have been regulated since the 1970s by the U.S. government and more stringently by the State of California (see AIR POLLUTION). Automobile companies have developed fuel metering and exhaust systems using the catalytic converter to meet emission regulations. Carbon dioxide emissions are indirectly controlled by corporate average fuel economy (CAFÉ) standards for passenger cars and small trucks.

Prior to emission control, passenger car and truck emissions together were the largest contributors to atmospheric pollution in the United States (1). By

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2004, the Tier 2 exhaust emission standards mandated by the Clean Air Act Amendments of 1990 required automobiles and small trucks to reduce emissions of hydrocarbons by 98%, carbon monoxide by over 90% and oxides of nitrogen by 98% as compared to 1970 pre-control emissions. California, having more severe pollution events, has established a system of the most stringent emission control regulations in the world. The California standards can be adopted by other states.

The key components of the spark-ignited engine emission control systems are the three-way catalytic converter and closed loop oxygen sensor (qv) (See SENSORS) controlled fuel metering system. Exhaust gas recirculation is used to reduce formation of engine NO_x and provides antiknock values. Over 600 million vehicles have been equipped with the catalytic converter which, has been rated among the top 10 engineering breakthroughs of the twentieth century (2). Emission control is achieved without negatively affecting fuel economy or performance.

Diesel engine emission control technology is not discussed in detail as very few light-duty diesel engines are now in service, and although the number is expected to rise in this coming decade, the emissions control technology has not been selected. Light-duty and medium-duty diesel engine powered vehicles have to meet the same Tier 2 standards (Table 1) as gasoline-fueled engines including a strict particle emission standard. Heavy-duty diesel engine trucks must meet very stringent standards starting with the 2007 model year.

2. Emission Regulation and Testing

United States Federal regulations require automobile manufacturers obtain a certificate of conformity indicating compliance with all applicable emission standards over the vehicle's useful life period. The Tier 2 useful life for car and light-duty vehicles is 160,000 km or 10 years or 11 years and 193,000 km for heavier light-duty vehicles.

2.1. Clean Air Act Amendments.

The Clean Air Act Amendments of 1970 set strict emission standards requiring 90% reduction of emissions of hydrocarbons, carbon monoxide and oxides of nitrogen. The resulting statutory emissions standard was 0.41 grams per mile of hydrocarbons, 3.4 grams per mile of carbon monoxide and 0.4 grams per mile of oxides of nitrogen. A series of interim standards were sequentially set that finally reached this level. The Clean Air Act Amendments of 1990 required more stringent standards and resulted in Tier 1 and Tier 2 standards—the later being initiated in 2004 through 2007 for light-duty vehicles and fully implemented for heavy light-duty vehicles in 2009. The Tier 2 standards essentially required all passenger cars and light-duty trucks (LDT) including sports utility vehicles (SUV) up to **3,856** kg (8,500 lb) gross vehicle weight (GVW) meet the same level standards as passenger cars for 193,000 kilometers or 10 years with a 25, 50, 75 and 100% phase-in schedule over 4 years. Heavier trucks and passenger carrying vehicles up to 4,536 kg (10,000 lb) GVW have to meet the same standards for 193,000 km or 11 years with a 50, 100% phase-in schedule starting in 2008. Table 1 summarizes the Tier 2 standards. Tier 2 also set fuel sulfur content in gasoline to an average of 30-ppm

Table 1. **US EPA-TIER 2 Emission Standards**[a,b]

Bin #	NO_x	NMOG	CO	HCHO	PM	Comments[c]
10[d]	0.372	0.097/0.143	2.61/3.98	0.011/0.017	0.056	a, b, c, d
9[d]	0.186	0.056/0.112	2.61	0.011	0.037	a, b, e
8	0.124	0.078/0.097	2.61	0.011	0.012	b, f
7	0.093	0.056	2.61	0.011	0.012	
6	0.062	0.056	2.61	0.011	0.006	
5	0.043[e]	0.056	2.61	0.011	0.006	
4	0.024	0.044	1.31	0.007	0.006	
3	0.019	0.034	1.31	0.007	0.006	
2	0.012	0.006	1.31	0.0025	0.006	
1	0.000	0.000	0.00	0.000	0.000	

[a] Ref. 3.

[b] Light-duty and medium-duty vehicles less than 4536 kg gross vehicle weight. Tier 2 light-duty full useful life exhaust emission standards (grams per kilometer). Full useful life: 10 yr. or 160,000 km up to 3856 GVW; 11 yr. or 193,000 km up to 4536 GVW for passenger carrying vehicles.

[c] Notes:

a. Bin deleted at end of 2006 model year (2008 for HLDTs).
b. The higher temporary NMOG, CO and HCHO values apply only to HLDTs and expire after 2008.
c. An additional temporary higher bin restricted to MDPVs is discussed in reference.
d. Optional temporary NMOG standard of 0.143 g/km applies for qualifying LDT4s and MDPVs only.
e. Optional temporary NMOG standard of 0.112 g/km applies for qualifying LDT2s only is discussed in reference.
f. Higher NMOG standard is deleted at end of 2008 model year.

[d] Temporary bins expire in 2006 (for LDVs and LLDTs) and 2008 (for HLDTs).

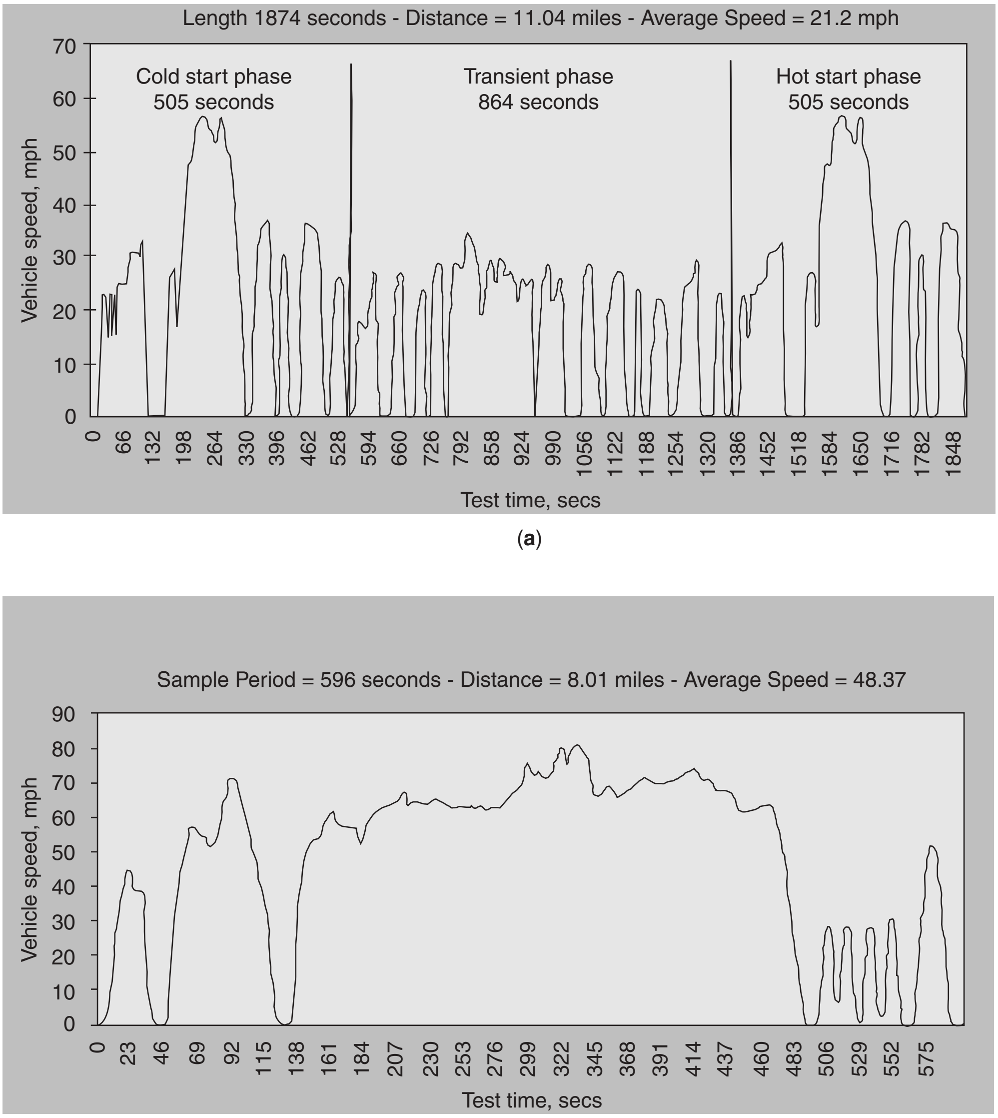
[e] Corporate average NO_x value.

with a cap at 80-ppm. For complete list of Federal emission standards, go to www.epa.gov/otaq/standards.htm (the Tier 2 Program) and State of California LEV-II emission standards www.arb.ca.gov. A new concept of “bins” was introduced. The heavier LDT and SUV vehicles can initially meet higher emissions of temporary Bins 9 and 10 but eventually have to meet Bin 6, 7, 8 or lower. Any vehicles sold by a manufacturer in one year in the higher bins must be offset by an equivalent number of vehicles sold by a manufacturer in that same year that meet the cleaner emissions of Bins 1, 2, 3, and 4, so as to counterbalance and meet an overall average 0.07 g/mile NO_x emission standard of Bin 5. California LEV2 standards are similar to those of Tier 2 with more emphasis on corporate average HC emissions. For California automobile manufacturers can choose to comply with voluntary emissions system durability of 15 years or 240,000 kilometers at slightly relaxed standards. Extended emission system durability requirements reflect much the improved and longer engine life now found in actual vehicle use as a result of clean unleaded gasoline. Highly corrosive leaded gasoline has been completely banned in the United States since 1996.

The U.S. Tier 2 and California LEV-II program will dominate advances in emission control in this next decade.

2.2. Test Procedure. Originally vehicle manufacturers had to actually run test track vehicles for 80,000 km as durability vehicles (3). Periodic exhaust emissions tests using the U.S. Federal Test Procedure (FTP) determined emissions at several mileages between 6,400 km and 80,000 km and a deterioration factor (DF) was computed. For example, a calculated DF factor of 1.1 for the durability vehicle could be applied to the emissions found on any number of 6,400 km emission data vehicles that represented various vehicle models within that engine family to predict compliance with the in-use standard at 80,000 km. Thus not all versions of vehicles had to be run for 80,000 km. Nevertheless, this original certification procedure was laborious and expensive. A simplified modern verification has been proposed for new emission durability procedures using a new standard road cycle (SRC) for whole vehicle durability or an alternative method of new standard engine bench cycle (SBC) for accelerated aging of the catalytic converter and oxygen sensor and other exhaust system components (4). The objective is to use durability procedures that are at least as severe as actual vehicle on-road use. The SRC would be used for whole vehicle durability using 7 laps (each different) in a 3.7 mile test track course or on a mileage accumulation dynamometer for the full useful life mileage. The SBC would be used to age catalytic converter, oxygen sensor and exhaust system under accelerated test conditions on a slave engine installed on an engine test bench. The aged components are then installed and tested on an actual new vehicle model undergoing compliance testing. The SBC uses a mathematical approach based on the Arrehenius equation to determine aging time and exhaust gas temperature to achieve catalyst and O_2 sensor aging effects equivalent to that found with the SRC whole vehicle durability cycle that are at least as severe as actual in-use vehicle aging. Auto manufacturers are permitted to develop their own SRC and SBC and have them approved. Tier 2 emission regulations require field surveys by automobile manufacturers to assure that vehicles in actual use are in compliance with the emission standards.

The Federal Test Procedure (FTP) specifies that a test vehicle is fueled with commercial unleaded gasoline and be stored in a temperature environment of between 20 and 29°C for at least 12 hours immediately prior to the emission test. The vehicle is placed on a chassis dynamometer which is calibrated for the vehicle weight and road load. The vehicle is started cold and driven for 41 minutes on a prescribed cycle of accelerations, cruises, decelerations, idle periods, a 10-minute shutdown (called the hot soak), and a hot start and period of rerun that matches the driving conditions of the first 505 seconds of the cold start. Total distance traveled is 17.8 km (11.115 miles). Fig. 1**a** is the USA FTP-75 Test Cycle for standard emission tests. Fig. 1**b** is the supplementary Federal Test Cycle US06 High Speed/High Load Cycle which reaches a maximum speed of 129.2 kmh (80.3 mph) implemented to assure emissions are controlled during higher rates of acceleration and higher speed. Exhaust emissions are sampled, analyzed and computed with a constant volume sampling system (CVS). All engine exhaust gases from test start to test end are fed into the (CVS) system where it is diluted with large amount of air drawn in by the CVS constant flow pump. Since CVS flow rate is constant throughout the test the air drawn in modulates inverse to vehicle exhaust flow. Total CVS system flow is recorded for each test period. Diluted exhaust samples are continuously collected from the well-mixed diluted exhaust CVS stream for each of the following portions of the entire test: The first cold start bag contains the continuous diluted gas



(**a**)

(**b**)

Fig. 1. (**a**) EPA federal test procedure. (**b**) US 06 or supplemental FTP driving schedule.

sample from the first 505 seconds of the test. The second transient portion bag is the diluted sample from 506 to 1372 seconds. The engine ignition is turned off for a 10-min hot soak. The third hot start bag is the diluted gas sample after the 10-min hot soak from the point of engine ignition of the hot restart for the last 505 seconds of the test. Each of the three bags are measured for concentration of hydrocarbons (HC), carbon monoxide (CO) and oxides of nitrogen (NO_x) using, respectively, a flame-ionization detector (FID) HC analyzer, an infrared CO analyzer, and a chemiluminescent NO_x analyzer. A CO_2 nondispersive infrared

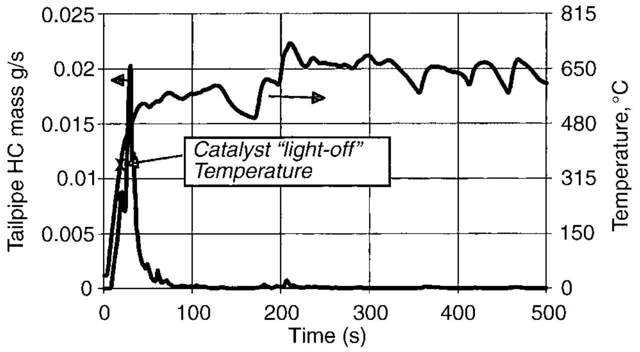


Fig. 2. Automotive emissions importance of cold start Tailpipe HC emissions (FTP bag 1) (19). Courtesy Ford Motor Company.

(ndir) is used as input to calculate dilution. The concentration measurements are converted into mass emissions per unit of distance utilizing the known inputs of distance traveled and total measured CVS system flow. FTP weighting factors are assigned for each phase to give a composite mass per unit of distance traveled values for each pollutant for the total test—for example: 0.25 g/km HC; 2.0 g/km CO and 0.25 g/km NO_x.

It is interesting to analyze the accumulation of emissions from a vehicle under test using the US FTP. Fig. 2 shows the typical cumulative grams (g) of HC emissions with respect to time from a Tier 2 vehicle undergoing the FTP. Fig. 2 shows the catalyst bed temperature for a typical vehicle meeting the U.S. Tier 2 emission standards (5). HC accumulation rate is high during the first ~50 seconds from engine start before the catalyst has started to function. Very little accumulation of HC occurs after the engine and catalyst is up to operating temperature as can be seen in Fig. 2. NO_x emissions occur during cold and hot starts and coincident with high speed modes. It can be clearly understood Tier 2 engines will have to be designed to heat up the catalytic unit in about 10 to 15 seconds. In fact, Tier 2 compliant engine design factors being examined to produce hotter exhaust gas are: (*1*) reduced exhaust system thermal mass; (*2*) lean air/fuel cold start; (*3*) retarded ignition timing; and (*4*) in some cases variable valve timing. The catalytic converter is located close to the exhaust manifold (close coupled) to heat up faster. New catalytic units have been developed with: (*5*) increased geometric surface area per unit of volume; (*6*) reduced thermal mass; and (*7*) improved thermal/physical properties of the catalyst layer. Clearer fuels with very low sulfur content are also needed.

These factors are explained in Section 5.

3. Exhaust Gas Composition

The exhaust composition from gasoline/air combustion is dependent on many factors. Total combustion in the internal combustion engine is not possible even when excess oxygen is present (6). The quality and formation of the air/

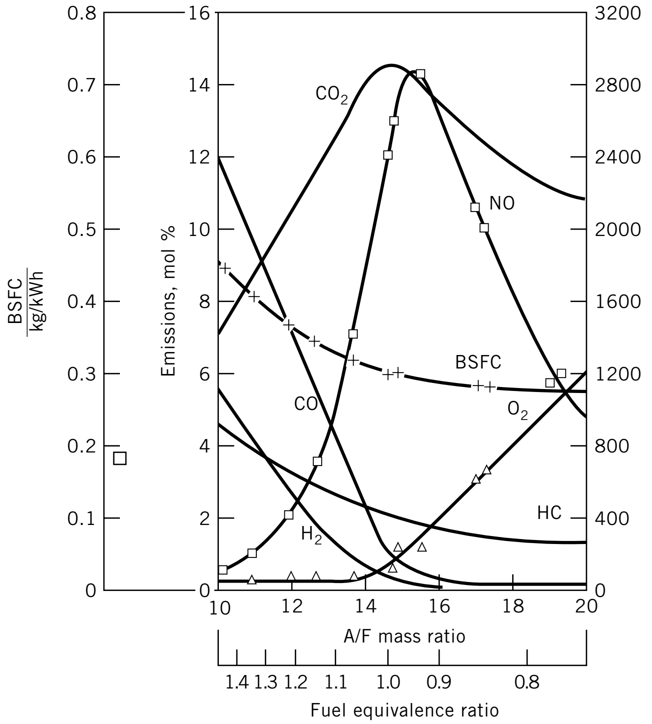


Fig. 3. Effect of mixture strength on exhaust gas composition (dry basis) and brake specific fuel consumption (BSFC) for an unsupercharged automotive-type engine using indolene fuel, H/C = 1.86, where the ignition is tuned to achieve maximum best torque (MBT), the brake mean effective pressure (BNEP) is 386 kPa at 1200 rpm (7).

fuel mixture as well as the design of the combustion chamber influence the combustion process, as do engine power and ignition timing. However in modern engines, for emission control, the main factor affecting exhaust gas composition is the air/fuel mixture or ratio as is shown in Fig. 3 (7) for a standard gasoline fuel where the hydrogen to carbon ratio (H/C) is 1.86. The values for a stoichiometric air/fuel mixture are given at $\lambda = 1.0$. The exhaust gas composition will change substantially as the H/C ratio changes (8), as shown in Fig. 4 (8–10).

Sources of exhaust unburned hydrocarbons are crevices in the combustion chamber, such as gaps between the piston and cylinder wall, where the combustion flame cannot burn. Unburned hydrocarbon composition is dictated by fuel composition (11). Carbon monoxide results from areas of insufficient oxygen. Oxides of nitrogen are produced in the high temperature flame zones during combustion by reaction of nitrogen molecules and oxygen atoms thermally produced from oxygen and oxygen-containing species, according to the Zeldovich mechanism (6,12).

Hydrocarbons and carbon monoxide emission can be minimized by lean air/fuel mixtures (Fig. 3), but lean air/fuel mixtures maximize NO_x emissions. Very lean mixtures (>20 air/fuel) result in reduced CO and NO_x, but encounter

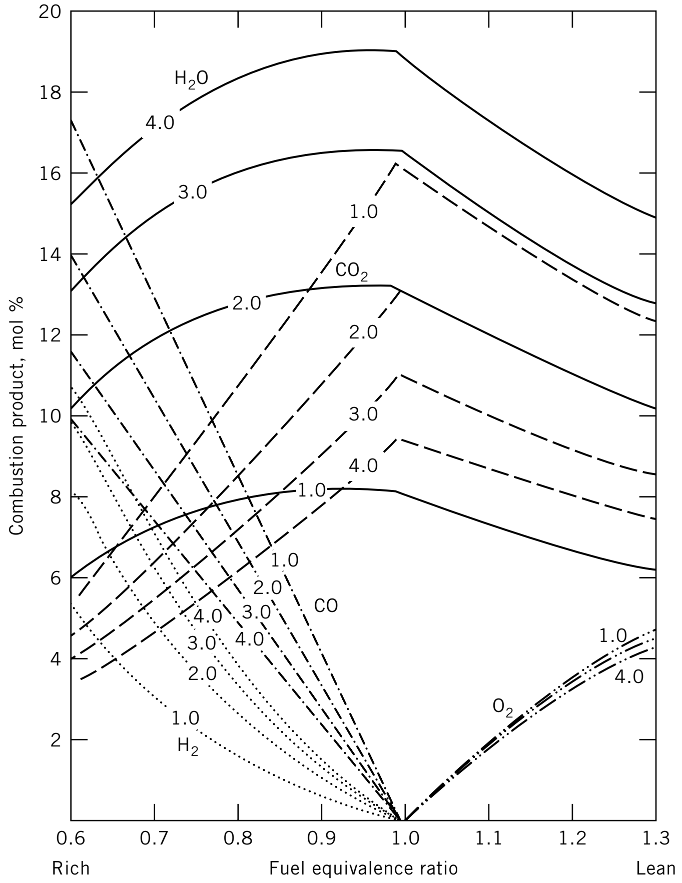


Fig. 4. Theoretical mole percent of the principal combustion products of hydrocarbon fuels for fuel hydrogen:carbon ratios from 1, eg, C_6H_6, to 4, eg, CH_4, wet basis, where (—) represents H_2O; (- - -) CO_2; (– · – ·) CO; (– · · – · ·) O_2; and (· · · · · · · · ·) H_2 (8).

increased HC due to unstable combustion at the lean limit. Improvements in lean-burn engines have extended the lean limit. Rich mixtures, containing excess fuel and insufficient air, produce high HC, CO and H_2 emissions in the exhaust. Very rich mixtures have been used in some engine applications at high engine speeds and loads where the cooling effect of gasoline as it is vaporized in the cylinder is used to limit high cylinder temperature. A recent supplementary US FTP procedure called US FTP 06 Fig. 1**b** is designed to limit such excessive emissions during high speed driving modes. Rich engine calibrations result in toxic CO exhaust concentrations of 4 to 5% or more.

The best engine power is achieved slightly rich and the best fuel economy is achieved slightly lean whereas the stoichiometric air/fuel is the optimal point for best power, fuel economy and emissions.

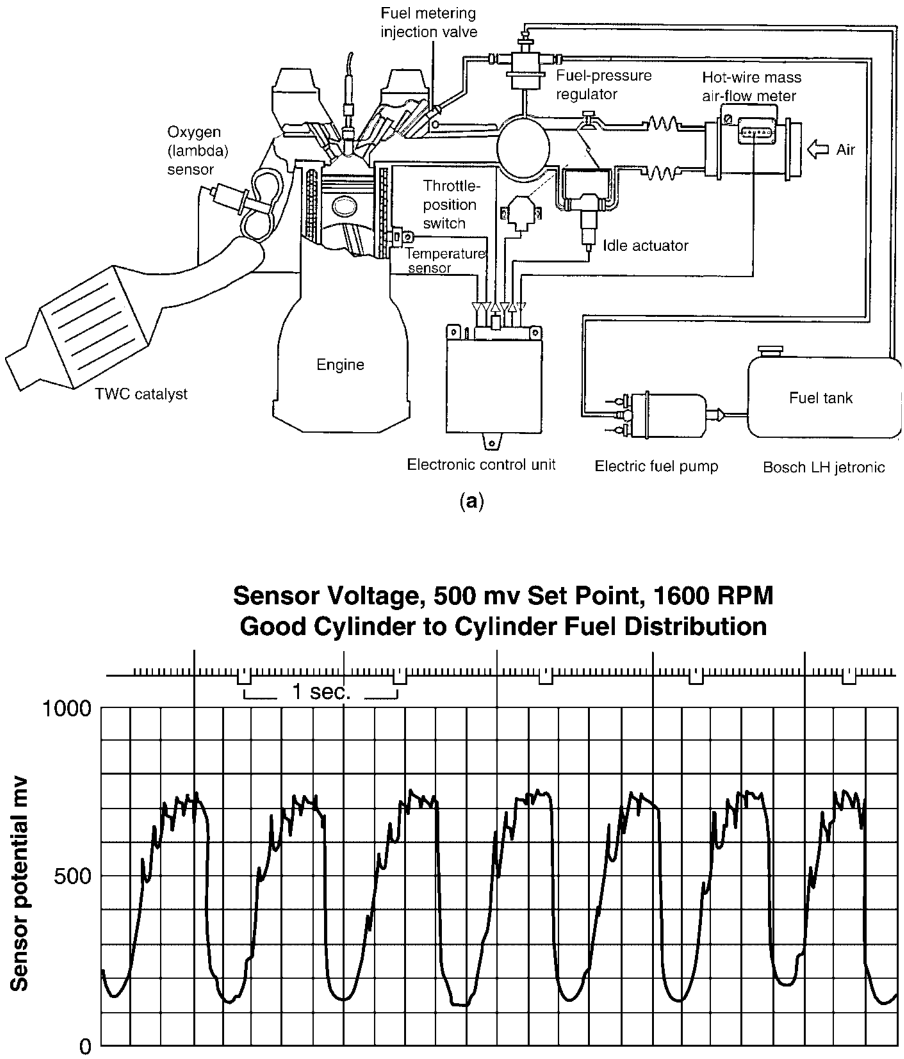
Over 150 hydrogen and carbon species are present in the exhaust mix of a gasoline fueled engine (13–17) including methane, various paraffins, olefins, aldehydes (qv), aromatics, and polycyclic hydrocarbons as well as unburned gasoline. Competitive catalytic oxidative reactions favor oxidation of the latter four classes before paraffins and methane. Analyses of older catalysts after long in-use on vehicles reveal that loss of catalytic performance is higher for the methane and paraffin hydrocarbons than for more reactive species.

Sulfur dioxide is present from the combustion of sulfur contained in the gasoline. The average U.S. gasoline sulfur content had been 350-ppm (20-ppm SO_2 in exhaust) ranging upwards to 1000-ppm in some sections of the U.S. From 2004 to 2006 the gasoline fuel sulfur specification will gradually change to an average of 30-ppm with 80-ppm maximum cap.

Exhaust gas also contains small amounts of hydrogen cyanide and ammonia depending on the air/fuel ratio.

4. Emission Control System

Fig. 5**a** is the schematic of the major components of the TWC Closed-loop Fuel Metering System. The catalytic converter is located at the engine exhaust manifold (in a close coupled position for Tier 2 compliant engines). An O_2 sensor is located ahead of the catalyst unit inlet and can be positioned in the converter inlet shell or in the exhaust manifold. A second O_2 sensor is located at the catalytic converter outlet. The inlet O_2 sensor generates the operating control signal to the electronic control unit (ECU). The outlet O_2 sensor provides a means for trimming the control point to correct for system aging changes over the life of the engine. Both the inlet and outlet O_2 sensors also perform a required emission control quality on-board diagnostic (OBD) function which is explained in Section 8. The operating O_2 sensor is exposed to raw exhaust emitted from the engine and generates an electrical signal indicative of the concentration of oxygen in the exhaust. The signal is sent to the ECU. The ECU also obtains an inlet airflow measurement signal from an engine inlet combustion air measurement meter. Inlet air flow varies in response to the throttle position and engine load (manifold vacuum). In addition, the ECU (*1*) obtains information from the throttle position switch and engine temperature sensor, (*2*) has a stored library of engine speed and load maps, (*3*) calculates the stoichiometric amount of fuel to be injected into the measured amount of inlet air, and (*4*) activates the fuel injector opening time to deliver the proper amount of fuel to a location just ahead of the inlet valve. After combustion in the cylinder, the exhaust gas is measured by the O_2 sensor ($\sim$3 millisecond response time) producing a millivolt signal indicating rich (insufficient oxygen) or lean (excess oxygen) combustion products. The ECU responds to deviations from the stoichiometric control point by correcting the quantity of fuel injected in the next fueling sequence. Thus the air/fuel ratio is constantly being adjusted slightly rich and slightly lean of the stoichiometric mixture (Fig. 5**b**). The three-way conversion (TWC) catalyst receives exhaust gas that reflects this constant change back and forth in intake air/fuel mixture that is stoichiometric centered, but because of the nature of the control system deviates widely in periodic fashion. The TWC is designed to operate under these conditions to convert NO_x by reduction and HC and CO by oxidation by over 95%.



(a)

(b)

Fig. 5. (**a**) Basic components of the TWC closed-loop fuel metering system. Courtesy of Robert Bosch. (**b**) The oxygen sensor controls the air/fuel mixture to an *average* mixture.

5. Three-Way Catalytic Converter: Physical

5.1. Catalytic Converter. The modern catalytic converter consists of three main components: the catalytic unit, a metal shell, and a resilient mounting media. The converter shell assembly surrounds and encloses the fragile ceramic or delicate metallic catalytic unit so that exhaust gas can easily flow into the inlet through the catalytic channels and out of the outlet. The steel shell serves to protect and insulate the catalytic unit from the elements and harsh road physical environments. The converter shell material is usually iron/chrome Series 409 muffler-grade stainless steel that is resistant to oxidation and external corrosion. For the ceramic catalytic unit version, a compliant resilient layer is positioned between the outside of the catalytic unit and the inside of the converter shell. The compliant layer grips the catalytic unit with sufficient force to prevent movement of the catalytic unit within the canister under all conditions of vibration and road shock forces, and compensates for thermal expansion differences of the catalytic unit and shell materials. Several types of compliant layers have been used and all have spring-like properties under compression that provide the necessary gripping force to prevent movement. The compliant layer mounting system has proven durable for the life of the vehicle. Converter design, physical properties, and flow and pressure drop characteristics are amply described in the literature (19–23). Tier 2 close coupled converters are designed to be more thermal resistant due to higher temperature exposure in the manifold location.

A pelleted catalytic converter was used by General Motors and a few other companies until the mid-1980s. It achieved a high level of development (18). However, high thermal mass limited rapid heat up needed to achieve the latest stringent emission standards and durability requirements. The monolithic catalytic converter has become universally used by automobile manufacturers because it is a smaller, lighter unit and can be mounted in any orientation with low pressure drop. Originally it was thought that the catalyst would have to be replaced sometime during engine life. The replacement of pellets was considered more easily managed. Experience has shown that the monolithic honeycomb catalytic converter remains active and fully functional for the life of the vehicle.

5.2. Catalytic Unit. Automotive catalysts for gasoline engines are known as three-way conversion (TWC) catalysts because it destroys all three regulated pollutants: HC, CO and NO_x. TWC catalysts were introduced for the 1977 model year Volvo sold in California. By the mid-1980s they predominated throughout the U.S. and Canada. As clean vehicle technology spread throughout the world TWC catalysts became the dominant system for gasoline spark-ignited engine automobiles and trucks. Oxidation catalysts are part of emission control systems for small engines used for lawnmowers, and hand-held 2-stroke engines emissions control for chainsaws and lawn and garden equipment. The active component of a catalytic unit is a thin activated catalyst layer that is applied uniformly through all flow channels of the monolithic substrate. The catalytic unit is designed to provide sufficient geometric surface so that all exhaust gas pollutants contact hot catalyst surfaces as they pass through its channels (20–23). In order to rapidly heat to operating temperature upon engine start the catalytic unit has low thermal mass and good heat-exchange and mass-transfer properties to extract heat and efficiently exchange pollutants to the catalyst surfaces and products back to the exhaust gas stream.

Activated Catalyst Layer. All catalytic chemical reactions occur on catalyst sites within the activated catalyst layer. The layer contains all the catalytically active ingredients consisting of precious metals, base metal promoter additives, stabilized alumina support particles, and oxygen storage components. The activated catalyst layer of a TWC is applied uniformly to all channel surfaces of the high geometric surface area substrate (ceramic or metallic). The activated catalyst layer consists of finely divided high BET (see explanation below) surface area particles that are porous and thermally resistant. The commonly used process of applying the catalyst layer to the substrate is one of preparing a water slurry of the particles and components and applying the slurry uniformly in a thin layer to the all surfaces of the catalyst substrate by: (*1*) dipping the substrate into a slurry bath; (*2*) pouring the slurry through the channels of the substrate; and (*3*) drawing the slurry up through the substrate by vacuum. The unit is dried and calcined. Small 2 to 5 nanometer precious metal crystals are uniformly dispersed on and within the porous particles of the catalyst layer. The thickness of the catalytic layer is usually between 25 and 100 μm. The substrate or monolith honeycomb body typically has a geometric surface area (the surface of all channels contained in the substrate) of between 35.1 and 43.7 cm^2/cm^3 so that l.6 L catalytic unit volume would contain 5.6 to 7.0 m^2 of geometric surface area. The activated catalyst layer increases the total surface to 7000 m^2/L, ie, about three orders of magnitude. The total surface area consists of the combined internal and external surface of all the minute particles contained in the activated catalyst layer. Total surface area is measured by the Brunauer-Emmet-Teller (BET) technique, which involves N_2 adsorption at low temperature (24).

The minute porous particles are typically aluminum oxide [1344-28-1], Al_2O_3. These particles can have BET surface area of 100 to 300 m^2/g. The thermal and physical properties of alumina crystalline phases vary according to the starting phase (aluminum hydroxide or hydrate) and thermal treatment (see ALUMINUM COMPOUNDS, ALUMINUM OXIDE).

Alumina is used because it is relatively inert and provides the high surface needed to efficiently and uniformly disperse the expensive active catalytic components in a thin effective catalyst layer throughout the entire catalytic unit. However, no one alumina phase possess the thermal, physical, and chemical properties ideal for the perfect activated catalyst layer. A great deal of research has been carried out in search of modifications that can make one or more of the alumina crystalline phases more suitable. For instance, components such as ceria, baria, lanthana, stronthana, or zirconia are added to enhance the thermal characteristics of the alumina. Most recent thermal resistant improvements, dictated by high temperature exposure of catalysts directly coupled to the engine (close coupled), include improved thermal properties of ceria / zirconia combinations (25–27).

A nonstabilized high surface area alumina sinters severely when exposed to 900°C hydrothermal conditions encountered in engine exhaust. Sintering is a process by which the small internal pores in the particles coalesce and lose large fractions of the total surface area. This process is to be avoided because it can occlude some of the precious metal catalyst sites. The network of small pores and passages for exhaust gas transfer collapses thus restricting free gas exchange into and out of the activated catalyst layer resulting in thermal deactivation of the catalyst.

The activated catalyst layer must possess two additional properties. It must adhere tenaciously to the substrate surface under a variety of extreme conditions including rapid thermal changes, high flow, and moisture condensation, evaporation, or freezing. It must have an open porous structure to permit easy gas passage into the catalyst layer and back into the main exhaust stream. It must maintain this porous structure up to exhaust temperature above 900°C. In fact, recent catalyst layer formulations maintain over 60% of original design open porous structure and surface area after exposure to hydrothermal conditions of 1050° to 1100°C.

Precious Metal Catalyst. Precious metals are deposited (impregnated) on and within the small particles throughout the TWC-activated layer. Rhodium plays an important role in the reduction of NO_x, and is combined with platinum and/or palladium for oxidation of HC and CO. Palladium only TWC catalyst have been developed. Various methods of precious metal impregnation are used including pre-impregnation of the stabilized alumina powder or post-impregnation after the activated layer has been applied to the substrate. Only a small amount of these expensive materials is used (28) (see PLATINUM-GROUP METALS). The metals are dispersed on the high surface area as precious metal salt solutions, and then reduced to small metal crystals (size range 2 to 10 nanometers in diameter) by various techniques. Catalytic reactions occur on the precious metal surfaces. A typical Palladium catalyst with 20% dispersion could contain 3.0×10^{21} catalyst sites within one liter of catalyst (29). The small precious metal crystals can agglomerate through in-use thermal processes into much larger diameter structure with consequent loss of catalyst site surface area. An important catalytic site factor is "strong metal to support interaction" (SMSI) plays an important role in influencing the electronic behavior of the catalyst site (30). Some exhaust gas reactions, for instance the oxidation of alkanes, require larger Pt crystals than other reactions, such as the oxidation of CO (31).

The small precious metal crystals can exist as metal crystallites or as metal oxides, both of which can be catalytic (28). Rhodium oxide has a tendency to react with alumina to form a solid solution (32). To minimize this reaction, zirconia is used with the aluminia (33). Publications regarding the TWC function of precious metal catalysts abound (34–38).

Catalyst Support Unit. Terms used to describe the high geometric area support material upon which the active catalyst layer is placed are substrate, monolith, honeycomb, and unitary body. Both ceramic and metallic forms are used for automobile catalysts and each possesses unique properties. The properties each has in common are a large amount of geometric surface per unit of volume, and inert surfaces that do not react with the catalyst layer but allow secure attachment of the catalyst layer.

Ceramic Substrate. The ceramic substrate is typically a cordierite compound [12182-53-5] material made from reacting silicon dioxide, talc, and kaolin at high temperature (~1200°C). The cordierite form is a micro-cracked body with a very low coefficient of thermal expansion that provides excellent thermal-shock resistance and is thermal-dimensionally stable. The manufacturing process is one that mixes, mulls and kneads the three primary materials with water into a sort of dough. The dough is formed into a round billet of about 24 to 36 mm diameter and 1 to 1.5 meters long and forced by an extruding machine through a complex die to form a high geometric area structure. The extruded piece, now in a wet clay-like form, is dried and fired in a kiln at about 1200°C to form the cordierite. The outside or circumferential dimension is formed by the die which shrinks to final dimension during the drying and calcining operation. Similarly, the length is cut to dimension. Variations of the process exist.

Some important substrate physical properties are given in Table 2. In the past the most common cell structure used was 62 cells/cm^2, 0.17 mm wall thick-

Table 2. **Physical Properties of Catalytic Converter Substrates**

Items	Unit	Cell structure [wall thickness, mm / cell density, cells/cm^2 – square cell shape]					
		0.17/62	0.115/62 [hexagonal]	0.11/93	0.09/93	0.064/140	0.05/180
material porosity	%	35	35	35	35	27	35
wall thickness [nominal]	mm	0.17	0.115	0.11	0.09	0.064	0.05
cell pitch [nominal]	mm	1.27	1.36	1.04	1.04	0.85	0.73
open frontal area	%	75.0	83.8	80.0	83.4	85.6	86.8
hydraulic diameter	mm	1.10	1.25	0.93	0.95	0.79	0.68
geometric surface area	cm^2/cm^3	27.3	26.9	34.4	35.1	43.5	50.8
pressure drop[a]	%	100	72	130	119	168	217
bulk density	g/cm^3	0.43	0.29	0.35	0.29	0.28	0.24
bulk density ratio	%[b]	100	67	81	67	65	55
specific heat	cal/g/°K		<—	0.2	—>		
thermal conductivity	cal/g/sec/°K		<–	3×10^{-3}	—>		

[a] Pressure drop values are calculated with the following conditions: Substrate size = 101.6 D × 101.6 L; Exhaust gas temp. = 850°C; Gas flow = 5 Nm^3/min.

[b] Ratio against 0.17mm wall thickness / 62 cell/cm^3 substrate. *Courtesy of NGK Ceramics, USA, Inc.*

ness, 27.3 cm^2/cm^3 geometric surface area, and 0.43 g/cm^3 bulk density as optimal to meet Tier 1 emission standards. Cell structure selected for the more stringent U.S. Tier 2 and California LEV2 standards are of higher geometric surface area and lower bulk density—for instance 93 and 140 $cell/cm^2$ with thinner walls of 0.11 and 0.06 mm wall thickness to create higher geometric surface area of 34.4 and 43.7 cm^2/cm^3 and lower bulk density of 0.34 and 0.24 g/cm^3 respectively. The combined factors of higher geometric surface area and lower bulk density allow for faster heat up of the catalytic unit to operating temperature during cold start where the important property of thermal mass is related to bulk density and specific heat. Care must be given to flow pressure drop, physical strength, and general ruggedness in an appropriate mounting system design (20–23,39–41).

Metallic Substrate. Metallic substrates are formed from thin metal sheets of metal alloys containing Fe, Cr, and Al stabilized with Y or Ce that have excellent oxidation resistance over the complete range of exhaust temperatures (42). Melting temperature is in the same range as ceramic cordierite (see HIGH TEMPERATURE ALLOYS). A feature is that when heated in air, an aluminum oxide surface layer is formed. The small amount of yttria or ceria present stabilizes the aluminum oxide surface to resist spalling of the alumina that may otherwise occur. The ceria- stabilized alloy develops a whisker-like surface. The activated catalyst layer has been found to adhere very well to either surface form.

The metallic substrate is designed to provide a cell density similar to that of the ceramic counterpart, and can be constructed in versions of 93, 124 and 155 $cells/cm^2$. However, the wall thickness is thinner, ie, 0.05 to 0.15 mm thick (43). The 0.05 mm thick wall material can be constructed in versions of 186 to 248 $cell/cm^2$. The unique advantage of metal substrate over its ceramic counterpart is that either the same geometric surface can be made into a smaller volume, or that the same volume and geometric surface area will provide lower pressure drop (44). The 186 to 248 $cells/cm^2$ metal substrates have a potential performance advantage over ceramic because of large increases in geometric surface area that are needed for Tier 2 emission standards. Metal substrate based catalytic converters find application on high performance vehicles such as Porsche, DaimlerChrysler Viper and others (42). The advantage here is lower exhaust gas pressure drop can result in increased horse-power ($\sim$1 or 2 hp at high engine speed) and performance. Other special niche applications exist.

5.3. Heat and Mass Transfer. The heat and mass exchange processes of exhaust gas to the catalytic surfaces takes place under hot pulsating exhaust flow conditions. Turbulent flow conditions (Reynolds numbers above 2000) exist in the exhaust manifold and inlet cone of the catalytic converter in response to the exhaust stroke of each cylinder (about 6 to 25 times per second) times the number of cylinders under fluctuating gas pressure. Upon entering the cell passages of the catalytic unit laminar flow conditions (Reynolds number below 2000) are developed in a distance of $\sim$0.6 cm (45–48).

Heat and mass transfer (qv) are driven by temperature and concentration differences, respectively, between catalyst surfaces and the bulk gas. Effective mass transfer of reactants and products commence at operating temperatures over 250°C as catalyst reactions take place with the catalytic layer.

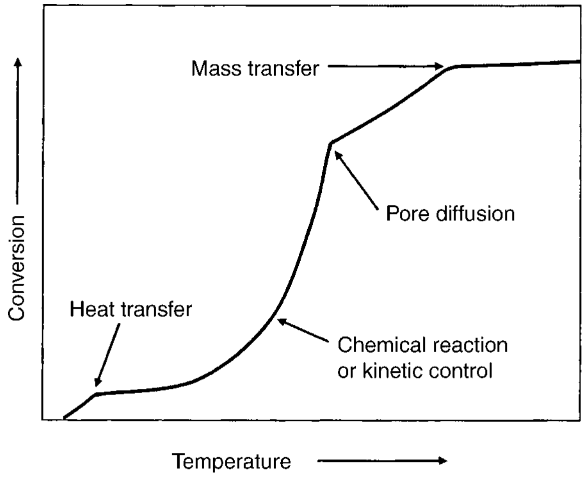


Fig. 6. Conversion vs temperature.

The process of catalyst heating and initiation of the catalytic functions involves three or four distinct regions as shown in Fig. 6. Depending on the location of the catalytic unit in the exhaust system, total thermal mass before and including the catalytic unit, and exhaust flow and temperature, it can take from 10 to 120 seconds for the catalyst unit to reach ignition temperature of approximately 250–300°C (Region I) where heat exchange processes dominate. At temperatures above the ignition point, catalyst function increases directly with temperature increase as catalyst activity increases sharply (Region II) involving both heat exchange and reactant/product mass transfer processes. Exothermic reactions contribute to temperature rise within the catalyst layer. Some catalysts reach a point where the sharp increase in catalytic activity with inlet temperature abruptly takes on an undesirable mild positive slope (Region III). Then a point is reached at which catalytic performance improves only slightly in response to further increases in temperature (Region IV) where reactant mass transfer processes dominate.

In Region I (below the ignition point) the process is one of heat exchange. Catalytic activity is prevented by lack of sufficient activation energy and because of chemisorption of other species. Within Region II, the specific activity of the catalyst is the rate-limiting step; this is the kinetically controlled region. Highly active catalysts have a lower ignition point and exhibit large increases in catalytic performance associated with small increases in catalyst temperature. The behavior of a catalyst in Region II is important to the selection of an automotive emission catalyst because catalyst light-off is a prime metric in achieving adequate emission control early in the FTP as shown in Fig. 7.

Region III is not present in most catalysts. It depends on the porous structure design of the catalyst layer and is often only found in used or spent catalyst. If present, the rate-limiting step is pore diffusion control. Catalysts clogged with masking agents such as lube oil ash and/or accumulations of metal oxides from gasoline organic metallic additives, ie, iron or manganese, would be expected to show Region III behavior. Region IV is a mass-transfer limited region, ie,

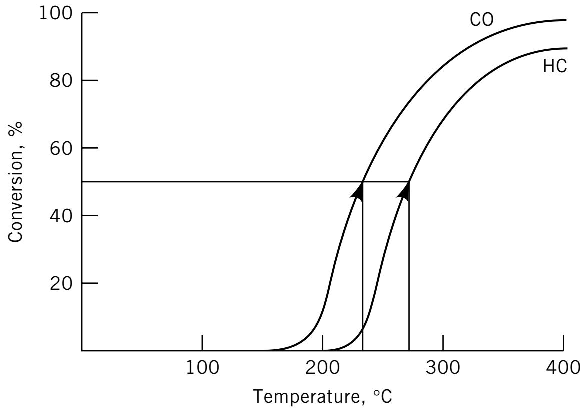


Fig. 7. Effect of temperature on catalyst performance using synthetic exhaust: 0.45% CO, 12% CO_2, 500 ppm NO,0.15% H_2, 3% O_2, 200 ppm C_3H_6, 10% H_2O, and remainder N_2. The T_{50} for CO and HC are 230°C and 270°C, respectively. See text.

catalytic reactions occur so fast that the rate-limiting factor is the rate of transfer of reactants and products to and from the surface of the catalyst. Mathematical models describing the entire process are found in several references (45–48).

6. Three-Way Catalytic Converter: Chemical Reactions and Surface Chemistry

Automobile exhaust catalysts are perfect examples of materials that accelerate chemical reactions toward thermodynamic equilibrium but are not consumed by the reactions. Reactions are completed on the catalyst surface and the products leave. Thus the auto exhaust 3-way catalyst performs its functions over and over again for the life of the vehicle. The catalyst permits reactions to occur at considerably lower temperatures. For instance, CO reacts with oxygen in bulk gas phase above 700°C at a substantial rate. An automobile exhaust catalyst enables the CO oxidation reaction to occur at a temperature of about 250°C and at a much faster rate and in a smaller reactor volume. This is also the case for the oxidation of hydrocarbons and the reduction of NO_x.

6.1. Selectivity. The reduction of NO_x in an automotive three-way catalyst involves a catalyst property called selectivity. Selectivity occurs when several reactions are thermodynamically possible but one reaction proceeds at a faster rate than another. The catalyst chooses the route with lowest activation energy. For instance the preferred three-way catalyst reduces NO to N_2 and not to N_2O or NH_3. In the case of the three-way catalyst, CO, HC and H_2 are potential reductants of NO. On the other hand, O_2 is present, which oxidizes CO, HC and H_2. If oxidation reactions are too rapid, no reductant would be available to reduce NO. Using modern TWC catalyst, however, NO reduction is substantially completed before reductants are consumed by O_2.

6.2. Catalyst Metals. Two classes of metals have been examined for potential use as catalytic materials for automobile exhaust control. These consist of some of the transitional base metal series, for instance cobalt, copper, chro-

Table 3. **Specific Reaction Rates**

	$CO + O_2$[a]		$C_2H_4 + O_2$[b]	
Catalyst	Temperature, °C	R^c	Temperature, °C	R^c
Pd (wire)	300	500	300	100
Pt (wire)	300	100	300	10
Au (wire)	300	15	300	0.03
Co_3O_4	200	25 + 5	300	0.33
CuO	200	11	300	0.6
$CuCr_2O_4$	200	5	300	0.8
$LaCoO_3$	200	2.3	400	0.53
$BaCoO_3$	300	5.3	400	0.1
SnO_2	300	5.2	400	0.4
MnO_2	300	3.4	300	0.04
$LaMnO_3$	300	2	400	0.3
$La_{0.5}Sr_{0.5}MnO_3$	300	1.2	400	0.26
$La_{0.5}Pb_{0.3}MnO_3$	300	0.5	400	<0.05
Fe_2O_3	300	0.4	400	0.06
$FeCr_2O_4$	300	0.33		
Cr_2O_3	300	0.03	300	0.006
NiO	300	1.5		
ZrO_2	300	0.013	400	0.002

[a] 1% O_2, 1% CO, 0% H_2O.

[b] 1% O_2, 0.1% C_2H_2, ~0.1% H_2O.

[c] Units in terms of CO_2 formation mL/(min · m^2).

mium, nickel, manganese, and vanadium; and the precious metal series consisting of platinum [7440-06-4], Pt; palladium [74409-05-3], Pd; rhodium [7440-16-6] Rh; iridium, [7439-88-5], Ir and ruthenium [7440-18-8], Ru. Specific catalyst activities are shown in Table 3.

The precious metals possess much higher specific catalytic activity than do the base metals. In addition, base metal catalysts sinter upon exposure to high engine exhaust gas temperatures thereby losing low temperature ignition and catalyst performance. Base metals deactivate due to reactions with sulfur compounds at the low temperature end of auto exhaust environments. Base metal catalysts would need to be considerably larger. Consequently, the larger volume would take more time to heat up quickly enough to achieve the catalytic performance demanded by stringent emission standards. Base metal catalytic components that provide positive synergistic effects on catalyst performance when combined with precious metal are called promoters. Reducible base metal oxides are very important to three-way catalyst designs as explained in a following section.

6.3. Diffusion of Pollutants to Active Catalyst Sites. A representation of gas transport from bulk gas to a catalyst reaction site is shown in Fig. 8. A gaseous pollutant such as CO diffuses from the main gas stream into the porous catalyst matrix. The rate of diffusion depends on molecular weight of the molecule—heavy gaseous hydrocarbons diffuse slower and hydrogen has the fastest rate of diffusion. There is a net CO flow from the main flow stream to the catalytic surface because CO is at a higher concentration in the exhaust stream and, once catalyst reactions take place, of lower concentration within the catalyst

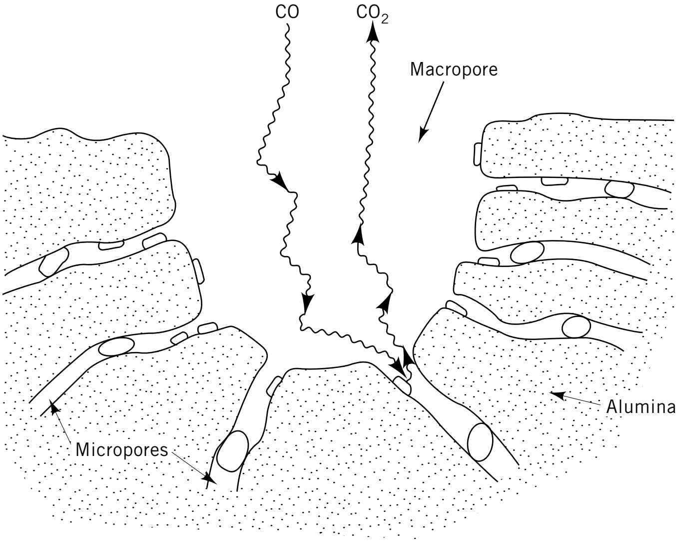


Fig. 8. Catalyst pore and reaction. The CO diffuses into a precious metal site □; reacts with O_2; and leaves as CO_2.

layer. The CO is attracted to a precious metal catalyst site that is temporarily unoccupied. For the same reason, O_2 molecules are attracted to the site. The O_2 molecule is chemisorbed on the precious metal surface where oxygen molecule bond stretching occurs, leading to dissociation into oxygen atoms and electron sharing with the clean precious metal catalyst site surface. The reaction of CO with adsorbed O atoms proceed to form CO_2, which in the product state is released and reenters the exhaust stream as there is less CO_2 in the exhaust stream and more within catalytic layer so there is a net flow of CO_2 away from the catalyst surface.

6.4. Chemical Reactions.

The principal chemical reactions of a TWC catalyst are

Oxidation reactions

$$H_2 + 1/2\,O_2 \longrightarrow H_2O$$

$$CO + 1/2\,O_2 \longrightarrow CO_2$$

$$C_mH_n + (m + n/4)\,O_2 \longrightarrow m\,CO_2 + n/2\,H_2O$$

TWC reaction at stoichiometric A/F mixtures

$$CO + NO \longrightarrow 1/2\,N_2 + CO_2$$

$$C_mH_n + 2(m + n/4)\,NO \longrightarrow (m + n/4)\,N_2 + n/2\,H_2O + m\,CO_2$$

$$H_2 + NO \longrightarrow 1/2\,N_2 + H_2O$$

$$\mathrm{CO + H_2O \longrightarrow CO_2 + H_2} \quad \text{water gas shift}$$

$$\mathrm{C_mH_n} + m\,\mathrm{H_2O} + m\,\mathrm{CO} + \left(m + \frac{n}{2}\right)\mathrm{H_2} \quad \text{steam reforming}$$

Other NO-reduction reactions

$$\mathrm{2\,NO + 5\,CO + 3\,H_2O \longrightarrow 2\,NH_3 + 5\,CO_2}$$

$$\mathrm{2\,NO + 5\,H_2 \longrightarrow 2\,NH_3 + 2\,H_2O}$$

$$\mathrm{NO} + \text{hydrocarbons} \longrightarrow \mathrm{N_2 + H_2O + CO_2 + CO + NH_3}$$

$$\left\{\begin{matrix}\mathrm{2\,NO + CO \longrightarrow N_2O + CO_2} \\ \mathrm{2\,NO + H_2 \longrightarrow N_2O + H_2O}\end{matrix}\right\} \text{at } 200\,^{\circ}\text{C (below exhaust gas temperature)}$$

Fuel sulfur reactions

$$\mathrm{S + O_2 \longrightarrow SO_2}$$

$$\mathrm{SO_2 + 1/2\,O_2 \longrightarrow_{Pt} SO_3}$$

$$\mathrm{3\,SO_3 + Al_2O_3 \overset{>600^{\circ}C}{\Longleftrightarrow} Al_2(SO_4)_3}$$

$$\mathrm{Al_2(SO_4)_3 + 12\,H_2 \longrightarrow_{PM\ catalyst} 3\,H_2S + Al_2O_3 + 9\,H_2O}$$

$$\mathrm{SO_2 + 3\,H_2 \longrightarrow_{PM\ catalyst} H_2S + 2\,H_2O}$$

Where PM is precious metal.

In the case of oxidation catalysts used for small engines or in any other similar applications only the *Oxidation reactions* and *Fuel sulfur reactions* apply.

6.5. Surface Chemistry and Reaction Mechanisms. Three-way catalytic oxidation of HC and CO must proceed in balance with the reduction of NO_x by CO, H_2 or HC. CO has been determined to be the predominant reductant of NO in a complex reaction series on a metal catalyst surface site. First two molecules of NO molecules are adsorbed on the catalyst site surface where they dissociate forming N_2 and leaving two O atoms remaining on the catalyst site. CO (nonabsorbed species) is required to remove the O atoms to complete the reaction cycle otherwise the cycle would be interrupted (49). A TWC catalyst must be able to partition enough CO present in the exhaust for each of these reactions and provide a surface that has preference for NO adsorption. For instance, Rhodium has a slight preference for NO adsorption rather than O_2 adsorption; Pt prefers O_2 adsorption. Rh does not catalyze the unwanted NH_3 reaction as does Pt, and Rh is more sinter-resistant than Pt (6). Double layered and multilayered catalysts are an effective means to partition the reactions, ie, an inner layer if Pt, Pd or Pt/Pd and an outer layer of Rh have been found particularly effective in this respect. Pd only TWC catalysts have been developed that are very thermally resistant for close coupled application in the new Tier 2 compliant vehicles. The catalyst layers can also be sequenced axially along the channel for instance with a Rh layer deposited on the inlet half followed by the Pt, Pd or Pt/Pd layer on the outlet half of the channel. Recently single layer structured designs have been reported effective.

A major performance factor for TWC catalysts is coping with the fluctuating air/fuel conditions common with O_2 sensor controlled fuel metering systems Fig. 6. In actual practice, the air/fuel mixture will fluctuate rich and lean of the stoichiometric point by $+-0.3$ to 1.0 air/fuel mixture ratio one to three times per second. Actually very little time is spent at the preferred stoichiometric air/fuel mixture point Thus there is too much oxygen present for one half of the time and too little for the other half. Incorporation of cerium oxide or other reducible oxides components, including Palladium oxide, solves this problem (53). For example, ceria reactions under these fluctuating air/fuel conditions are: Under lean conditions with excess O_2

$$Ce_2O_3 + 0.5\ O_2 \longrightarrow 2\ CeO_2$$

Under rich conditions with insufficient O_2

$$2\ CeO_2 + CO \longrightarrow CO_2 + Ce_2O_3$$

The cerium $+3$ species captures O when in excess that would otherwise exit the tailpipe and cerium $+4$ releases O for oxidization reactions when in short supply. These reactions provide a counterbalance chemical force toward maintaining stoichiometric conditions within the catalyst layer even though the dynamic of the fuel metering system provide cycles “rich – lean – rich – lean” in response to the O_2 sensor feedback control signal.

Nevertheless, the fuel metering system dynamic (or lag time) has a profound effect on any three-way catalyst formulation. Fig. 9**a** shows a single-point fuel injection system with the injector located in the main tube of the inlet manifold and Fig. 9**b** show a multi-point fuel injection system with a fuel injector located at each inlet valve. Fig. 10 is the catalytic performance evaluation of the same TWC when evaluated on an engine sweep test equipped with a variable closed-loop feed back O_2 sensor controlled fuel metering system so that different fuel metering systems can be simulated: (**a**) Actual multi-point fuel injection. (**b**) Simulated single-point fuel injection. (**c**) Simulated closed loop carburetor. It is proven here that advanced fuel metering is needed to extract the optimal catalytic performance of a three-way catalyst (54).

The CO oxidation reactions steps proceed as factors. An O_2 molecule is chemisorbed on Pt metal surface as well as two CO (absorbed) species, resulting in CO_2 formation that enters the exhaust stream as mentioned above.

7. Factors Related to Long Term Durability

7.1. Catalyst Durability.

The actual in-use overall durability of the three-way catalyst has proven to be very good even under extreme operating conditions. A durability test of an advanced three-way catalytic converter that was

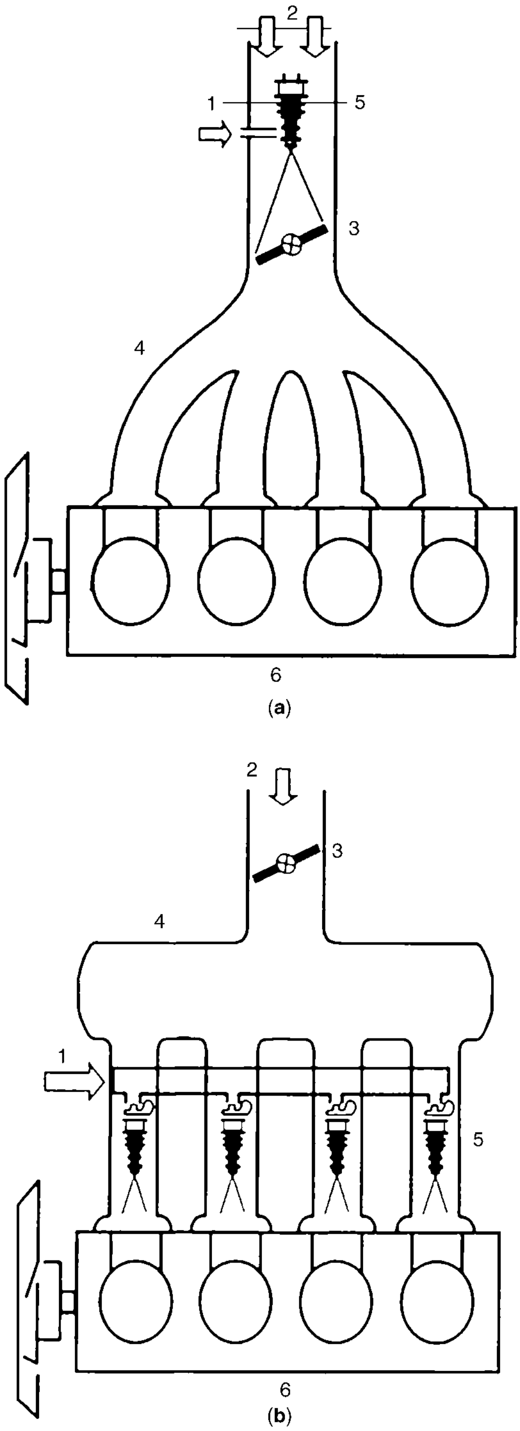


Fig. 9. (**a**) Single-point fuel injection (TBI). 1 Fuel, 2 air, 3 throttle valve, 4 intake manifold, 5 injector, 6 engine. (**b**) Multipoint fuel injection. 1 Fuel, 2 air, 3 throttle valve, 4 intake manifold, 5 injectors, 6 engine. Courtesy of Robert Bosch.

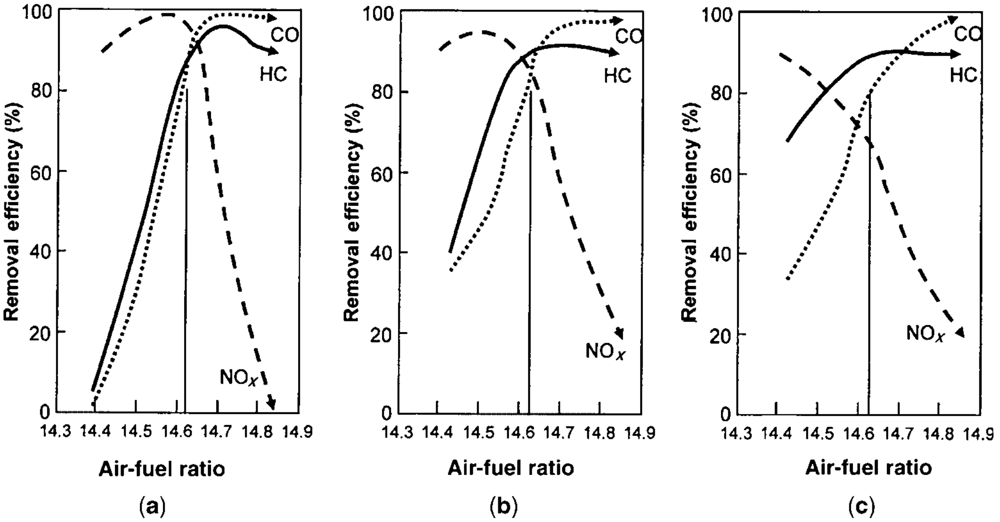


Fig. 10. The quality of the closed-loop system is very important to catalyst function. (**a**) Closed loop ±0.3 A/F at 1.5 Hz (multi-point fuel injection). (**b**) Closed loop ±0.5 A/F at 1.0 Hz (single-point fuel injection). (**c**) Closed loop ±1.0 A/F at 1.0 Hz (closed-loop carburetor) (51). For (**b**) and (**c**) Simulated Utilizing Frequency Generator.

aged on the MVEG-Cycle (European automobile manufacturers aging cycle that mimics autobahn driving) for 160,000 km. The decline in HC, CO and NO*x* emissions control performance is minor over 20,000 to 160,000 km. The result shows that very robust three-way catalysts have been developed.

Automobile catalysts last for the life of the vehicle and still function well at the time the vehicle is scrapped. However, there is potential for decline in total catalytic performance from exposure to very high temperatures, accumulation of catalyst poisons, or loss of the active layer (52–57).

7.2. Thermal Processes. Exposure to temperatures above 1050°C can cause the active layer surfaces to sinter, collapse, agglomerate, shrink, and possibly exfoliate. Collapse of the open porous structure can occlude precious metal sites and prevent free exhaust gas passage to these sites. Also, the small precious metal crystals can unite and grow into larger crystals, thereby diminishing the total precious metal surface and thus the total number of active catalyst sites. If catalyst temperatures exceed 1200°C, the substrate softens and perhaps shrinks. At about 1465°C, the substrate melts and is destroyed.

High catalyst temperatures are caused by two types of factors. The first is engine operating conditions and the second is due to exothermic chemical reactions within the catalysts. Ignition timing, air/fuel mixture, and engine load govern the exhaust gas temperature and thus the catalyst inlet temperature. High engine speed and load can result in exhaust temperature up to 900°C. When the catalyst consumes exhaust hydrocarbons, carbon monoxide or hydrogen exhaust components, these exothermic reactions result in increased catalyst temperatures. For instance the combustion of 1% CO would result in 87°C adiabatic temperature rise of the exhaust gas (58); the combustion of 1000-ppm C_6H_6 would yield 103°C temperature rise. If an engine was calibrated rich and air was added to the exhaust prior to an oxidation catalyst with an air pump an exothermic reaction could result in 300 to 700°C exhaust gas temperature rise. The three-way catalyst closed-loop feedback system does not normally have an air pump and avoids such mishaps. Misfire or partial misfire results in non-combusted fuel/air mixtures which undergo catalytic combustion in the catalyst and can produce very high exothermic reactions.

Misfire or partial misfire of the air/fuel charge in the combustion chamber results in unburned fuel mixed with air passing to the catalyst, where complete combustion occurs. The temperature rise can be considerable. Two misfiring cylinders in a four-cylinder engine could cause the temperature in the catalyst to approach the softening temperature (1200°C) of the substrate or melting temperature (1465°C) (59).

There are many reasons for misfire. The principal causes are: (*1*) any interruption of ignition energy, for instance, caused by faulty or wet ignition wiring; and (*2*) extreme lean or rich noncombustible air/fuel mixtures. Modern engines have electronic ignition, very durable and moisture proof ignition wiring and connections, and highly improved fuel metering systems, and fuel shut off during deceleration, all of which have greatly lessened the chances and occurrence of misfire. Shorted-out ignition failure due to wet wiring has become rare. Unleaded fuel does not corrode, clog, or wear spark plugs, as leaded gasoline quickly did, and extends combustion quality and spark plug life by 4 to 10 times or more. Thus the ignition, fuel metering systems and combustion quality are vastly improved over pre-1975, pre-catalyst equipped vehicles. Catalysts have now been designed to resist thermal degradation by incorporation of base metal oxide stabilizers (25–27,60,61).

7.3. Poisons and Inhibitors. Catalyst poisons and inhibitors can come from the fuel, the lubricating oil, from engine wear and corrosion products, and from air ingestion of various materials. The two types are: poisons of catalyst active sites; and, masking agents.

Fuels. The most serious catalyst poison resulted from combustion of a tetraethyl lead (TEL) [78-00-2] and ethylene dibromide or chloride (EDB,EDC), cocktail mixture additive to gasoline to improve octane. Octane enhancement of gasoline is the only positive feature of TEL with many negative consequences. Exhaust of leaded gasoline produces ultra-fine air borne lead perfect for inhalation deep into the lung directly contributing to mental development impairment of children (unrecoverable loss of up to 10 IQ points in urban areas) and serious detriments to classroom learning processes. Serious life-shortening health problems for adults and children are also documented (62,63). Combustion of the TEL cocktail produces acid components that saturate lube oil resulting in severe engine corrosion and wear resulting in shortened engine life. Continuous deterioration of spark plugs resulted in decline of ignition and combustion quality and shortened spark plug life. The entire exhaust system was corroded from the inside out resulting in reduced exhaust system life.

Leaded gasoline (about 10% of world gasoline) is still used in many parts of the world—Africa, former Soviet Union countries and Middle East countries. Leaded gasoline use in North America is banned. The only remaining U.S. source of leaded gasoline is aviation grade gasoline and thus mechanics and a sector of the population near airports are still exposed to this poison. Also, tetraethyl lead in containers is reported available in auto supply stores for individuals for their own vehicles. Catalytic converters are permanently poisoned and rendered ineffective from small amounts due to contamination of leaded gasoline in unleaded gasoline—30 mg Pb/gal caused rapid decline in catalyst performance in a short period. The mechanism of lead poisoning of automobile exhaust catalysts has been identified by Ford researchers (64).

Other metal-based fuel additives (Fe, Mn) also create engine debris and accumulate within the engine and exhaust system. Catalysts have been found clogged with inlet face surface debris/deposits. See reference 5 for a comprehensive analysis of the engine, oxygen sensor and catalyst component functions where one set of engine components was exposed to clear unleaded gasoline and an identical set exposed to a Mn-additive containing gasoline. The study is complete with revealing photographs. The components were interchanged between the respective engines used for clear unleaded and Mn-additive in a sound scientific study to reveal: (*1*) engine out emissions effects; (*2*) negative effects of O_2 sensor performance; and (*3*) declines in catalyst performance. The negative effects appear to be a direct consequence of accumulation of Mn deposits on and within the O_2 sensor and catalyst (5). In recognition of the negative effects of fuel-borne metal-organic additives, the World-Wide Fuel Charter (WWFC), a document produced in cooperation with all world engine manufacturers and automobile manufacturers, specify metal content of unleaded gasoline (Fe, Mn, Pb and other) be non-detectible for all world in-use vehicle markets (65).

7.4. Fuel Sulfur. Fuel sulfur is responsible for inhibition of TWC catalyst performance. Fuel sulfur combustion produces sulfur oxides–(SO_2/SO_3). Sulfur compounds react with catalyst layer materials and catalyst sites in a complex manner. Fuel sulfur has been found to contribute to a decline in HC, CO, and NO_x catalyst performance directly associated with the level of fuel sulfur in two separate studies (66). Sulfur is stored on catalyst sites and within the catalyst layer in various forms and is released under certain conditions. One mechanism is the release of H_2S yielding a rotten egg odor to the exhaust. A small amount of nickel oxide incorporated into the TWC captures H_2S and releases it inoffensively later as SO_2 under higher temperature operating conditions (50,67). The U.S. EPA Tier 2 specification for gasoline sulfur content is 30-ppm average with a maximum cap of 80-ppm to start phasing-in from 2004 to 2006. When the lower sulfur gasoline phase-in is complete it is expected that all current on- and off-road in-use vehicles will improve emissions control performance by up to 30%. The World Wide Fuel Charter (65) recommends similar fuel sulfur specifications. It is noted that TWC catalysts avoided a major fuel sulfur problem with respect to the in the U.S. light-duty emission control program. Oxidation catalysts, originally used from 1975 through the early 1980s, oxidized SO_2 to SO_3 resulting in H_2SO_4 emissions in the order of 0.2 g/km—100 times higher than TWC catalysts. Had oxidation catalysts continued to be needed for emissions control fuel sulfur content would have had to be addressed in the early 1980s.

7.5. Lubricating Oil. Masking agents deactivate catalysts by plugging the open porous surface of the catalytic layer. Oil ash compounds resulting from lubricating oil combustion accumulate on catalyst layer surfaces, or lubricating oil emitted from the exhaust valve stems deposit on the surfaces of the catalyst where the organic portion is oxidized leaving inorganic ash compounds of zinc, phosphorous, calcium and barium (see LUBRICATION AND LUBRICANTS) on the catalyst surface. Significant quantities can accumulate depending on lube oil consumption. The ash compounds tend to partially or fully block some of the surface pores of the catalyst layer called pore mouth plugging. It only takes a small amount of material on the surface of the catalyst to restrict the free passage of exhaust gases into and out of the porous catalyst layer. A zinc pyrophosphate glaze had been found to form on the catalyst surface under certain temperature conditions (68,69) masking large areas of catalyst surface and preventing passage of gases into and out of the catalyst porous structure. Materials such as calcium inhibit the formation of this glaze. Because modern engines using clean unleaded fuel have a much longer life, masking mechanisms are becoming a more important in catalyst performance decline for high mileage engines. Metal contents of lubricating oils are currently being studied and it is expected they will be reduced to match engine needs fueled with Tier 2 low sulfur unleaded gasoline (70).

7.6. Catalyst Layer Loss. Partial loss of the catalyst layer via attrition, erosion, or loss of adhesion and exfoliation could result in some loss of catalyst performance. The monolithic catalyst is designed to resist all of these mechanisms. Nevertheless, catalyst materials have been found in roadside dust extending a few meters from the roadway indicating some loss is occurring. Analyses of the leading inlet face edge of catalytic units have revealed evidence of small loss via a gas erosion process at the leading edge. If this becomes an issue it can be addressed by a hardening procedure.

8. Oxygen Sensor and the Closed Loop Fuel Metering System

The first commercial application of the TWC catalyst and closed loop fuel metering system using an oxygen sensor was on the 1977 Volvo (four models) sold in the California market (71–74). The catalyst was invented by Engelhard (50). Volvo, Bosch, and Engelhard cooperated to bring the system to production over a 2.5 year period. Several other car companies adopted the system the following year, and by the 1990s almost all cars sold in the United States and Canada utilized it. The fully developed system is described in the literature (see SENSORS). It is now used on almost all light-duty, medium-duty and heavy-duty SI engine vehicles produced in the world.

A brief description of the system follows. The function of the oxygen sensor, electronic control unit (ECU), and fuel metering system is to deliver a stoichiometric air/fuel mixture to the engine cylinder combustion process, ie, there should be neither excess air nor excess fuel. The main purpose is to provide optimal exhaust conditions for the TWC catalyst to reduce NO_x while at the same time to oxidize HC and CO within the same catalyst bed forming nonpollutants N_2, H_2O, and CO_2. In actual operation, the O_2 sensor continuously senses whether there is an excess or lack of O_2 present in the exhaust products. The O_2 sensor signal is continuously monitored by the ECU. The ECU also receives a continuous air flow measurement signal from a mass-flow inlet airflow measurement device (usually a hot wire anemometer) (75,76); calculates the proper amount of fuel for the measured amount of air, and controls each fuel injector opening time to deliver the calculated amount of fuel. The ECU uses the O_2 sensor signal as a correction signal to the computed amount of fuel to be injected into a measured flow of input air. This control approach is known as a feed-back system and by its nature is always correcting after the cylinder combustion event has taken place. The result is a correction cycle above and below the stoichiometric air/fuel mixture centering at stoichiometric. The TWC is designed to operate effectively in such an environment. It is found that minimizing the deviation from the stoichiometric control point and minimizing the frequency with which it occurs is very beneficial to the performance of any TWC catalyst (51).

8.1. Oxygen Sensor. The O_2 sensor is also referred to as lambda sonde or lambda sensor (lambda is the Greek letter used to denote the air/fuel ratio), and as an exhaust gas oxygen sensor (EGO). The O_2 sensor is a concentration cell that responds to a changes in exhaust oxygen content in 3 milliseconds yielding a millivolt output signal, ie, 50 mV at $i = 1.05$ (lean) to 900 mV at $i = 0.99$ (rich) as shown in Fig. 11. The voltage changes sharply in the immediate vicinity of the stoichiometric ratio ($i = 1.0$). The sensor consists of (qv) ceramic porous solid electrolyte that is ionically conductive at operating temperatures >350°C. The outside of the ceramic is coated with platinum electrodes: one electrode exposed to the exhaust gas, the second to ambient air. Between these electrodes is a zirconia solid electrolyte. The voltage generated depends on the oxygen concentration difference between each electrode. The exhaust porous platinum electrode is a catalyst at the exhaust gas surface and equilibrates the mixture, consuming, by catalytic action, unreacted oxygen and CO, H_2,and HC, yielding

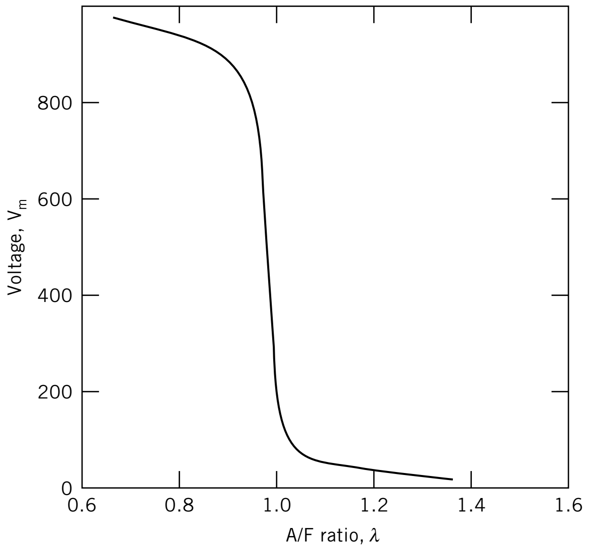


Fig. 11. The A/F ratio ad the lambda sensor's voltage signal. Courtesy of Robert Bosch.

a net amount of oxygen present. Near the stoichiometric point, ie, $i = 1.0$, the difference between atmospheric O_2 and exhaust O_2, and thus the voltage generated, approach a maximum. Thus a control point sensor signal of about 450 to 500 mv is used to detect whether the exhaust is above or below the stoichiometric control point (75–77). In order for the sensor to function properly, it needs to be heated to above 350°C. To accommodate the need for quick O_2 sensor catalyst function, a heated version of the O_2 sensor is used.

8.2. Computer Controller. The computer controller also known as the electronic control unit (ECU), is used for various engine management and other vehicle functions. It is rightly claimed that the TWC closed-loop system brought the ECU into dominant use. The ECU has a stored library of engine speed and load maps. The input signals of mass inlet air measurement, engine temperature, throttle position and O_2 sensor in conjunction with stored data are employed to assist the engine in cold starting and to calculate the proper amount of fuel to be injected by each fuel injector for its current operating condition. The ECU control system uses the O_2 sensor signal as a switching device using the logic “rich! Go lean!” or “lean! Go rich!” Advanced closed loop systems use the input of a second O_2 sensor located downstream of the catalyst for minor correction to the system due to long term system drift. An advanced Honda system using an observer O_2 sensor to anticipate rate of change (rate adjustment) has had a dramatic effect in maximizing the performance of the TWC. Utilizing these improvements was a key to a Honda emission control system able to meet the California super ultra-low emission vehicle standard (SULEV) and partial zero emission vehicle standard (PZEV) with a single bed TWC catalyst.

The oxygen sensor closed loop system automatically compensates for changes in fuel composition or air density. For instance, the system corrects for stoichiometry differences in winter and summer grades of gasoline or those fuels containing various amounts of oxygenated hydrocarbons such as MTBE or ethyl alcohol. Also the stoichiometric air/fuel mixture is maintained even when the vehicle climbs from sea level to high altitudes where the air density is lower.

The oxygen sensor signal indication for the stoichiometric point can be a bit different for certain gases, for instance H_2 has a high rate of diffusion. Natural gas and methanol have high H_2 in the exhaust (see Fig. 4). This has to be taken into account for flexible fuel vehicles that operate on two different fuels; ie methanol and gasoline.

8.3. On-Board Diagnostics. An on-board diagnostic system (OBD-II) is required on all new vehicles since 1994. The object is to assure and monitor continued functional performance of combustion quality (engine misfire), the performance of the catalytic converter, and the evaporative emission control system. The ECU would record incidents of failure by displaying a notice to the vehicle driver/owner and for use in annual vehicle inspection purposes.

An OBD-II system, during an assessment event, compares the output signal of two O_2 sensors: (*1*) the standard operating sensor is located in front of the TWC catalyst; and (*2*) a second OBD-II O_2 sensor located downstream of the catalytic converter (or behind the first converter when more than one is used). The assessment event is conducted by the ECU which schedules a series of distinct air/fuel ratio step changes from rich to lean and back to rich air/fuel at a defined frequency of 2 Hz. During an assessment event, a fully functional TWC catalyst will produce a characteristic OBD-II O_2 sensor signal indicating proper catalyst performance. An impaired or failed TWC catalyst would produce a different characteristic OBD-II O_2 sensor signal indicating catalyst performance below a desired rate. The component of the TWC being measured is the ceria function as described earlier in Section 6 and in Refs. 49,78. A fully functional TWC catalyst containing activated ceria would capture O_2 when in excess and release O_2 when in short supply. Thus the OBD-II O_2 sensor located downstream of the catalyst would sense a stoichiometric A/F mixture and produce a steady 450 to 500 millivolt signal indicating that the catalyst function is normal. However, if the OBD-II O_2sensor produced a millivolt signal of 50 to 700 at 2 Hz that mirrored or approached that of the operating O_2 sensor signal, it would indicate that the TWC catalyst ceria function was damaged or no longer able to perform the oxygen storage and release reactions and by inference had lost catalyst functional performance (79–82).

9. Other Emission Control Systems

9.1. Exhaust Gas Recirculation. NO_x control within the engine can be achieved by recycling a fraction of the exhaust gases into the engine air inlet stream. The resultant mixture upon combustion results in lower peak combustion temperature and lowers the amount of thermal NO_x produced within the combustion flame. The reaction of $N_2 + O \rightarrow NO_x$ is strongly dependent on the combustion flame temperature (75,83). The degree of NO_x suppression is dependent on the amount of exhaust gas recirculation (EGR). EGR reduces flame speed of the mixture, and thus also provides a certain antiknock quality to the combustion process. The impact of EGR on engine parameters has been detailed (84).

EGR in modern engines are quite transparent to the driver/operator with respect to engine power and performance. In the 1970s vehicle engine performance had been noticeably degraded due to early EGR systems; especially at idle, under load at low speed, and during cold start. This negative public memory lingers but is only of historic importance.

9.2. Evaporative Emissions. Gasoline fumes from the on-board fuel tank, from fuel left in the fuel delivery system, and from running losses are regulated by U.S. EPA standards. Gasoline is a wide mixture of hydrocarbon species from high volatility butane (C-4) to lower volatility C-8 to C-10 hydrocarbon compounds. High volatility fractions are needed for choked engine cold start. Winter and summer grade fuels vary the volatile fractions accordingly.

Evaporative sources are (*1*) Diurnal emissions due to daily fluctuations in ambient temperature where evaporative emissions depend on the combined vapor pressure of the fuel hydrocarbon components and the fuel tank temperature; (*2*) Hot soak emissions due to fuel left in the fuel metering system or the inlet manifold after the engine is turned off. Engine and exhaust system thermal energy heats the left over fuel causing evaporation and emission loss; (*3*) Running loss emissions which occur during vehicle operating modes such as low speeds on a hot day when the rate of vapor generation in the entire fuel system exceeds engine fueling demand; and (*4*) filling vapor losses during fuel tank filling where the liquid gasoline displaces the fuel tank vapor. Fuel tank filling losses are controlled by a fuel filling pump device at the gasoline filling station (85,86).

The current EPA evaporative emission regulation prohibits more than 0.95 to 1.2 grams per test to escape to the atmosphere depending on the vehicle class (**3**). The test is a 3-day diurnal temperature cycle and an immediate hot soak in a shed enclosure following the dynamometer run.

The vehicle evaporative control system typically consists of a charcoal canister that connects to the intake manifold. At engine shut off a valve permits hydrocarbon fumes to be absorbed and stored by a carbon canister. When the engine is operating, the stored hydrocarbons are purged into the inlet manifold where they enter the combustion process.

9.3. Crankcase Emissions.

Exhaust gases enter the crankcase by what is known as blow-by gases that escape the combustion chamber past the piston rings or inlet and outlet valve stem seals. The exhaust gases would enter the atmosphere via the crankcase breather tube. As the engine wears, blow-by increases. A positive crankcase ventilation (PCV) valve is required by regulation (with specified test procedure) to assure these blow-by gases are fed into the inlet manifold so that they pass through the engine and exhaust emission control system (87,88).

10. Emissions Control for Alternative Fuels

The National Energy Policy Act of 1992 requires that nonpetroleum-based transportation fuels steadily replace petroleum fuels in the United States. Such fuels include natural gas (see GAS, NATURAL), liquid petroleum gas (qv) (LPG), methanol (qv), ethanol (qv) and hydrogen (qv) (see also ALCOHOL FUELS; HYDROGEN ENERGY).

10.1. Natural Gas.

Natural gas fueled passenger cars and light-duty trucks are produced by U.S. automobile manufacturers (89). Emission control systems are developed for natural gas fueled engines. The preferred emission control TWC catalyst is based on Pd and Rh rather than Pt and Rh. Engine out emissions are shown in Fig. 4 for 4/1 H/C ratio. Natural gas combustion produces larger amounts of H_2 and H_2O, lesser amounts of CO and CO_2, and CH_4 is the predominant HC emission species with formaldehyde as minor. Formaldehyde is carcinogenic and has it own regulated emission standard (Table 1). TWC catalysts are quite effective for formaldehyde emission control. The U.S EPA and California emission standards exclude CH_4 emissions in the definitions of NMOG (nonmethane organic gas) and NMHC (nonmethane hydrocarbons) emission standards. CH_4 has low reactivity in the atmosphere and low ozone (qv) formation potential (90). Pd-based TWC catalysts require exhaust gas temperature over 450°C to oxidize CH_4. The symmetrical methane molecule is the most refractory of the hydrocarbon family and resists catalytic reactions on traditional TWC catalysts below 450°C. The CH_4 oxidation performance of Pd and Pd-Rh TWC catalysts are quickly impeded by very small amounts of sulfur in natural gas. Interesting catalyst work in this area can be found in work by R. Hicks (91). Natural gas fuel metering systems must assure sufficient CO be present to permit efficient reduction of NOx with CO. For this purpose a 2/1 ratio of CO/NO_x appears sufficient.

10.2. Liquid Petroleum Gas (LPG). LPG is a transportation fuel used for special vehicle and equipment applications. Emission control systems are developed and typically use Pt-based (Pt-Rh) TWC catalysts which exhibit lower light off temperature for propane (C_3H_8), the major HC species in LPG.

10.3. Alcohol Fuels. Emission control systems have been developed for methanol and ethanol transportation fuels which normally contain 15% gasoline and are known respectively as M85 and E85 alcohol fuels. Engines have been designed for these fuels and emission control systems have been modified for efficient emission control (92–94). M85 fuel exhaust formaldehyde emissions are the order of 0.60 g/m. Pd-Rh TWC catalysts are found very effective in controlling formaldehyde emission. E85 fuel exhaust emissions contain acetaldehyde and formaldehyde. Standard TWC catalyst formulations effectively control aldehyde emissions. Ethanol is added to gasoline as an oxygenated additive to meet fuel composition requirements for certain non-attainment or non-compliance regions in the United States. The closed loop TWC catalyst fuel metering system is able to accommodate the change in air/fuel stoichiometry induced by the addition of alcohols without loss in its ability to control exhaust emission.

11. Diesel Engine Emission Control

Light-duty, high speed, diesel compression ignition (CI) engine powered vehicles must meet the same emission standards as gasoline spark ignited (SI) engines (Table 1). The CI engine has been greatly improved over that last decade with respect to fuel efficiency and engine performance. Diesel engines are found in light and medium trucks but in very few passenger cars. Penetration into the light-duty vehicle market is expected to increase sharply over the next decade. Light-duty diesel vehicles have reached 50% of sales in France and a substantial percentage in most European countries because of improvements in fuel efficiency and dramatic improvements in performance due to excellent engine torque at low speeds. Diesel fuel has more energy per liter than gasoline (35,785 vs 31,845 kJ/L). Fuel efficiency for light-duty diesel vehicles can range from 13% to 24% better than for similar gasoline vehicles in similar service (39). Higher gasoline prices and growing concern for global warming could increase attractiveness of diesel engines for the North American market.

11.1. Emission Standards. Emission standards for light- and medium engines are shown in Table 1. Diesel engine has to meet all standards without exception. The most difficult standards for diesel engines are the particulate matter (PM) and NO_x standards whereas HC and CO are easily removed with diesel oxidation catalysts.

11.2. Nature of Diesel Exhaust. Modern high speed compression ignition engines used for passenger cars and LDV are equipped with turbochargers and electronically controlled fuel injection utilizing a common rail fuel feed line, individual electronically actuated injectors and very high pressure fuel injection. The individual injectors provide full flexibility of fueling timing and fueling rates within the start of injection and finish of injection event; ie, (*1*) a small amount of fuel can be added early in the compression stroke referred to as pilot injection; (*2*) the main amount of fuel can be injected in one squirt, in several squirts and with modulated fuel rates or shapes that are adjustable during the fueling event; and (*3*) post ignition injection can be scheduled to activate downstream emission control regeneration when necessary. Base engine emissions from these diesel engine have lower NO_x and PM mass. However, ultra-fine particles (30 to 100 nanometer diameter in size) have not been reduced with any of these improvements.

Combustion air is inducted into the engine in response to engine RPM and fueling rate without a throttle. Excess air is present for every condition of engine speed and load. Mass emissions of carbon monoxide and hydrocarbons are low compared to a SI gasoline engine. NO_x generation is high even though overall air/fuel is very lean because most combustion is diffusion flame combustion of fuel droplets rather than homogeneous combustion.

11.3. Emission Control Technology. The light-duty vehicle emission control system that will conform to Tier 2 emission light-duty vehicle emission standards is currently under development. In 2006 the vehicles would have to meet at lease Bin 8 NO_x 0.124 and PM 0.0124 g/km (Table 1). There two major challenges: 1) control of NO_x and 2) control of particle emissions:

NO_x Control. Two approaches under consideration are: (*1*) Use of large fractions of EGR (see Section 9) to prevent formation of thermal NO_x; or (*2*) Catalytic approaches such as NO_x adsorbers. Catalytic reduction of NO_x in the oxidizing conditions of diesel exhaust is difficult at the 90% effective reduction rates needed. One effective approach that is under intense development is one that stores and releases NO_2. In this respect the NO_x adsorber is much like a TWC catalyst the latter stores and releases O_2 whereas the NOx adsorber stores and releases NO_2. The feat is accomplished by oxidizing $NO \rightarrow NO_2$ on a Pt component of the NO_x Adsorber and storing it chemically as $Ba(NO_3)_2$ for instance. Periodically, the engine is calibrated slightly rich of stoichiometric for a few seconds and NO_2 is released and catalytically reduced by the Rh component in a TWC catalytic reaction. This technology requires ultra-low sulfur diesel fuel.

Particle Emission Control. Catalyst-based diesel particulate filter (CB-DPF) are a fully developed and proven technology for removal of all soluble organic and elemental carbon particles. They remove over 99% of the dangerous fine carbon particle fraction that has the most serious health concern. Several types of CB-DPFs exist. The exhaust gas containing particles are passed through the filter where the particles are removed and collected. The collected carbonaceous particles have to be removed by combustion either in a continuous or periodic fashion. The collected particles can be slowly oxidized by several means. One method involves the oxidation of $NO \rightarrow NO_2$ on a Pt component contained within the inlet channel surface catalytic layer of the CB-DPF. NO_2 react chemically with carbon pariticle forming NO and CO_2. Reducible oxides such as ceria are incorporated to transfer oxygen atoms to carbon. In another method NO_2 is generated by a separate inlet Pt catalyst and delivered to the non-catalyzed filter where the carbon particles are oxidized. At a temperature of about 375 to 400°C direct catalytic oxidation of carbon with oxygen takes place. Above 550°C the thermal supported oxidation of collected soot proceeds. This technology will likely be part of any Tier 2 light-duty diesel engine emission control system for diesel engines sold in the 2006 or 2007 model year depending upon whether ultra-low sulfur diesel fuel becomes generally available. Currently

CB-DPF technology is planned to be incorporated into heavy-duty on-road diesel engines by the 2007 model year to meet the heavy-duty diesel engine 2007 rule when low sulfur diesel fuel is required to available.

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