Post-flame Oxidation of HC and Transport to Exhaust

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Post-flame HC Oxidation

During expansion stroke, the hydrocarbons from the quench layer, oil film and crevices diffuse back into the bulk combustion gases. These hydrocarbons that diffuse back into the burned gases oxidize inside the cylinder and in the exhaust depending upon the burned gas temperature and the availability of oxygen. HC levels in the cylinder prior to opening of exhaust valve are 1.5 to 2 times higher than the concentrations in the exhaust. Empirical correlations have been obtained from the experimental data to estimate HC oxidation in the cylinder and exhaust as given below:

$$\frac{d[HC]}{dt} = -6.7 \times 10^{15} \exp\left(\frac{-18{,}735}{T}\right) \tilde{x}_{HC}\tilde{x}_{O_2}\left(\frac{p}{RT}\right) \qquad (2.35)$$

where [ ] denotes concentration of reactants in moles per cm3, X_{HC} and X_{O2} are the mole fractions of HC and O2, respectively, *t* is time in seconds, temperature *T* in K and the density (*p/RT*) is in moles per cm^3. From the oxidation rate given by the above expression, oxidation time, t_{ox} for a given concentration [HC] can be estimated as below:

$$t_{ox} = [\mathrm{HC}] / (d[\mathrm{HC}]/dt) \qquad (2.36)$$

As the quench layers on the cylinder walls are thin, HC from these diffuse rapidly into burned gases and get oxidized. When the bulk gas temperatures are higher than 1300-1400 K, the HC oxidize rapidly. The unburned hydrocarbons from the crevices between piston and cylinder expand back into the bulk gases later in the expansion and exhaust strokes when temperatures have fallen below 1300 K. Just before exhaust valve opens, the gas temperatures are generally around 1250 K, but decrease below 1000K after exhaust blows down. Thus, a significantly large fraction of HC emerging from crevices and oil layers may not be oxidized.

It is estimated that about two third of the hydrocarbons stored in the crevices and absorbed in oil film get oxidized inside the cylinder of the conventional gasoline engines under steady state, mid-load and mid-speed engine operation. At lower loads, extent of postflame HC oxidation would be lower.

During postflame oxidation, partial combustion products and intermediate hydrocarbons due to decomposition of fuel molecules are also produced. These compounds are not present in the original fuel and constitute about 50% percent of the exhaust HC.

Oxidation to an extent of up to 45% of HC which leave the cylinder is possible if high enough temperatures are maintained and the oxidation reactions are not quenched by sudden cooling. In the exhaust port and manifold if residence time is of the order of 50 ms or longer and temperatures greater than 1000 K are maintained, significant oxidation of HC is possible. The engine could be run at stoichiometric or richer mixtures and with retarded spark timing to obtain a high exhaust gas temperature, and calibrated amount of secondary air is injected at the exhaust port to oxidize and reduce HC emissions. This technique was employed on production engines prior to catalytic emission control.

HC Transport to Exhaust

Four quench zones basically exist in the engine cylinder. These zones are

- cylinder head quench layer wall including spark plug crevice
- cylinder wall quench layer and head gasket crevice
- the quench layer on piston head, and
- the quench zone around the piston above the top land crevice.

Depending upon the gas-dynamic flow during exhaust, the flow from these regions is expected to be different. At the end of combustion, hydrocarbons are present in high concentrations along the combustion chamber walls trapped in the deposits, oil films and crevices. During expansion stroke, hydrocarbons flow out of crevices. Some of the hydrocarbons flowing out of crevices and desorbed from oil film and deposits diffuse into the bulk gas, but most of these remain close to the walls. When the exhaust valve opens, gases blow out of the cylinder at a high velocity. During the exhaust blow down process, in the beginning the exhaust gas takes along HC from the quench zones (1) and (2), spark plug and head gasket crevices which are closer to the exhaust valve and part of the hydrocarbons released from crevices, oil films and deposits. Thus, the initial exhaust blow down gas is rich in unburned hydrocarbons and about half of the total unburned HC are emitted.

During expansion, hydrocarbon -rich boundary layer is present along the cylinder walls as the fuel vapours expand out of piston-cylinder crevice and desorbed from the oil film. Upward motion of the piston during exhaust stroke scraps this hydrocarbon –rich boundary layer and gases from quench zone (3) rolling these into a vortex along the periphery of piston crown.. The piston motion pushes it towards cylinder head and this vortex may be detached from the piston crown and is partly exhausted. This vortex mechanism leads to high HC concentration in the exhaust gases towards the end of the exhaust stroke.

Typical variation in exhaust HC concentration and mass flow rate exiting the cylinder is shown in Fig. 2.15. Hydrocarbon concentration peaks during blow down and towards the end of the exhaust stroke. The peak in HC concentration at the end of exhaust stroke is very high as it contains HC mostly originating from the piston ring crevice, but the exhaust flow rate is small. Mass HC emission rates peak during the exhaust blow down process as the exhaust flow rates are high. About half of the mass of HC is exhausted during blow down itself and the remaining half later in the exhaust stroke. Another peak in the HC mass flow rate occurs towards the end of exhaust stroke when the HC from the piston-cylinder crevice region are flowing out as HC concentration is very high, although the exhaust flow rates are small.

it has been estimated that under wide open throttle operation, about 2/3rd of the total unburned HC in the cylinder are exhausted, the balance remaining in the residual gases. Under part load conditions, about half of the unburned HC exit the cylinder.

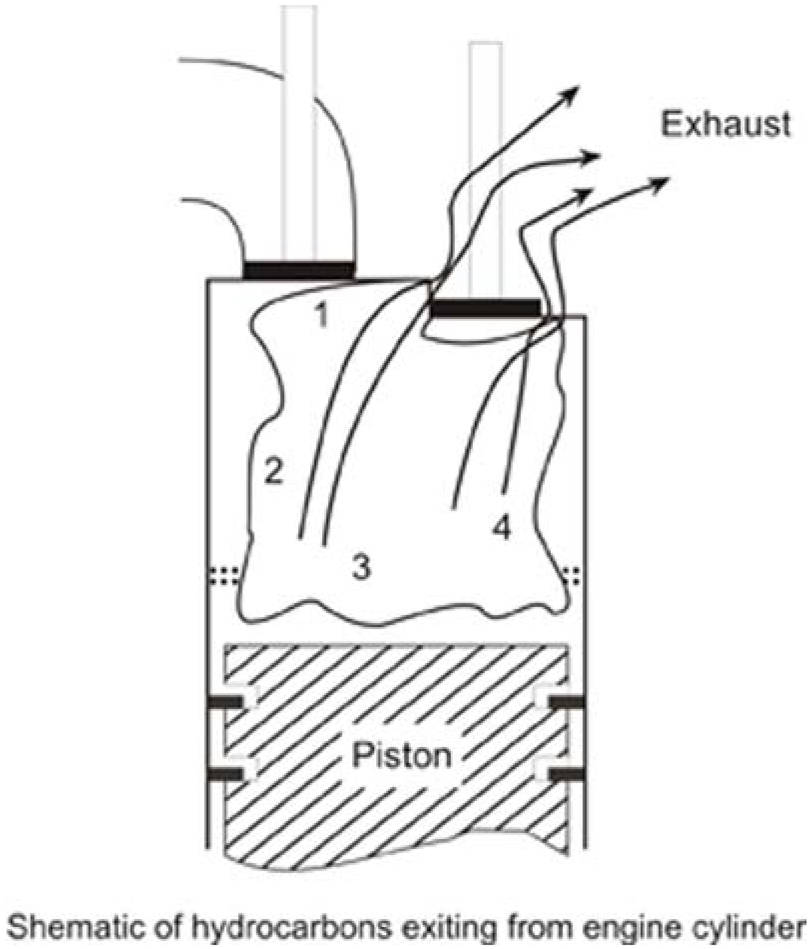

Figure 2.14	Schematic of hydrocarbons exiting from engine cylinder

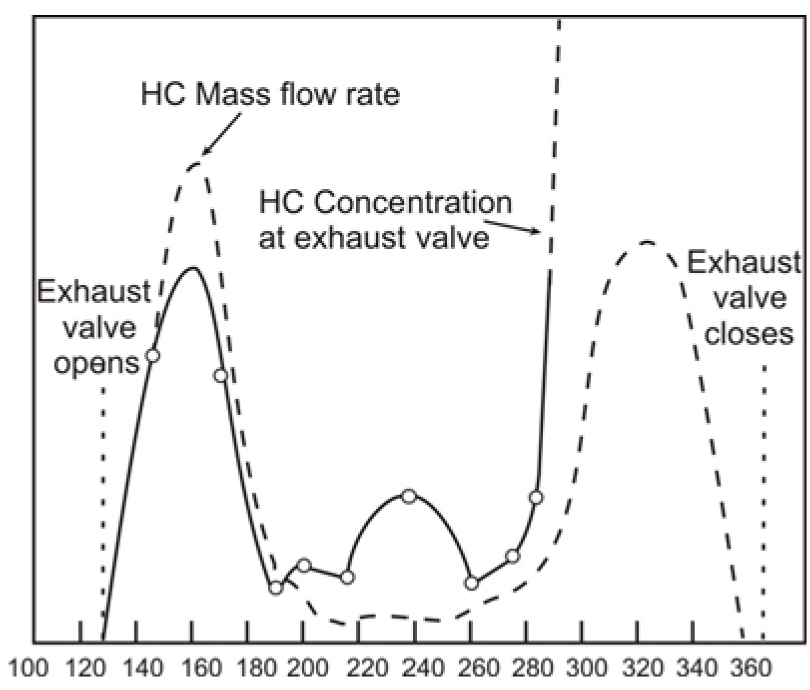

Figure 2.15	Trends in variation of HC concentration and HC mass flow rate at the exhaust valve during the exhaust process of an SI engine.

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Summary of HC Emission Processes in SI Engines

In a port fuel injection SI engine, typically:

- About 9 percent of the total fuel supplied escapes normal combustion. Of the this Approximately 3 percent escapes as fuel itself through absorption in oil and deposits routes, and as liquid fuel films deposited in the cylinder.
- About 5 percent as fuel-air mixture due to flame quenching on walls and crevices, and leakage through exhaust valves.
- Around 1% of fuel –air mixture escapes as crankcase blow by.
- Of the fuel contained in crevices and quench layers about 2/3rd is oxidized inside the cylinder.
- Of the fuel in oil layers, deposits and liquid fuel film only about 1/3rd is oxidized inside the cylinder.
- About 2.7 % of fuel exits the exhaust port and nearly 1 % is retained in the residual burned gases.
- Of the hydrocarbons exiting the exhaust port about 1/3rd is further oxidized in the exhaust system.
- Under warmed up operation, engine out HC emissions from a PFI are approximately 1.8 percent of the fuel supplied. The balance 7.2 percent fuel that does not leave the cylinder is either oxidized in the cylinder or at exhaust port and manifold or recycled in the residual gases and crankcase blow by gases.

Approximate contribution of different sources to HC emissions for a port fuel injected SI engine is shown in Fig. 2.16

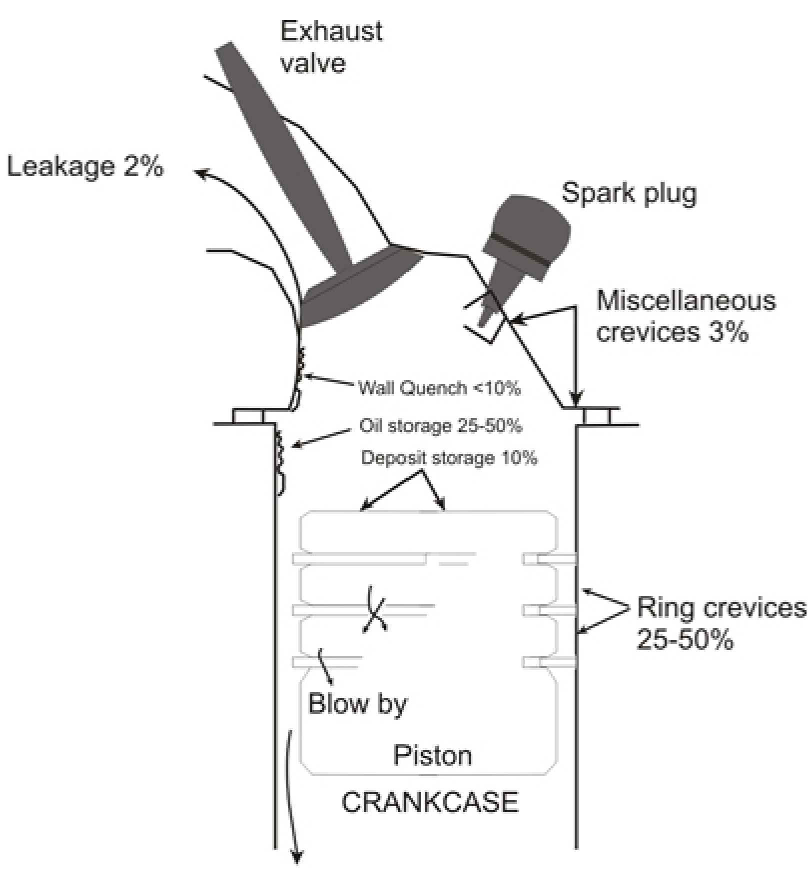

Figure 2.16	Different sources of hydrocarbon emissions in homogeneous charge SI engine.

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