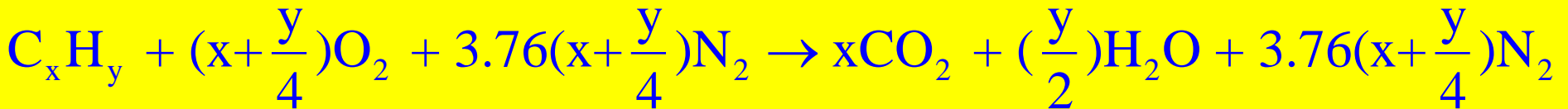


Combustion

- The best method to reduce the pollution in local issue is to do the complete combustion.

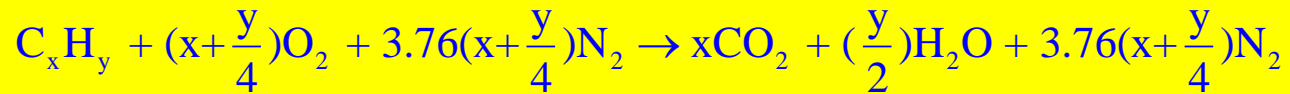
General Equation:



$(A/F)_{\text{actual}} > (A/F)_{\text{stoichiometric}} \rightarrow \text{Lean mixture}$

$(A/F)_{\text{actual}} < (A/F)_{\text{stoichiometric}} \rightarrow \text{Rich mixture}$

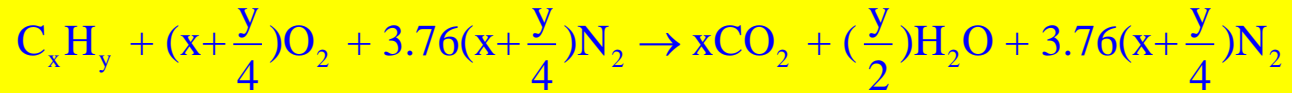
Example: A/F ratio for n-heptane



HC	Moles of O ₂	Moles of N ₂	Mass of O ₂	Mass of N ₂	A/F ratio (mass/mass)
C ₇ H ₁₆ Mol wt = 100	11	41.4	352	1158	1510/100 = 15.1

$$\text{Equivalence ratio} = \frac{(\text{Fuel-Air ratio})_{\text{actual}}}{(\text{Fuel-Air ratio})_{\text{stoichiometric}}}$$

Concentration of Unburned Hydrocarbon (C_xH_y)



Reactants	Products
$(x + \frac{y}{4})$ moles of O_2 $3.76(x + \frac{y}{4})$ moles of N_2 <hr/> $\Sigma = 4.76(x + \frac{y}{4})$ moles = F(say)	x moles of CO_2 $\frac{y}{2}$ moles of H_2O $3.76(x + \frac{y}{4})$ of N_2 <hr/> $\Sigma = (x + \frac{y}{2}) + 3.76(x + \frac{y}{4})$ moles = M(say)

Example:

If 'f' fraction of C_xH_y escaped unburned inspite of supplying stoichiometric amount of air. Find concentration of C_xH_y in the exhaust.

Soln:

F = Reactants and M = Products

$$\text{Unburned HC (ppm) in exhaust} = \frac{f \times 10^6}{(1-f)M + f + fF}$$

Other than fuel in the reactant

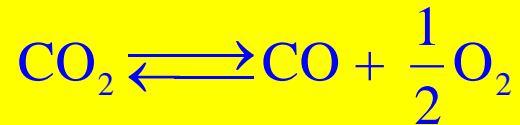
Fuel goes out

Air going out without taking part

Suppose $f=0.001$, then unburned concentration=19.2

CO Formation

- In this system of combustion, the compounds are: CO, CO₂, O₂
- Equilibrium Mole Fraction:



$$K = 3 \times 10^4 \exp(-67,000/RT)$$

$$= \frac{x_{\text{CO}} (x_{\text{O}_2})^{1/2}}{x_{\text{CO}_2}} \quad (1)$$

$$x_{\text{CO}_2} + x_{\text{CO}} + x_{\text{O}_2} = 1 \quad (2)$$

$$\frac{2x_{\text{CO}_2} + x_{\text{CO}} + 2x_{\text{O}_2}}{x_{\text{CO}} + x_{\text{CO}_2}} = \alpha = \frac{\text{moles O}_2}{\text{moles C}} \quad (3)$$

Using eqn 1 and 3, K can be obtained as function of x_{CO} and α . Choosing T and α , x_{CO} can be solved. Some of the results are reported as follows:

α	T, K		
	2000	3000	4000
2	0.0157	0.383	0.630
3.125	0.0015	0.213	0.448
5	0.00074	0.125	0.302

Temp up(\uparrow) \Rightarrow CO(\uparrow)

α (\uparrow) \Rightarrow CO(\downarrow)

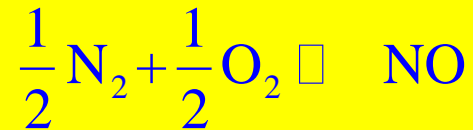
NO_x Formation

First Route: Thermal NO_x (formed during the combustion of all fuels in the regions of peak flame temperature)

Second route: Fuel NO_x (during the oxidation of nitrogen-containing compounds in the fuel)

Most of the NO_x are from thermal route. High temperature and high O₂ concentration favor NO formation and preventing one or both of the conditions is the basis of most thermal NO_x control technology.

Equilibrium:



$$K = \frac{x_{\text{NO}}}{(x_{\text{N}_2})^{1/2} (x_{\text{O}_2})^{1/2}} = 4.69 \exp\left(-\frac{21600}{RT}\right) \quad (1)$$

$$x_{\text{N}_2} + x_{\text{NO}} + x_{\text{O}_2} = 1 \quad (2)$$

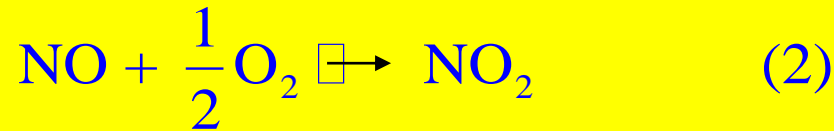
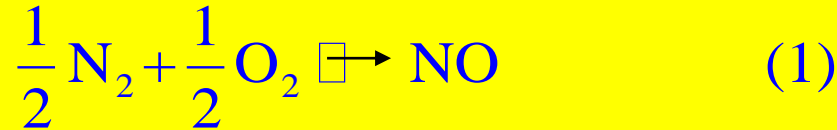
$$\begin{aligned} \beta &= \frac{\text{Moles of N}}{\text{Moles of O}} \\ &= \frac{x_{\text{NO}} + 2x_{\text{N}_2}}{x_{\text{NO}} + 2x_{\text{O}_2}} \end{aligned} \quad (3)$$

β	T, K		
	2000	3000	4000
4	0.00785	0.045	0.1
40	0.00295	0.0152	0.02

Temp up(\uparrow) \Rightarrow x_{NO} (\uparrow)

β (\uparrow) \Rightarrow x_{NO} (\downarrow)

NO₂ Equilibrium:



$$K_1 = \frac{x_{\text{NO}}}{(x_{\text{N}_2})^{1/2} (x_{\text{O}_2})^{1/2}} = 4.69 \exp\left(-\frac{21600}{RT}\right) \quad (3)$$

$$\text{So, } K_2 = \frac{x_{\text{NO}_2}}{(x_{\text{NO}}) (x_{\text{O}_2})^{1/2}} = 2.54 \times 10^{-4} \exp\left(-\frac{13720}{RT}\right) \quad (4)$$

$$x_{\text{NO}_2} + x_{\text{NO}} + x_{\text{O}_2} + x_{\text{N}_2} = 1 \quad (5)$$

$$\begin{aligned} \beta &= \frac{\text{Moles of N}}{\text{Moles of O}} \\ &= \frac{2x_{\text{N}_2} + x_{\text{NO}} + x_{\text{NO}_2}}{x_{\text{NO}} + 2x_{\text{NO}_2} + 2x_{\text{O}_2}} \end{aligned} \quad (6)$$

$$x_{\text{NO}} = K_1 (x_{\text{N}_2})^{1/2} (x_{\text{O}_2})^{1/2}$$

$$x_{\text{NO}_2} = K_1 K_2 (x_{\text{N}_2})^{1/2} (x_{\text{O}_2})$$

At 3.3% O₂ and 76% N₂
Assume N₂ and O₂ not change

β	T, K		
	298	1273	1873
4	3.6×10^{-10}	9.69×10^{-6}	2.64×10^{-5}
40	5.59×10^{-11}	1.49×10^{-6}	4.05×10^{-6}

Temp up (\uparrow) \Rightarrow x_{NO_2} (\uparrow)

O₂ (\uparrow) \Rightarrow x_{NO_2} (\uparrow)

Virtually all NO_x is NO

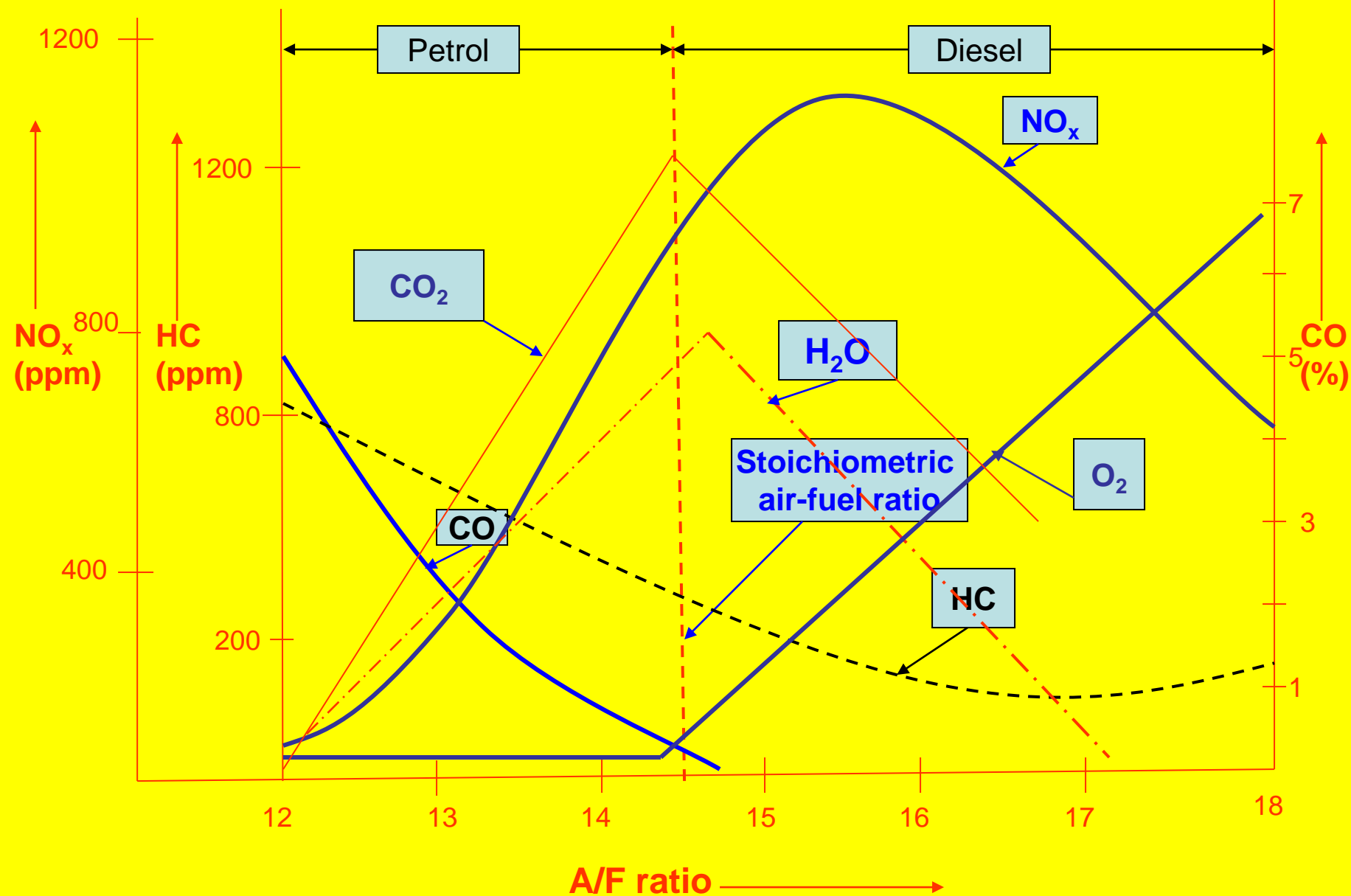


Fig: Exhaust hydrocarbon, carbon monoxide, nitric oxides etc as a function of air-fuel ratio.

value, Btu/lb ^g								Heating	% by weight of U.S. electric generation coal, 1997 ^a
Ultimate analysis, weight %, dry basis, typical values								Average wet basis, as delivered, U.S., 1991 ^a	
Material	C	H	O	N	S	Ash	Dry basis ^h		
Wood ^b	52.3	6.3	40.5	0.1	<0.1	0.8	9050		
Peat ^c	57.0	5.5	31.0	1.5	0.2	4.8	9300		
Lignite (also called brown coal) ^d	55.0	4.4	13	1.0	1.7	24.9	9727	6372	8.4
Subbituminous coal ^e	72.5	6.1	17.2	0.7	0.4	3.1	13006	8741	40.3
Bituminous coal ^f	75.8	5.0	7.4	1.5	1.6	8.7	13600	11964	51.2
Anthracite coal	82.1	2.3	2.0	0.8	0.6	12.2	13258		0.1

^h The dry basis heating values are computed from the equation

$$(\text{Higher heating value, Btu/lb}) = 14544C + 62028(H - O/8) + 4050S$$

Solid Fuel

Pollutant Emissions from the Internal Combustion Engine

The type and quantity of exhaust contaminants from an internal combustion engine depend on a number of factors, including the following:

1. Air-fuel ratio.
2. Ignition timing.
3. Compression ratio.
4. Combustion chamber geometry.
5. Engine speed.
6. Type of fuel.

Description of pollutants

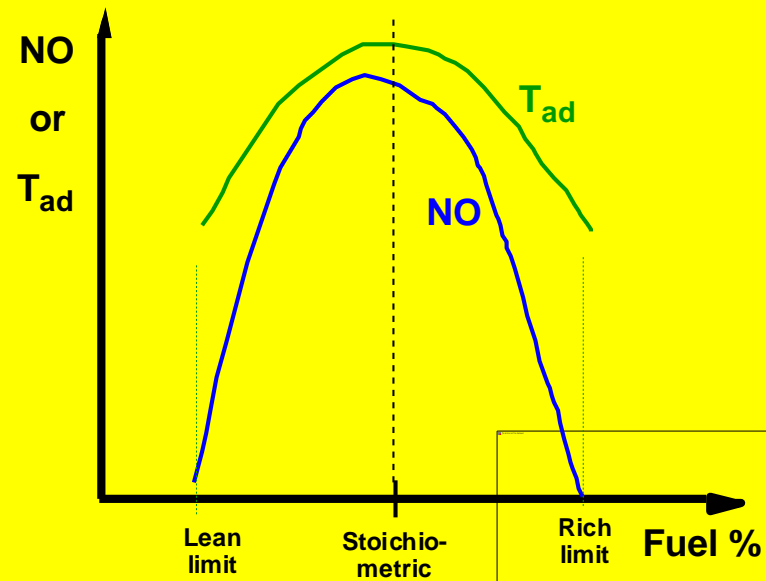
- Mantra - “emissions are a NON-EQUILIBRIUM PROCESS”
- If we follow two simple rules:
 - Use lean or stoichiometric mixtures
 - Allow enough time for chemical equilibrium to occur as the products cool down
- ... then NO, CO, UHC and C(s) (soot) are practically zero
- So the problem is that we are not patient enough (or unable to allow the products to cool down slowly enough)

Pollutants in the Combustion Processes

- Nitrogen oxides
- CO
- Hydrocarbons
- Soot

Nitrogen oxides

$$\phi = \left[\frac{(\text{fuel/air})_{\text{act}}}{(\text{fuel/air})_{\text{stoich}}} \right]$$



- **Typical experimental result**

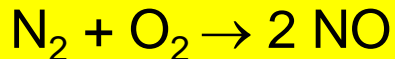
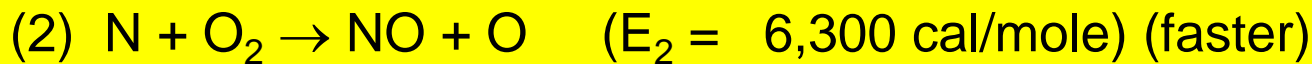
- Peak NO slightly lean of stoichiometric ($\phi \approx 0.9$) since N_2 is plentiful at all ϕ , but surplus O_2 is present only for lean mixtures
- Very sensitive to temperature (high activation energy) so peak still close to $\phi = 1$ where T is highest (thermal NO)
- Slower decrease on rich side than lean side due to prompt NO formation

- **Two flavors of NO**

- “Thermal” or “Zeldovich”
- “Prompt” or “Fenimore” (actually 2 sub-flavors):
 - Due to O atoms in flame front
 - Due to CH & C_2 molecules in flame front

Zeldovich mechanism

- Extremely high activation energy due to enormous strength of $\text{N}\equiv\text{N}$ bond (≈ 220 kcal/mole)



- Zeldovich NO occurs in the burned gases downstream of the flame front, not in the flame front itself.
- ...but this doesn't tell the whole story - experiments show that some NO forms *inside the flame* ("Prompt" NO)
- Plot $[\text{NO}]$ vs. distance from flame, extrapolate back to flame front location, $[\text{NO}]$ there is defined as prompt NO
- Experiments show that prompt NO is more prevalent in hydrocarbon flames (not CO , H_2), and for fuel-rich flames (even though less O in rich mixtures, thus Zeldovich less important)

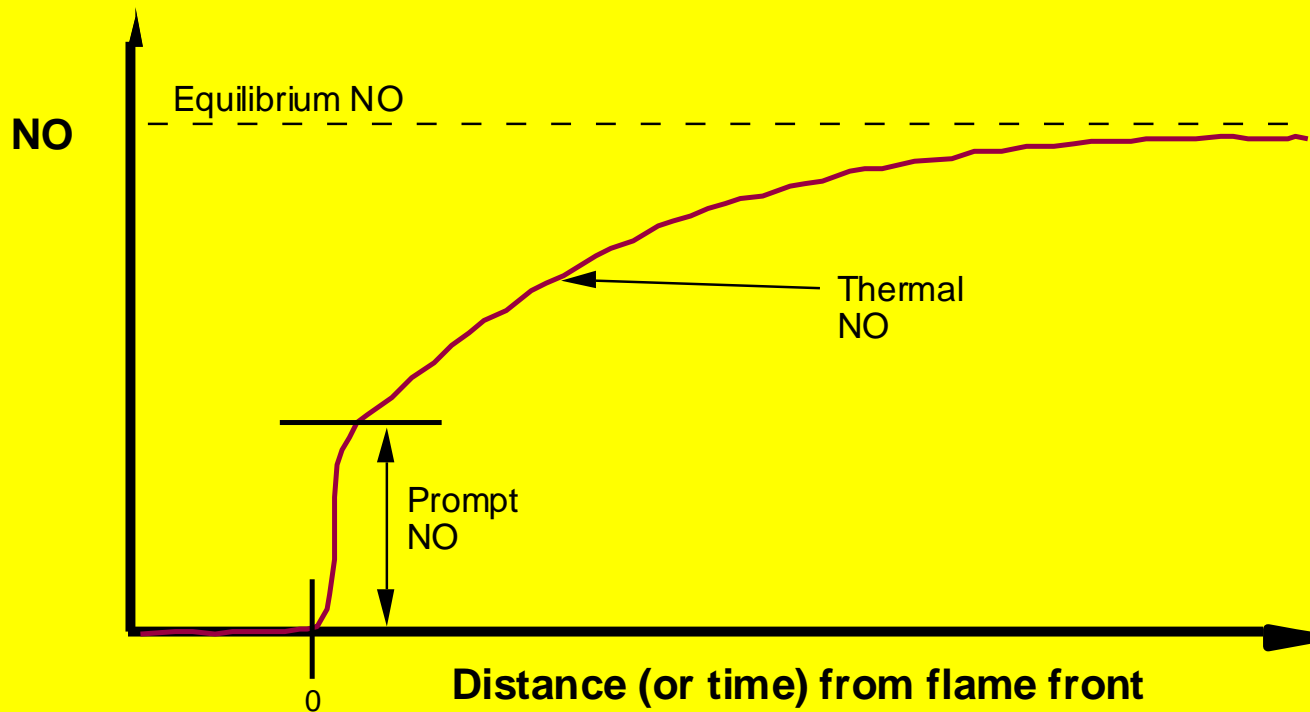


Figure showing the formation of thermal and prompt NO_x

Prompt mechanism

Fenimore (1971) proposed either

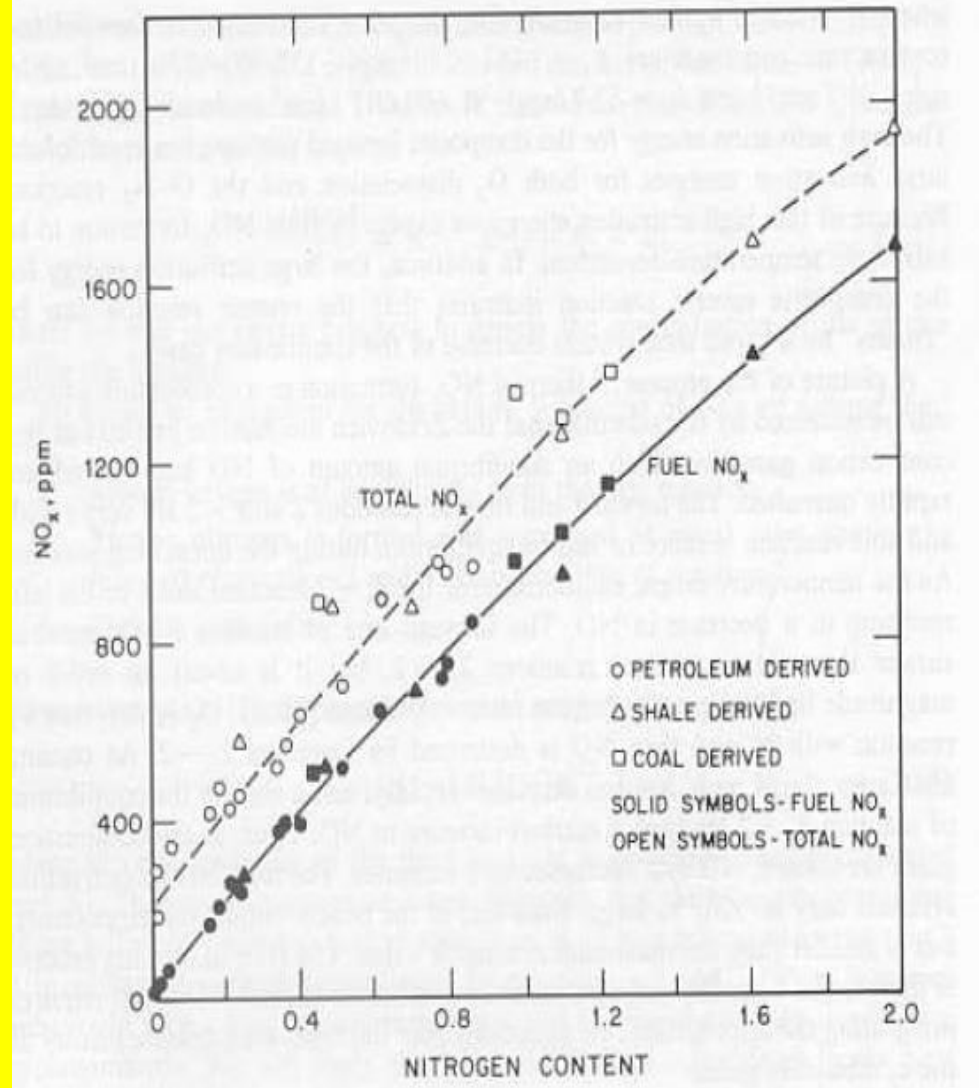
- (a) $\text{CH} + \text{N}_2 \rightarrow \text{HCN} + \text{N}$ followed by (e.g.) $\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}$
($E = 20,130$ cal/mole; much faster than $\text{N}_2 + \text{O}$ due to lower E)

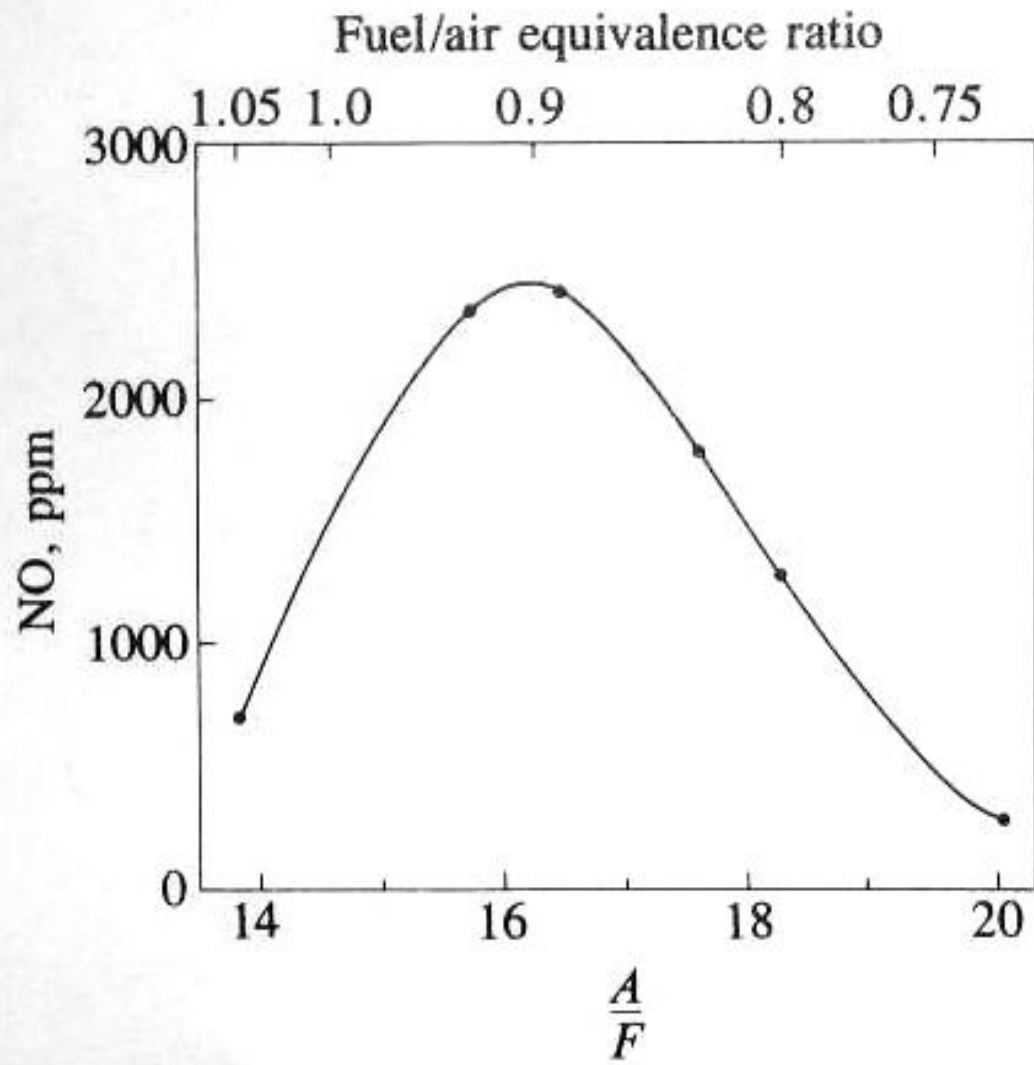
Or

- (b) $\text{C}_2 + \text{N}_2 \rightarrow 2\text{CN}$ followed by $\text{CN} + \text{O}_2 \rightarrow \text{CO} + \text{NO}$

Fuel NO_x Formation

- Fig 1 → the correlation between NO_x emissions and fuel nitrogen content for liquid fuels burned under fuel lean conditions.
- The lower curve shows the fuel nitrogen conversion as determined by substituting an argon/oxygen mixture for the combustion air.
- The difference between the two curves in the Fig. represents the thermal NO_x.





Unburned hydrocarbons (UHC)

- In the engine, emissions of UHCs come from
 - Raw unburned fuel
 - Fuel that didn't burn all the way to CO₂ and H₂O
 - Lubricating oil (especially in 2-stroke engines using fuel + oil mixtures)
- Other than tailpipe, UHCs may come from
 - Crankcase fumes (older engines without crankcase gas recycling)
 - Fuel tank (older cars without evaporative emission controls)
 - Filling station (in regions without 2nd hose to recover gas tank vapors)
 - Tires (!!!)

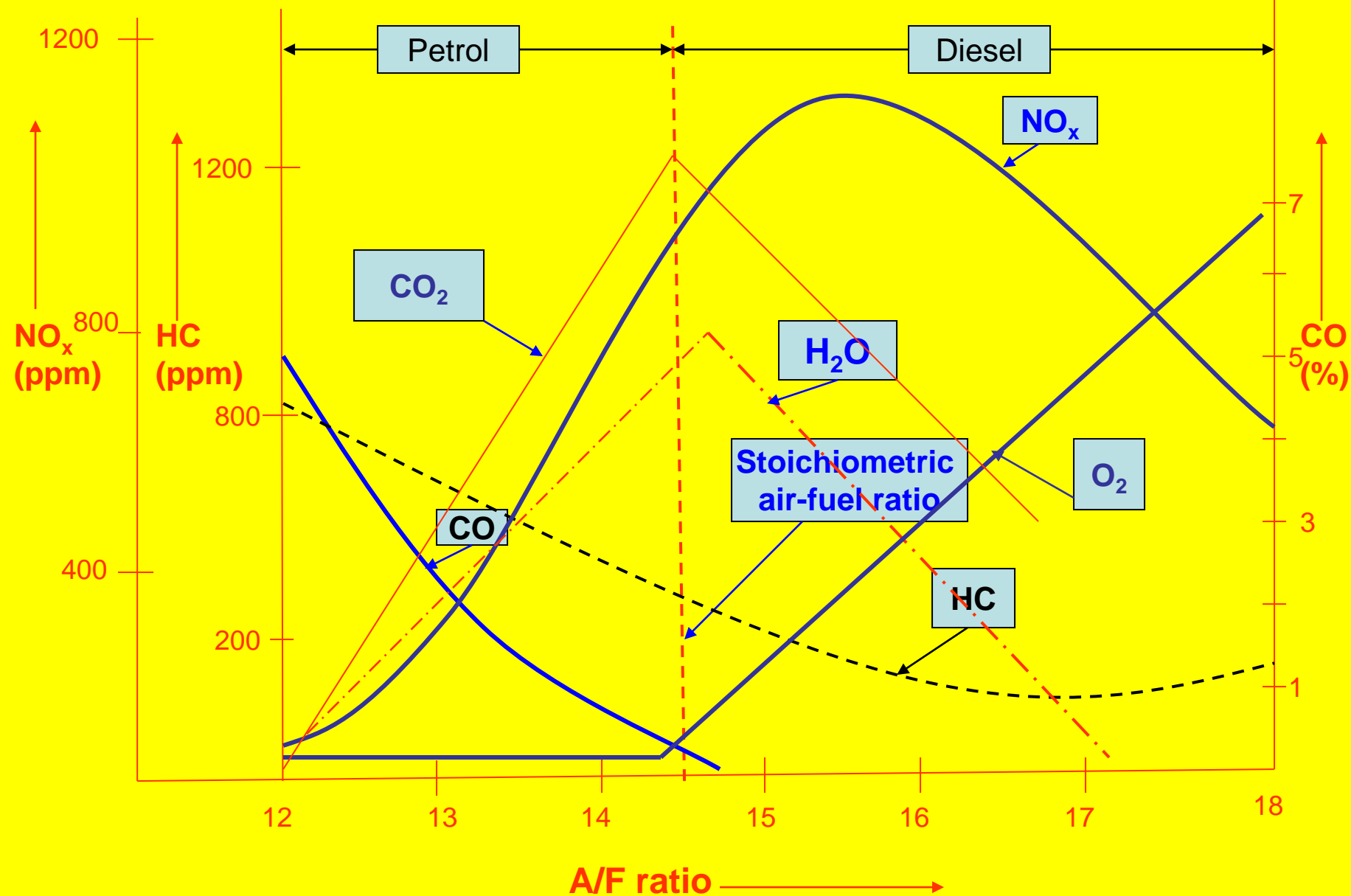


Fig: Exhaust hydrocarbon, carbon monoxide, nitric oxides etc as a function of air-fuel ratio.

Summary of the figure 1:

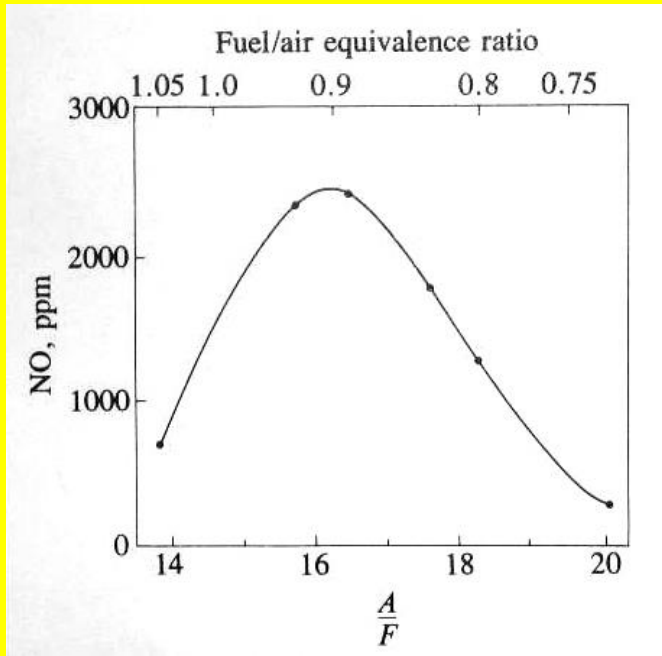
- The petrol driven vehicles have A/F ratio ranging from 12-15.
- The diesel engine has A/F ratio greater than 15.
- After stoichiometric, O₂ content increases.
- When A/F ratio low, HC emission high
- In petrol engine, the major pollutant come out is HC.
- NO_x decreases as larger air is consumed.

Pollutants from Engines

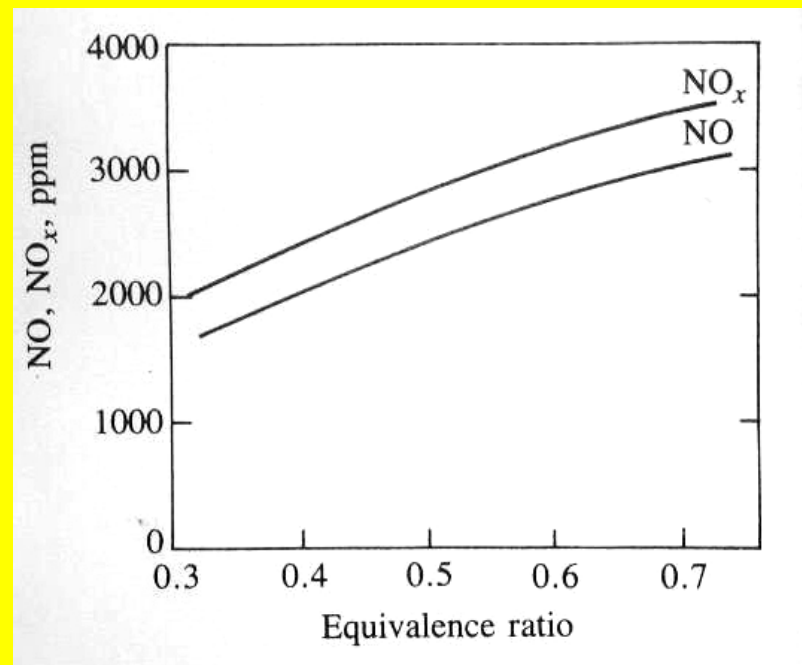
Petrol/gasoline engine	Diesel engine
HC	NO _x
CO	Soot
Soot	HC

How to reduce NO during combustion?

- Premixed - every parcel of gas experiences same peak temperature - lean mixtures will have **much** lower NO
- Non-premixed flames
 - Always have hot stoichiometric surfaces with $T \approx T_{ad,stoich}$ - **even when overall ϕ is very low** \Rightarrow thermal NO; $NO \sim$ fuel used
 - Always have fuel-rich, “warm” regions - Fenimore NO
 - \therefore Hard to control NO in Diesel (non-premixed charge) engines



Premixed-charge
Heywood (1988)



Non-premixed-charge
Heywood (1988)