

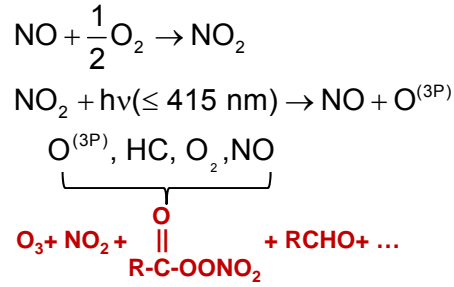
**Lectures 11 and 12**  
**Air Pollution and SI Engine Emissions**

**Atmospheric Pollution**

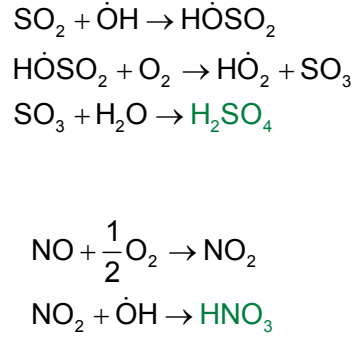
- **SMOG**
    - $O_3$        $NO_2$        $\begin{array}{c} O \\ || \\ R-C-OONO_2 \end{array}$
    - Ozone      Nitrogen dioxide      PAN(Peroxyacyl Nitrate)
  
  - **TOXICS**
    - CO, Benzene, 1-3 butadiene, POM (Polycyclic organic Matters), Aldehydes
- Primary Pollutants:**      Direct emissions from vehicles
- CO, HC, NO<sub>x</sub>, PM(Particulate matters), SO<sub>x</sub>, aldehydes
- Secondary Pollutants:** From interaction of emissions with the atmosphere
- O<sub>3</sub>, PAN, NO<sub>2</sub>, Aldehydes

## Atmospheric Pollution

### Smog formation:

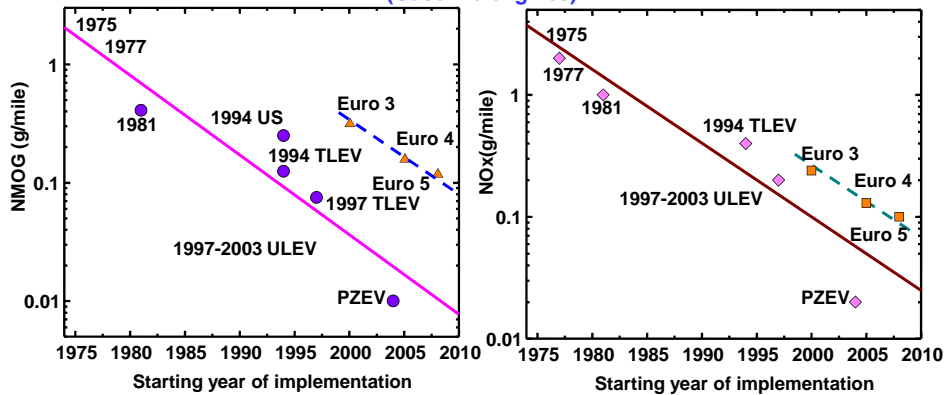


### Acid rain:



## Emission requirements

(Gasoline engines)

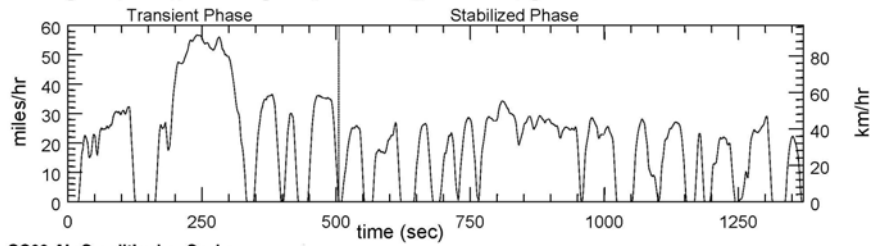


Historic trend: Factor of 10  
reduction every 15 years

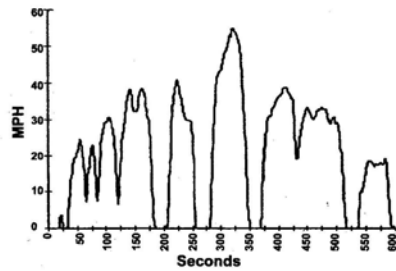
At 28.5 miles per gallon, 100 g of fuel is burned per mile.  
Emission of 0.01 g/mile means  $10^{-4}$  g/g-of-fuel

PZEV regulation  
(120,000 miles guarantee):  
 NMOG 0.01 g/mile  
 CO 1.0 g/mile  
 NOx 0.02 g/mile

**FTP 23 cycles** – Each cycle consists of idle, accel., cruise, and decel. Three test phases:  
 Transient phase (0-505s); stabilized phase (505 to 1376s); warm start (repeat of first 505 s test after 10 min. shut down)

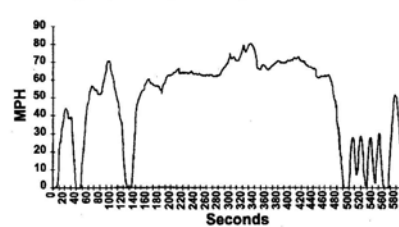


**SC03 Air Conditioning Cycle**



Total duration : 594 s Max. speed : 54.8 mph

**US06 High speed/High load cycle**



Total duration : 600 s Max. speed : 80.3 mph  
 Max. acceleration: 8 mph/second

**Air Conditioning Cycle:**

10 min. soak, 95°F ambient temperature, 40% relative humidity,  
 850W/m<sup>2</sup> solar load, AC max cooling

## EMISSIONS MECHANISMS

- CO emission
  - Incomplete oxidation of fuel under fuel rich conditions
- NOx emission
  - Reaction of nitrogen and oxygen in the high temperature burned gas regions
- Particulate matter (PM) emission (most significant in diesel engines; there are significant PM emissions in SI engines in terms of number density, especially in direct injection engines)
  - Particulates formed by pyrolysis of fuel molecules in the locally fuel rich region and incomplete oxidation of these particles
  - Lubrication oil contribution
- Hydrocarbon emissions
  - Fuel hydrocarbons escape oxidation (or only partially oxidized) via various pathways

### Typical steady state SI engine-out emissions

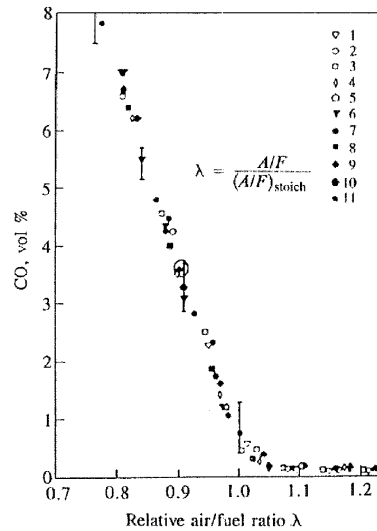
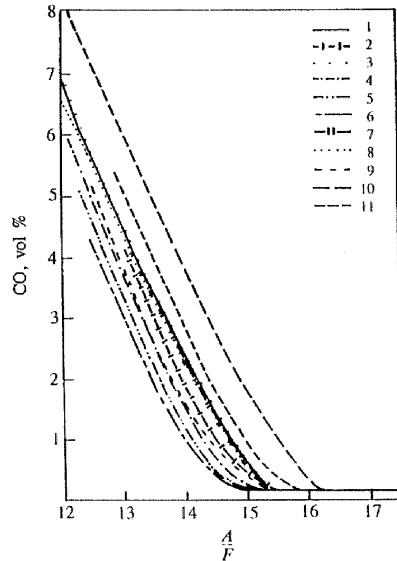
- NO<sub>x</sub> is a few thousand parts per million
- CO is around 0.5-1% for stoichiometric operation
- HC is 500-2000 ppm for fully warm up engine
- PM very small by mass

### CO Emissions Mechanism

- CO is the incomplete oxidation product of the fuel carbon
- Significant amount in fuel rich condition
- Immediately following combustion, CO is in chemical equilibrium with the burned gas
- During expansion, as the burned gas temperature decreases, CO is 'frozen'
  - Empirical correlation

$$\frac{[\text{CO}][\text{H}_2\text{O}]}{[\text{CO}_2][\text{H}_2]} \approx 3.7$$

## CO is mostly an A/F equivalence ratio issue

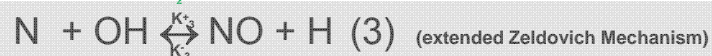


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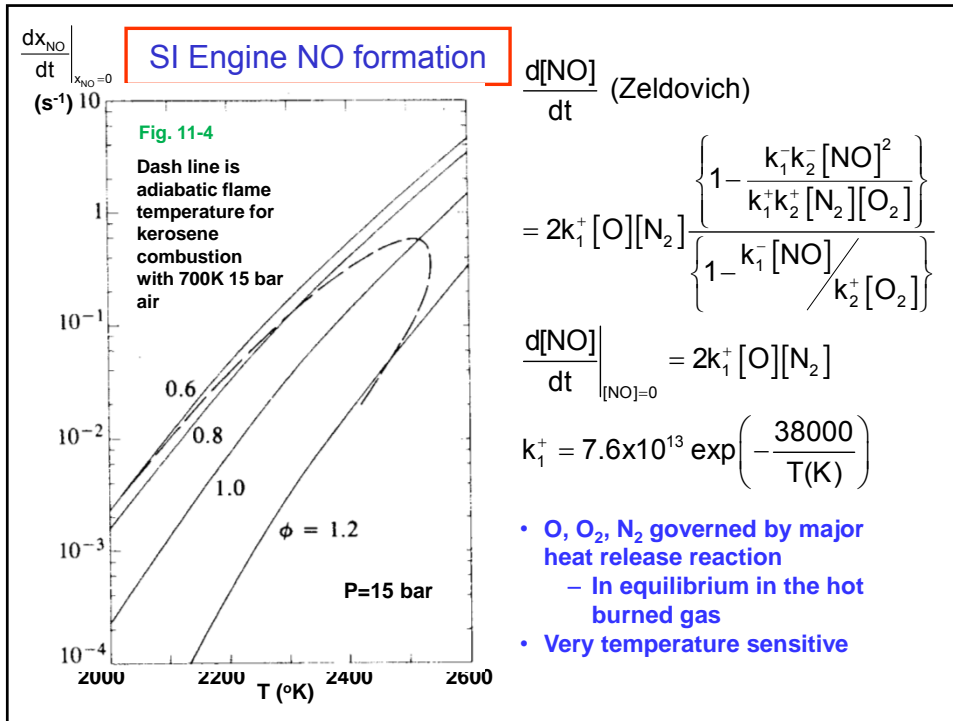
## NO FORMATION CHEMISTRY

- Zeldovich Mechanism

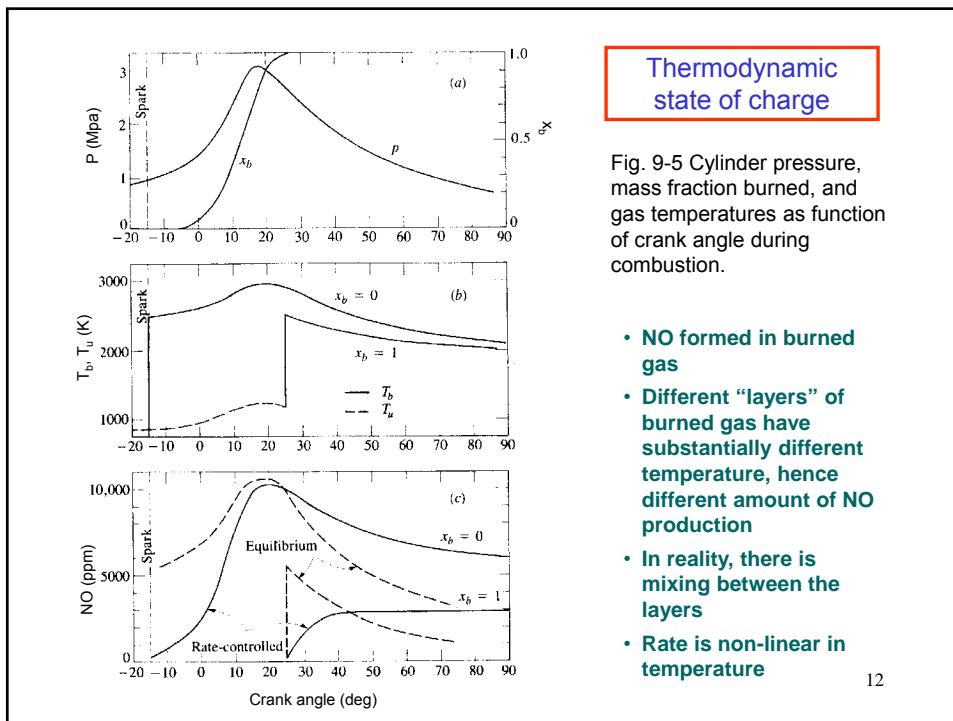
See table 11.1 for rates



- NO formation is kinetically controlled
- Reactions involving N is fast; N is in steady states ( $d[\text{N}]/dt \approx 0$ )
- Very temperature sensitive
- At high temperature ( $\geq 1000\text{K}$ ), equilibrium favors NO versus  $\text{NO}_2$  formation
  - Engine-out  $[\text{NO}_2]/[\text{NO}_x] \leq 2\%$

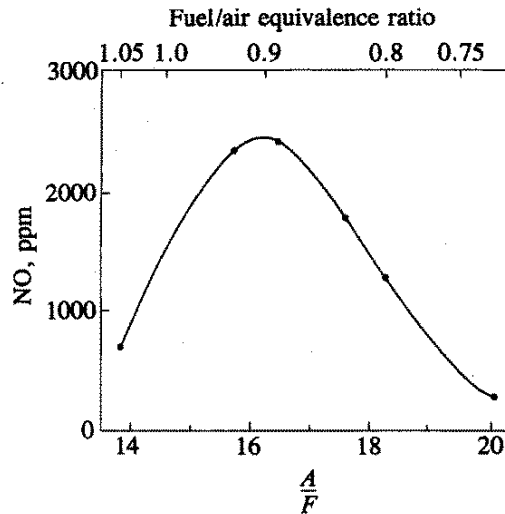


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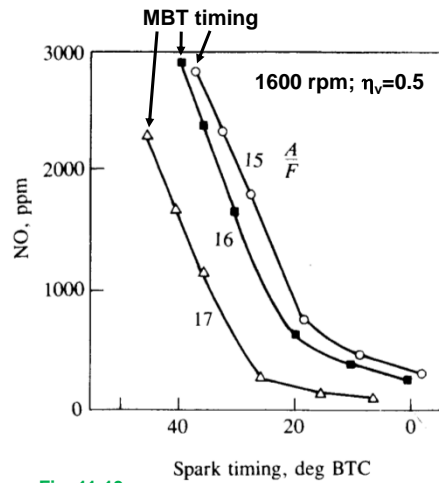
## Engine-out NO emission as function of $\Phi$



**Fig. 11-9**  
SI engine, 1600 rpm,  
MBT timing,  $\eta_v=50\%$

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## In-cylinder NO control



**Fig. 11-13**

- **Temperature is the key**
  - Spark retard
  - EGR (Exhaust Gas Recirculation)

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## NO control by EGR

- EGR is a dilution effect
  - Reduce burned gas temperature via increase in thermal inertia

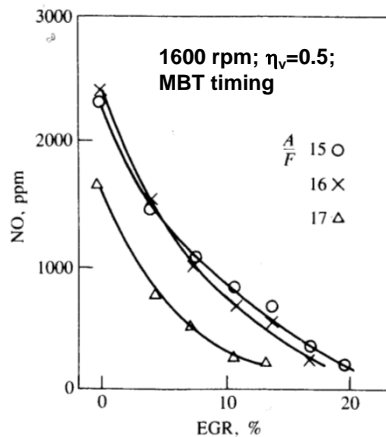


Fig. 11-10

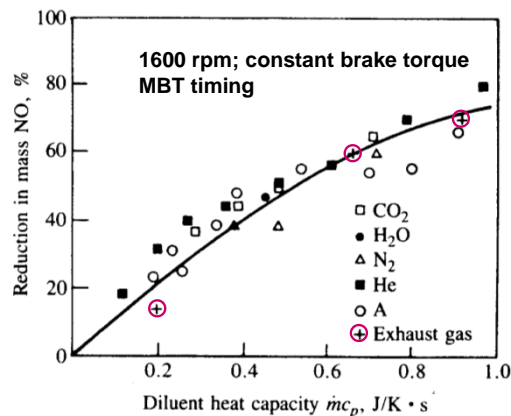


Fig. 11-11

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## HC emissions

- Importance
  - Photochemical smog (irritant; health effects)
  - Significant loss of fuel energy
- Measurement
  - Flame Ionization Detector (FID)
    - Chemi-ionization process
    - Signal proportional to C atom concentration
- Emissions regulation: NMOG as g/mile
  - EPA definition of HC
    - Normal gasoline CH<sub>1.85</sub>
    - Reformulated gasoline CH<sub>1.92</sub>
    - Compressed natural gas CH<sub>3.78</sub>
  - Need speciation to detect CH<sub>4</sub>



## HC Impact on smog formation

- Species dependent
  - Assessed as MIR of individual VOC
- VOC = volatile organic compounds

$$\text{Kinetic reactivity} = \frac{\text{VOC reacted}}{\text{VOC input}}$$

$$\text{Mechanistic reactivity} = \frac{\text{Ozone formed}}{\text{VOC input}}$$

Maximum Incremental Reactivity (MIR)

$$\text{MIR} = \frac{m_{\text{ozone, test case; max}} - m_{\text{ozone, base case; max}}}{\text{VOC increment to base case}}$$

**EKMA (Empirical Kinetic Modeling Approach) methodology: follow air column (Lagrangian) from 0800 using O3 as indicator. Maximum O3 formation occurs at about 1500-1700 hr.**

APPENDIX		Maximum Incremental Reactivity Values Used in This Paper	
	MIR (g O <sub>3</sub> /g NMOC)		MIR (g O <sub>3</sub> /g NMOC)
Ethane	0.250	Ethene	7.290
Propane	0.483	Ethyl	0.500
2-Methylpropane	1.210	Propene	0.400
n-Butane	1.020	Propadiene	7.290
2,2-Dimethylpropane	0.370	Propyne	4.100
2-Methylbutane	1.390	2-Methylpropane	5.310
n-Pentane	1.040	1-Butene	0.910
2,2-Dimethylbutane	0.820	1,3-Butadiene	10.890
Cyclopentane	2.300	i-2-Butene	0.940
2,3-Dimethylbutane	1.070	1-Butyne	9.240
2-Methylpentane	1.070	i-2-Butyne	0.940
3-Methylpentane	1.520	c-2-Butene	0.940
n-Hexane	0.980	3-Methyl-1-Butene	6.220
2,2-Dimethylpentane	1.400	2-Butyne	0.240
Methylcyclopentane	1.400	1-Pentene	6.220
2,4-Dimethylpentane	2.620	2-Methyl-1-Butene	4.900
2,2,3-Trimethylbutane	1.320	2-Methyl-1,3-Butadiene	9.080
Cyclohexane	1.290	i-2-Pentene	0.800
2-Methylhexane	1.090	c-2-Pentene	0.800
2,3-Dimethylpentane	1.510	2-Methyl-2-Butene	4.410
Cyclohexane	1.510	Cyclohexadiene	7.660
1,3-Dimethylcyclopentane	1.850	Cyclopentene	7.660
1,1,3-Dimethylcyclopentane	1.850	4-Methyl-1-Pentene	4.420
2,2,4-Trimethylpentane	0.930	3-Methyl-1-Pentene	4.420
n-Heptane	0.810	3-Hexene	6.690
Methylcyclohexane	1.850	1,2-Hexene	6.690
2,5-Dimethylhexane	1.630	3-Methyl-1,2-Pentene	6.690
Ethylcyclopentane	2.310	2-Methyl-2-Pentene	6.690
Cyclohexane	1.510	c-3-Hexene	6.690
3,3-Dimethylhexane	1.200	c-2-Hexene	6.690
2,3,4-Trimethylpentane	1.620	3-Methyl-c-2-Pentene	6.690
2,3-Dimethylhexane	1.320	3-Methylcyclopentene	5.690
2-Methylheptane	0.960	3-Methyl-1-Hexene	3.490
3-Methylheptane	1.200	c-2i-3-Heptene	5.530
3-Methylhexane	0.920	2-Methyl-Hexene	6.630
4-Trimethylcyclic C5/C6	1.940	c-2-Heptene	5.530
2,2,5-Trimethylhexane	0.970	1-Methylcyclohexane	5.520
Octane	0.610	1,4-Octene	5.290
1-3-Dimethylcyclohexane	1.850		
2,4-Dimethylheptane	1.940		
c-1,2-Dimethylcyclohexane	1.940		
3,5-Dimethylheptane	1.140		
2-Methyloctane	1.140		
3-Methyloctane	1.140		
n-Nonane	0.540		
2,2-Dimethyloctane	1.010		
2,4-Dimethyloctane	1.010		
Branched C10's	1.010		
Branched C10's	1.010		
3-Methylnonane	1.010		
n-Decane	0.470		
n-Undecane	0.420		
n-Dodecane	0.380		
Benzene	0.420		
Toluene	2.730		
Ethylbenzene	2.700		
m-Xylene	8.160		
p-Xylene	6.560		
Styrene	2.220		
o-Xylene	6.460		
Isopropylbenzene	2.240		
n-Propylbenzene	2.120		
1,3-Dimethylbenzene	7.200		
1,4-Dimethylbenzene	7.200		
1,3,5-Trimethylbenzene	10.120		
1,2-Dimethylbenzene	7.200		
1,2,4-Trimethylbenzene	8.830		
Isobutylbenzene	1.890		
1,2,3-Trimethylbenzene	8.850		
Indane	1.050		
1,3-Dialkylbenzene	6.450		
1,4-Dialkylbenzene	6.450		
1,2-Dialkylbenzene	6.450		
1-Methyl-2-Propylbenzene	6.450		
1,4-Dimethylstyrene	9.070		
1,2-Dimethyl-2-Ethylbenzene	9.070		
1,3-Dimethyl-2-Ethylbenzene	9.070		
1,2,4,5-Tetramethylbenzene	9.070		
1,2,3,5-Tetramethylbenzene	9.070		
Methylindane	1.060		
1,2,3,4-Tetramethylbenzene	9.070		
Methyl-1-Butyl Ether	0.820		
Ethyl-1-Butyl Ether	1.980		
Methanol	0.560		
Ethanol	1.340		
Formaldehyde	7.150		
Acetaldehyde	5.520		
Acrolein	6.770		
Propionaldehyde	6.530		
Acetone	0.560		

Carter Index for Ozone Forming Potential (CARB July, 1992)

Table from SAE Paper 932718 (Tauchida et al.)

Methodology explained in SAE Paper 900710 (Low and Carter)

## HC sources

- Non-combustion sources
  - Fueling loss
  - Diurnal emissions
  - Running loss
  - Hot soak
  - Blow by
    - A few L/min; depends on load and RPM
    - At light load, 1500 rpm, blow by ~ 4L / min

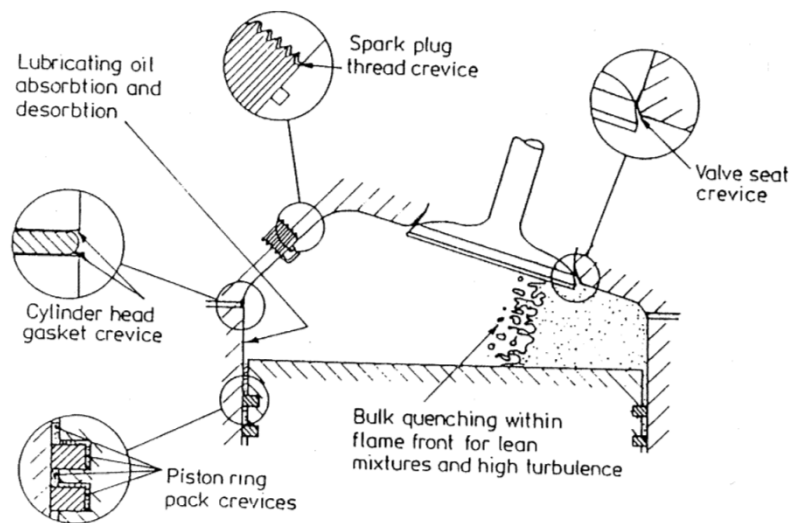
## HC sources (cont.)

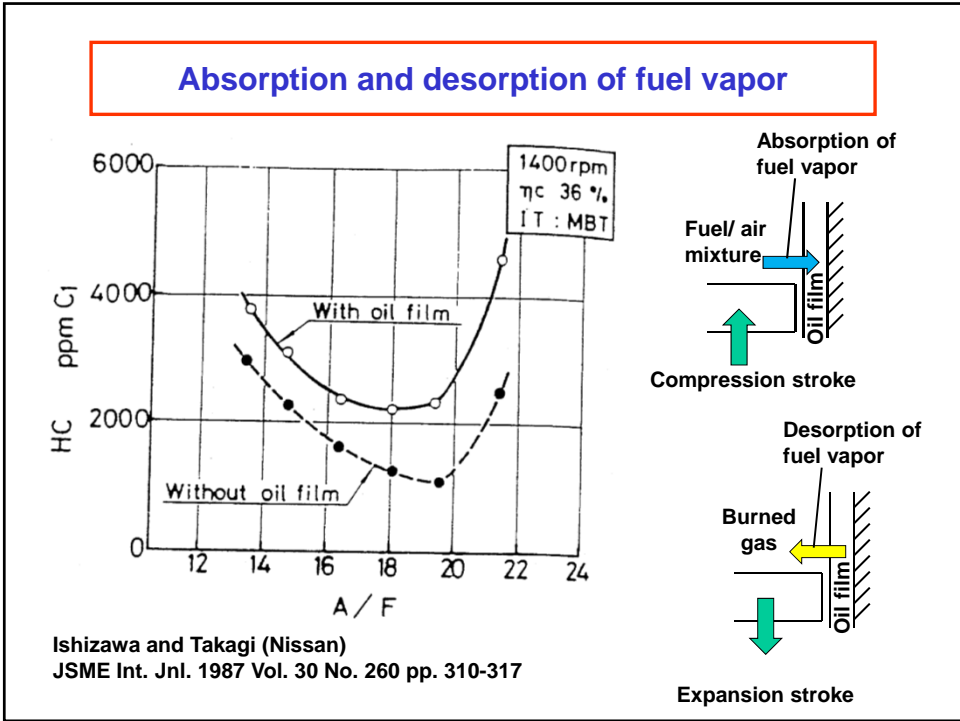
- Combustion sources
  - 300 to 3000 ppmC1 typical
    - Stoichiometric mixture is ~120,000 ppmC1
  - Main combustion: very little HC except for very lean/ dilute or very late combustion (misfires/ partial burns)
    - Various mechanisms for HC to escape from main combustion
  - Cold start emissions (wall film) especially important

## SOURCES OF UNBURNED HC IN SI ENGINE

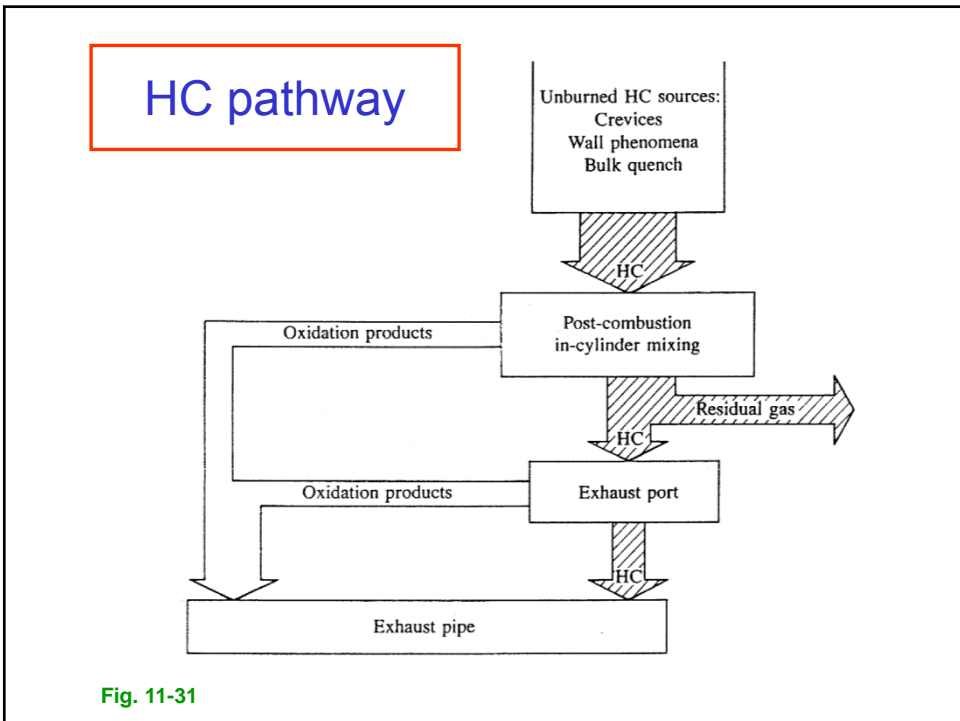
- a) Crevices
- b) Absorption and desorption in oil layers
- c) Absorption and desorption in deposit
- d) Quenching (bulk and wall layer)
- e) Liquid fuel effects
- f) Exhaust valve leakage

## Crevice HC mechanism

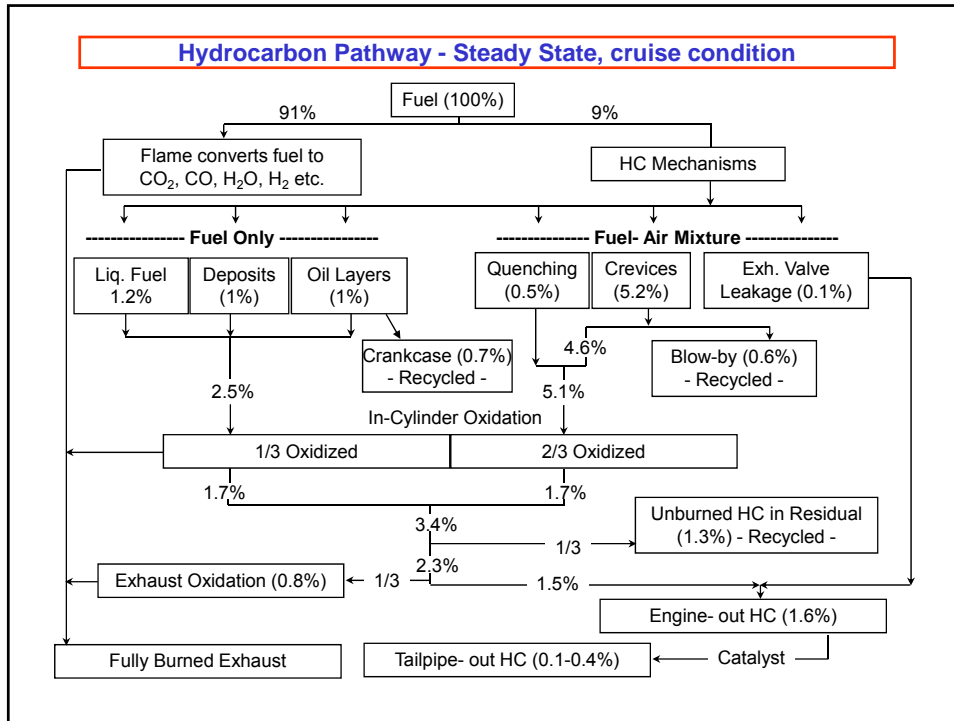




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**HC Sources: Magnitudes and Percent of Total Engine-out Emissions\***  
(SAE Paper 932708)

Source	% Fuel Escaping Normal Combustion	Fraction Emitted as EOHC	% Fuel as HC Emissions	% of Total EOHC Emissions
Crevices	5.2	0.15*	0.682*	42.6
Quench	0.5	0.15	0.074	4.6
Oil Layers	1.0	0.09**	0.090**	5.6
Deposits	1.0	0.30	0.300	18.7
Liquid Fuel	1.2	0.30	0.356	22.2
Valve Leakage	0.1	1.00	0.100	6.3
Total	9.0		1.60	100

\* Blowby (0.6%) subtracted  
\*\* Amount to crank case (0.7%) subtracted

\*steady state cruise condition (1500 rpm, 2.8 bar NIMEP)

## HC control

- Reduce crevice volume
- Keep liner hot
- Spark retard
  - Higher burned gas temperature in the later part of expansion stroke and higher exhaust temperature
- Comprehensive cold start strategy
  - Retard timing, fuel rich followed by exhaust air injection

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2.61 Internal Combustion Engines  
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