



SWANSEA METROPOLITAN UNIVERSITY

PRIFYSGOL FETROPOLITAN ABERTAWE

Emissions Control & Diagnosis

Pollution

Pedro Monteiro Ferreira

pedro.monteiro-ferreira@smu.ac.uk

- What is pollution?
 - In pairs agree a definition for pollution stating the most common known types of pollution.

For vehicles the most critical forms of pollution are

1. Air Pollution
2. Noise
3. Soil and water contamination

- First concerns raised about automobile exhaust emissions in 1915
- Smog problem in California attributed to vehicles in 1945
- Air Pollution definition by the Council of Europe (1967)
 - *“Air pollution occurs when the presence of a foreign substance or a large variation in the proportion of its components is liable to cause a harmful effect, according to the scientific knowledge of the time, or create a discomfort”* (Degobert, 1995)
 - *Knowledge of the time*: new risks may be determined
 - *Create a discomfort*: bad odours, reduced visibility, etc.

Emissions Control and Diagnostics

Atmosphere

Main Constituents	%	Pre I A (ppm)	Current (ppm)
Nitrogen N ₂	78.084		
Oxygen O ₂	20.984		
Argon Ar	0.934		
Carbon Dioxide CO ₂	0.033	270	340
Neon Ne	18 10 ⁻⁴		
Helium He	5.3 10 ⁻⁴		
Methane CH ₄	1.7 10 ⁻⁴	1.0	1.7
Krypton Kr	1.1 10 ⁻⁴		
Hydrogen H	0.5 10 ⁻⁴		
Nitrous Oxide NO	0.3 10 ⁻⁴	0.28	0.30
Xenon Xe	0.09 10 ⁻⁴		
Ozone O ₃	0.02 10 ⁻⁴		



- Nitrogen
 - Non toxic, in very high concentrations disperses essential oxygen
 - Essential as retained by soil bacteria to life sustaining process
- Oxygen
 - Necessary to aerobic life
 - Toxic at very high concentrations
 - Danger of combustion of certain materials at high concentrations
- Carbon Dioxide
 - Non toxic at normal concentrations but an asphyxia at 100x
 - Essential to life as major component of plant's photosynthesis of chlorophyll



- Water Vapour
 - Necessary constituent for life
 - Limited in concentration as saturation leads to formation of clouds and subsequent rain!
- Ozone
 - Essential in Stratosphere as a UV radiation filter
 - Occurs by the dissociation of Oxygen molecule into free atoms though solar radiation and their subsequent link to an Oxygen molecule
 - At ground level it is formed as a sub product of other emission and is a pollutant.

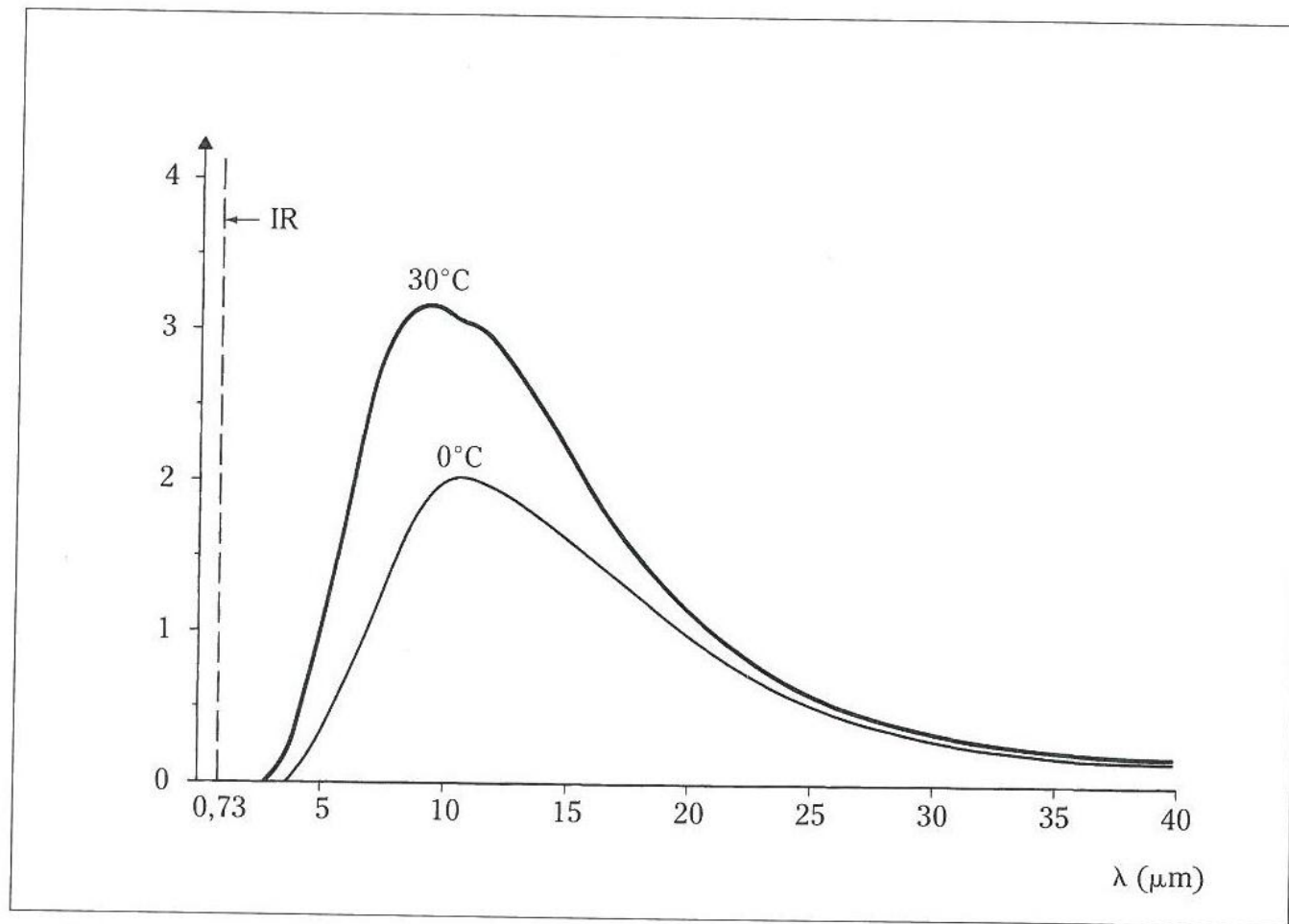
- Atmospheric gases participate in filtering wavelengths of sunlight
 - Ozone absorbs UV radiation at high altitude
 - Water vapour absorbs near infra-red radiation 0.4 to 0.8 μm (both ways)
 - CO_2 absorbs wavelengths around 15 μm – same as maximum energy is radiated by the Earth that pass through the water vapour
 - Other trace gases absorb infrared at the wavelengths that both Carbon Dioxide and water are transparent

Emissions Control and Diagnostics

Earth's Radiation



SWANSEA METROPOLITAN UNIVERSITY
PRIFYSGOL FETROPOLITAN ABERTAWE



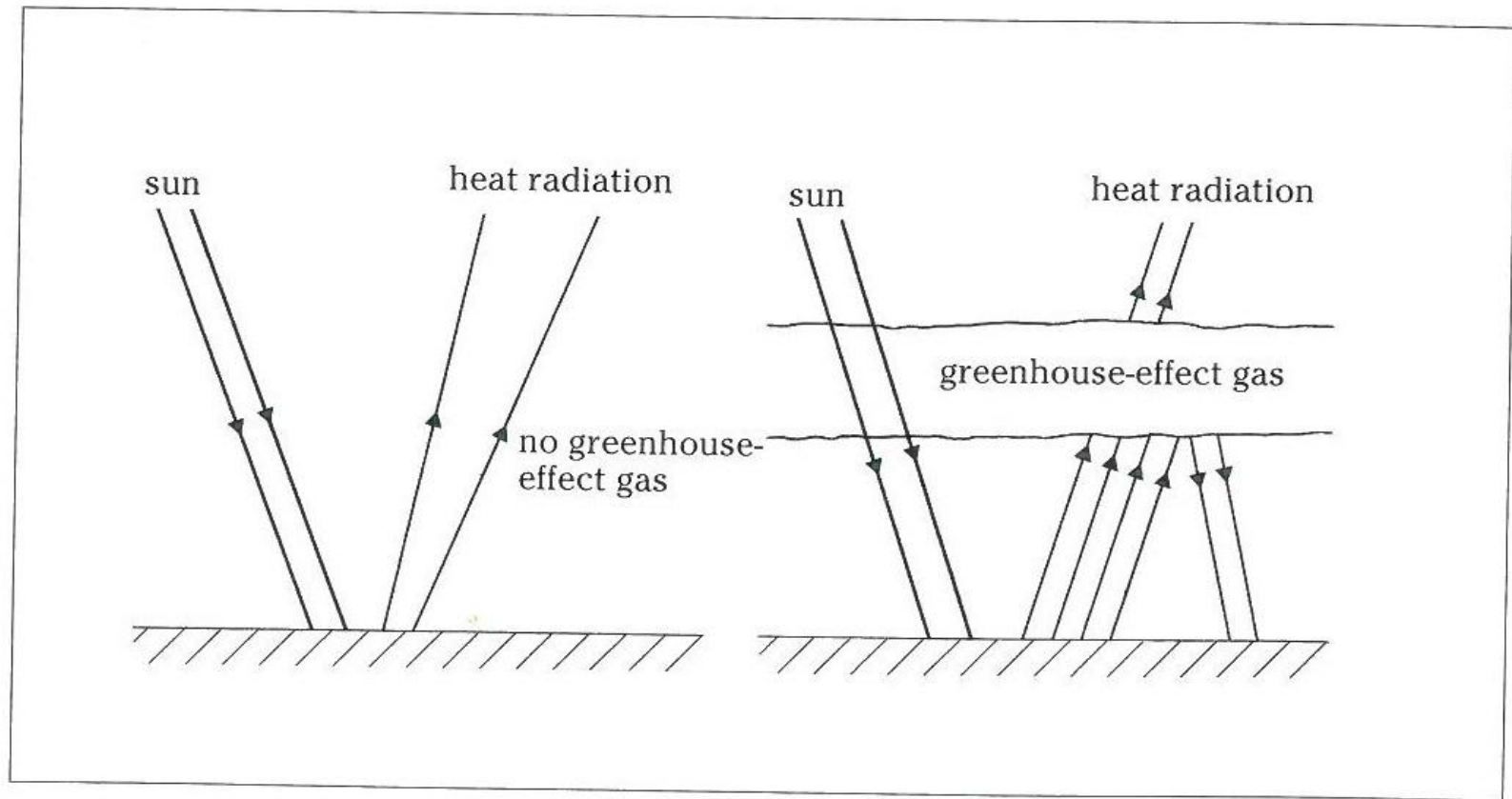
Spectrum of re-emission by the Earth's surface

Emissions Control and Diagnostics

Greenhouse effect



SWANSEA METROPOLITAN UNIVERSITY
PRIFYSGOL FETROPOLITAN ABERTAWE



- What are the main air pollutants resulting from vehicle and industrial emissions?
- Definition
 - *Normally applied to any substance added to the environment is sufficient concentration to have a measureable effect on humans, animals, vegetation or building materials (Chambers,1968)*
- Primary
 - Emitted directly by identifiable polluting sources
- Secondary
 - As a result of interactions from primary pollutants or between these and the normal constituents of the atmosphere with or without sunlight radiation assistance

Emissions Control and Diagnostics

Pollutants

New Constituents	Pre Ind Age (ppm)	Current (ppm)	% / year
Carbon Dioxide CO ₂	270	340	0.4
Carbon Monoxide CO	0.05 – 0.2	0.13	3
Nitrous Oxide NO	0.28	0.30	0.25
Sulphur Dioxide SO ₂	0.001	0.002	2
Ammonia NH ₃	0.004	0.006	2
Ethylene C ₂ H ₄	0.0	0.0002	2
Hydrogen Sulphide H ₂ S	0.00005		
Chlorofluorocarbons CFC's	0.0	0.00015	8



- Carbon Dioxide CO₂
 - End product of the combustion of every carbon fuel (wood, coal, biomass, oil and petroleum derivatives, etc.); and of anaerobic breathing (respiration)
 - Recovered by plants during photosynthesis and converted back to carbon.
 - Known effects of increased concentrations and the green house effect
- Carbon Monoxide CO
 - Colourless, odourless and highly toxic – known as the silent killer
 - As a result of excessively rich combustions – E.g Steel Works
 - As a high 40 times higher affinity to haemoglobin than oxygen and can be fatal very quickly.
 - Easily dissipates via reaction with other atmosphere elements

Emissions Control and Diagnostics

Nitrogen compounds

- Generically known as NO_x
- Nitric Oxide NO and Nitrogen Peroxide NO_2
 - NO naturally emitted by soil bacteria
 - 32% of total annual emissions are of human origin (up to 80% of which from automotive traffic emissions)
 - Significant in 4 stroke petrol engines
 - Main issue is the by-products of NO_x oxidation and its combination with other atmospheric constituents
- Nitric Acid
 - Not significant in direct exhaust emissions – diesel – but large as a result of the oxidation of NO_x

- Nitrous Oxide N_2O
 - Dealt with separately from No_x since it is more stable (125 yrs)
 - Also emitted by soil
 - Difficult to analyse and measure
 - Results from the combustion of the atmospheric air Nitrogen N_2
 - Although industrial emissions are high automotive emissions represent only 3.3%
 - Is relatively inactive as a pollutant in the troposphere but is an active factor in the depletion of the Ozone layer in the stratosphere
- Ammonia NH_3
 - Mostly resultant from livestock urea leads to Nitrogen Oxides
 - Automobile emission only due to malfunction in catalytic converters

- Volatile organic compounds
 - Includes a variety of different products
 - VOC's are defined as any compound that once released into the atmosphere stay there long enough to take part in photochemical reactions.
 - Mainly composed of compounds that evaporate rapidly at ambient temperature.
 - From a range of sources
 - Oil industry – refining and distribution (gasoline evaporation)
 - Mobile sources – automobile, aviation, railroad (2/3 emissions 1/3 evaporation)
 - Industries employing solvents – rubber, plastics paints, adhesives, alcoholic fermentation

- Typical exhaust composition of gasoline and diesel engines and vapours from gasoline tanks (VOC)
- Come in a variety of compositions from alkanes, alkenes and aromatics
- Of these Benzene is the most critical as it is highly toxic and carcinogenic
 - In gasoline engines benzene emissions 44% has survived combustion and 56% have been created during the combustion
 - Catalytic converters are crucial in the reduction of Benzene emissions.
- Polynuclear aromatic hydrocarbons are particularly nasty as they are formed by two or more Benzene rings
 - Also found in cigarette smoke and BBQ!

- Compounds containing Carboxyl – CO – in their molecule structure
- Ketones not as a result of combustion
- Aldehydes on the other hand result from incomplete combustion
 - The most common found in air is formaldehyde HCOH
 - Can also take place by the combination of hydroxyl radical OH⁻ with methane
 - Aldehydes are irritant and with higher molecular weight the odour effects is significant
 - Formaldehyde in the atmosphere due to vehicle emissions can be as much as 34% but the use of 3 way catalytic converters can again reduce this by over 10x.

- Sulphur Dioxide SO_2 is the major factor in acid rain
- Is a by product of the combustion of fossil fuels that contain Sulphur
- In automotive applications mostly present in diesel emission
- Industries – specially the burning of coal with 5% Sulphur content – are a major contributor
- In recent years low sulphur diesel has been introduced to try and tackle the problem
 - Draw back is low sulphur diesel has poorer lubrication properties and injection systems sometimes suffer as a result
- Major problem is the creation of Sulphur Trioxide and sulphuric acid in atmospheric interactions – O_2 and water.

Halogenated & Metallic Compounds

- Halogenated
 - Essentially Hydrochloric, hydrobromic and hydrofluoric acids
 - As a result of anti-knock additives in fuel
 - The hydrolysis of the volatile salts in the atmosphere produces the acids
 - These tend to be absorbed by atmospheric dust
- Metal
 - Biggest one of all used to be Lead
 - Highly toxic and now banned as an anti-knock additive
 - Precious metals such as platinum and palladium can be emitted as a result of the deterioration of catalytic converters
 - Cadmium and Zinc can also be seen mainly in lubricant additives where Cadmium – toxic – is an impurity

- Term applies to aerosols - gaseous suspension of fine solid or liquid particles – and includes dust, fines, soot, mist, fog and smog
- Of interest are “particles in suspension” - $10\mu\text{m}$ and low sedimentation rate.
 - Health hazard because they penetrate deep in pulmonary system
 - Soil the environment – buildings and monuments
 - Visibility and climate – diffusion of sunlight (cooling) or absorbing radiation (warming)
- Mineral – from road surfaces and lining friction materials
- Organic – as a result of very rich mixtures and mainly on diesel engines – carbon skeleton impregnated with mixture of unburned compounds

- Considered as a form of pollution
- Detected in small concentrations considered hazardous
- Are mostly an annoyance but can have a negative impact on behaviour – aggressiveness, loss of attention, etc.)
- Diesel emissions notably unpleasant where smoke can be visible and smelt.
 - Irritant to eyes, nose and throat: irritant compounds
- Some are harder to describe as they result from specific combinations of emissions compounds that can be felt
 - Some highly appreciated by petrol heads!

Emissions Control and Diagnostics

Influencing parameters

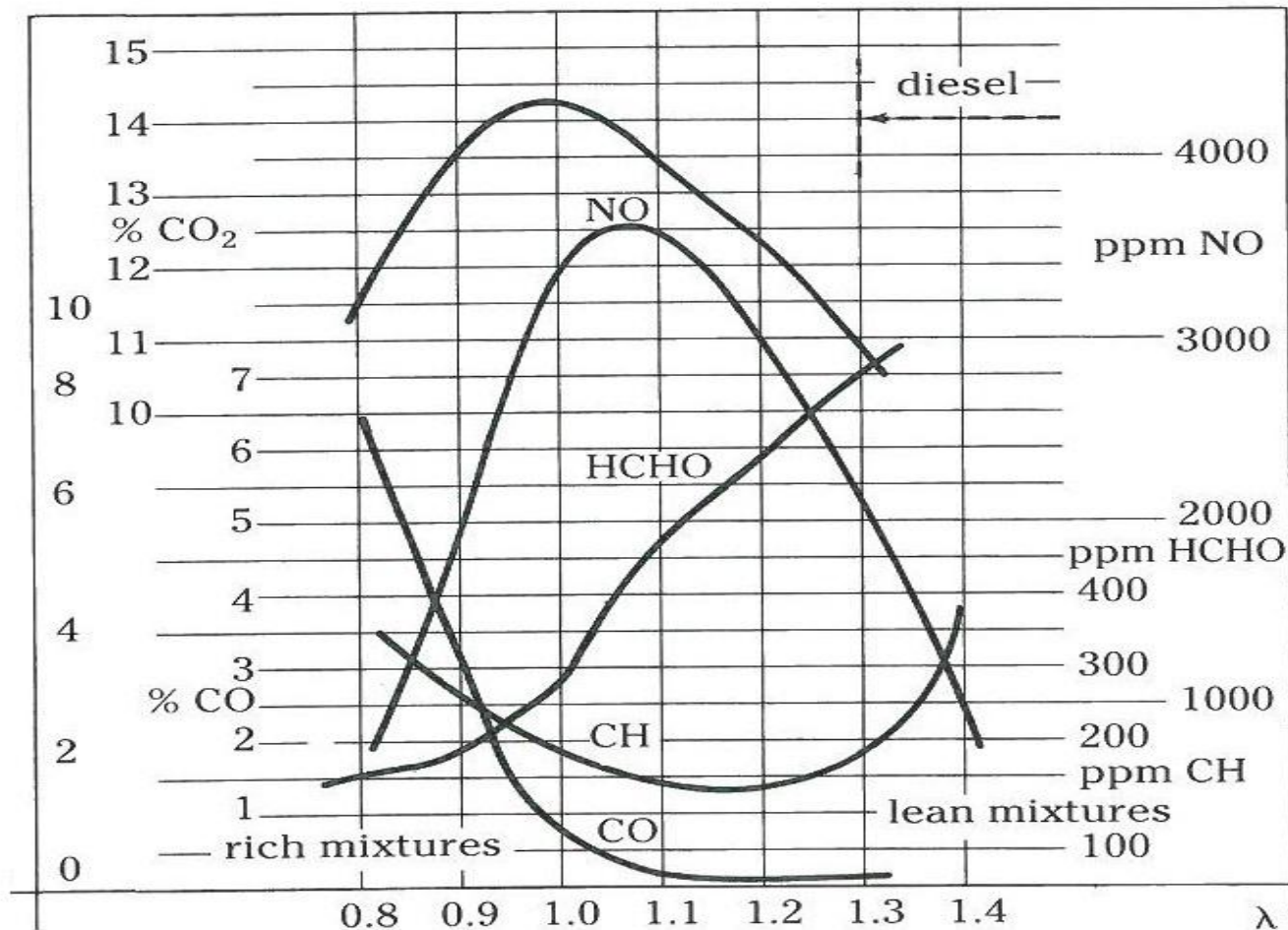
- Automotive emissions are dependant on a series of factors beyond the type of engine or power
- An expression that incorporates both vehicle parameters and travel parameters has been suggested by Plaßmann:

- $$Be = \frac{b_e}{\mu_u} (m(\eta f + g \sin \alpha + b) + \frac{1}{2} C_w A \rho V^2)$$

- $\frac{b_e}{\mu_u}$ = engine efficiency
- m = vehicle mass
- η = condition of transmission and tyres
- $\frac{1}{2} C_w A \rho V^2$ = aerodynamic drag
- f = state of driving surface
- $g \sin \alpha$ = path profile
- b = circulation flow – impact on acceleration
- V = traffic velocity



- All the pollutants mentioned so far are emitted by both petrol and diesel engines with the exception of particles
- Only the relative quantities vary with the type of engine, its design, internal geometry and running conditions
- Due to the very short combustion period, the heterogeneities of temperature and mixture composition, pollutant concentrations in the exhaust differ substantially from the values calculated assuming thermodynamic equilibrium.
- The most important variable is?

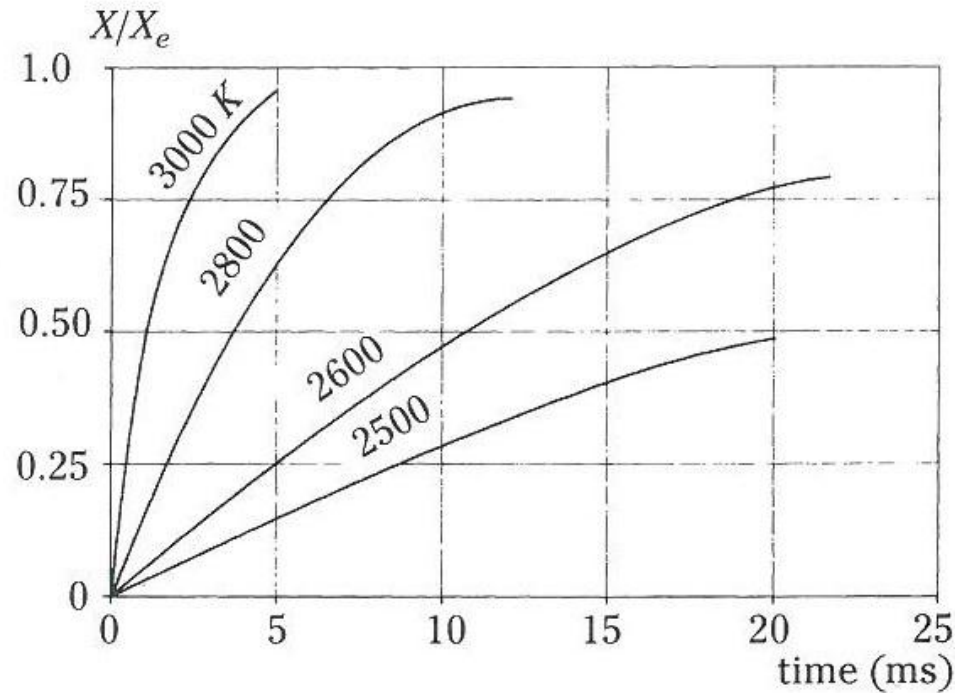


Pollutants as a function of air/fuel ratio

Formation of NO_x



- Takes place due to the oxidation of atmospheric N₂
- The main reactions for the formation of NO are
 - $\text{O} + \text{N}_2 \leftrightarrow \text{NO} + \text{N}$
 - $\text{N} + \text{O}_2 \leftrightarrow \text{NO} + \text{O}$
 - $\text{N} + \text{OH} \leftrightarrow \text{NO} + \text{H}$
- Takes place mainly in rich mixtures and is formed both in the flame front and the gas leaving the flame
- In engines – high pressure combustion – the flame reaction is very small but high temperature of burnt gases leads to most of it being generated within those
- Temperature is a key factor as is oxygen concentration



fuel/air ratio 0.9
pressure 100 atm
 X instantaneous NO concentration
 X_e NO concentration at equilibrium

Effect of temperature on advancement of
the reaction $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$ [221]

Formation of NO₂



- Taking into account the temperatures in the flame NO should prevail, However, in diesel engines 30% of NO_x is actually NO₂.
- One explanation is the reaction that can take place
 - $\text{NO} + \text{HO}_2 \leftrightarrow$

Formation of NO₂



- Taking into account the temperatures in the flame NO should prevail, However, in diesel engines 30% of NO_x is actually NO₂.
- One explanation is the reaction that can take place
 - $\text{NO} + \text{HO}_2 \leftrightarrow \text{NO}_2 + \text{OH}$

Formation of NO₂



- Taking into account the temperatures in the flame NO should prevail, However, in diesel engines 30% of NO_x is actually NO₂.
- One explanation is the reaction that can take place
 - $\text{NO} + \text{HO}_2 \leftrightarrow \text{NO}_2 + \text{OH}$
- NO₂ can then be reconverted to NO

Formation of NO₂



- Taking into account the temperatures in the flame NO should prevail, However, in diesel engines 30% of NO_x is actually NO₂.
- One explanation is the reaction that can take place
 - $\text{NO} + \text{HO}_2 \leftrightarrow \text{NO}_2 + \text{OH}$
- NO₂ can then be reconverted to NO
 - NO₂ +

Formation of NO₂



- Taking into account the temperatures in the flame NO should prevail, However, in diesel engines 30% of NO_x is actually NO₂.
- One explanation is the reaction that can take place
 - $\text{NO} + \text{HO}_2 \leftrightarrow \text{NO}_2 + \text{OH}$
- NO₂ can then be reconverted to NO
 - $\text{NO}_2 + \text{O} \leftrightarrow$

Formation of NO₂



- Taking into account the temperatures in the flame NO should prevail, However, in diesel engines 30% of NO_x is actually NO₂.
- One explanation is the reaction that can take place
 - $\text{NO} + \text{HO}_2 \leftrightarrow \text{NO}_2 + \text{OH}$
- NO₂ can then be reconverted to NO
 - $\text{NO}_2 + \text{O} \leftrightarrow \text{NO} +$

Formation of NO₂



- Taking into account the temperatures in the flame NO should prevail, However, in diesel engines 30% of NO_x is actually NO₂.
- One explanation is the reaction that can take place
 - $\text{NO} + \text{HO}_2 \leftrightarrow \text{NO}_2 + \text{OH}$
- NO₂ can then be reconverted to NO
 - $\text{NO}_2 + \text{O} \leftrightarrow \text{NO} + \text{O}_2$

Formation of NO₂



- Taking into account the temperatures in the flame NO should prevail, However, in diesel engines 30% of NO_x is actually NO₂.
- One explanation is the reaction that can take place
 - $\text{NO} + \text{HO}_2 \leftrightarrow \text{NO}_2 + \text{OH}$
- NO₂ can then be reconverted to NO
 - $\text{NO}_2 + \text{O} \leftrightarrow \text{NO} + \text{O}_2$
- Nitrous Oxide N₂O is of low concentration since it is easily destroyed due to the presence of Hydrogen in the mixture
 - $\text{N}_2\text{O} + \text{H} \leftrightarrow \text{NH} + \text{NO}$
 - $\text{N}_2\text{O} + \text{H} \leftrightarrow$

Formation of NO₂



- Taking into account the temperatures in the flame NO should prevail, However, in diesel engines 30% of NO_x is actually NO₂.
- One explanation is the reaction that can take place
 - $\text{NO} + \text{HO}_2 \leftrightarrow \text{NO}_2 + \text{OH}$
- NO₂ can then be reconverted to NO
 - $\text{NO}_2 + \text{O} \leftrightarrow \text{NO} + \text{O}_2$
- Nitrous Oxide N₂O is of low concentration since it is easily destroyed due to the presence of Hydrogen in the mixture
 - $\text{N}_2\text{O} + \text{H} \leftrightarrow \text{NH} + \text{NO}$
 - $\text{N}_2\text{O} + \text{H} \leftrightarrow \text{N}_2 + \text{H}_2\text{O}$

Formation of NO₂



- Taking into account the temperatures in the flame NO should prevail, However, in diesel engines 30% of NO_x is actually NO₂.
- One explanation is the reaction that can take place
 - $\text{NO} + \text{HO}_2 \leftrightarrow \text{NO}_2 + \text{OH}$
- NO₂ can then be reconverted to NO
 - $\text{NO}_2 + \text{O} \leftrightarrow \text{NO} + \text{O}_2$
- Nitrous Oxide N₂O is of low concentration since it is easily destroyed due to the presence of Hydrogen in the mixture
 - $\text{N}_2\text{O} + \text{H} \leftrightarrow \text{NH} + \text{NO}$
 - $\text{N}_2\text{O} + \text{H} \leftrightarrow \text{N}_2 + \text{OH}$

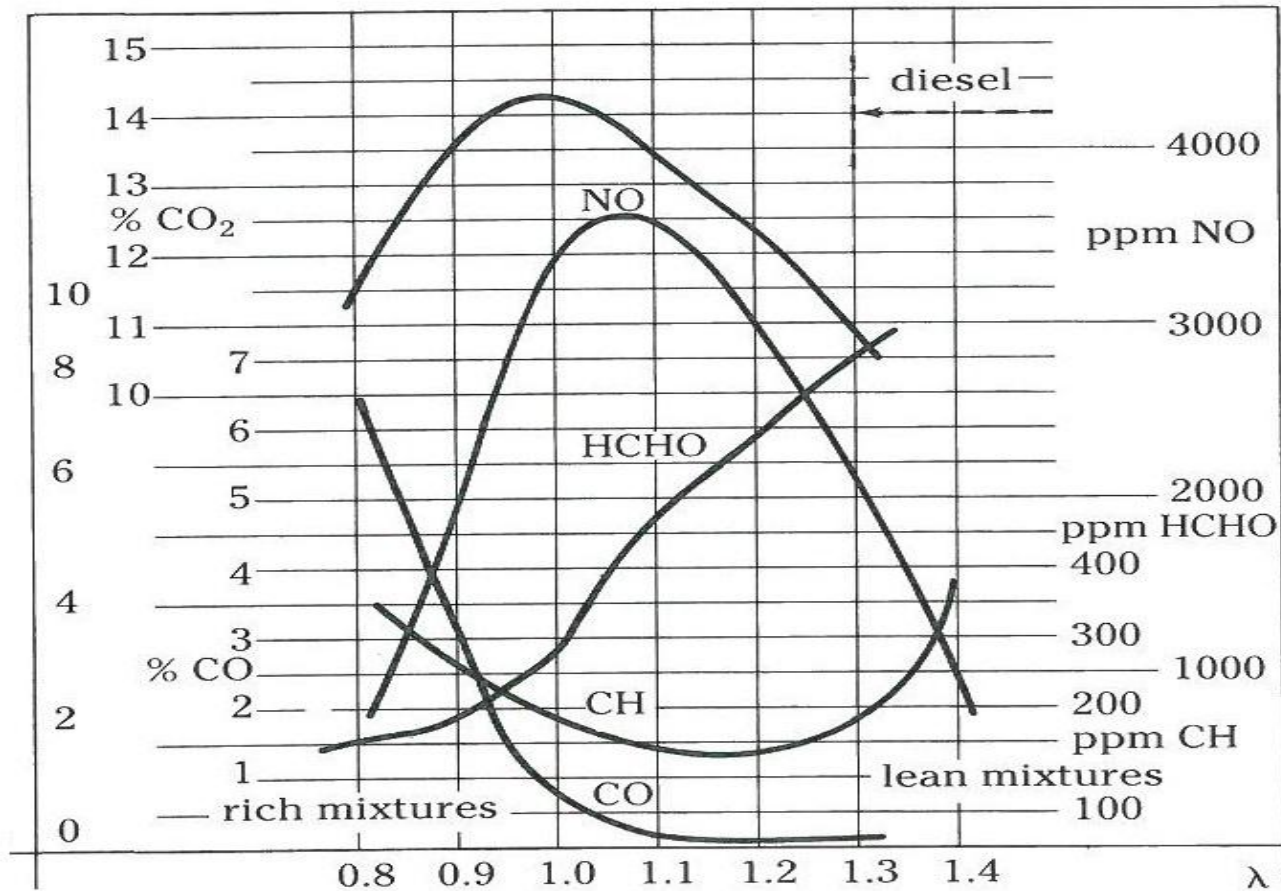
- Emissions of NO in Spark Ignition engines result from:
 - Fuel/air ratio
 - Fraction of unburned gases in the unburnt mixture
 - Ignition timing
- Air/fuel ratio
 - At 1.1 (slightly rich) burnt gas temperatures peak but oxygen concentration low
 - At 0.9 (slightly lean) NO_x tends to peak
 - Leaner than that and the temperature drops and so does NO formation
 - During expansion, NO formation will mostly carry on in rich mixtures whereas in lean it would have all been formed

Emissions Control and Diagnostics

SI Engines



SWANSEA METROPOLITAN UNIVERSITY
PRIFYSGOL FETROPOLITAN ABERTAWE



Pollutants as a function of air/fuel ratio

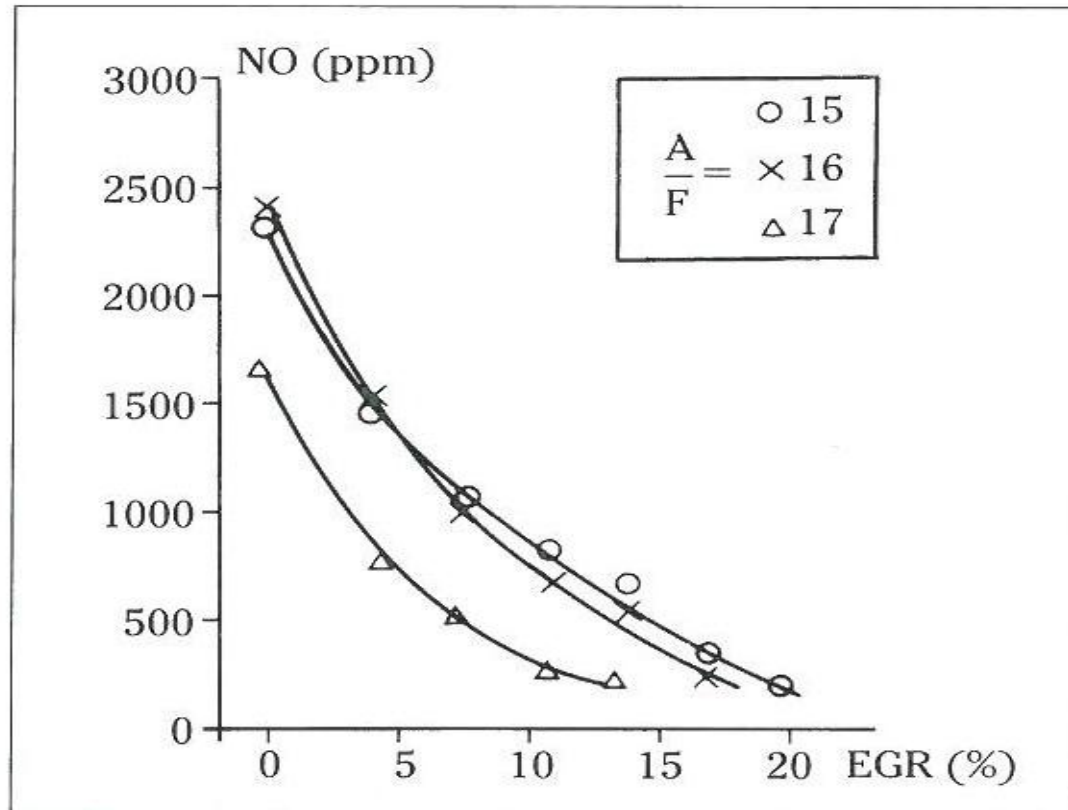
- Burnt gases fraction
 - Either via residual gases or recycled exhaust gases (EGR)
 - Depends on:
 - Load
 - Valve settings
 - Valve overlap!
 - Higher overlap increases the dilution and therefore reduces NO emissions
 - Engine speed
 - Fuel/air ratio
 - Compression ratio – lower ratio causes reduction in NO emissions
 - Dilutes the fuel mixture reducing the temperatures after combustion and therefore the emissions of NO
 - However, too much dilution will cause engine running instabilities
 - Maximum 20% EGR for partial engine load
 - ECU control of EGR gives best solution

Emissions Control and Diagnostics

SI Engines



SWANSEA METROPOLITAN UNIVERSITY
PRIFYSGOL FETROPOLITAN ABERTAWE

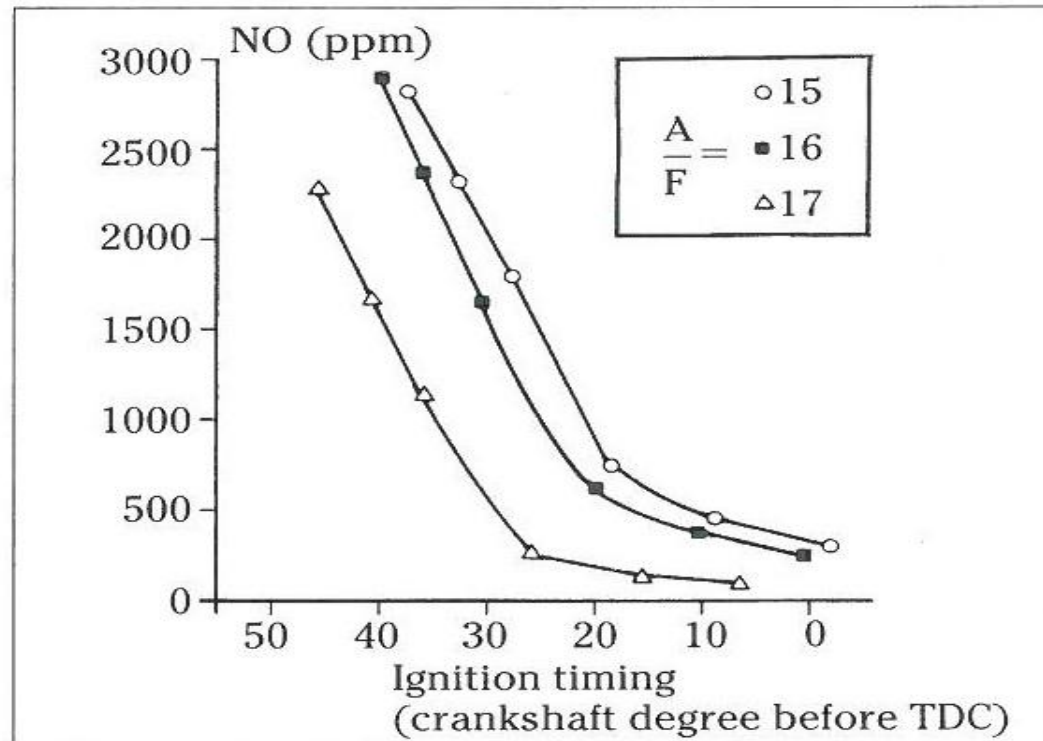


NO concentration in the exhaust as a function of % EGR, Spark ignition engine, 1600 rpm, Volumetric efficiency 50%, Minimum advance for the best torque

- Ignition timing
 - Has a great effect on NO emissions
 - Too advanced
 - Raises the value of the pressures peak as more fuel is burned before TDC (where volume is smaller)
 - Higher peak pressures mean higher peak temperatures – and for longer
 - Therefore NO emissions rise
 - Retarding ignition has the opposite effect
 - Retarding ignition by 10° can reduce NO emissions by 20 to 30%
 - This also causes rise in exhaust temperature and the promotes post combustion of residual hydrocarbons
 - The drawback is a reduction in fuel consumption and specific power

Emissions Control and Diagnostics

SI Engines



NO concentration at the exhaust as a function of spark retard, Spark ignition engine, 1600 rpm, Volumetric efficiency 50%, Minimum advance for the best torque for the points on the left-hand end of the curves

- Fuel is injected into cylinder just before combustion
 - Leads to heterogeneous mixtures
 - Results in heterogeneity of temperature and composition of burnt gases
- Two phases
 1. Combustion phase in a pre-mixed flame - varies from stoichiometric
 2. Diffusional flame phase – closer to stoichiometric
- Burnt mixture during phase 1 will be further heated as it is compressed on the way to TDC thus increasing the NO formation
- During the power stroke the formation of NO freezes as the mixture is mixed with cold air and colder burned gases(EGR)

- All NO is formed in the 20° after combustion initiation
- Delayed injection means later combustion and in turn later NO
 - Lower peak temperature = lower NO emission
 - Trick used in large diesel engines to meet NO emission regulations
 - Results as before in slightly higher fuel consumption
- Fuel/air ration again a contributing factor
 - However, less significant than in SI due to poorer distribution of fuel in mixture
 - Hence richer mixture means higher NO
- In indirect injection diesel 35% of NO is formed in main chamber but 65% in the pre-combustion chamber!



- CO is an intermediate step in the oxidation of an hydrocarbon fuel on its way to being converted into CO₂ and water
 - $RH \rightarrow R \rightarrow RO_2 \rightarrow RCHO \rightarrow RCO \rightarrow CO$
 - Where R is the hydrocarbon radical
 - Oxidation rate depends on:
 - the available Oxygen! – fuel/air ratio
 - The temperature of the gases
 - Time for reaction to take place – i.e. engine speed
 - Air/fuel ratio
 - Inevitably a rich mixture will result in higher CO emissions
 - A lean mixture tends to not be so affected by the other parameters

Emissions Control and Diagnostics

CO in SI engines

- SI engine run F/A ration of 1 at partial load
- but rich under full loads and on choke = high CO
- Nonetheless exhaust CO is lower than chamber CO
- To improve CO emissions
 - good mixture is required = good oxygen presence around fuel
 - Make the intake mixture leaner
 - Have a tight control over F/A ration during acceleration and deceleration
 - Minimise dispersion of F/A ration between cylinders in multi cylinder engines

Emissions Control and Diagnostics

CO in Diesel engines

- Diesel engine run on an overall leaner mixture = less CO
- However, poor homogeneity of the mixture leads to
 - areas of poor oxygenation
 - Not enough time for full combustion to take place
 - Non uniform temperature distribution throughout the mixture
- All the above lead to the formation of CO at both low load and full load at maximum speed.

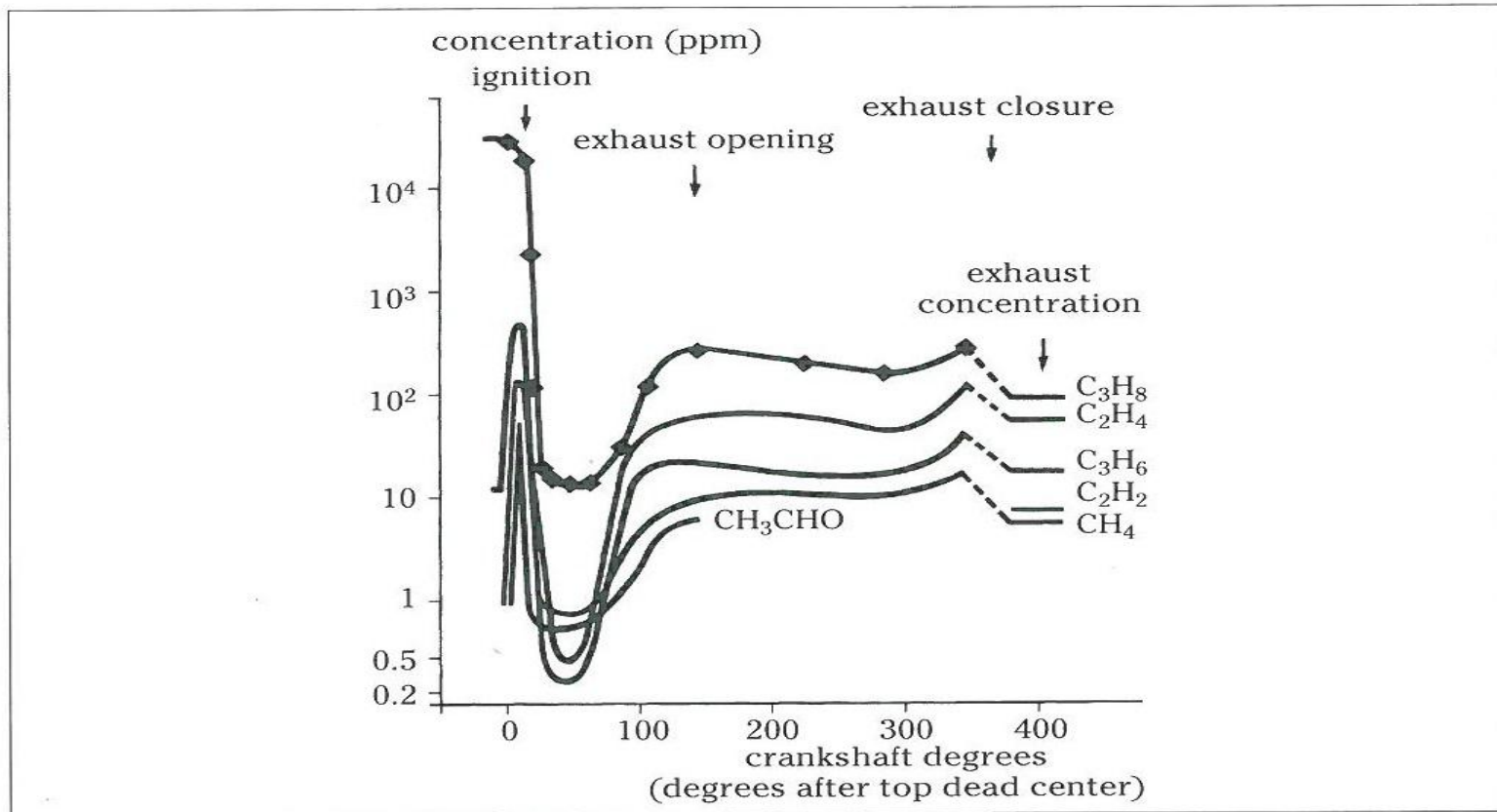
- Result from the incomplete combustion of the long chain complex fuel hydrocarbon
- Result from:
 - Poor mixture homogeneity of mixture
 - Lower temperatures in the region of the cylinder walls
- Take the form of different hydrocarbons with varying level of harmfulness and reactivity with the atmosphere
 - Most HC detected in emissions is methane
 - Also present are oxygenated compounds that as seen before can be quite nasty and reactive
- Also, there is fuel that escapes completely the combustion process

Emissions Control and Diagnostics

Unburnt Hydrocarbon



SWANSEA METROPOLITAN UNIVERSITY
PRIFYSGOL FETROPOLITAN ABERTAWE



Concentrations of unburnt hydrocarbons during the cycle

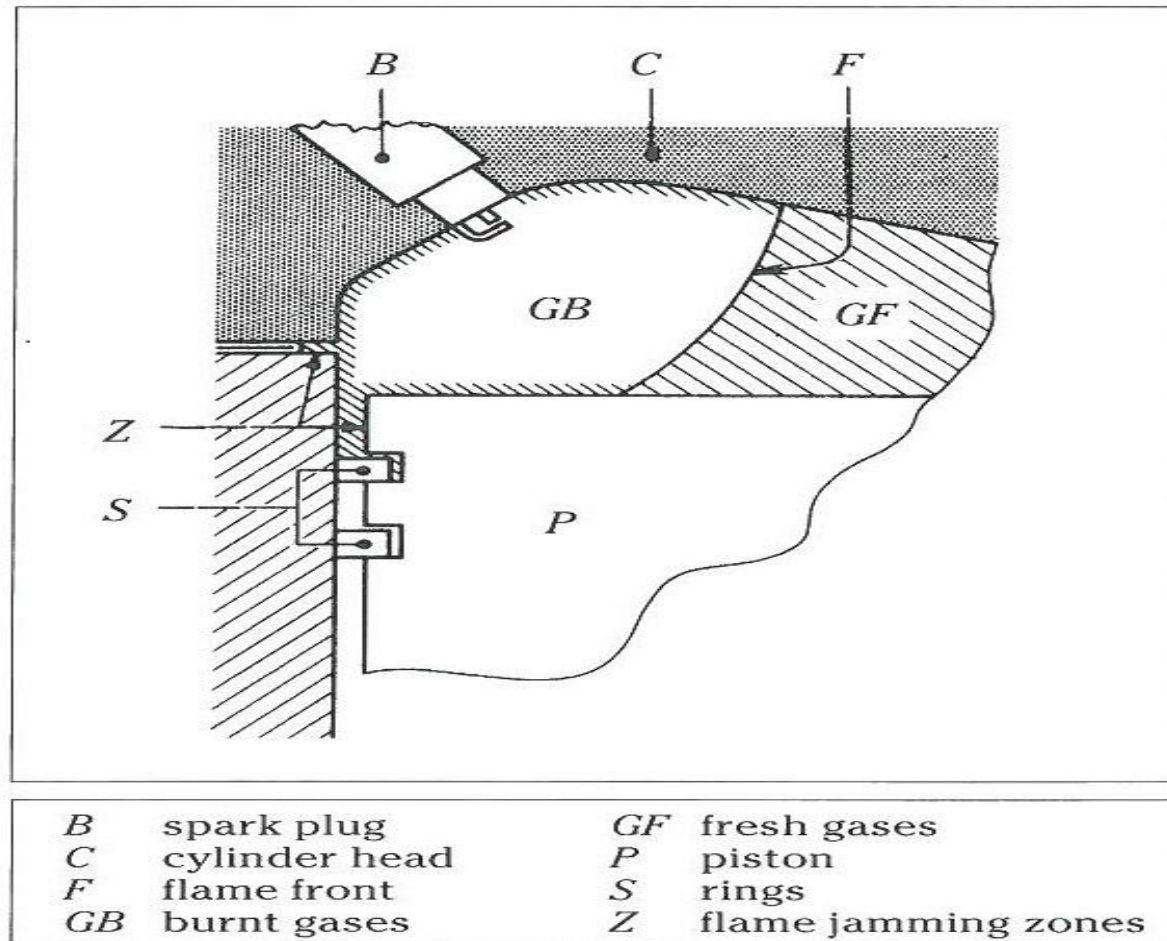
- Flame quenching or even extinction takes place at the cooled walls of the combustion chamber
- It can also take place at crevices within the combustion chamber
- Trapped by the oil layer absorbs unburnt fuel during compressions and delivers them during expansion
- F/A ration, timing and excessive EGR are also a cause
- Excessive deposits in combustion chamber aggravates all the above!
 - As a result of unburnt HC from previous cycles

Emissions Control and Diagnostics

Unburnt Hydrocarbon



SWANSEA METROPOLITAN UNIVERSITY
PRIFYSGOL FETROPOLITAN ABERTAWE



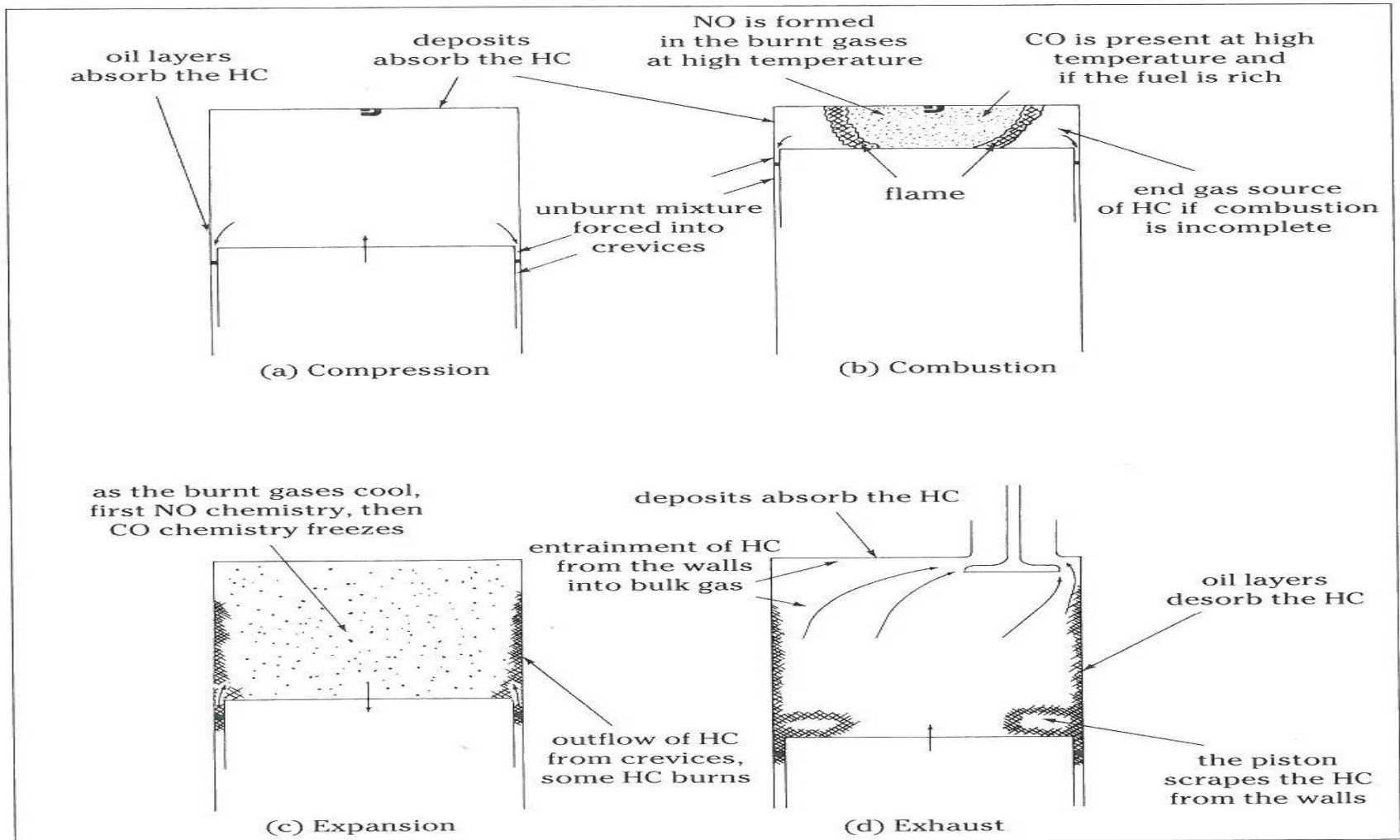
Formation of unburnt hydrocarbons by
quenching at the wall

Emissions Control and Diagnostics

Unburnt Hydrocarbon



SWANSEA METROPOLITAN UNIVERSITY
PRIFYSGOL FETROPOLITAN ABERTAWE



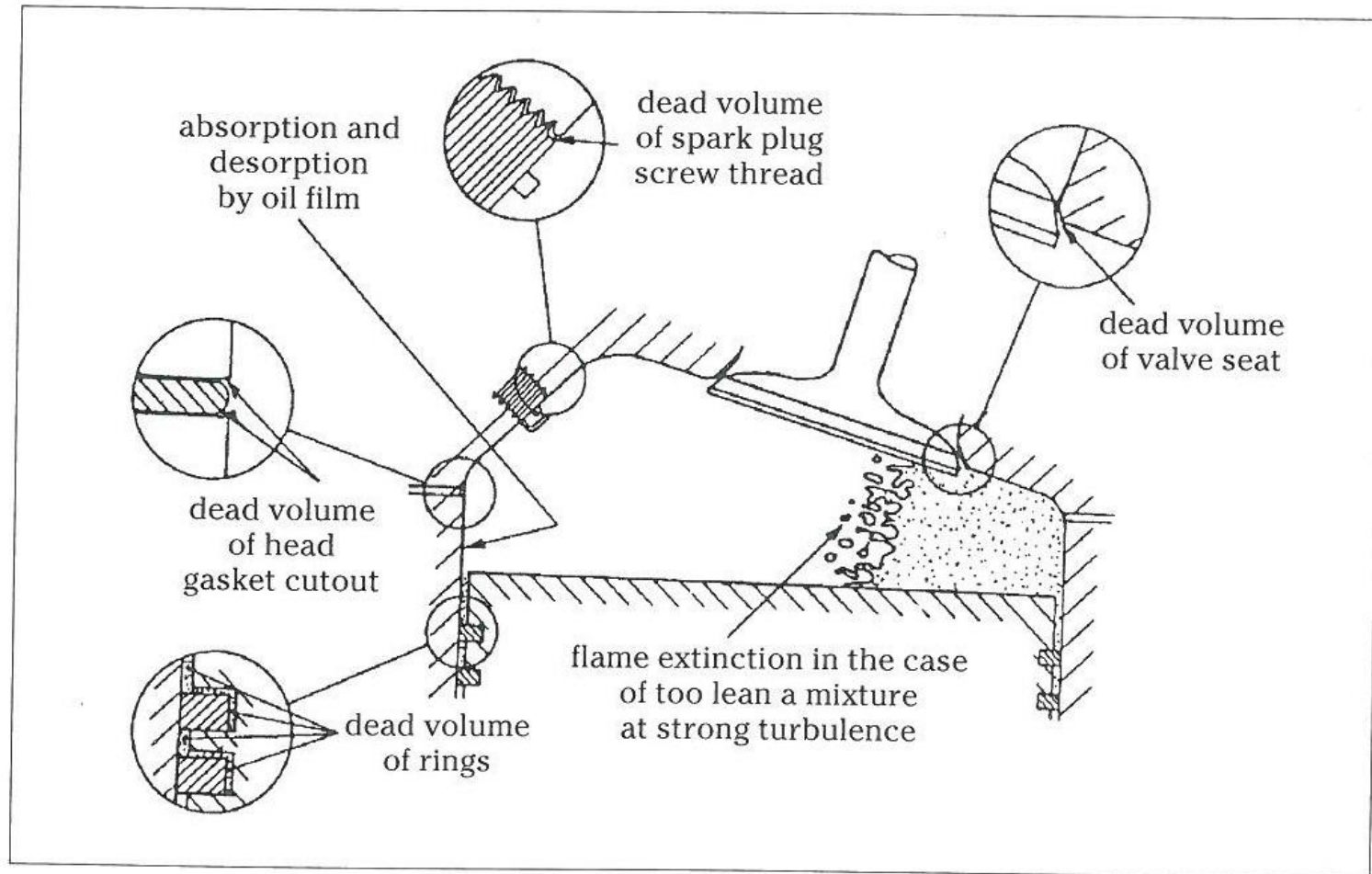
Schematic sources of HC, NO and CO in a four-stroke spark ignition engine

Emissions Control and Diagnostics

Unburnt Hydrocarbon



SWANSEA METROPOLITAN UNIVERSITY
PRIFYSGOL FETROPOLITAN ABERTAWE



Cylinder head showing possible sources of unburnt HC