

Module 2:Genesis and Mechanism of Formation of Engine Emissions

Lecture 7:Mechanisms of CO and HC Formation in SI Engines

Mechanisms of CO and HC Formation in SI Engines

The Lecture Contains:

- FORMATION OF CARBON MONOXIDE
- FORMATION OF UNBURNED HYDROCARBONS
- HC EMISSIONS FROM SI ENGINES

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FORMATION OF CARBON MONOXIDE

Carbon monoxide is formed during combustion of fuel-rich mixtures due to deficiency of oxygen. Combustion of hydrocarbon fuels may be considered as a two-step process leading to complete combustion when carbon dioxide is the final product.

Step 1

Conversion of hydrocarbons to CO: oxidation reactions involving intermediate species like smaller hydrocarbon molecules, aldehydes, ketones etc lead to formation of CO as schematically shown below are.



RH represents a hydrocarbon where R stands for the hydrocarbon radical

Step 2

Conversion of CO to CO₂ : when sufficient oxygen is available. Hydroxyl radical OH is one the principal oxidizing species and converts CO to CO₂,



The reaction (2.29) is quite fast and is under equilibrium at high temperatures. In fact, the reactions involving C-O-H system may be taken in chemical equilibrium during combustion and large part of expansion stroke when temperatures are above 1800 K.

CO emitted is higher than the equilibrium concentrations corresponding to the temperature and pressure conditions at the end of expansion. The calculations show that until about 60 degrees after top dead centre, the burned gases are close to equilibrium. However, late in the expansion stroke and during exhaust blow down on opening of the exhaust valve as the gases cool down, the CO concentrations differ from the equilibrium value. The predicted CO levels at the end of expansion computed by equilibrium considerations during early part of expansion and CO oxidation kinetics (Reaction 2.29) in the later part of expansion correlated well with the experimental data as shown on Fig. 2.11 These CO values may be considered as partial equilibrium values. Detailed investigations have shown:

- For rich mixtures ($f > 1$), the average exhaust CO concentrations are close to equilibrium concentrations during expansion.
- For near stoichiometric mixtures ($f \sim 1$) exhaust CO is close to computed partial equilibrium values.
- For lean mixtures the measured CO is higher than the computed values using kinetic models. This discrepancy may occur due to partial oxidation of unburned hydrocarbons released from crevices and lubricating oil film and deposits on the combustion chamber walls during expansion.

For estimation of CO concentration a good approximation is to assume chemical equilibrium frozen at 1750 K.

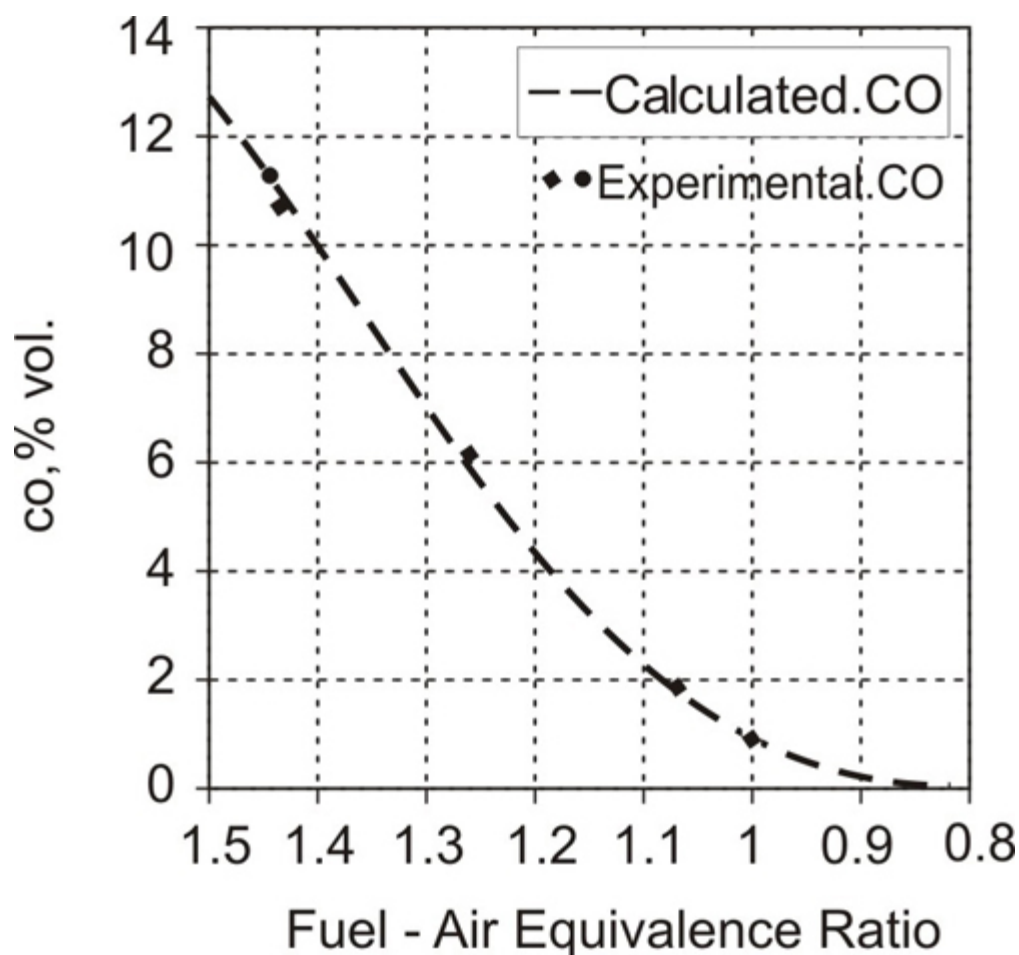


Fig 2.11

Comparison of calculated CO using partial equilibrium (kinetics in later part of expansion stroke) and experimental data

CO emissions in real engines:

- Mixture mal-distribution in multicylinder engines causes cylinder-to-cylinder variation in air-fuel ratio. It results in significant increase in the average CO emissions. This is especially prominent in the carburetted or single point throttle body-injected (TBI) engines.
- Another contributing factor to higher CO emissions is non-uniform mixture distribution within the cylinder.
- During cold start of engine and acceleration rich mixtures are used resulting in higher CO emissions

Overall, the air-fuel ratio is the most important engine parameter affecting CO emissions. Other factors influence CO mostly indirectly through changes in mixture composition and/or promotion of slow oxidation reactions resulting in incomplete combustion.

FORMATION OF UNBURNED HYDROCARBONS

- The unburned hydrocarbons are also called volatile organic compounds (VOCs).
- Unburned hydrocarbon emissions result as part of the fuel inducted into the engine escapes combustion. Most of hydrocarbons in exhaust HC are the same compounds as in the fuel. A typical petroleum fuel contains 100 to 200 different hydrocarbons (10 to 20 are the major constituents) and other organic compounds. Thus, if the fuels are rich in aromatics and olefins the exhaust hydrocarbons also consist of a high fraction of aromatics and olefins, which are photo-chemically more reactive.
- Almost 400 hundred different organic compounds are present in the engine exhaust. A number of these compounds are formed during combustion process in the engine cylinder.
- Nearly 50% mass of organic compounds emitted in the exhaust is similar to fuel in composition. The balance 50% is composed of the chemical species which are produced by thermal cracking, pyrolysis, chemical synthesis and partial oxidation of the fuel molecules during combustion.
- Methane is also present in significant amounts in the exhaust of gasoline and diesel engines. As methane is not photo-chemically reactive, hydrocarbon emissions now, are also measured neglecting methane emissions and these are termed as non-methane hydrocarbons or non-methane organic gases (NMHC/NMOG).
- Hydrocarbon concentration in the exhaust is measured by flame ionization analyzer (FIA), which is basically a carbon atom counter. The total hydrocarbon concentration measured by this method is specified in parts per million as methane or C1 (ppmC₁ or simply ppmC). It means that if the FIA is calibrated with propane (C₃H₈), the HC measurement reading is to be multiplied by a factor of 3 to obtain HC concentration in ppmC.

Several engine processes contribute to the unburned fuel emissions. The sources of unburned hydrocarbon emissions also vary with the engine design; whether it is a homogeneous SI or a heterogeneous CI ignition engine, whether 4-stroke or crankcase scavenged 2-stroke engine. In the crankcase scavenged, small two stroke SI engines, fuel-air mixture bypasses combustion and is directly 'short-circuited' to the exhaust port during scavenging period and the mixture short-circuiting is the main source of hydrocarbon emissions in these engines.

HC EMISSIONS FROM SI ENGINES

Main sources of hydrocarbon emissions in the four-stroke, homogeneous charge spark ignition engines are:

(i)	Flame quenching on the cylinder walls
(ii)	Flame quenching in crevices
(iii)	Absorption and desorption in oil film on cylinder walls
(iv)	Absorption and desorption in carbon deposits in the chamber
(v)	Misfired combustion or bulk gas quenching
(vi)	Liquid fuel in the cylinder
(vii)	Exhaust valve leakage, and
(viii)	Crankcase blow by gases

In the vehicles, fuel evaporation from fuel tank and fuel system is another source of unburned HC emissions.