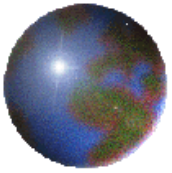


Internal Combustion

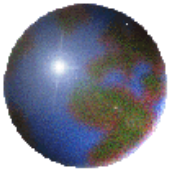


GASEOUS POLLUTION AND PHOTOCHEMICAL SMOG

Formation

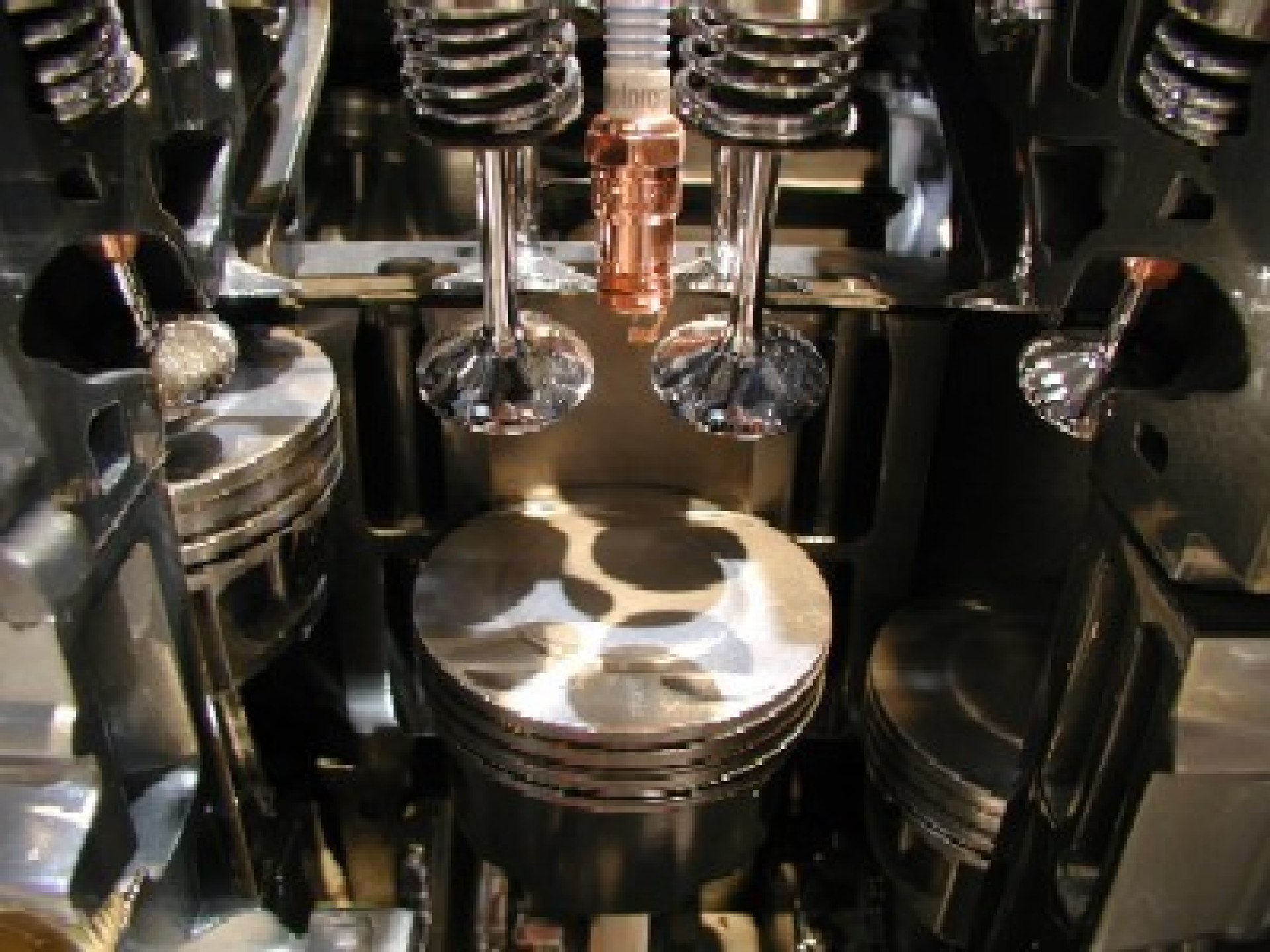
I. The Automobile Internal Combustion (Otto cycle)

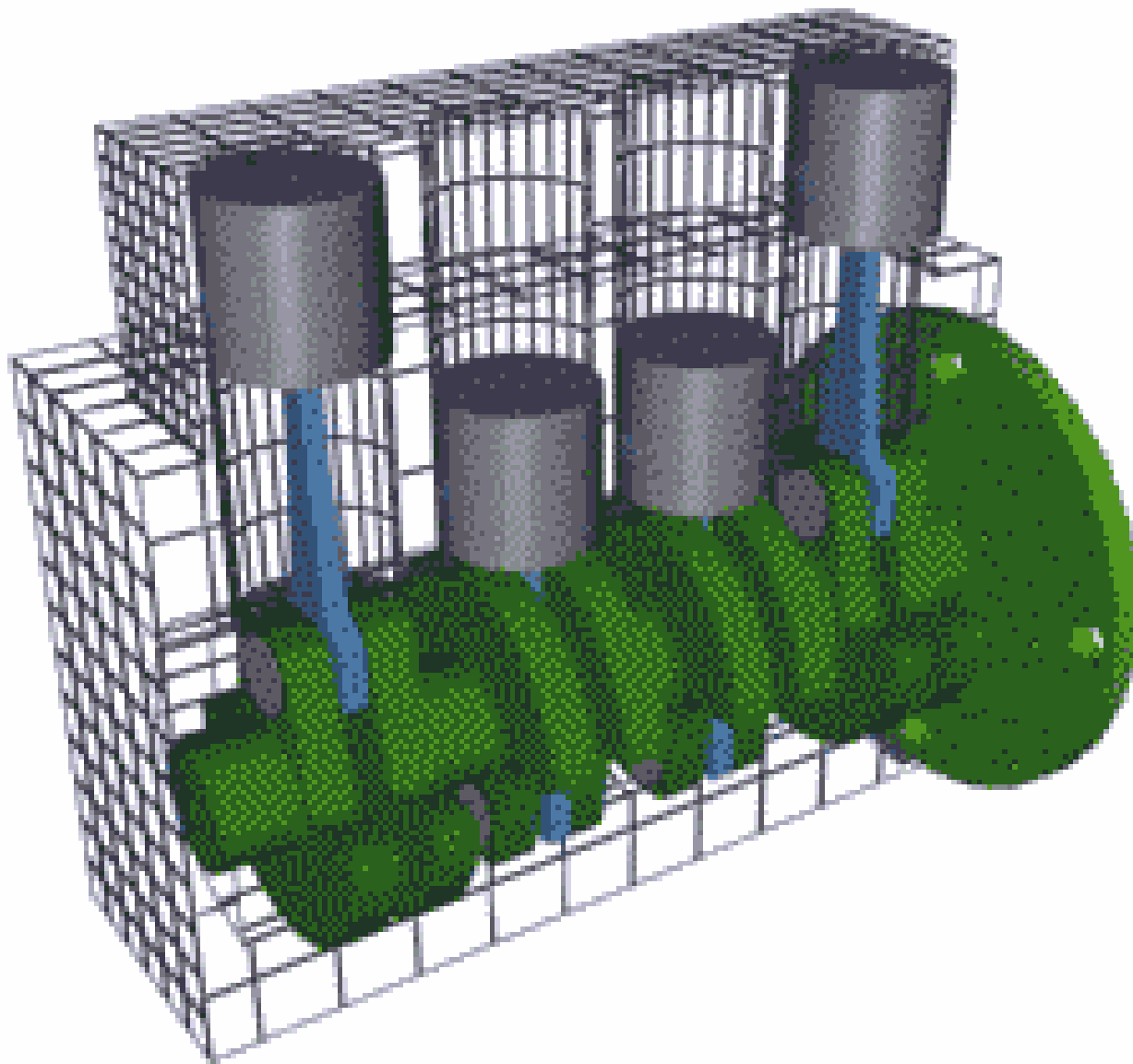
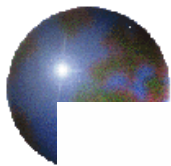
- ⊕ Main cause of smog
- ⊕ Main source of CO, NMHC, NO_x, and Pb in developing countries.
- ⊕ Mobile sources much stronger source than stationary sources for all but NO_x.

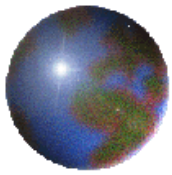


Image

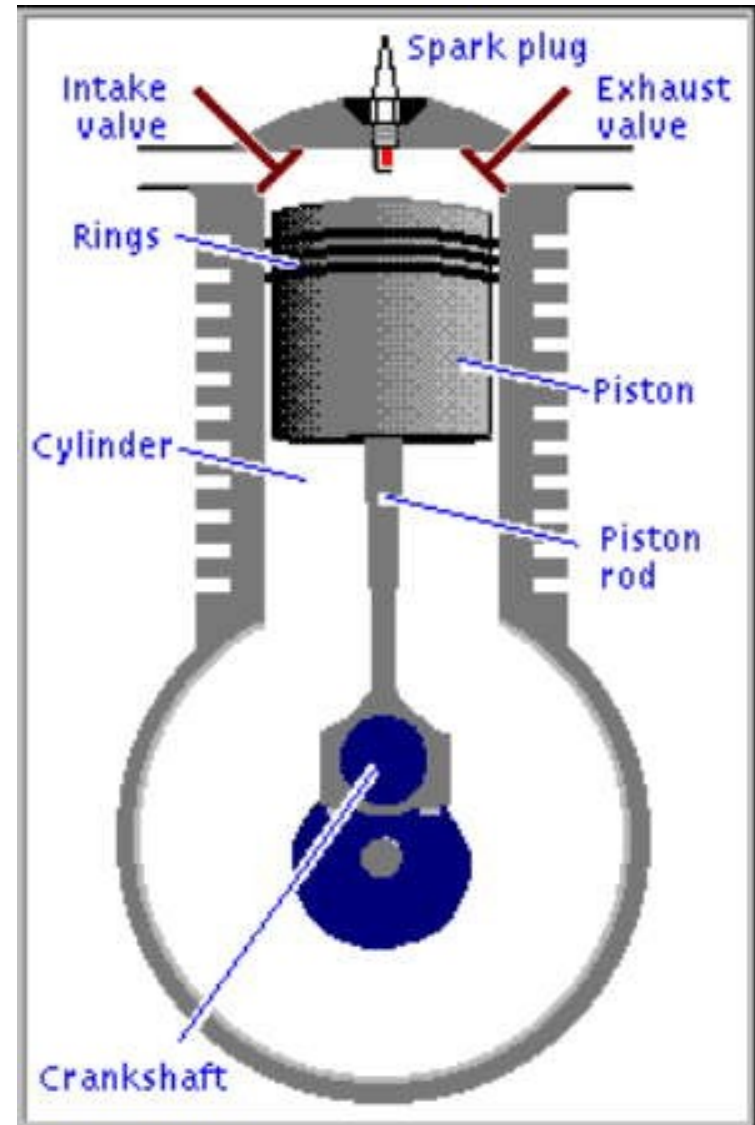
- ✚ **INTAKE** - Downward motion draws in air/fuel mixture
- ✚ **COMPRESSION** - For higher efficiency
- ✚ **POWER** - Combustion initiated by spark plug
- ✚ **EXHAUST** - Push out burned hydrocarbons

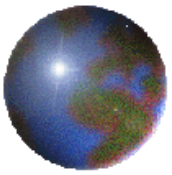




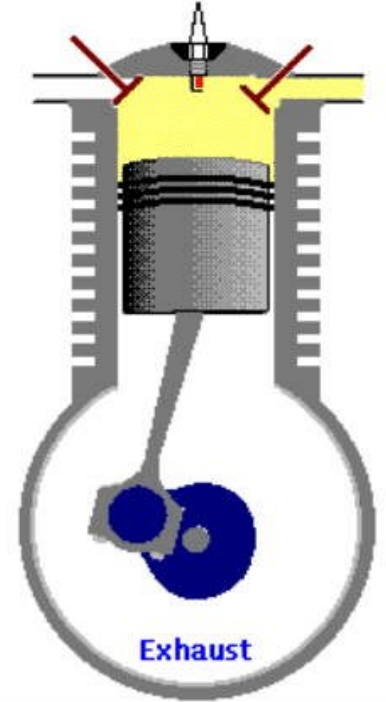
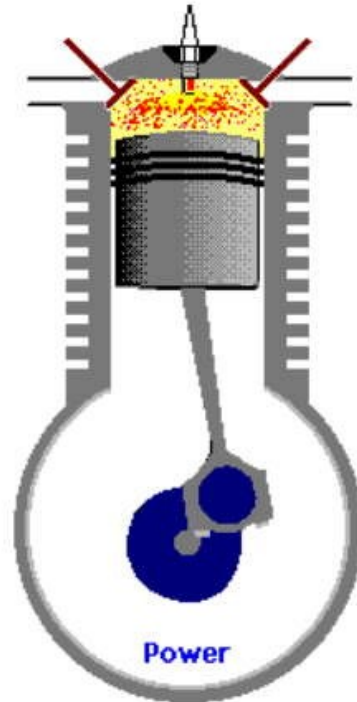
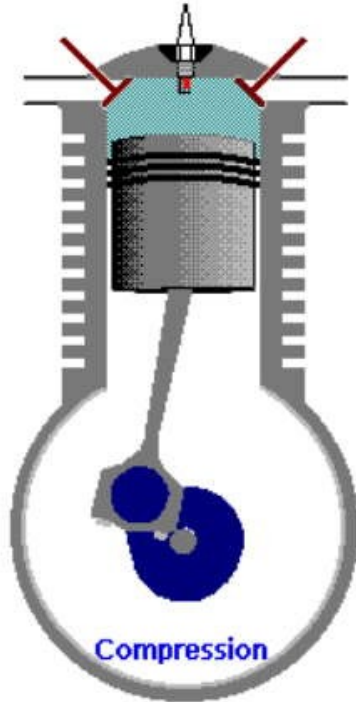
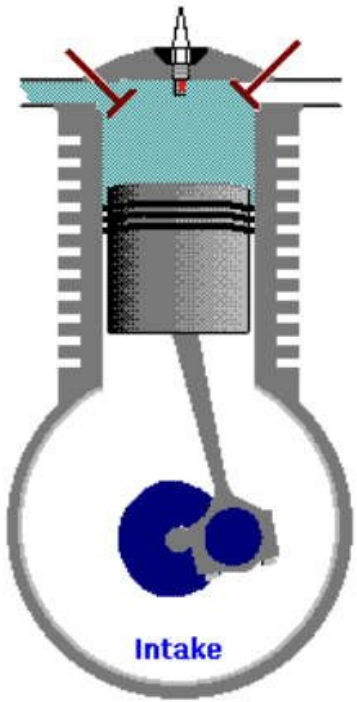


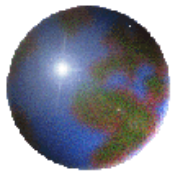
Four-Stroke Engine



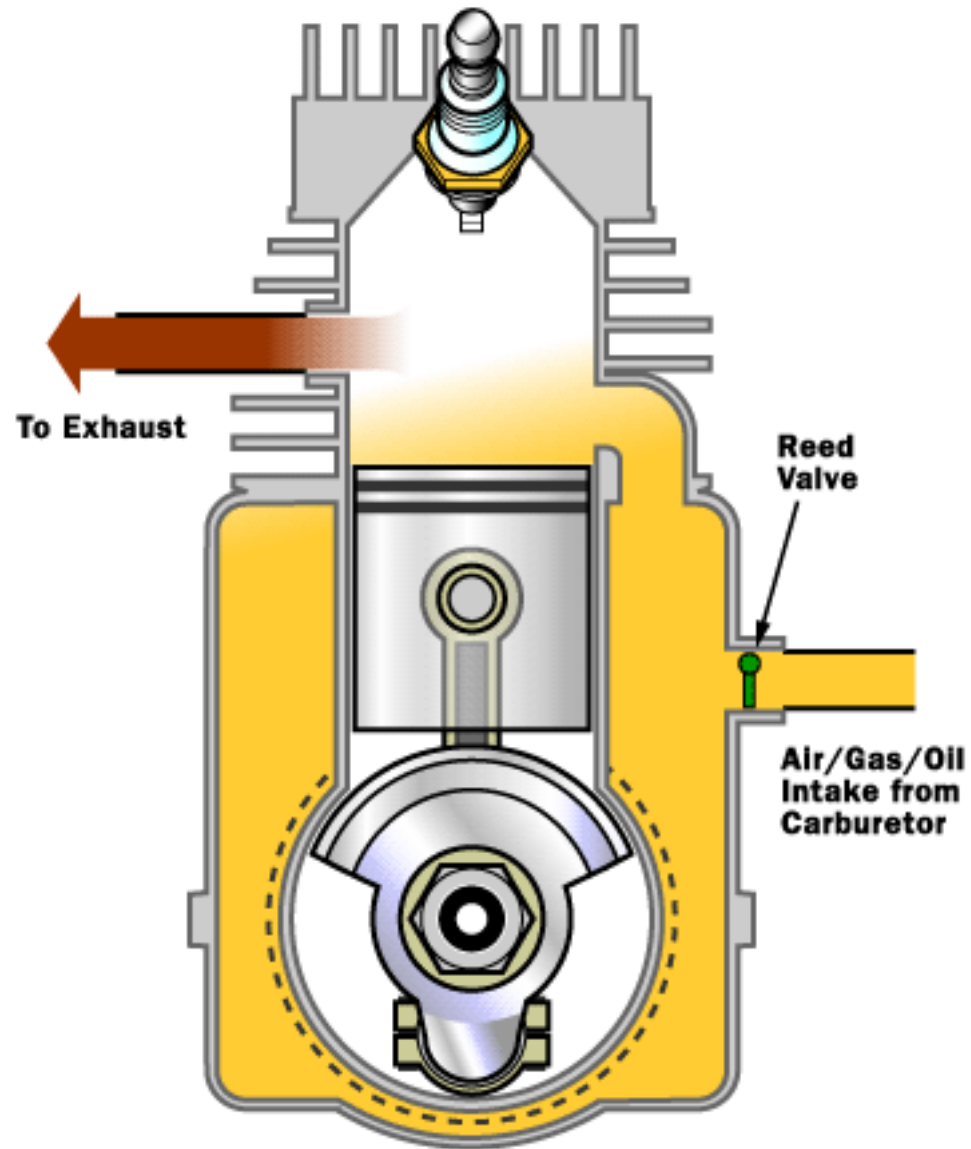


Four Strokes of an Engine

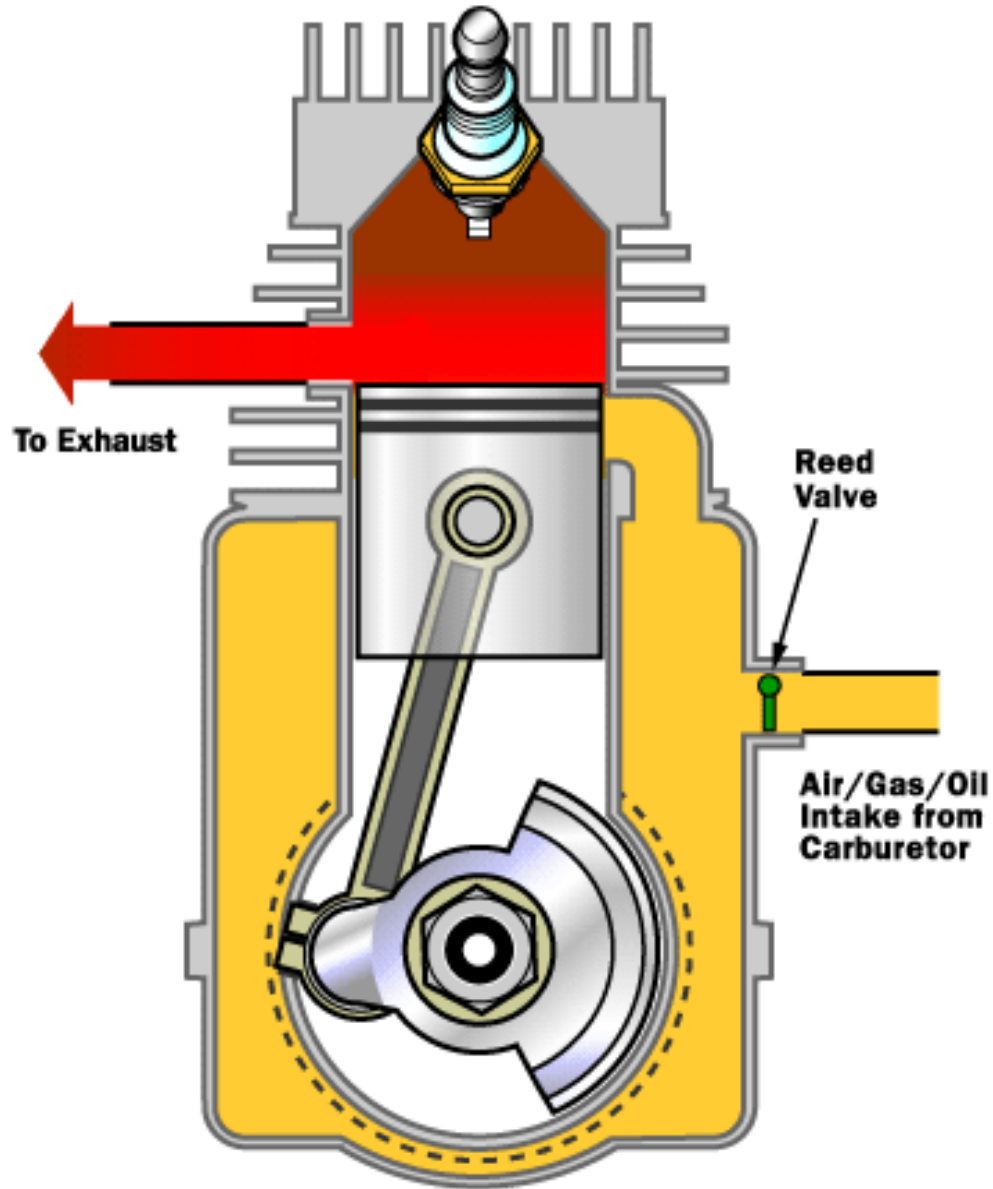
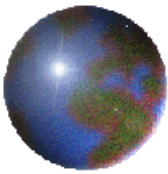




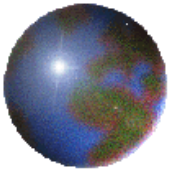
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Fuel-intake position of a two-stroke engine



Exhaust position of a two-stroke engine

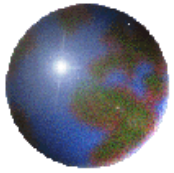


Exhaust is not the only source of air pollutants. In an unregulated auto:

Hydrocarbon Sources in an Unregulated Auto

Gas tank	10%
Carburetor	10%
Crankcase*	25%
Exhaust	55%
Total	100%

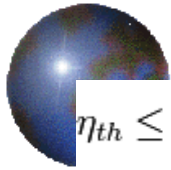
*** Called "Blowby"**



Evaporation from gas tank and carburetor are easy to control, but essentially all of the NO_x, CO, and Pb comes from the exhaust.

Recirculation System

- Engine off - vapors onto charcoal
- Engine on - intake sucks air and HC out of charcoal
- Positive crankcase ventilation
- Without controls 3% of the fuel would be lost



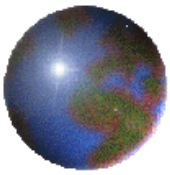
$$\eta_{th} \leq 1 - \frac{T_C}{T_H}$$

II. How to Tune a Car

Equilibrium calculation told us to burn *lean* and at *high compression* to produce less CO. High compression also ups thermodynamic efficiency; Carnot cycle efficiency is defined from the ratio of cold to hot temperatures:

A. **Air-Fuel-Ratio**
$$\eta_{th} \leq 1 - \frac{T_C}{T_H}$$

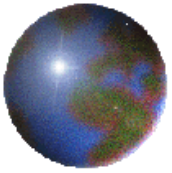
- ✦ Best power at AFR of 12.5 (rich)
- ✦ Best mileage at 15.5 (lean)
- ✦ ARF above 17 causes misfiring
- ✦ ARF below 10 causes flooding and plug fouling
- ✦ ARF of about 14.5 ($\Phi = 1.0$) is stoichiometric



• **Automobiles: Otto cycle** the cycle used in spark-ignition internal combustion engines run on gasoline. Its theoretical efficiency depends on the compression ratio r of the engine and the specific heat ratio ($C_p/C_v = \gamma$) of the gas in the combustion chamber.

$$\eta_{th} = 1 - \frac{1}{r^{\gamma-1}}$$

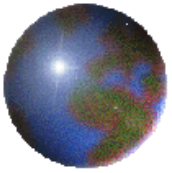
The higher the compression ratio, the higher the temperature in the cylinder as the fuel burns and so the higher the efficiency. The maximum compression ratio usable is limited by the need to prevent preignition (knocking), where the fuel ignites by compression before the spark plug fires. The specific heat ratio of the air-fuel mixture $\gamma \sim 1.40$. Compression ratios for gasoline powered cars range from 10:1 to 14:1 for racing engines. Alcohol powered cars have 15:1; Diesel 14:1 to 23:1.



B. Compression

Higher compression means higher power

- Problem - *Detonation* occurs when the fuel beyond the flame front initiated by the sparkplug burns. This is also called autoignition or *knocking*.
- Octane rating proportional to the detonation temperature.
- Higher octane allows higher compression.
- An enormous search found lead, in the form of tetraethyl lead, $\text{Pb}(\text{C}_2\text{H}_5)_4$, inhibits detonation. More on this later.

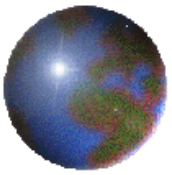


C. Timing

Definition of Crank angle, *advance* vs. retard

Image

- Combustion takes time, about 5 ms.
- Combustion should occur at Top Dead Center (TDC), therefore spark must precede piston.
- The higher the engine speed (RPM's) the more advanced the spark must be. Vacuum or centrifugal advance.
- As lower octane fuel is used, the spark must be retarded. Effectively reduces compression thus reducing power and fuel economy.
- Retarding the spark reduces the maximum and end temperatures of combustion and thus reduces both CO and NO formation.



Image

D. Fuel

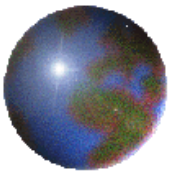
An octane rating of 100 means the same antiknock properties as isooctane (2,3,4-trimethyl-pentane). Without lead in the fuel more aromatic and branched HC must be mixed into the fuel. But these species are more reactive with respect to photochemical O_3 formation.

Fuel Lead

To produce higher octane gasoline from n-heptane (cheap gasoline) add the following:

0.8 g Pb per gal. produces 100 octane fuel

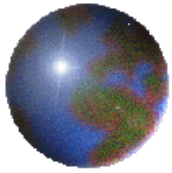
0.4 g Pb per gal. produces 90 octane fuel



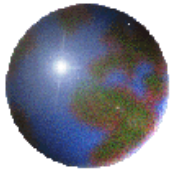
In the United States, lead in gasoline has been phased out altogether, but some of the developing world still uses lead. Lead forms a solid oxide ash after combustion, and fouls sparkplugs. To prevent the formation of ash on the plugs, scavengers such as 1,2-dibromoethane ($\text{CH}_2\text{Br}-\text{CBrH}_2$) were added to the fuel. These cause the burned lead to form halides such as $\text{Pb}(\text{Br})_2$ which stay in the vapor phase longer, and can act as a valve lubricant for some older cars. Unfortunately, 1,2-dibromoethane is carcinogenic.

Where does the lead go?

- At 20 MPH 90 % of the lead goes onto the exhaust system; 10 % is expelled out the tailpipe.
- At 70 MPH 90 % of the lead is expelled.
- Most of the lead falls as particles to the ground within 100m of roadways.



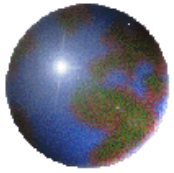
Lead is an insidious, cumulative poison. High serum (blood) lead has been linked to reduced intellect, although the research is controversial. Symptoms are hard to distinguish because they include anemia, constipation, and abdominal pain, in short the malaise of modern man.



Diesel Engines

There are no sparkplugs in a diesel engine. The fuel is injected at the time of maximum compression (near TDC) and the heat of compression causes combustion.

- ⊕ Diesel Engines have no throttle on the air.
- ⊕ Detonation impossible.
- ⊕ Low octane, "cheap," fuel may be used.
- ⊕ Compression must be higher (ca. 18:1 vs. 9:1 for Otto cycle).
- ⊕ Improved efficiency, but bigger and heavier engine block required.
- ⊕ Fuel mix is *leaner*, i.e. $\Phi < 1.0$.
- ⊕ Low CO and HC, but high NO_x.
- ⊕ Lots of particles including soot and PAH.



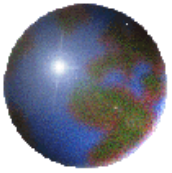
III. Exhaust Emissions

a) Hydrocarbons

Some fuel remains unburned even after combustion; why? The Temperature at the time of combustion is 2500 - 3000 C, but the walls of the cylinder are around 200 C. The exhaust starts at 1000 C, but cools quickly.

- ✚ Poor mixing and absorption of HC into oil on walls creates a *quench zone*.
- ✚ HC are concentrated in the first and last components of the exhaust.
- ✚ The NO profile is opposite.

To control HC emissions from the quench zone, the surface to volume ratio should be kept to a minimum, but that reduces stroke and compression.



b) Carbon Monoxide



$$K_{\text{eq}} = e^{(-\Delta G/RT)}$$

The process becomes kinetically limited as expansion occurs. The formation of CO is quick, but the removal is slower, especially at temperatures below about 1000 K. Thus the [CO] is close to the [CO] calculated by the above equilibrium method based on the temperature of the exhaust gases at the *end* of expansion.

Image



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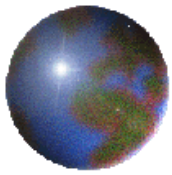




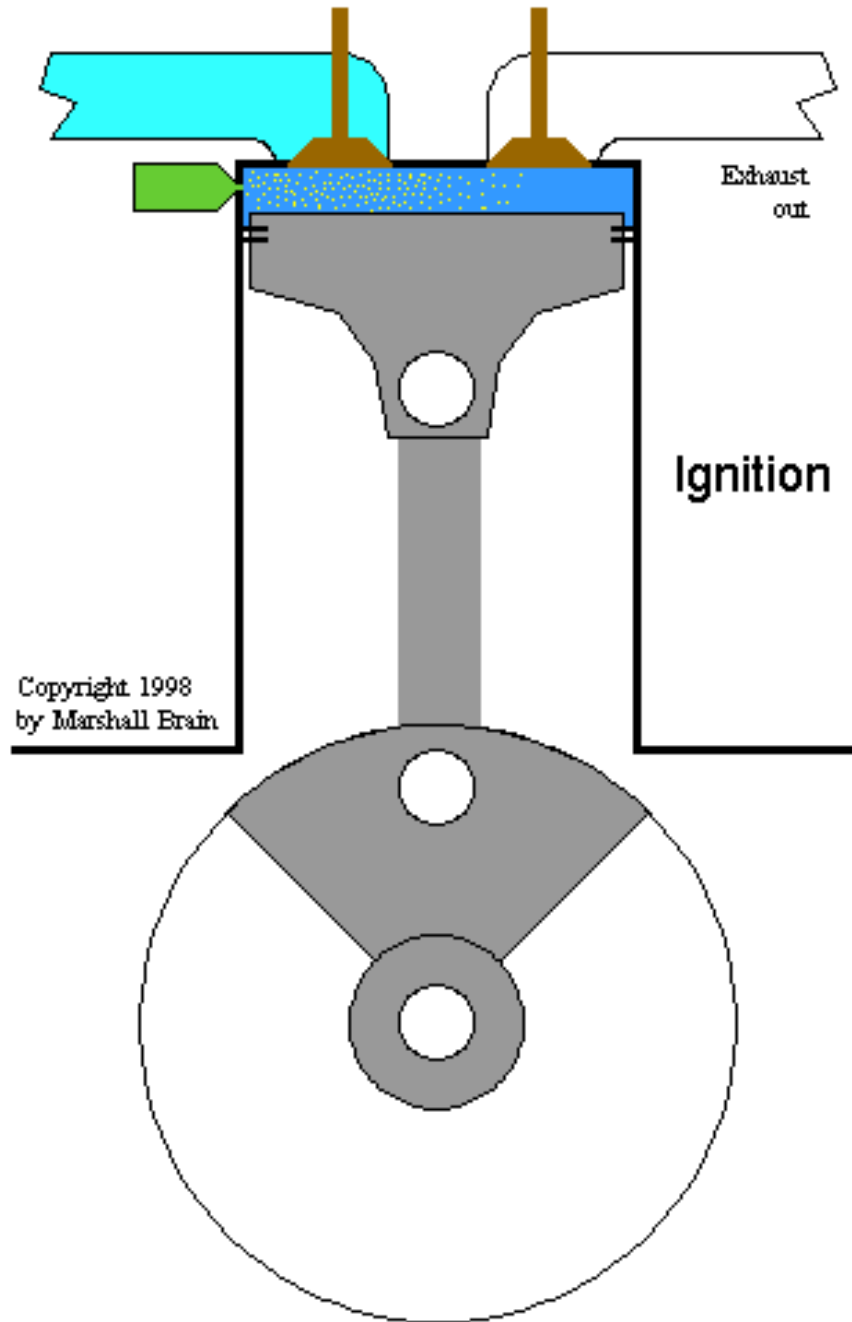
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2万年水之精华
瑞丰食品饮料批发部

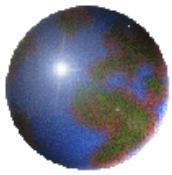


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Diesel Engine





Major advantages, cont.

* Diesel fuel (longer HC chains) is safer than gasoline in many applications. Although diesel fuel will burn in open air using a wick, it will not explode and does not release a large amount of flammable vapor. The low vapor pressure of diesel is especially advantageous in marine applications, where the accumulation of explosive fuel-air mixtures is a particular hazard. For the same reason, diesel engines are immune to vapor lock.

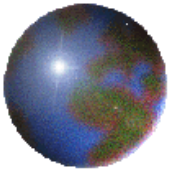
* For any given partial load the fuel efficiency (mass burned per energy produced) of a diesel engine remains nearly constant, as opposed to petrol and turbine engines which use proportionally more fuel with partial power outputs.

* They generate less waste heat in cooling and exhaust.

* Diesel engines can accept super- or turbo-charging pressure without any natural limit, constrained only by the strength of engine components. This is unlike petrol engines, which inevitably suffer detonation at higher pressure.

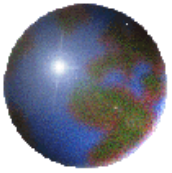
* The carbon monoxide content of the exhaust is minimal.

* Biodiesel is an easily synthesized, non-petroleum-based fuel (through transesterification) which can run directly in many diesel engines, while gasoline engines either need adaptation to run synthetic fuels or else use them as an additive to gasoline e.g., ethanol added.



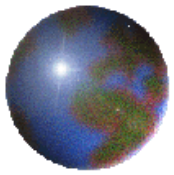
Diesel engines, Major disadvantages:

- Diesel engines are larger, heavier and more expensive than spark ignited engines.
- Tolerances on valves and rings stricter due to higher compression.
- Noise
- Greater NO_x and soot generation



Take Home Messages for Internal Combustion Engines.

1. Generate most of the CO and NO_x.
2. Four stroke spark ignited engines generate a lot of CO and substantial NO_x.
3. Two-stroke spark ignited engines generate aerosols, CO, VOC's, but little NO_x.
4. Diesel engines run hot and lean and generate NO_x and soot, but little CO.



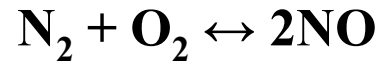
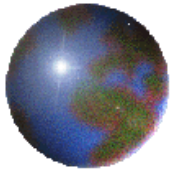
The Role of Internal Combustion in gaseous pollution and Photochemical Smog

Formation

4. Exhaust Emissions

c) Nitric Oxide, NO

The formation of NO is controlled by kinetics, not thermodynamic equilibrium. High temperatures favor the formation of NO, and as the exhaust gases cool the NO is frozen out because the reformation of N₂ and O₂ is slow. Our objective here is to derive an expression for the rate at which [NO] approaches the equilibrium concentration, [NO]_{eq}.

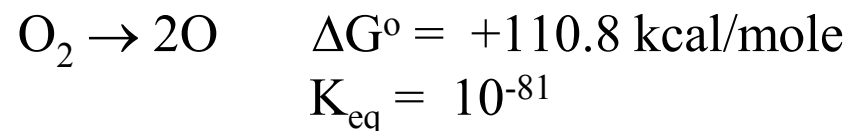
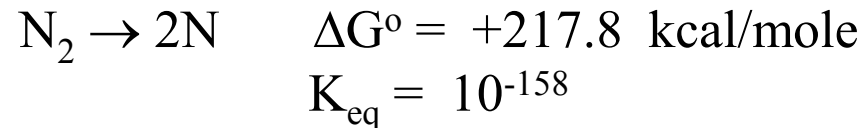


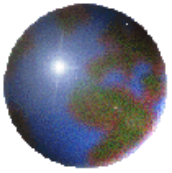
Derive an expression for the rate of NO formation.

Equilibrium Calculation

$$K_{\text{eq}} = \exp(-\Delta G / RT) = (\text{P}_{\text{NO}})^2 / (\text{P}_{\text{N}_2} \text{P}_{\text{O}_2})$$

The limit to the formation of NO is the slow rate of N₂ dissociation, which is hindered by a large positive ΔG. Oxygen dissociates more readily.





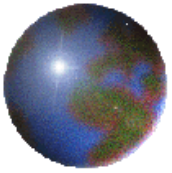
We can represent the formation of NO as a two step process.





$$\frac{d[\text{NO}]}{dt} = k_1[\text{O}][\text{N}_2] - k_{-1}[\text{NO}][\text{N}] + k_2[\text{N}][\text{O}_2] - k_{-2}[\text{NO}][\text{O}] \quad (\text{I})$$

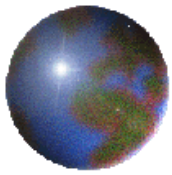
We will assume that N is in steady state. This is *not* the same as assuming it is in thermodynamic equilibrium.



$$d[\text{N}]/dt = k_1[\text{O}][\text{N}_2] - k_{-1}[\text{NO}][\text{N}] - k_2[\text{N}][\text{O}_2] + k_{-2}[\text{NO}][\text{O}]$$

$$[\text{N}]_{\text{ss}} = \frac{k_1[\text{O}][\text{N}_2] + k_{-2}[\text{NO}][\text{O}]}{k_{-1}[\text{NO}] + k_2[\text{O}_2]}$$

$$[\text{N}]_{\text{ss}} = \frac{[\text{O}]\{k_1[\text{N}_2] + k_{-2}[\text{NO}]\}}{k_{-1}[\text{NO}] + k_2[\text{O}_2]} \quad (\text{II})$$



From I and II

$$d[\text{NO}]/dt = \frac{2[\text{O}]k_1[\text{N}_2] - (k_{-1} k_{-2}[\text{NO}]^2 / k_2[\text{O}_2])}{1 + (k_{-1}[\text{NO}] / k_2[\text{O}_2])} \quad (\text{III})$$

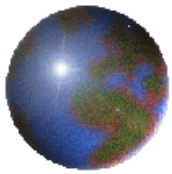
Where:

$$k_1 = 1.3\text{E-}10 \exp(-38000/T) \text{ cm}^3 \text{ s}^{-1} \quad k_1 (2400 \text{ K}) = 1.7\text{E-}17 \text{ cm}^3 \text{ s}^{-1}$$

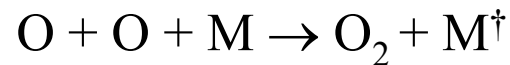
$$k_{-1} = 3.4\text{E-}11 \text{ cm}^3 \text{ s}^{-1} \quad k_{-1} (240\text{K}) = 3.4\text{E-}11 \text{ cm}^3 \text{ s}^{-1}$$

$$k_2 = 1.5\text{E-}11 \exp(-3600/T) \text{ cm}^3 \text{ s}^{-1} \quad k_2 (2400 \text{ K}) = 3.3\text{E-}12 \text{ cm}^3 \text{ s}^{-1}$$

$$k_{-2} = 2.5\text{E-}15 \text{ T} \exp(-19500/T) \text{ cm}^3 \text{ s}^{-1} \quad k_{-2} (2400 \text{ K}) = 2\text{E-}15 \text{ cm}^3 \text{ s}^{-1}$$

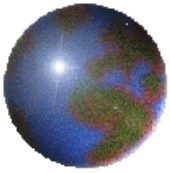


In a qualitative sense, at combustion temperature Reaction 1 is fast; Reaction 2 is fast *if* there is any O₂ around, and Reactions -1 and -2 are slow. So the formation of NO is much faster than the destruction. As the temperature drops, O atoms react with each other to reform O₂, preventing Reaction -2 from removing much NO:



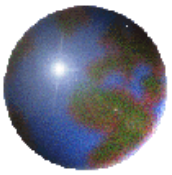
The superscript dagger represents translational kinetic energy.

In deriving a quantitative expression for the rate of formation of NO, the following relations will prove useful. Remember that rate constants are much harder to measure than thermodynamic properties, thus thermodynamic data are generally better (more accurate) than kinetic data. Anywhere we can substitute K_{eq} for k , we will.



$$K_1 K_2 = (k_1 / k_{-1})(k_2 / k_{-2}) = (P_{\text{NO}})^2 / \{ P_{\text{N}_2} P_{\text{O}_2} \} \quad (\text{IV})$$

$$d[\text{NO}]/dt = \frac{2k_1[\text{O}][\text{N}_2] \{1 - ([\text{NO}]^2 / K_{\text{eq}} [\text{N}_2] [\text{O}_2])\}}{1 + (k_1[\text{NO}] / k_2 [\text{O}_2])}$$



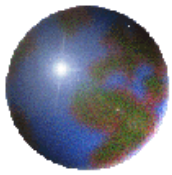
For a given temperature, Equation IV can be integrated to yield an expression for the concentration of NO as a function of time, but this is a tedious process. See Wark and Warner, p. 384. The result is:

$$[\text{NO}]_t = [\text{NO}]_{\text{eq}} (1 - (\exp(-Mt))^{1/2})$$

Where $[\text{NO}]_{\text{eq}}$ is the equilibrium concentration of NO and

$$M = 5.7\text{E}15 \text{ T}^{-1} \text{ P}^{1/2} \exp(-58400/\text{T}) \text{ s}^{-1}$$

Note that M is a strong function of temperature, but not pressure. We have assumed that Reactions 1 and 2 control, that the temperature is constant throughout the process, and that N₂ and O₂ are present at a ratio of 40:1. The actual process is very complicated because the temperature does not remain constant.

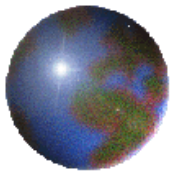


CONCLUSIONS Tuning to Reduce Automotive Pollution Emissions

The kinetics of CO formation and destruction are rapid. The emission of CO follows thermodynamic equilibrium, and is regulated by the temperature at the *end* of combustion. With slow kinetics, NO is seldom in thermodynamic equilibrium, and the emission is regulated more by the *maximum* combustion temperature.

A) Air-Fuel-Mixture

AFR	POWER	ECONOMY	CO/HC	NO_x
LEAN	LOW	HIGH	LOW	HIGH
RICH	HIGH	LOW	HIGH	LOW

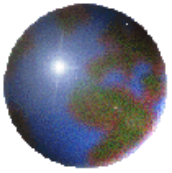


B) Compression

Increases power and reduces CO, but puts structural demands on the engine, and requires higher octane fuel to prevent knocking. Higher octane fuel cannot be produced with lead or the catalytic converters will be poisoned. High octane fuel without lead is more reactive with respect to photochemical ozone formation.

C) Timing

For maximum power, combustion should take place at the point of maximum compression, therefore the spark is usually advanced, and occurs before top dead center. But if a low octane fuel is used with an engine that has the spark advanced for maximum power, knocking occurs. By retarding the spark, the octane demand of the engine is reduced. Retarding the spark also lowers both the maximum temperature and the end temperature of combustion, reducing both NO and CO production.



D) Exhaust gas Recycling

Adding exhaust, rich in relatively inert CO_2 , N_2O and N_2 , to the combustion mixture reduces the temperature enough to help reduce NO production.