tutorial

Nitric Oxide Emission From Combustion

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Nitric oxide (NO) emission is one of the regulated pollutants produced as a result of the combustion of gasoline, natural gas, coal, and oil. The automobile is an important source of NO production in industrial societies. The adverse health effects of NO are lung damage, and illnesses of breathing passages and lungs (respiratory system). Also, nitric oxide is an ingredient of acid rain (acid aerosols), which can damage trees and lakes. Acid aerosols can reduce visibility and eat away stone used on buildings, status, and monuments. Therefore, a solid understanding of the mechanism of formation of NO during the combustion process is of vital importance to its mitigation strategy.

To attain the gist of the matter on formation of nitric oxide, one needs to understand or discover its chemical formation mechanism. Once it is found, the rest becomes a matter of systematic application of known mathematical and physical principles to the engine environment to construct a tool guiding the designers in reducing the NO emission from the engine combustion process. Also, the chemical formation mechanism provides a logical framework and clear direction on reduction strategies.

Three reaction mechanisms, each having unique characteristics (see Figure 1), are responsible for the formation of NOX during the combustion processes. NO and NO_2 are collectively referred to as NO_x . NO, the primary form in combustion products, is typically 95% of the total NO_X. NO is subsequently oxidized to NO_2 in the atmosphere. There are three formation paths are:

1. Thermal NO_X, which is formed by the combination of atmospheric nitrogen and oxygen at high temperatures largely in the burned gases.

2. Fuel NO_X, which is formed from the oxidation of fuel-bound nitrogen.

3. Prompt NO_X, which is formed by the reaction of fuel-derived hydrocarbon fragments with atmospheric nitrogen.

By far, the most important of these mechanisms in internal combustion engines is the thermal NOx. Therefore, we will not discuss other mechanisms any further than what is indicated in Fig. 1. The formation mechanism for the thermal NO_x is through the so-called Zeldovich mechanism as shown:

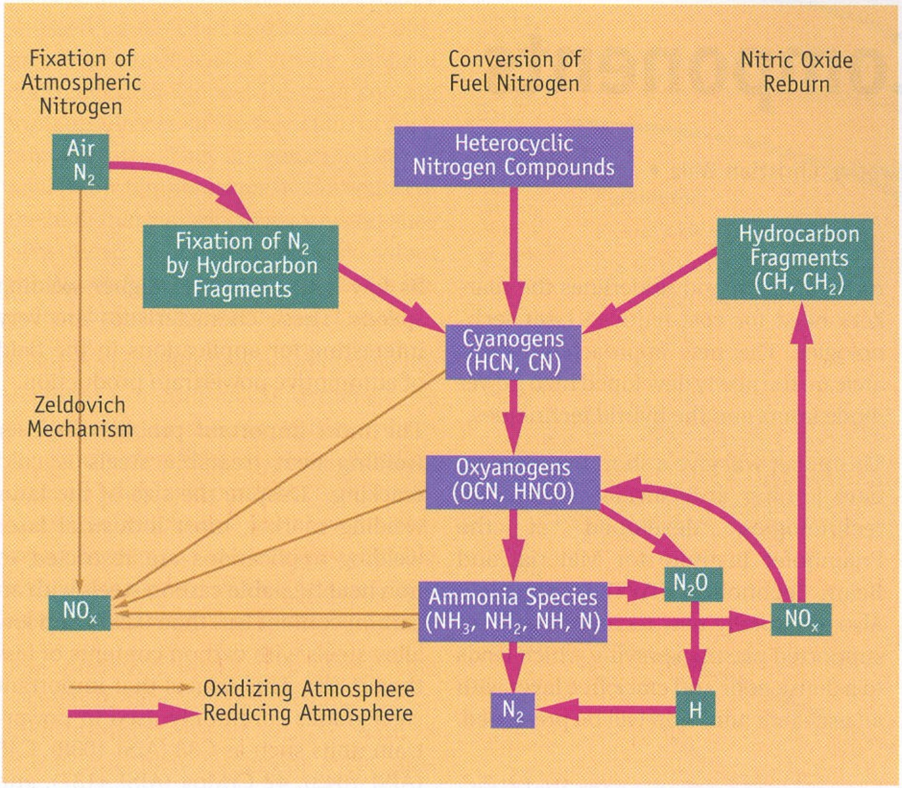

Figure 1: Nitrogen oxide formation mechanisms in combustion

$$N_2 + O \rightleftharpoons NO + N$$
$$N + O_2 \rightleftharpoons NO + O$$
$$N + OH \rightleftharpoons NO + H$$

The first reaction controls the overall rate of formation of the nitric oxide (i.e. it is rate-limited). Assuming that the concentration of the O and O_2 are in partial equilibrium, the NO formation rate can be formulated as:

$$\frac{d[NO]}{dt} = A[N_2][O_2]^{1/2} \exp\left(\frac{-E}{RT}\right)$$

As can be seen from the exponential function in the above equation, the rate of formation of NO is strongly affected by the temperature of the burned gases. Thus, thermal NOx formation is rapid in the high-temperature burned gases zones and when the fuel/air mixture is slightly on the lean side to have excess oxygen. A typical NO emission trend in a warmed-up spark-ignited engine with no catalyst as a function of the equivalence ratio is shown in Figure 2. Note that the peak of the NO is slightly on the lean side. The term equivalence ratio, Φ, is defined as the ratio of the (actual fuel/air mass ratio) to the (stoichiometric or theoretical fuel/air mass ratio); when $\Phi < 1$, the fuel-air mixture is lean; when $\Phi = 1$, it is at the stoichiometric value; and when $\Phi > 1$, it is on the rich side.

The above understanding clearly guides the direction one should take for reduction of the engine-out NO emission. Reduction of the burned gas temperature is central to all strategies used for NO emission reduction measures. For example, exhaust gas recirculation (EGR), a mainstream method, tends to reduce the burned gas temperature on account of its heat capacity and hence exponentially reduces the formation rate of the nitric oxide. As is obvious in Figure 2, lean operation of engines inherently produces low levels of nitric oxides. This is due to the reduction of the burned gas temperature under lean operation.

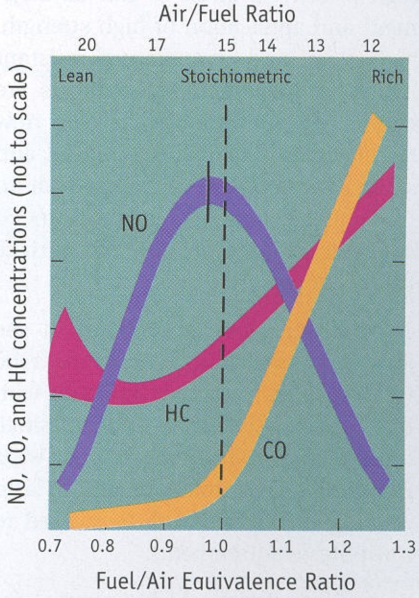

Figure 2. Major engine-out emission trends in a warmed-up spark-ignited engine