The Lecture Contains:

- NO Formation in CI Engines
- NO₂ Formation
**NO Formation in CI Engines**

In the compression ignition engines, rapid combustion of fuel and air that are mixed during delay period occurs. This rapid combustion phase is termed as 'premixed combustion' and is followed by mixing controlled diffusion combustion process. The diffusion combustion rates are controlled by the rate at which fuel and air mix and hence the name 'mixing controlled combustion'. Fuel-air equivalence ratio varies widely from very rich at the core of spray to very lean at the spray boundaries and, the formation of emissions is governed by the local air-fuel ratio besides other factors like temperature and pressure. In the premixed combustion phase, mixture formed within the flammable limits burns spontaneously. On the other hand, in the mixing controlled combustion phase, it is believed that combustion occurs in those regions of spray where equivalence ratio is close to stoichiometric.

In the classical spray combustion models, formation of NO starts in the burned gases produced on combustion of close to stoichiometric and lean flammable mixtures during premixed combustion phase. New combustion research on turbocharged/supercharged engines suggests that most NO is formed in mixing controlled diffusion combustion at spray boundaries and in the post combustion high temperature gases. The diffusion combustion takes place at near stoichiometric conditions. In the supercharged/turbocharged engines the delay period is rather short and overall a significantly smaller fraction of fuel burns in premixed phase. In the modern turbocharged, high-pressure direct injection engines with retarded injection timing, more than half of NO\textsubscript{x} in the cycle is produced in the post combustion gases after peak pressure. In the naturally aspirated engines with long ignition delays and sufficient time available for premixing of fuel and air, the contribution of premixed combustion to NO formation is considered to be substantial.

The hypothesis that most of NO\textsubscript{x} in diesel engines is formed in the burned gases produced by combustion at near stoichiometric conditions has been demonstrated by the following results. NO formation index (E\textsubscript{INOx}) in diesel engines has been correlated with the stoichiometric adiabatic flame temperature, \( T_{f,\varphi=1} \) using the following Arrhenius type expression

\[
E\text{INO}_x = \text{constant} \times \exp(E/RT_{f,\varphi=1})
\]

\( T_{f,\varphi=1} \) = Adiabatic flame temperature for stoichiometric mixture, K

\( E \) = overall activation energy, J/gmol

\( R \) = universal gas constant J/gmol.K

\( T_{f,\varphi=1} \) was evaluated at tdc motoring conditions using polytropic compression process. With polytropic index, \( n = 1.33 \). The use of diluents like nitrogen, exhaust gas, oxygen and water varies the intake air composition and hence the stoichiometric adiabatic flame.
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temperature. The measured NO\textsubscript{x} emissions with varying amounts of diluents at different engine loads and speeds correlated well with \( T_{f,\varphi = 1} \) according to the relationship given in Eq. 2.23. On a log plot, the (EINO\textsubscript{x}) data normalized with emissions obtained for standard air (without diluents) for several engines had linear correlation with the reciprocal of \( T_{f,\varphi = 1} \) as shown on Fig 2.9. The activation energy for DI engine was determined to be - 285.0 kJ/gmol, and for IDI engines equal to - 304.9 kJ/gmol. A single value of \( E \) correlated the emission data varying by a factor of nearly 40 times. The good correlation obtained between EINO\textsubscript{x} and \( T_{f,\varphi = 1} \) demonstrates the dominant importance of NO formation in close-to-stoichiometric burned gas regions.

![Correlation of NO\textsubscript{x} emission index with adiabatic flame temperature of stoichiometric mixture (\( T_{f,\varphi = 1} \)) varied by addition of nitrogen and oxygen as diluents and determined for mixture conditions at top dead centre for motored engines [14].](image)

The engine design and operating conditions too affect the NO\textsubscript{x} formation process. The above model is a very simple model and it showed good correlation for the engines of 1980s. For advanced engines with very different injection parameters and fuel-air mixing processes, single overall activation energy was found to have a poorer correlation than shown on Fig. 2.9.
Depending upon the burned gas temperature, the contribution of different reactions to kinetics of NO formation also changes and hence the deviations may be observed from the simple stoichiometric adiabatic flame temperature model. However, the dominant contribution to NO formation still results from the spray regions that burn in near stoichiometric conditions. NO is formed at varying rates in the spray depending upon the local equivalence ratio and temperature. As the combustion progresses, the already burned gases keep on mixing with colder air and fuel vapour, changing its composition and temperature and hence the NO formation chemistry. Temperature of the reacting gases also changes due to compression and expansion. Sudden cooling of the burned gases may result due to mixing with cooler air and consequently resulting in freezing of NO kinetics and the NO decomposition reactions. Thus, cooling of burned gases by mixing with cooler air and fuel-air mixture in diesel engines causes more rapid freezing of NO kinetics, which results in NO concentration frozen at higher levels compared to those in the SI engines. Kinetic models based on the extended Zeldovich mechanism discussed earlier are widely used for calculations of engine-out NO emissions from the DI diesel engines. At high pressures typical of diesel combustion with high residual gas dilution (EGR), the Zeldovich mechanism alone may not predict adequately NO formation. Additional reactions involving N₂O in formation of NO as given in reactions 2.24 – 2.25 have been proposed.

\[
\text{N}_2 + O + M \rightarrow \text{N}_2O + M \quad (2.24)
\]

\[
\text{N}_2O + O \rightarrow 2\text{NO} \quad (2.25)
\]

The significance of N₂O mechanism for NO formation in the real engines however, is yet to be established.

**Summary of NO Formation in CI Engines**

- In the CI engines, most NO is formed in the burned gases resulting from near stoichiometric combustion
- Kinetically formed NO is frozen at higher levels compared to SI engines as sudden cooling of the burned gases may be caused due to mixing with cooler air or cylinder charge, thereby freezing the NO decomposition reactions
**NO₂ Formation**

Nitrogen dioxide emissions from the spark-ignition engines are negligibly small and constitute less than 2% of the total NOₓ emissions. NO emissions range from a few hundred ppm to several thousands of ppm while, the maximum NO₂ emissions are around 60 to 70 ppm only compared to 3000-4000 ppm of NO at full load conditions. In diesel engines however, the NO₂ emissions account generally for 10 to 30 percent of the total NOₓ emissions. In diesel engines, NO₂ concentration may be in the range of 200 to 400 ppm compared to NO concentrations typically in the range of 1500 to 3000 ppm. NO₂ is rapidly formed in the combustion zone by reaction of NO with HOO⁻ radical.

\[ \text{NO} + \text{HOO}^- \rightarrow \text{NO}_2 + \text{OH}^- \]  

(2.26)

Later in the post combustion gases NO₂ on reaction with atomic O⁻ is converted back to NO and O₂.

\[ \text{NO}_2 + \text{O}^- \rightarrow \text{NO} + \text{O}_2 \]  

(2.27)

However, if the high temperature burned gases due to presence of high turbulence mix rapidly with colder air or air-fuel mixture, the reactions that decompose NO₂ back to NO and oxygen are frozen and relatively higher concentrations of NO₂ result. The relative concentration of NO₂ with engine power typically observed in diesel engines is shown in Fig.2.10. An increase in relative concentration of NO₂ with decrease in engine load as seen in Fig 2.10 supports this mechanism. As the engine load decreases the air to fuel ratio increases and the probability of high temperature gases coming suddenly in contact of cooler air/charge in the engine cylinder also increases. Hence, there is a higher probability of freezing of NO₂ decomposition reactions in diesel engines at lighter loads.
Figure 2.10 Exhaust NO$_2$ concentration as percent of total NO$_x$ for a DI diesel engine