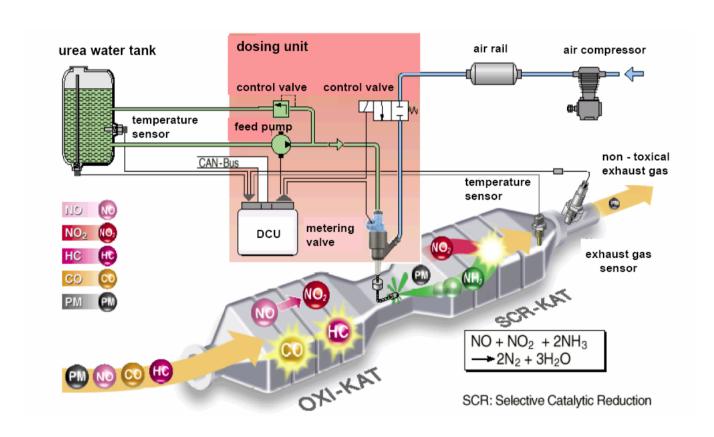


Chapter 6: Pollution Control & Abatement





Learning objectives of Chapter 6

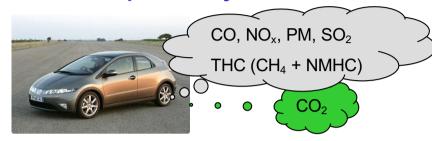
- ⇒ Recognize different "upstream methods" and the means of emissions reduction through the Electronic Control Unit (ECU)
- ⇒ Know the operating principles of after-treatment technology ("downstream methods") like 3-way cat, SCR, DPF, NOx trap



- Pollutants
- Emission standards
 - Passenger Vehicles
 - Trucks and Off-Road vehicles
- Upstream pre-treatment methods
 - Cylinder mixture dilution
 - Influence of ECU parameters
- Exhaust-gas after-treatment systems
 - 3-way catalyst & λ regulation
 - Oxidation catalytic converter
 - NO_x treatment in lean-burn operation
 - Diesel Particulate Filter (DPF)



Main primary and secondary pollutants



Secondary pollutants = reactions between primary pollutants & the atmosphere

 O_3 (Ozone) H_2SO_4 , HNO_3

Environmental impacts :

- CO: toxic for breathing beings († in high concentrations)
- HC: toxic (benzene and PAH are highly carcinogenic)
 Ozone precursors (O₃): contribute to "smog" formation
- CH₄: greenhouse gas (GWP ≈ 20): CH₄ = THC NMHC
- NO: non-toxic gas but NO₂ precursor
- NO₂: Ozone precursor (O₃): contributes to "smog" formation, toxic for pulmonary system
- N₂O: greenhouse gas (GWP ≈ 300)
- PM: toxic for human beings (volatiles < 50 nm)

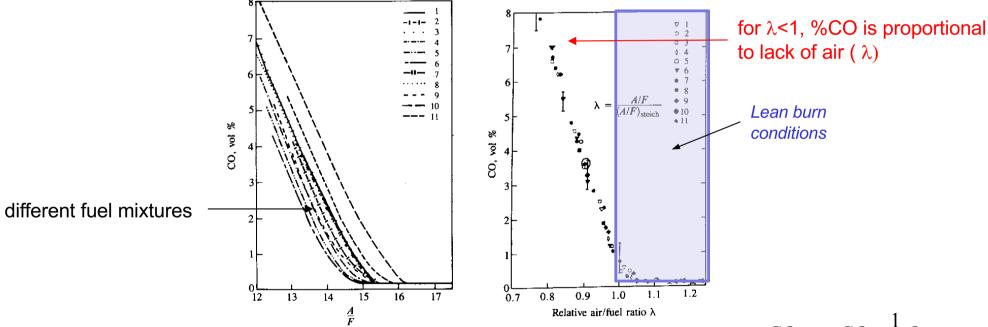


Pollutants (1)

- Pollutant formation <u>during</u> the combustion process
 - 1) CO: formed by an O_2 lack \Rightarrow O_2 is necessary in order to burn all carbon fully to CO_2

Origin of formation:

1. Combustion in rich (=fuel excess) burn mixture \Rightarrow highly dependent on the λ ratio (A/F ratio)



- 2. For $\lambda > 1$, reactions of dissociation at high temperature
 - ⇒ oxidation reactions are frozen during the expansion stroke:

$$CO_2 \rightarrow CO + \frac{1}{2}O_2$$

$$CO + OH \times CO_2 + H$$



Pollutants (2)

- Pollutant formation <u>during</u> the combustion process
 - 2) NO_x : NO_x are composed of NO (\approx 98% Otto, \approx 70% Diesel) and NO_2 Formed in the burned gases zone at high temperature (> 2300K)

$$EX : \frac{d[NO]}{dt} = \frac{6 \cdot 10^{16}}{T^{0.5}} \cdot \exp\left(\frac{-69090}{T}\right) \cdot [O_2]_e^{0.5} \cdot [N_2]_e$$

Origin of formation:

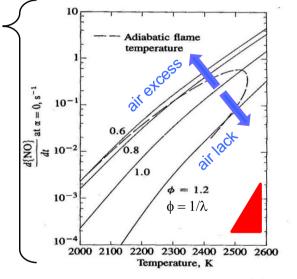
1.Formed by chemical reactions between N_2 (air) and O_2 NO = Zeldovich mechanism :

$$O + N_2 \leftrightarrow NO + N$$
 (1)

$$N + O_2 \leftrightarrow NO + O$$
 (2)

$$N + OH \leftrightarrow NO + H$$
 (3)

 NO_2 = NO oxidation reaction



+100K=>NO*10!

- ⇒ residence time at high temperature facilitates [NO_x] concentration
- 2. These reactions are frozen with the cooling process of the combustion gases during the expansion stroke. (back-reduction of NO_x to N_2 is kinetically too slow)
 - ⇒ [NO]_{real} are higher than the theoretical values computed via chemical equilibrium



Pollutants (3)

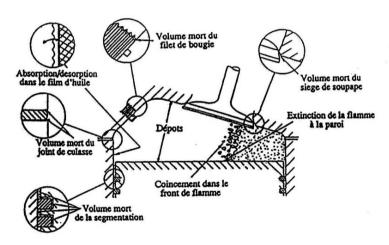
- Pollutant formation <u>during</u> the combustion process
 - 3) HC: formed mostly by an incomplete fuel combustion

Origin of formation (for **S.I.** engine):

1.Flame quenching / Trap zone within the combustion chamber:

Fuel/Air mixture penetrates into small clearance volumes (interstices) during compression stroke

Example: Piston rings, spark-plug, head gasket ⇒ avoid the oxidation by flame propagation and HC are released during expansion stroke



- 2.Fuel absorption/desorption phenomena in engine oil layer on cylinder walls
- **3.Incomplete combustion**: flame propagation speed too slow or poor comb. quality
- 4.Combustion misfire (cold start) and rich burn mixture



Pollutants (4)

- Pollutant formation <u>during</u> the combustion process
 - 4) PM: PM (Particulate Matter) are composed of:
 - ⇒ carbonaceous material (soot)
 - ⇒ other components coming from fuel or adsorbed lubricant on PM (sulfates, metallic oxides, heavy organic compounds)

Resulting from a complex chemistry in a mixture locally <u>fuel-rich</u> and at <u>high temperature</u>

Origin of formation:

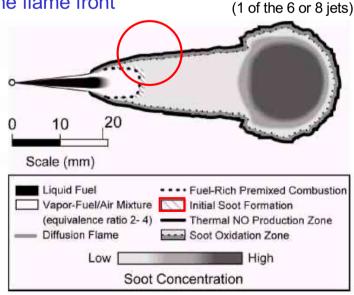
1.Process of PAH formation (Polycyclic Aromatic Hydrocarbons):

After injection, the fuel temperature is elevated near the flame front

and fuel molecules are oxidized and/or pyrolysed This will form initial light products ($C_{2n}H_2$, PAH) which will be the soot precursors in flames

 \Rightarrow depends on the mixture preparation: $\nabla \lambda$, turbulence, fuel atomization

=> Fuel injection pressure is a means of action



Top view of a diesel fuel injector



Pollutants (4)

Pollutant formation during the combustion process

Origin of formation:

Soot particle growth
 Starting with two single types of molecules (precursors)
 Particles will grow by coagulation, aggregation and dehydrogenation (=> long C-chains)

3. Soot oxidation

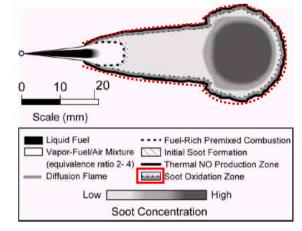
Soot is formed until the flame front extinction where they start to be oxidized with O_2 by air contact. Pressure, temperature, $[O_2]$ and residence time facilitate the soot post-oxidation (=>post-injection)

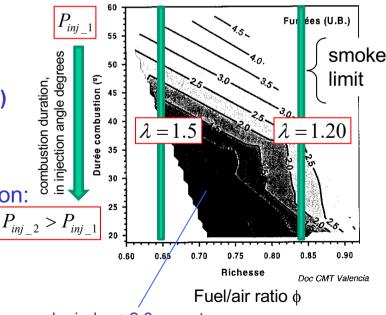
[PM] A when P and T decrease too quickly before the end of the combustion, that depends on:

- ⇒ engine speed
- ⇒ delivery period / timing of the combustion

 Soot is reduced the faster the combustion

=> act on fuel injection pressure





smoke index >2.0 = soot smoke index <2.0 = no soot



Pollutants (summary)

Pollutant formation <u>during</u> the combustion process
 In summary, the formation of the 4 main pollutants depends on:

• [CO] \Rightarrow A/F ratio (λ)

S.I.

• $[NO_x]$ $\Rightarrow [O_2]$ concentration (lean mixture), hence λ

C.I.

 \Rightarrow T (K) of combustion process

 \Rightarrow residence time at high T

• [HC]

⇒ geometry / design of the combustion chamber

 \Rightarrow combustion in rich mixture (λ < 1)

S.I.

[PM]

⇒ local F/A ratio (fuel atomisation, turbulence)

C.I.

⇒ combustion duration (residence time for post-oxidation)



- Pollutants
- Emission standards
 - Passenger Vehicles
 - Trucks and Off-Road vehicles
- Upstream pretreatment methods
 - Cylinder mixture dilution
 - Influence of ECU parameters
- Exhaust-gas after treatment systems
 - 3-way catalyst & λ regulation
 - Oxidation catalytic converter
 - NO_x treatment in lean-burn operation
 - Diesel Particulate Filter (DPF)



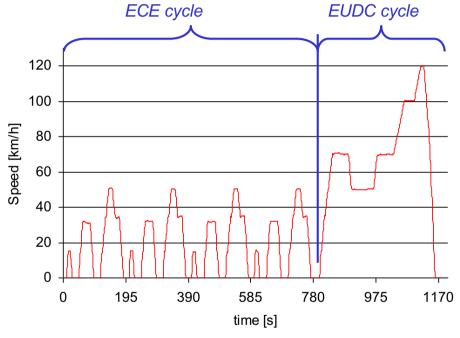
Passenger vehicles

Pollutants are measured in [g/km] on a normalized cycle (>1990)

including:

Urban driving cycle or **ECE 15** \Rightarrow 4 consecutive phases (L \approx 4 km, t = 780 s, v_{avg} = 18.7 km/h)

Extra-urban driving cycle or **EUDC** (L \approx 7 km, t = 400 s, v_{avg} = 62.6 km/h)



Total of the mixed cycle : ECE + EUDC = NEDC (or MVEG)

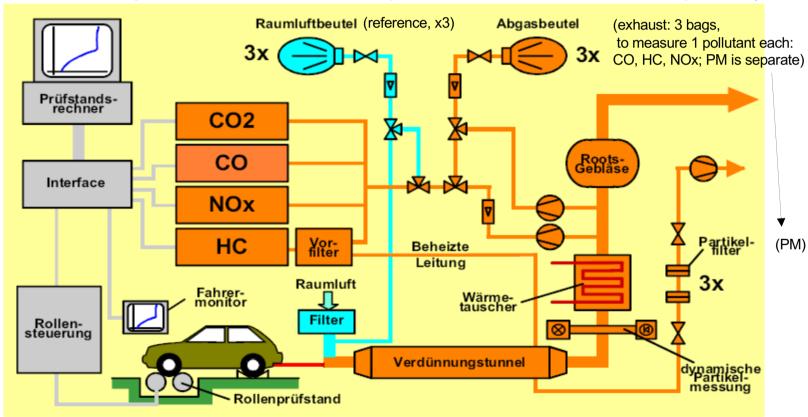
 $L = 11.0 \text{ km}, t = 1180 \text{ s}, v_{avg} = 32.5 \text{ km/h}$

- → New European Driving Cycle
- → (Motor Vehicles Emission Group)



Passenger vehicles

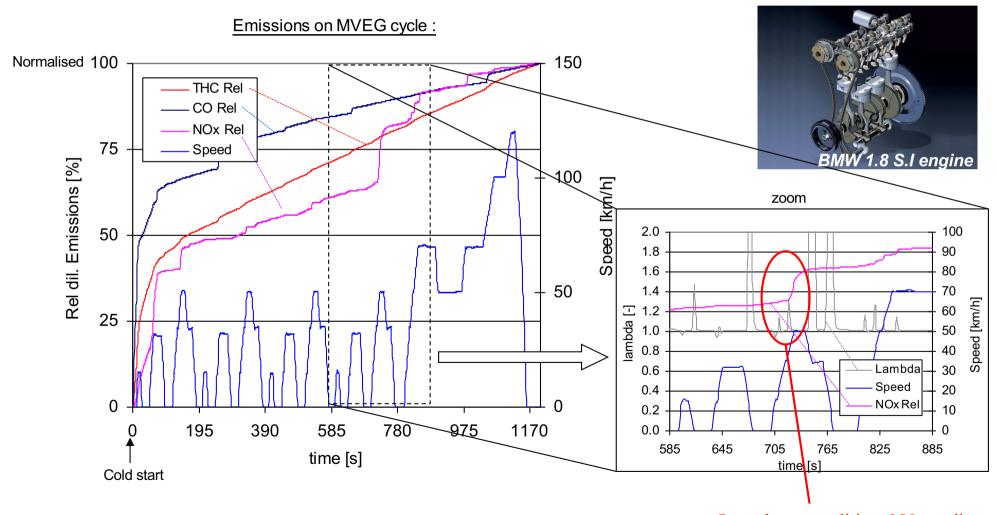
 During the cycle, exhaust gases are stored into separated bags and analyzed at the end of the driving cycle (continuous measurements are also accomplished in real time for post-treatment and development)





Passenger vehicles

• Analysis of the NEDC cycle: example on a BMW 318i Valvetronic





Passenger vehicles

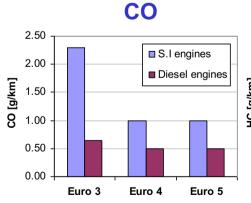
Maximal permissible values (for European Union) – in g/km :

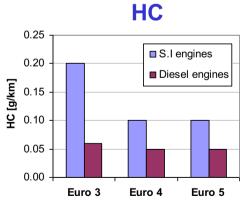
Gasoline vehicle

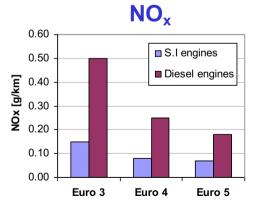
g/km	year	СО	HC	NO _x	PM
Euro 1	1992	2.72	Tot : 0.97		-
Euro 2	1996	2.20	Tot : 0.50		ı
Euro 3	2000	2.30	0.20	0.15	1
Euro 4	2005	1.00	0.10	0.08	-
Euro 5	2009	1.00	0.10	0.07	0.005
Euro 6	2014	1.00	0.10	0.07	0.0045

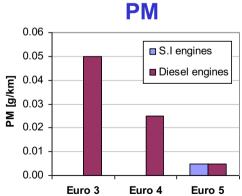
Diesel vehicle

g/km	year	СО	HC+NO _x	NO _x	PM
Euro 1	1992	2.75	1.36	1	0.19
Euro 2	1996	1.00	0.90	1	0.10
Euro 3	2000	0.64	0.56	0.50	0.05
Euro 4	2005	0.50	0.30	0.25	0.025
Euro 5	2009	0.50	0.23	0.18	0.005
Euro 6	2014	0.50	0.17	0.08	0.005











Passenger vehicles: now

In 2017, the NEDC cycle was replaced by the WLTP:
 Worldwide harmonized Light vehicles Test Procedures

⇒ harmonized (Worldwide)

⇒ more dynamic

⇒ 3 different vehicle class defined by power-weight ratio: kW / ton

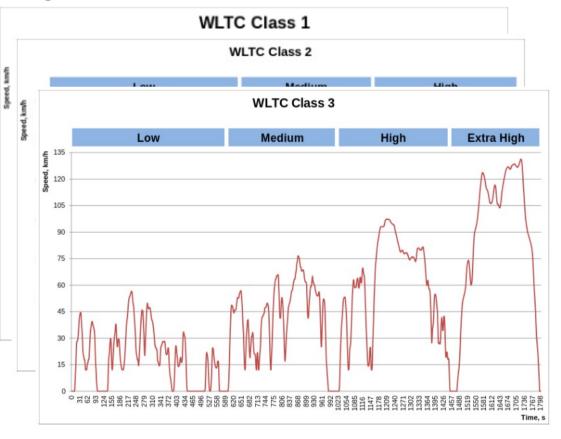
Class 1: PWr < 22

Class 2: 22 < PWr < 34

Class 3: PWr > 34

Actual cars in EU:

40 < PWr < 70 kW/tons



test to be repeated every 10'000 km



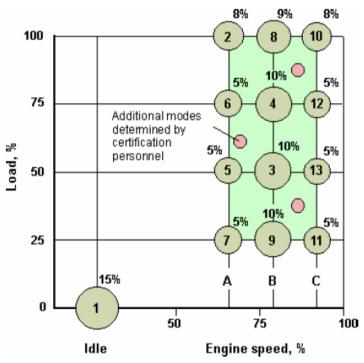
Trucks

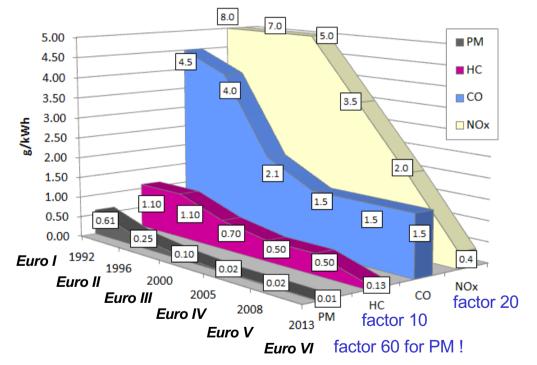
≠ g/km!

Pollutants are measured in [g/kWh] on a 13 modes cycle:

13 modes test cycle:

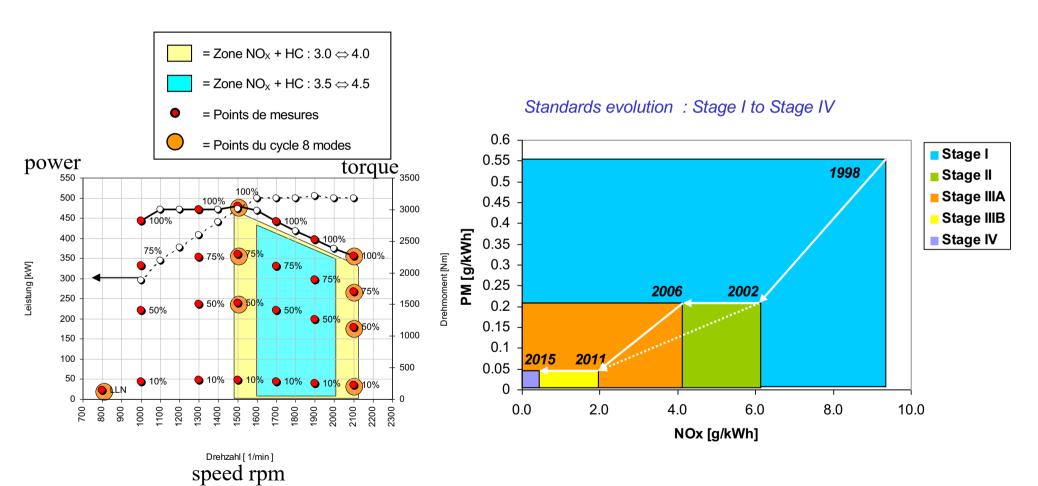
Standards evolution:







- Off-road vehicles (=> diesel => NOx, PM)
 - Pollutants are measured in [g/kWh] on a 8-modes cycle:





Off-road vehicles

• Comparison of Emission Standards: passenger car / off-road vehicles

Passenger vehicles (Diesel engine): [g/km]

Available from:	Name	Unit	СО	NO _x + HC	PM
> 2000	Euro 3	g/km	0.64	0.56	0.05
> 2005	Euro 4	g/km	0.50	0.30	0.025

> 2000	Eq. EU3	g/kWh	3.84	3.36	0.30
> 2005	Eq. EU4	g/kWh	3.00	1.80	0.15

Off-road vehicle (Diesel engine): [g/kWh]

> 2006	Stage 3A	g/kWh	3.5	4.0	0.20
> 2011	Stage 3B	g/kWh	3.5	2.0 + 0.19	0.025





Vehicle @ 120 km/h

 \Rightarrow $P_{mean} \approx$ **20 kW**

- \Rightarrow with a delay of 5 years offset, emission levels are quite identical!
- ⇒ from 2011, the standards on PM are all almost at the same level



Content of Chapter 6

- Pollutants
- Emission standards
 - Passenger Vehicles
 - Trucks and Off-Road vehicles
- Upstream pre-treatment methods
 - Cylinder mixture dilution
 - Influence of ECU parameters
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■ "Pretreatment" ⇒ 4 methods

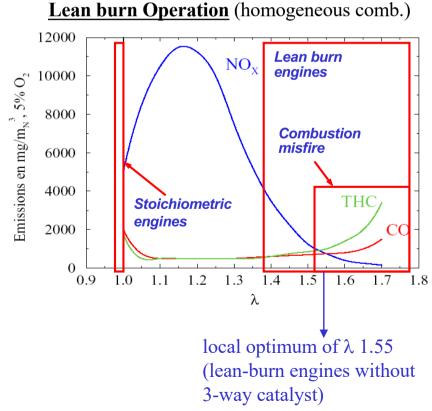
Objective: reducing the emission values before the aftertreatment itself, i.e. <u>inside</u> the combustion chamber

- 1. Cylinder mixture dilution by air $(\lambda \triangleleft)$
 - \Rightarrow increase the oxygen fraction inside the combustion chamber by increasing the λ ratio *Reminder*:

$$\lambda = \frac{R_{A/F}}{R_{A/F,sto}} = \frac{\left(\frac{M_A}{M_F}\right)}{\left(\frac{M_{A,sto}}{M_F}\right)} = \frac{M_A}{M_{A,sto}}$$

Consequence of a lean burn mixture:

1 <
$$\lambda$$
 < 1.5 : [NO_x] \circlearrowleft and [HC], [CO] \hookrightarrow λ > 1.5 : [NO_x] \hookrightarrow and [HC], [CO] \vartriangleleft





Pretreatment methods by cylinder mixture dilution

1. Cylinder mixture dilution by air (continued)

Diesel engine:

Permanent operation in air excess (lean burn) to avoid the formation of black smoke \Rightarrow explains the higher [NO_x] concentration for C.I. engines

Otto engine (non-stoichiometric)

This type of operation is called **lean burn**, we find 2 types:

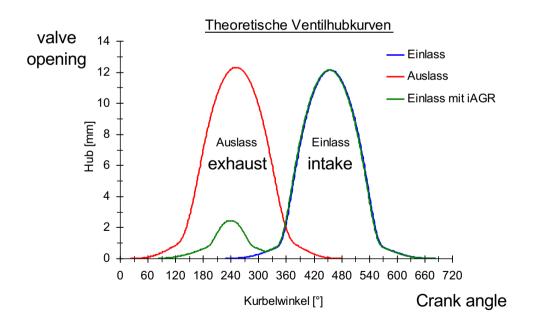
- A) Homogeneous lean burn engines
 - ⇒ beware at the « lean flammability range », so $\lambda_{max} \approx 1.5$ -1.7 Example : gas engine with a prechamber
- B) Stratified lean burn engines

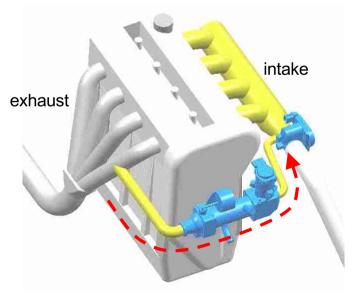
Need the use of a direct injection system (for the mixture air/fuel stratification) and an <u>after</u>-treatment system for the [NO_x]

=> NOx trap



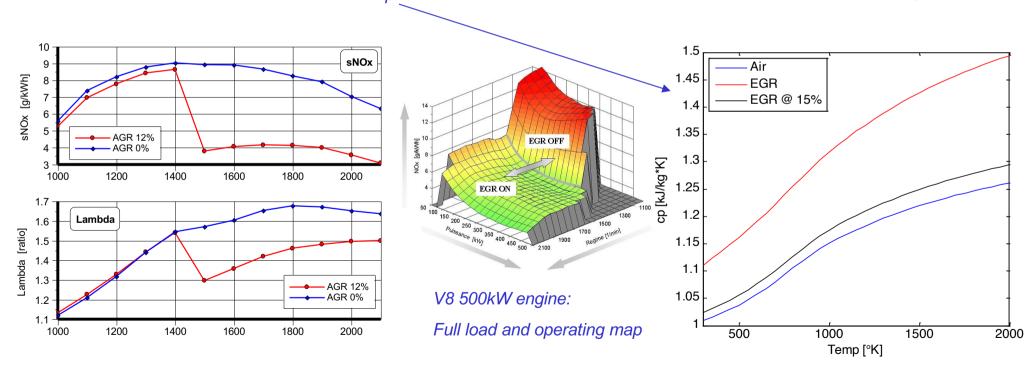
- Pretreatment methods by cylinder mixture dilution
 - 2. Cylinder mixture <u>dilution</u> by exhaust gas recirculation (**EGR**)
 - Objective: NO_x reduction
 - Type of technology for exhaust gas recirculation (~10-30%):
 - A) Internal recirculation
 - ⇒ with valve train system
- B) External recirculation (cooled)
 - ⇒ reintroduced at the intake







- Pretreatment methods by cylinder mixture dilution
 - 2. Cylinder mixture dilution by exhaust gas recirculation (**EGR**)
 The fresh gases dilution by the combustion gases has 2 consequences:
 - Reduction of $[O_2] \Rightarrow$ reduction of the λ ratio
 - Increase of the c_p (of the introduced mixture) \Rightarrow reduction of T_{max}

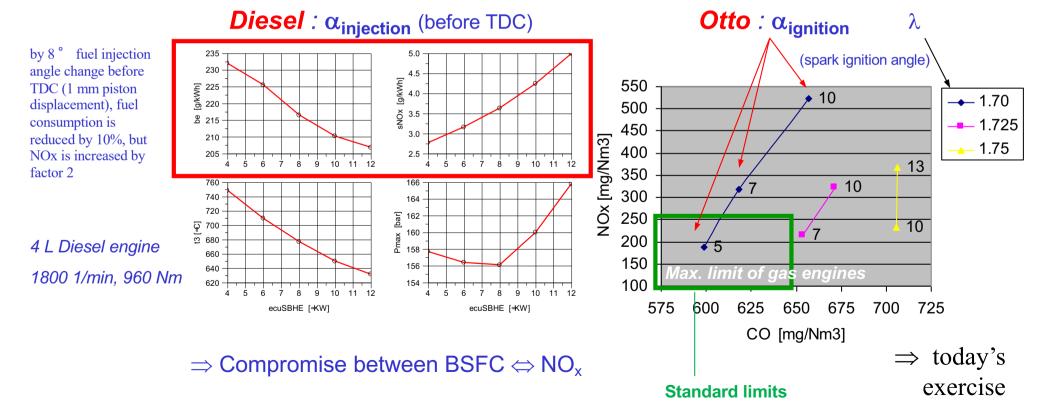


NOx divided by factor 2 (left), up to factor 5 (map)

EGR is now standard on all diesel cars



- Pretreatment methods by engine parameters (ECU)
 - 3. Combustion timing (=most important means of action)
 - The <u>timing</u> of the combustion process in the engine cycle directly influences the cylinder temperature and pressure \Rightarrow influence on the [NO_x]
 - The increase of exhaust gases T° improves the post-oxidation ⇒ influence on [CO] and [PM]



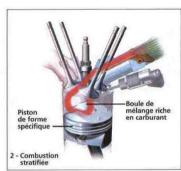


- Pretreatment methods by engine parameters (ECU)
 - 4. Combustion speed

Reminder: an increase of the <u>turbulence</u> intensity involves an increase of the flame propagation speed (therefore the combustion speed)

(Otto:) Influence on [CO] and [HC] with lean burn engines (combustion becomes more stable)





⇒ Turbulence generator enable / disable (swirl or tumble)

Diesel: Influence on [PM]

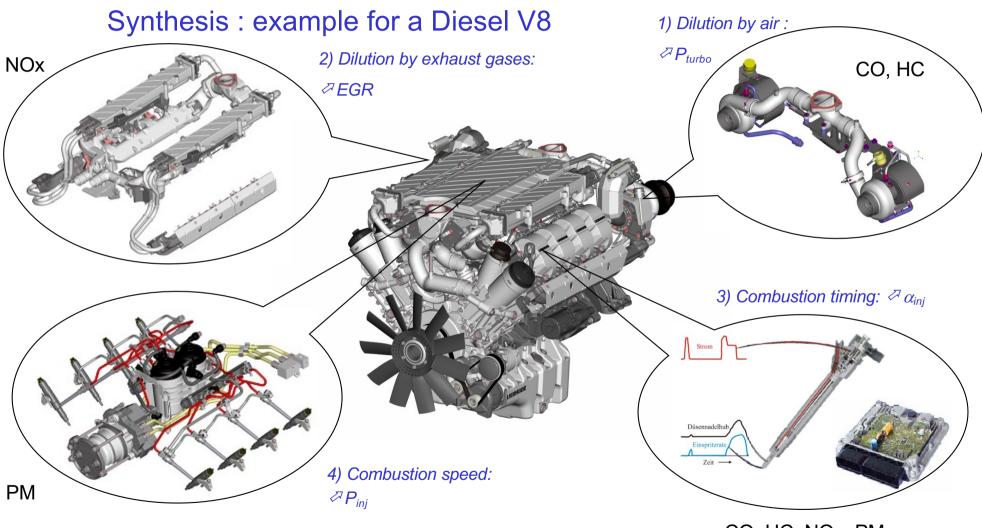
On Diesel engines, the combustion **duration is reduced** if the <u>injection duration</u> of the fuel is reduced by an **increase of the injection pressure** (\Rightarrow better atomisation)

⇒ increase of P_{ini} in order to reduce the PM emissions



Upstream pretreatment methods: summary

Pretreatment methods by engine parameters (ECU)



CO, HC, NOx, PM

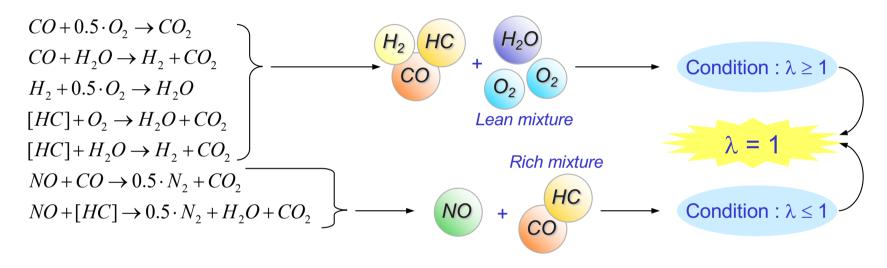
(injection during expansion stroke to burn off PM)



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- After-treatment systems: (1) 3-way catalyst (late 1980'ies)
 - Simultaneous action on: CO, HC and $NO_x \Rightarrow 3$ pollutants
 - Reactions to consider:

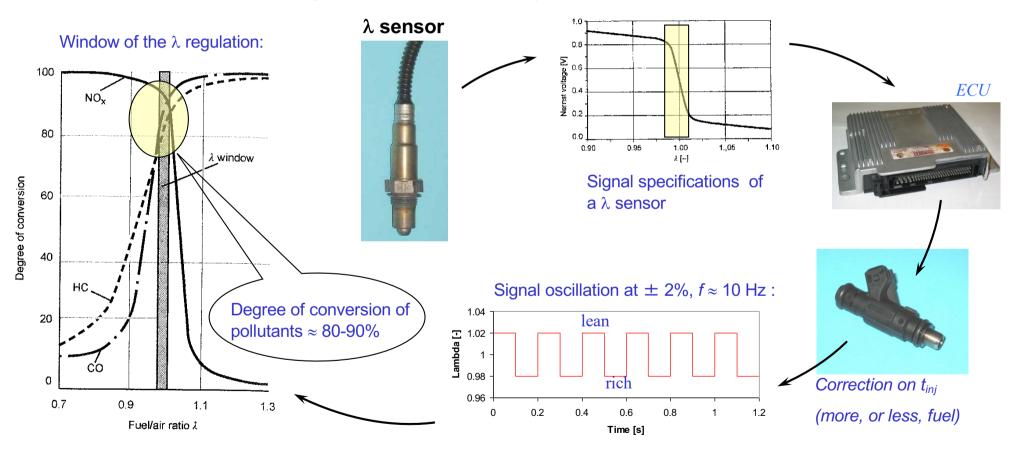


Problem:

- <u>Kinetic</u> constraints: the required time for (homogeneous) reactions is longer than the residence time of the gases in the exhaust line (< 1s)
 - \Rightarrow acceleration of the reactions thanks to a catalyst
- Needs an operation in both lean burn AND rich burn conditions
 - \Rightarrow regulation by an O_2 sensor (lambda sensor) close to the stoichiometric conditions

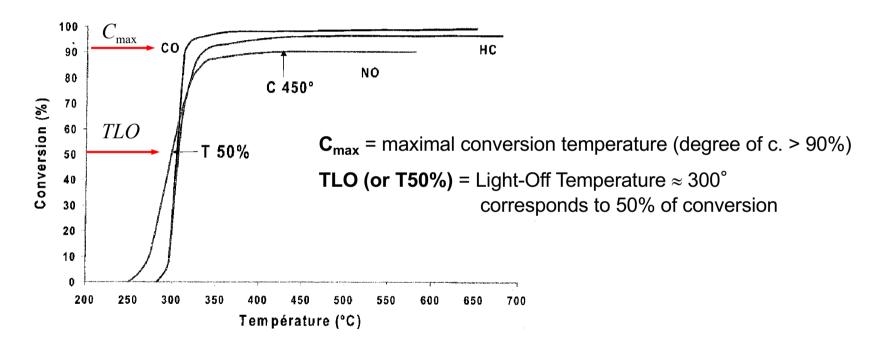


- After-treatment systems: 3-way catalyst & λ regulation
 - Regulation at λ = 1 possible only on S.I. stoichiometric engines
 - The F/A ratio regulation is controlled by a lambda sensor:





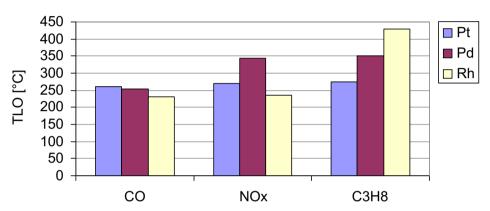
- After-treatment systems: 3-way catalyst
 - Influence of the main parameters:
 - Temperature of combustion gases at the catalyst inlet



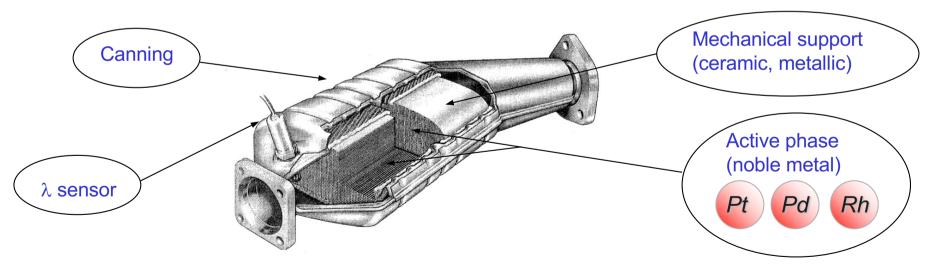
 \Rightarrow 90% of the measured emissions on the normalized cycle are generated during the 200 first seconds before catalyst Light-Off (when $T_{exhaust}$ < TLO) (= cold start)



- After-treatment systems: 3-way catalyst
 - Influence of the main parameters:
 - type of noble metal used on catalytic support ⇒



Converter components :





- After-treatment systems: (2) Oxidation catalytic converter
 - Operation in <u>lean burn</u> condition
 - \Rightarrow application for **Diesel** engines (with a constant operation at λ >1.2)
 - Composition of the combustion gases for Diesel engines (with respect to stoichiometric engines):
 - CO and HC content clearly lower
 - NO_x level slightly higher
 - O₂ always in excess
 - presence of particulates (PM)
 - T° of exhaust gases lower
 - \Rightarrow 3-way catalyst is impossible because of O₂ presence:





- (3) 'NO_x treatment in lean-burn operation' (=intrinsically contradictory)
 - The NO_x treatment by catalyst requires a stoichiometric regulation (NO_x reduction is impossible in an oxidizing environment)
 - ⇒ Problem for lean-burn engines:
 - 1. Spark ignition engines with lean burn operation (FSI)
 - 2. Diesel engines
 - The reduction of emission standards caused upstream pretreatment measures to be insufficient (for example: EGR, late combustion timing) and required specific new after-treatment solutions:

$$\Rightarrow$$
 (a) NO_x trap (S.I.)

 \Rightarrow (b) Selective Catalytic Reduction (SCR) (C.I.)



- (3) NO_x treatment in lean-burn operation:
 - (a) NO_x trap / absorber
 - Principle:
 - 1. Catch the NO_x on an absorbent material during the lean-burn operating phases (storage (few min) on the catalyst surface like a sponge filled with water)
 - 2. Release the NO_x and reduce them to N_2 during short transitions in rich burn operation (similar mechanism to the one used for the 3-way catalyst)
 - Adaptation on S.I. engines:
 - The change of the A/F ratio is done by switching from one combustion mode to another:
 - lean burn (stratified or homogeneous) ⇔ stoichiometric
 - Strategies of regeneration occur e.g. during vehicle accelerations (rich burn)
 - (Adaptation on <u>Diesel</u>)
 - More difficult because black smoke emissions are enormous at λ < 1
 - ⇒ Combination of NO_x Trap & Particulate filter

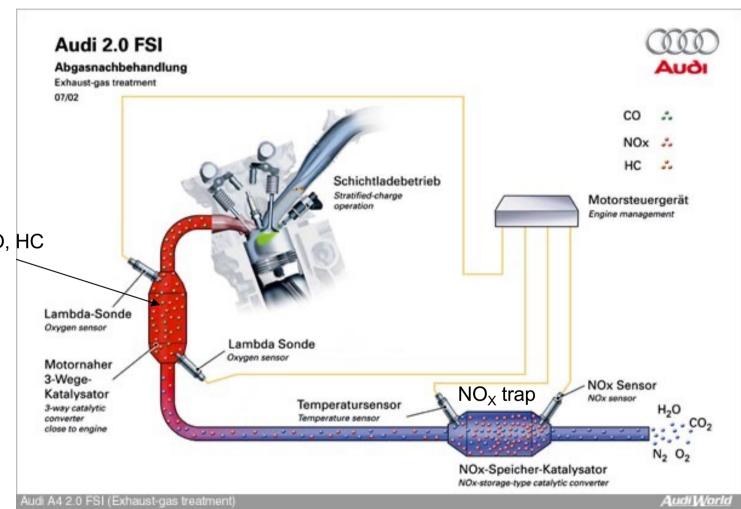


■ (3) NO_x treatment in lean-burn operation: (a) NO_x trap / absorber

Only for S.I.E.

oxidation of CO, HC

3-way cat works normally at $\lambda=1$ At $\lambda>1$, it can only oxidize CO, HC, hence NOx pass through.

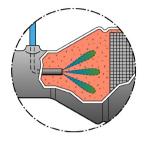


(maybe +PM filter in future)

Cost: 3 kFr Life: 8-10 yrs NOx trap filled during lean burn $\lambda > 1$. The trap is cleaned to N_2 by a short rich burn phase $\lambda < 1$ every 10 min. or so.



- (3) NO_x treatment in lean-burn operation: (b) SCR (for <u>Diesel</u>)
 - Principle of selective catalytic reduction (SCR):
 - ⇒ Injection at the exhaust system of a <u>reducing</u> agent having a strong <u>selectivity</u> towards NO_x:



- Reducing agent mostly used: urea (=>ammonia after dissociation) 'ADBLUE'
 - 1. Thermal dissociation of urea and hydrolysis into ammonia (NH₃)

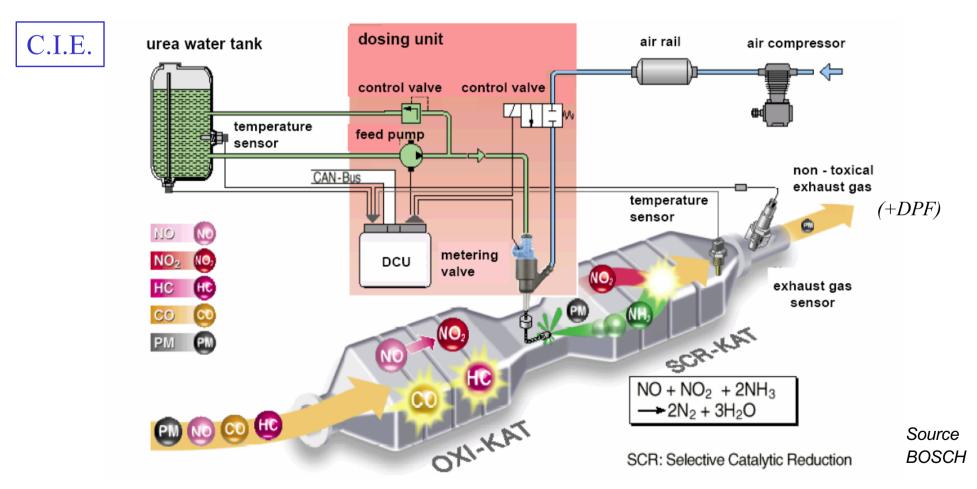
$$\overbrace{NH_2 - CO - NH_2}^{Ur\acute{e}e} \rightarrow HNCO + NH_3$$

$$HNCO + H_2O \rightarrow CO_2 + NH_3$$

- 2. NO_x reduction thanks to ammonia (NH₃)
- The use of (toxic) ammonia directly is avoided
- High conversion degree of the system ≈ 90%



- (3) NO_x treatment in lean-burn operation: (b) SCR
 - Example of a SCR system with urea injection:

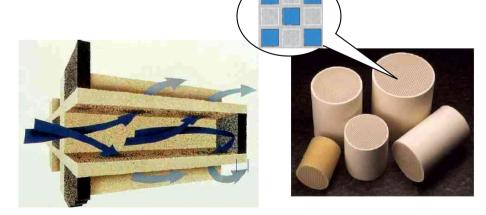




- After-treatment systems:(4) Diesel Particulate Filter (DPF)
 - Utilization only on Diesel engines
 - Due to a massive reduction of the PM emission limit, the upstream pretreatment measures (like increase of injection pressure) reached its limits
 - ⇒ need to equip with Particulate Filters all the Diesel engines of the market (Passenger vehicles, Trucks, Heavy-duty machines, cogeneration)

 Principle: solid particles present in the exhaust gases are retained on a porous material until a regeneration phase

Type of filtration: « Wall-Flow »
 The hot gases pass through a porous wall (ex.: ceramic monoliths) and leave the particles behind ⇒

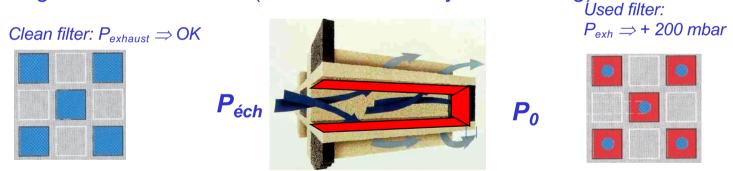


Filtering « Wall-Flow »

Ceramic monoliths



- After-treatment systems: Diesel Particulate Filter (DPF)
 - Degree of filtration : > 90% in mass of all particles
 - Filter regeneration:
 - The accumulation of particles causes an increase in back-pressure at the exhaust, penalizing the engine operation
 - ⇒ regeneration is needed (=burn-off of soot by filter heating)



- DPF regeneration strategy (PM are composed of carbon: T_{comb} ≈ 500-600° C):
 - ⇒ Increase the exhaust-gas temperature (burn-off soot) by **post-injection**
 - ⇒ Decrease the soot combustion temperature





- After treatment systems: Diesel Particulate Filter (DPF)
 - The regeneration strategy depends on the filter type:

Passive filters: Utilization of additives mixed in the fuel in order to reduce

the temperature of soot combustion and so accelerate the

combustion process

⇒ the filter is « passive » for the engine

Active filters: The engine management knows the charge load of the filter

(by measuring the ΔP_{exh}) and is able to elaborate strategies to increase the exhaust-gas temperature if a regeneration

phase is required:

 \Rightarrow action on engine parameters or external heating (electrical

or thermal)

- Example of possible modifications on the engine parameters:
 - Reduction of λ ratio (EGR *or* air throttle)
 - Combustion timing (reduction of $\alpha_{injection}$)
 - Post-injection
 - injection at or close to *BDC* (fuel combustion into the oxidation catalytic converter)