White Paper

Title: Exhaust Gas Readings and the Combustion Process
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Overview:

In the past 30 years, the Exhaust Gas Analyzer has become a standard feature in many workshops. This need has been driven by a combination of requirements – the promulgation of EPA-dictated gas emission standards (CO, HC, and NOx), OSHA workplace safety standards (CO), the need to diagnose and repair increasingly complex engine operation and emission control systems, and the desire to obtain better tuning and performance by using exhaust gas analysis for performance tuning.

The NDIR and Electro-chemical gas analysis technology used in these is cost effective, robust, and well proven – with 100,000's of installations operating worldwide. The awareness of the potential benefits of using exhaust gas information has gradually increased with the use us EGAs as standard workshop instruments, but not to the level that it could if a better understanding of the relationship between exhaust gas constituents and the combustion process existed.

The purpose of this White Paper is to increase this understanding.

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Combustion Fundamentals

This paper contains essential information required to understand and interpret analyzed combustion byproducts and information provided by the analyzer. Included is a description of how and where combustion byproducts form in an engine and common methods used to help reducing their formation.

Combustion and Air-Fuel Ratios

In a gasoline-powered internal combustion engine, normal combustion is burning a compressed mixture of hydrocarbon fuel and air in the combustion chamber. This action causes the compressed fuel mixture to expand, producing the pressure required to move the pistons downward. Figure 1 shows the air-fuel mixture inside a cylinder being ignited by the spark plug.

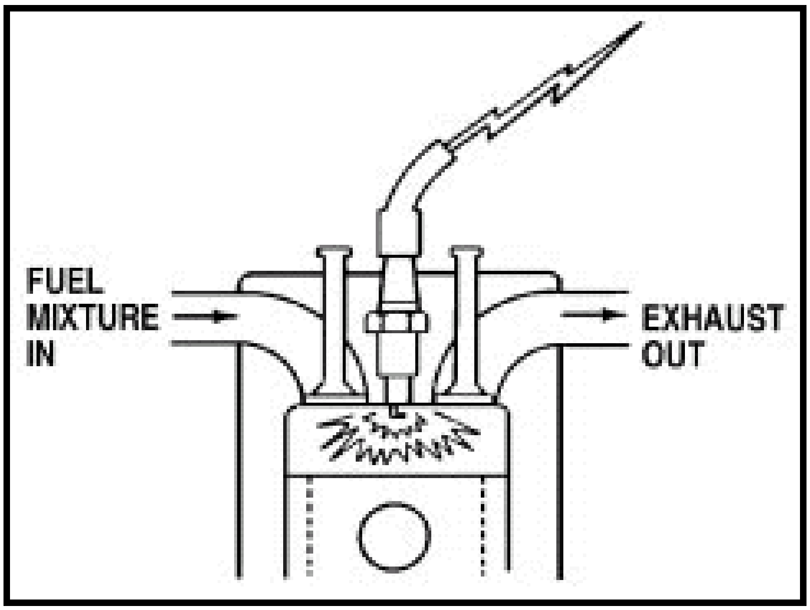

Figure 1: Combustion Process

The fuel induction system of a gasoline engine mixes vaporized gasoline, a hydrocarbon, with air in a given proportion. There must be more air than fuel to keep the vaporized fuel in suspension and to supply oxygen for combustion.

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NOTE: Air-Fuel ratios are measured by weight, not volume. An air-fuel ratio of 12:1 is 12 pounds of air mixed with one pound of fuel.

The ideal air-fuel ratio for perfect combustion in a gasoline engine is 14.66:1, commonly referred to as 14.7:1. This is the stoichiometric ratio or stoichiometric fuel mixture. Under perfect conditions, the combustion of a stoichiometric air and fuel mixture results in carbon dioxide (CO2), water (H2O) and nitrogen (N2), all of which are harmless.

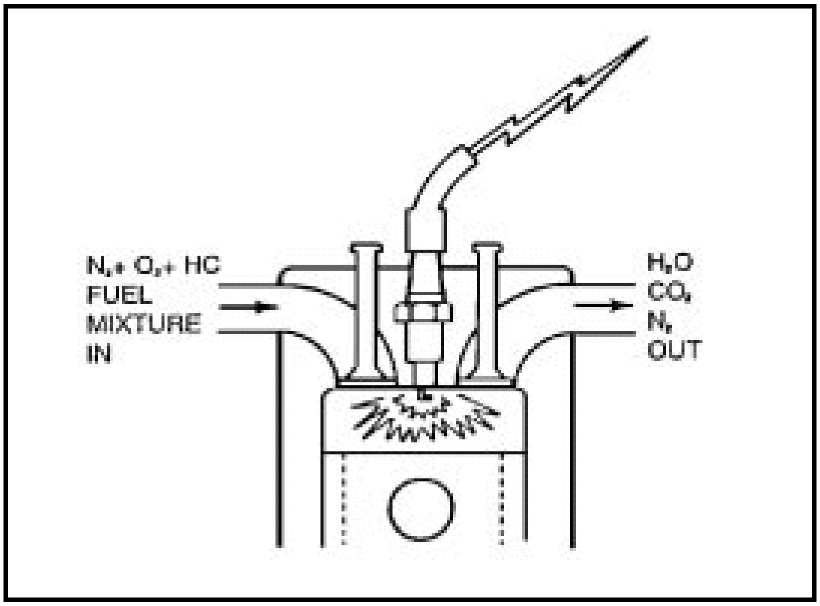

Figure 2: Ideal Combustion Byproducts

A lean fuel mixture has too much air or too little fuel. A rich fuel mixture has too much fuel or too little air.

Combustion Emissions

Internal combustion engines are not 100 % efficient, even with ideal fuel mixtures. For this reason, other substances form in the combustion chamber during combustion and exhaust from the engine.

Natural products of combustion are:

- Carbon dioxide (CO_2) – produce by the oxidation of the carbon contained in the fuel.
- Water (H_2O) – produced by the oxidation of the hydrogen contained in the fuel.

Secondary constituents of "real-world" combustion exhaust gases include:

- Carbon monoxide (CO) – due to incomplete oxidation of Carbon to CO_2.
- Hydrocarbons (HC) – fuel which has not been oxidized.

• Oxides of nitrogen (NOX) – the unwanted combination of Nitrogen with Oxygen.
• Oxygen (O_2) – unused oxygen from the air.

Because exhaust gases relate to health and environmental concerns, federal and state agencies regulate several of the unwanted "real-world" automobile emissions.

Carbon Monoxide (CO)

CO is an exhaust byproduct formed when combustion occurs with less than the ideal volume of oxygen (rich fuel mixture). This combines a carbon atom with an oxygen atom. Carbon in the combustion chamber comes from the HC fuel, and oxygen from inducted air. When the fuel mixture in the combustion chamber is richer, meaning more HC and less air, the concentration of CO in the exhaust is higher. Therefore, anything causing a rich air-fuel ratio results in high CO concentrations in the exhaust.

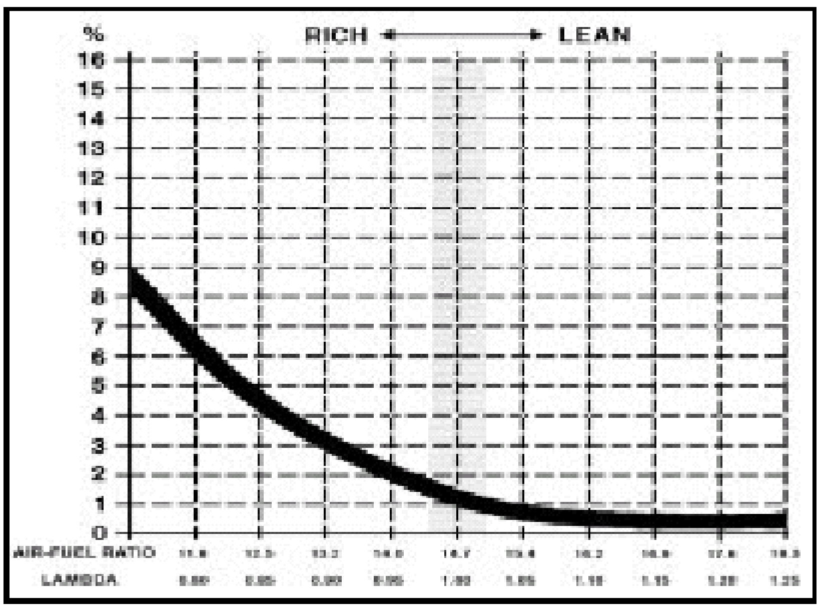

Figure 3: Carbon Monoxide Versus Air-Fuel Ratio

Figure 3 shows that at high combustion efficiencies, the CO level decreases as the air-fuel ratio approaches about 15:1, and maintains this low level even while the mixture is further leaned out. Because of this, CO is a good indicator of fuel mixture richness, but a poor indicator of leanness. However, CO also increases with combustion inefficiency (poor engine operation), which mitigates its use alone as a robust indicator of Air-Fuel ratio.

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Hydrocarbons (HC)

HC is an organic compound composed of Hydrogen (H) and Carbon (C) atoms. The HC in gasoline engine exhaust is unburned gasoline vapor (a mix of Hydrocarbon compounds) that is measured in parts per million (ppm) equivalent Hexane (C_6H_{14}). HC levels in engine exhaust vary with the air-fuel ratio.

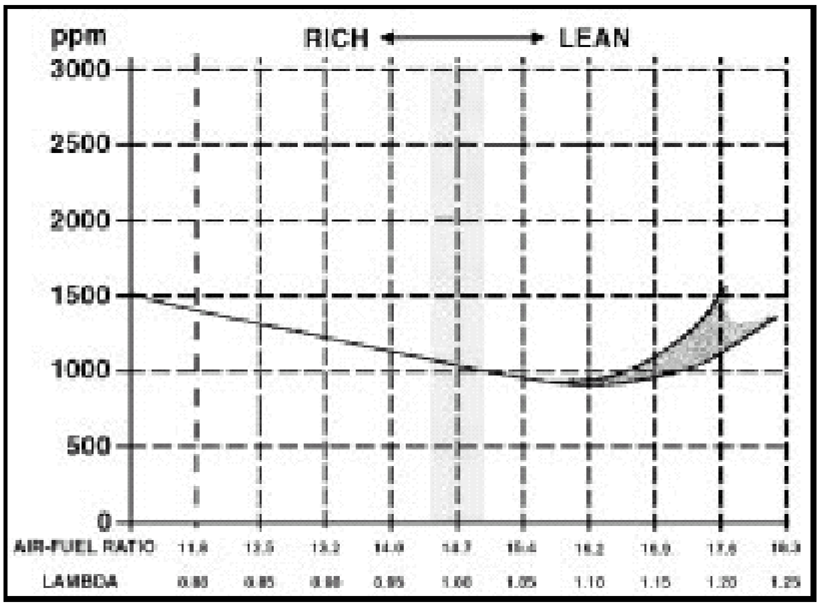


Figure 4: Hydrocarbons Versus Air-Fuel Ratio

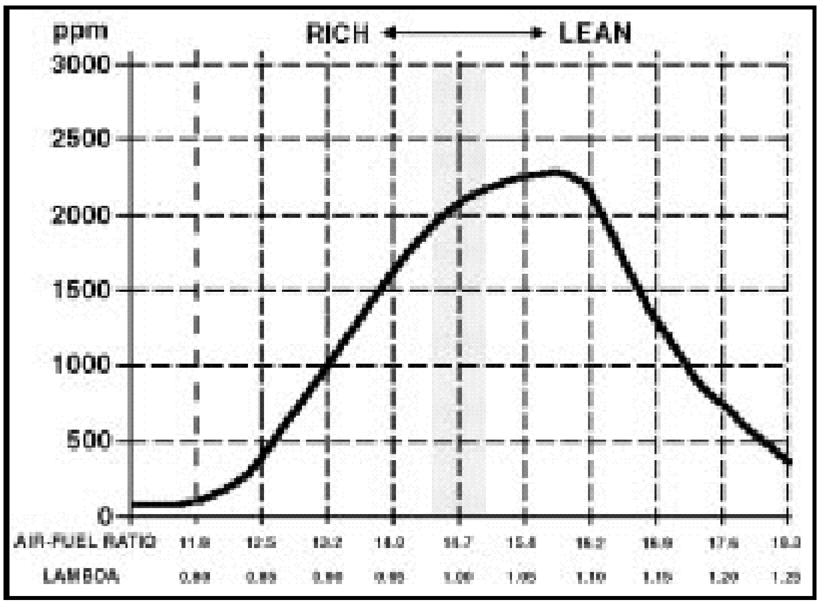
The lowest HC emissions occur at an air-fuel ratio of about 16:1. Since no engine combustion is perfect, some vaporized HC in the combustion chamber remains unburned and leaves the engine with exhaust gases. The amount of HC depends largely on combustion chamber design. Also, HC increases dramatically when the fuel mixture is too lean or rich to support complete combustion, or when ignition does not occur in the combustion chamber at all – as it is a strong indicator of combustion efficiency. When compared along with O_2 and CO_2 readings, HC can also indicate catalytic converter efficiency. Gasoline evaporating from the fuel system plumbing and the fuel tank are also sources of HC, known as evaporative emissions.

Oxides Of Nitrogen (NOX)

Air in the atmosphere, and air admitted into the combustion chamber of an engine, consists of about 78 % nitrogen (N_2) and about 21 % oxygen (O_2) by volume. Nitrogen does not contribute to, or detract from, combustion. When exposed to heat above 1093 °C, oxygen and nitrogen combine.

Since combustion chamber temperatures easily exceed 1371 °C under some engine conditions, such as under load, O_2 combines with N to form harmful oxides, including nitrogen monoxide (NO) and nitrogen dioxide (NO_2). These are part of a group of oxides commonly known as oxides of nitrogen (NOX).

NOX is an engineering term for an unknown mixture of nitrogen oxides. NOX includes



all the N compounds formed in the combustion chamber of an engine, especially NO and N O2. The X subscript in place of numbers indicates that all NO compounds are included.

Of the nitrogen oxide compounds, NO is the only compound with appreciable importance to engine combustion. NO formed in the combustion chamber persists during the exhaust stroke where it reacts with additional O_2, forming N O2. NO is one of the gases that may be checked to determine if the vehicle complies with specifications.

Figure 5 shows the concentration of NOX in relation to air-fuel ratio before treatment in a three-way catalytic converter.

Figure 5: NOX Versus Air-Fuel Ratio

When based only on air-fuel ratio, NOX levels peak at about 15.8:1. Many other factors affect actual NOX formation besides air-fuel ratio. The formation of NOX does not affect engine performance. However, some devices used to prevent the formation of N

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OX can affect engine performance and contribute to higher levels of HC and CO when not functioning properly.

Some of the devices and factors that affect the formation of NOX are:

Note: The following descriptions should be considered individually, that is with minimal effect from other dynamic variables.

- **Exhaust Gas Recirculation (EGR)**
  EGR dilutes the air-fuel mixture, lowers combustion chamber temperature, and reduces flame speed. When operated at a steady state of about 50 km/h, five percent EGR on a typical engine can reduce NOX emissions by as much as forty percent. Ten percent EGR can reduce NOX emissions about eighty percent. However, HC emissions increase with higher EGR rates. An inoperative EGR system will not decrease NOX emissions.
- **Valve Timing**
  Intake and exhaust valve timing, (amount of overlap, lift and duration) can affect inlet charge dilution and combustion chamber temperature the same as EGR, but can not be easily changed.
- **Spark Timing**
  Increasing spark advance at any load and speed will increase NOX emissions.
- **Intake Manifold Vacuum**
  A decrease in intake manifold vacuum increases load and temperature, and decreases the mass of residual gases. As a result, combustion time decreases. This increases maximum cycle temperature which increases NOX emissions.
  An increase in intake manifold vacuum decreases load and temperature, and increases the mass of residual gases. As a result, combustion time increases. This decreases maximum cycle temperature which decrease N OX emissions.
- **Engine Speed**
  An increase in engine speed increases flame speed due to turbulence. This reduces heat losses per cycle and tends to raise compression, combustion temperature and combustion pressure. An increase in engine speed with rich mixtures (which burn faster) increases NOX formation because of reduced heat losses at higher speeds. An increase in engine speed with lean mixtures (which burn slower) decreases NOX formation because of late burning.
- **Compression Pressure**
  An increase in compression pressure causes an increase in combustion chamber temperature. This increases the formation of NOX. Engine design, camshaft design, valve timing, and supercharging/turbocharging affect compression.
- **Intake Air Temperature**

High intake air temperatures can increase NOX formation.

- **Coolant Temperature**
  Higher coolant temperature increases cylinder and gas temperature. This increases NOX formation. Improper coolant temperature can cause cylinder and combustion chamber deposit build-up, increasing compression ratio and, consequently, NOX concentration.
- **Carbon Build-up**
  Carbon in the combustion chamber reduces combustion chamber volume. This increases compression pressure and increases the air and fuel mixture temperature which contributes to NOX formation.
- **Fuel Octane**
  Low octane fuel burns faster and less controlled than higher octane fuel. This can cause NOX formation.
- **Air and Fuel Mixture**
  — Lean Engine Operation
  Engine pinging indicates lean engine operation and the formation of NOX. Any condition that causes the engine to run lean can cause an increase in the formation of NOX. If the mixture and exhaust are too lean, the converter can convert HC and CO but can not control NOX.
  — Rich Engine Operation
  Rich mixtures and high CO can mask an NOX problem. When an engine has carbon build-up from the rich condition and the cause of excessive richness is corrected, the resulting leaner condition can cause increased NOX formation. Also, the three-way catalytic converter requires CO to convert NOX to N and CO2. So, high CO levels can mask high NOX levels. If the mixture and exhaust are too rich, the converter can reduce NOX but can not control HC and CO.
- **Catalytic Converter**
  A dual-bed or three-way type catalytic converter in good working order can reduce NOX emitted from the engine as it passes through the catalytic converter. If the mixture and exhaust are rich, the converter can reduce NOX but can not control HC and CO. If the mixture and exhaust are too lean, the converter can convert HC and CO but can not control all of the NOX.
- **Humidity**
  An increase in mixture humidity can help reduce formation of NOX due to the drop in maximum combustion chamber flame temperature.
- **Air Pump Operation**
  Air pump pressure can overcome the exhaust pressure in a three-way catalytic converter if, during deceleration, air is pumped into the converter instead of diverted

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into the atmosphere. Under this condition, air can backflow into the reducing portion of the catalyst, increasing NOX formation.

- **Fuel Injector Problems**

  Restriction of one injector on an engine with port fuel injection causes that cylinder to run lean and the cylinder temperature to increase, forming NOX. NOX levels in other cylinders remain normal, therefore, NOX levels at the tailpipe will only be slightly high. When an injector spray pattern is abnormal, hot spots can form within the cylinder and increase NOX formation.

  Note: Excessive NOX emissions may be caused by the effects of several of these devices or factors at one time.

Carbon Dioxide (CO2)

CO2 is a combustion product formed when one carbon atom bonds with two oxygen atoms, and by the oxidation of CO in the catalytic converter. Unlike CO, CO2 is comparatively harmless. CO2 is a good indicator of combustion efficiency because its volume in the exhaust peaks just before the stoichiometric air-fuel ratio. CO2 peaks when the combustion chamber fuel mixture approaches about 15:1, and decreases when the mixture becomes more lean or more rich. CO2 level is also used to check exhaust system and sampling system integrity, since significant air leaks lower CO2.

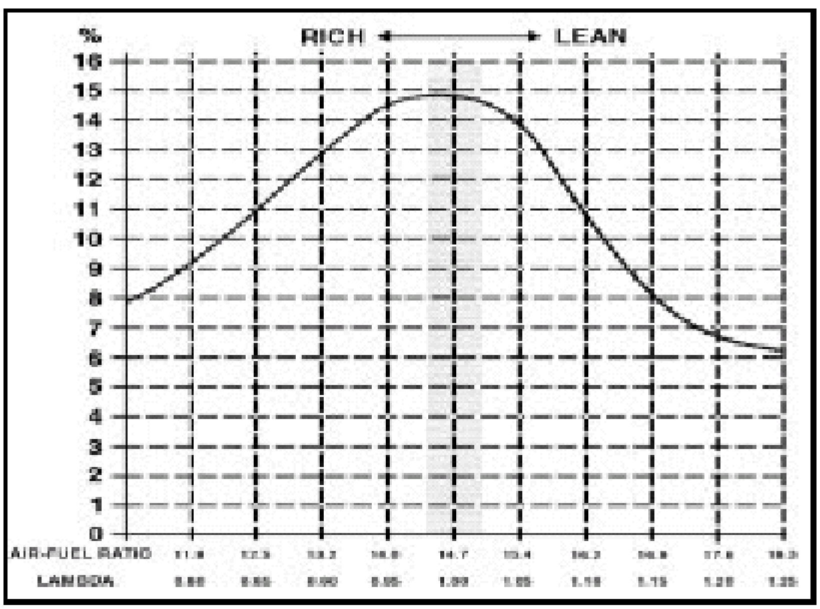
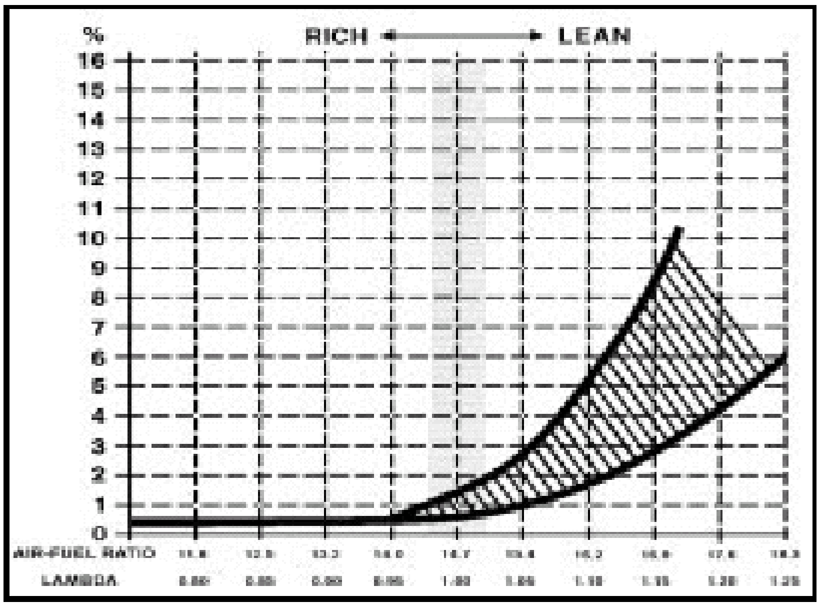


Figure 6: Carbon Dioxide Versus Air-Fuel Ratio

Oxygen (O2)

The level of O2 in exhaust gas is an indicator of air-fuel ratio leanness. The O2 is present in the air the engine inducts and mixes with the HC for combustion. Since the atmosphere is about 21 % O2, the percentage of O2 in the exhaust gas after combustion indicates air-fuel ratio leanness.

In Figure 7, the O2 concentration is at a steady low level when the fuel mixture is richer than about 15:1, because all available O2 is consumed in the combustion process. As the mixture gets leaner, O2 steadily increases, because less is used in combustion. Higher



concentrations of O2 in the exhaust are therefore directly proportional to leaner air-fuel ratios.

Figure 7: Oxygen Versus Air-Fuel Ratio

Interpreting Air-Fuel Ratios and Emissions

The relationship between the air-fuel ratio and exhaust gases monitored by the analyzer are:

- **HC is lowest when the air-fuel ratio is ideal because most of the fuel is consumed in combustion. Richer or leaner mixtures, or ignition problems cause HC to increase because of incomplete combustion.**
- CO is lowest when the air-fuel ratio is nearly ideal because there is less O2 and C left over. This is due to more complete combustion occurring at stoichiometric ratios.

Richer than ideal mixtures cause CO levels to increase; leaner mixtures have little effect.

• CO2 levels are highest when air-fuel ratios are close to ideal, and decrease when the mixture becomes richer or leaner.

• O2 levels are near zero when the air-fuel ratio is near stoichiometric, since most of the O2 consumed in combustion. It remains low with richer mixtures, and increases when the mixture leans out.

• NOX is lowest when the air-fuel ratio is either very rich or very lean and highest when the air-fuel ratio is slightly lean and when the engine is under load.

Stoichiometric Fuel Mixture

The stoichiometric air-fuel ratio (14.71:1) is near the point where the emission levels drastically change. The stoichiometric air-fuel ratio, where the HC and CO levels are lowest, is as close to perfect combustion as can be attained.

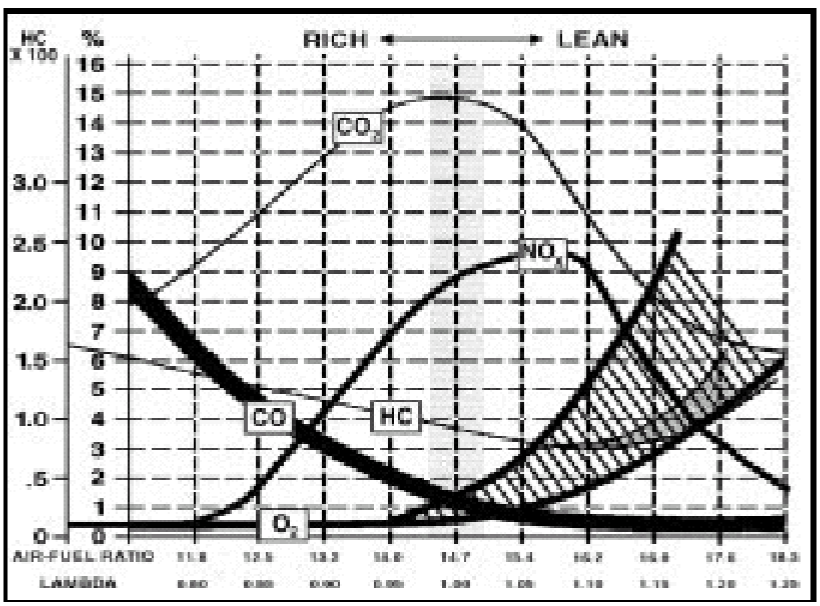


Figure 8: Major Combustion Byproducts Versus Air-Fuel Ratio

Note: The term **Lambda** is often used instead of air-fuel ratio. Lambda is a numerical value of the measured air-fuel ratio relative to the ideal air-fuel ratio. Lambda equals one (1.000) when the air-fuel ratio is stoichiometric. Lambda is less than one when the air-fuel ratio is rich, and is greater than one when lean.

Because combustion temperatures and the air-fuel ratio requirements can change in engines under dynamic load, the only way to ensure that the air-fuel ratio remains close to stoichiometric under most operating conditions is to use a feedback system to monitor oxygen content of exhaust gas. This feedback system reports back to a computer that calculates fuel delivery and commands the fuel injector or carburetor to deliver the necessary amount of fuel required to maintain the correct air-fuel ratio.

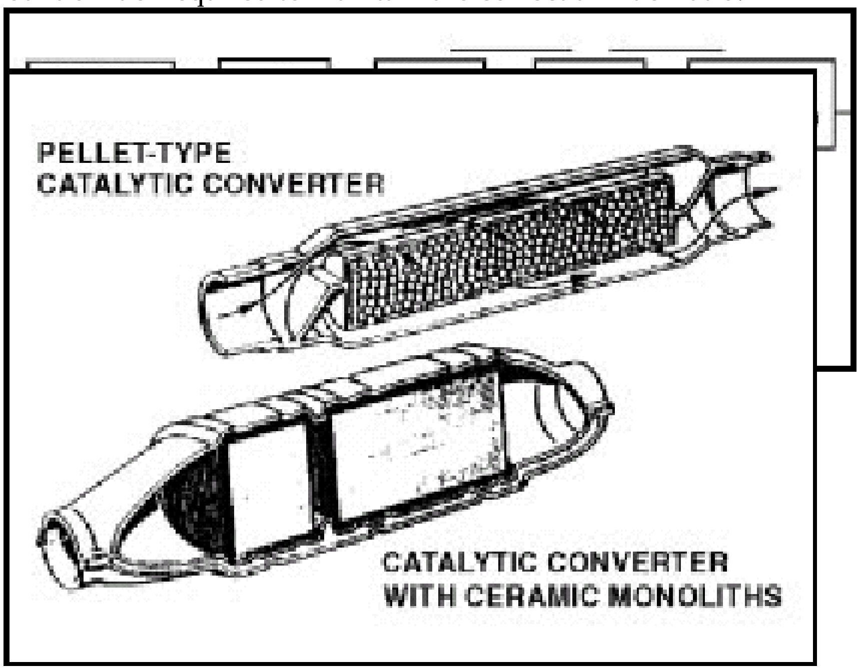


Figure 9: Closed-loop Fuel Feedback System

Catalytic Converters

The first attempt at reducing emission levels in automobiles was to get air-fuel ratios as close to stoichiometric as possible. However, even engines designed for low emissions and that are operating properly, may not have HC and CO emission levels low enough to meet clean air standards. To assist in lowering these emissions, catalytic converters were installed. A catalyst is a substance that increases the rate of a chemical reaction without being used up itself. Automobile catalytic converters contain a combination of three noble metals - platinum (Pt), palladium (Pd) and rhodium (Rh). These metals are applied to small beads or ceramic baffle materials, called substrates, that provide a tremendous surface area for exhaust gases to contact the noble metal catalysts.

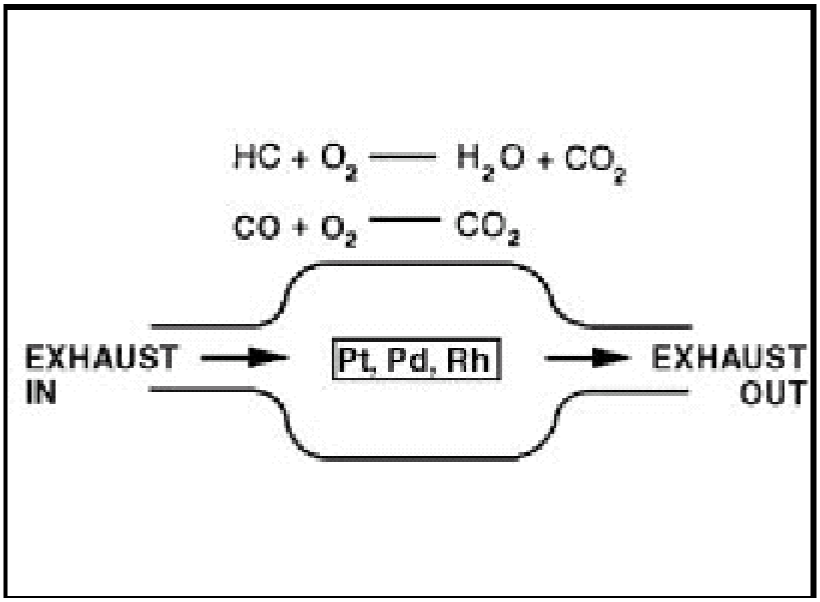


Figure 10: Typical Catalytic Converters

In operation, exhaust gases pass into the catalytic converter from the engine, where the exhaust gases flow past the catalytic metals. Contact of the exhaust gases with these metals facilitates oxidation reactions, completing the oxidation of the CO and HC contained in the engine-out gases. This oxidation turns the CO into Carbon Dioxide (CO2) and the HC into water (H2O) and the Carbon Dioxide (CO2). These converters are called oxidation or two-way converters since they only treat two gases.

> Note: Oxidation and reduction catalytic converters (three-way converters) usually have a two-way catalytic bed after the NOx reduction catalytic bed at the front.

Figure 11: HC and CO Oxidation in a two-way Catalytic Converter

Oxidation of any compound requires an abundance of O2. Some engines use Air Injection Reaction (AIR) or pulse air type systems to provide the supplemental O2 needed. These systems supply additional air to the exhaust manifold or catalytic converter. As converter technology has progressed, catalysts treating NOX compounds were developed. With a reduction reaction, these catalyst reduced NOX to N2 and O2. Three-way converters reduce NOX and oxidize CO and HC. These converters are even more sensitive to air-fuel ratio because the reduction of NOX is efficient only at stoichiometric air-fuel ratio.
Two-way and three-way catalytic converters only lower HC, CO and NOX by a certain amount. When an engine operates properly, the converter decreases emissions to levels lower than the amount specified by state and federal regulations.

Figure 12 shows NOX versus air fuel ratio after being treated by a three-way catalytic converter. NOX levels are typically low when the air-fuel ratio is more rich than stoichiometric. When the air-fuel ratio is near stoichiometric and more lean than stoichiometric, NOX levels increase, then fall to slightly lower values as the air-fuel mixture continues to get leaner.

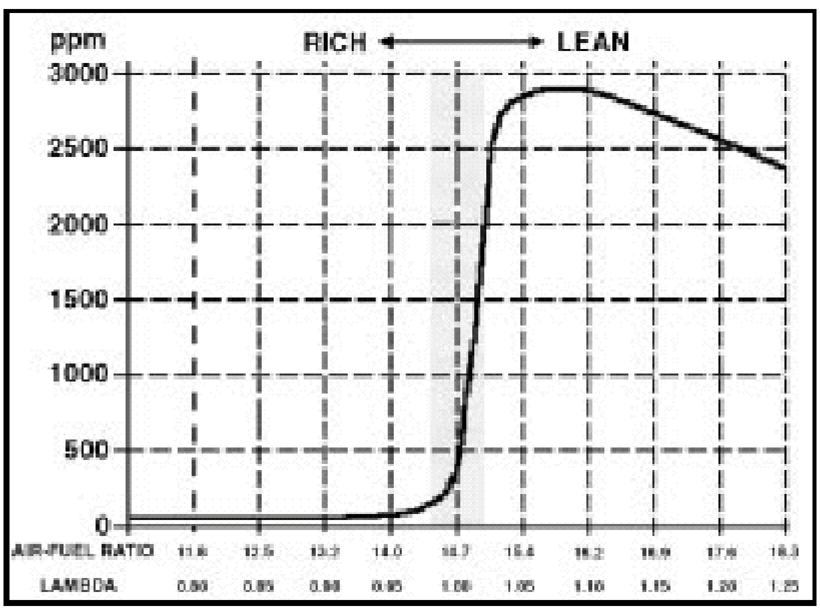


Figure 12: NOX Versus Air Fuel Ratio After Three-Way Converter

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Three-way catalytic converters oxidize HC, CO and reduce NOX, producing H2O, CO2 and N2. Therefore, monitoring just HC and CO alone does not give an accurate picture of engine performance because the catalytic converter alters these gases. Using the analyzer to monitor O2, CO2, HC, CO and NOX provides a more accurate method of monitoring engine operation on vehicles with a catalytic converter.

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