

Ciências ULisboa

Faculdade
de Ciências
da Universidade
de Lisboa

DISCIPLINA MIEA 2018



Technologies of combustion

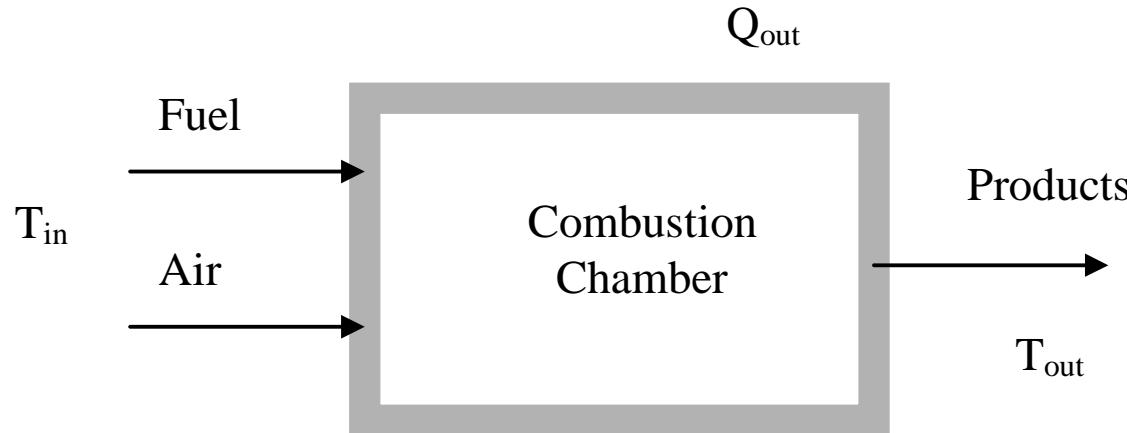
Corpo docente

Carla Silva (Teóricas e práticas) /Theory and practice
camsilva@ciencias.ulisboa.pt

P#10 Following table list the results of an experiment of boiler that is used to produce superheated vapour. The boiler is feed by natural gas trough a conventional burner.

- a) The air/fuel ratio
- b) The higher heating value of the fuel
- c) Heat transfer to water, assuming that heat loss through boiler walls are 3% of the lower heating value.

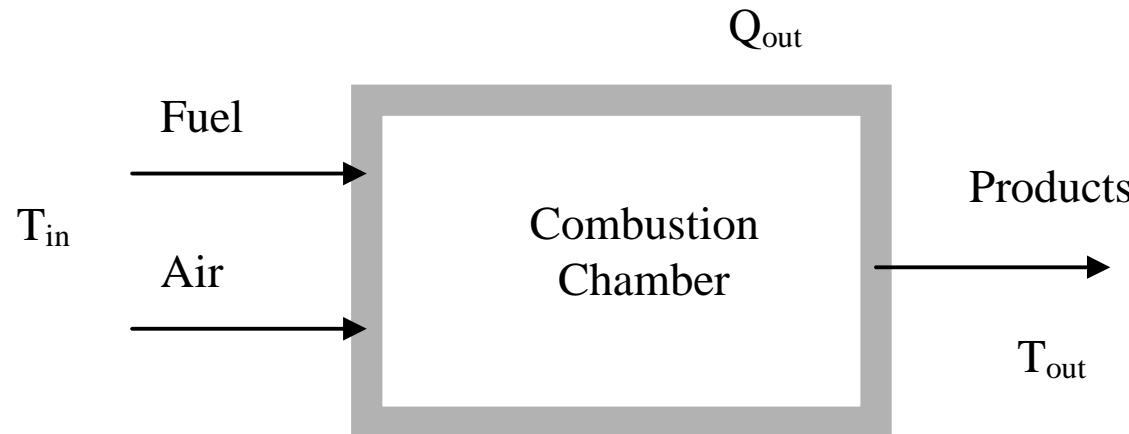
Fuel rate	150 m ³ /h
Reactants temperature@ entrance	25°C
Products temperature @exit	227°C
Fuel composition by volume(%)	CH ₄ : 88 H ₂ : 2 CO ₂ : 3 N ₂ : 7
Dry analysis combustion products (%)	O ₂ : 1.1 CO ₂ : 10.8 N ₂ : 88.1



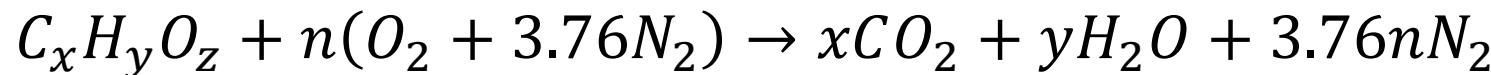
- Maximum heat release, $\max Q_{out}$: $T_{out} = T_{in}$
- Maximum flame temperature, T_{ad} :

$H_{reag}(T_{in}) = H_{prod}(T_{ad})$ (constant pressure, e.g. Diesel engine, gas turbine, furnace)

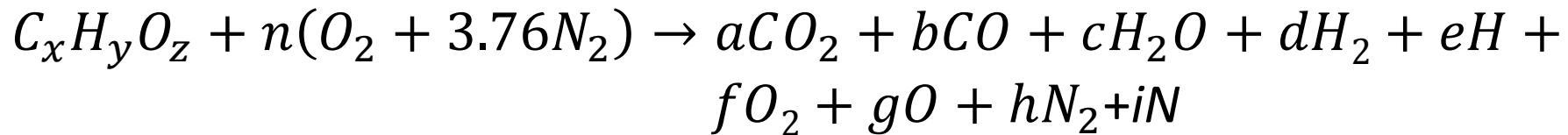
$H_{reag}(T_{in}) = H_{prod}(T_{ad}) - R(n_{prod}T_{ad} - n_{reag}T_{in})$ (constant volume, e.g. gasoline engine)



- Ideal stoichiometric combustion



- Real stoichiometric combustion



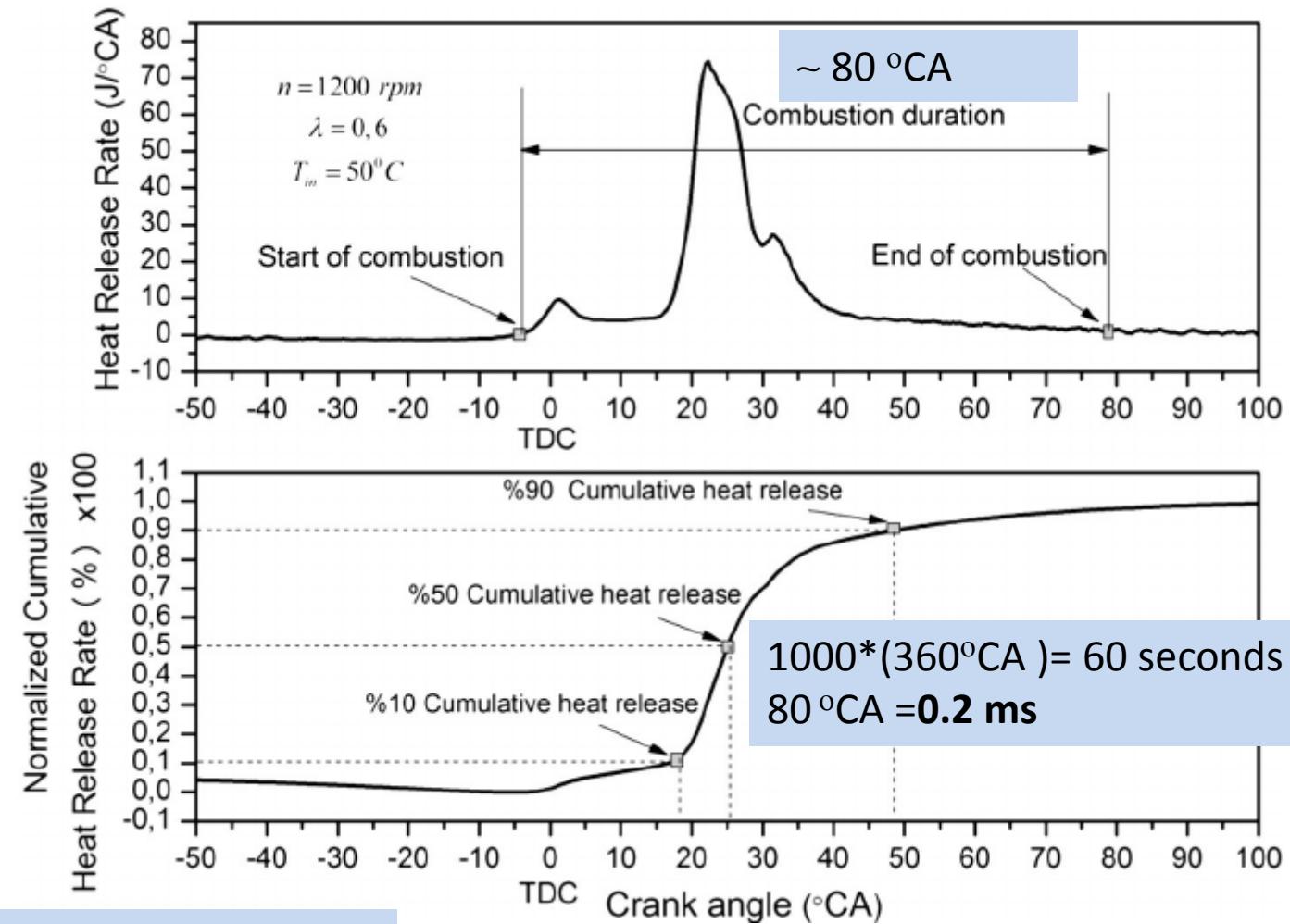
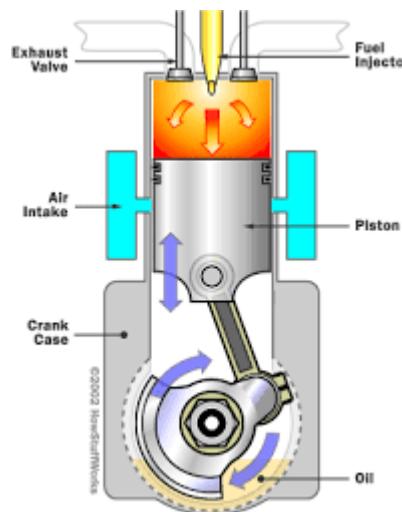
K is tabulated as a function of temperature for different equilibrium reactions

**APÊNDICE 4
CONSTANTES DE EQUILÍBRIO**

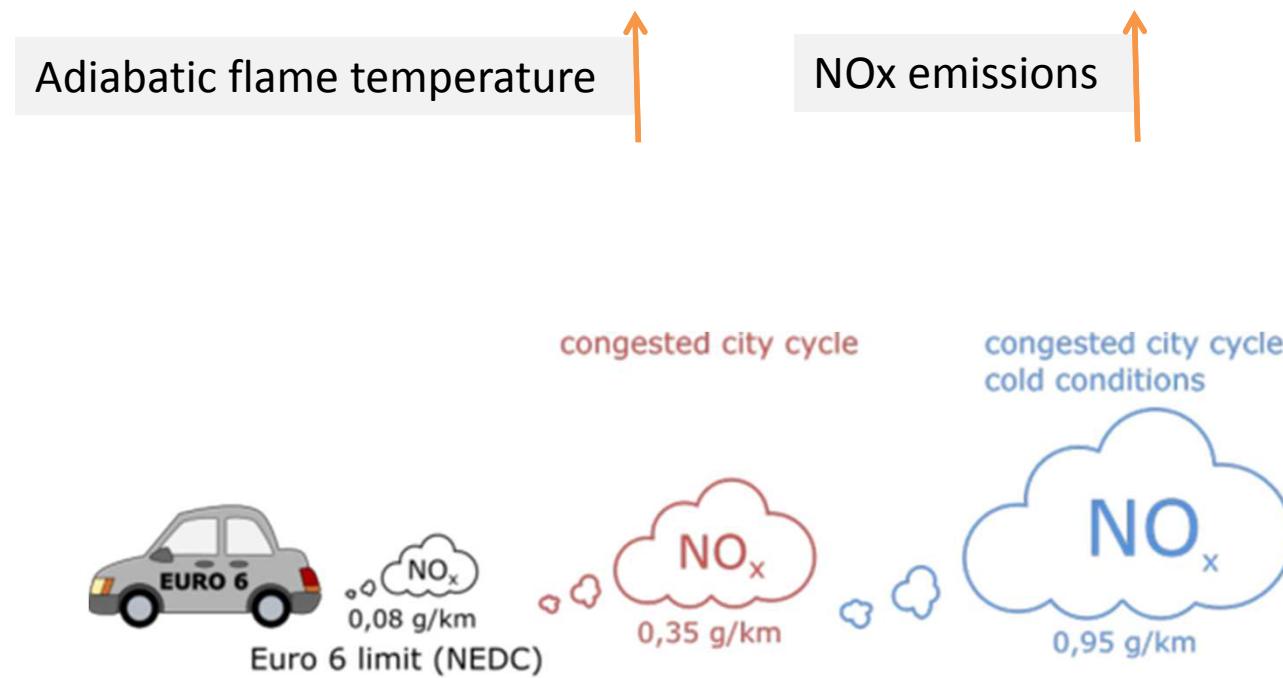
$T(K)$	$\log_{10} K_p$ com as pressões parciais em atmosferas							
	$\frac{P_{H_2O}}{P_{H_2} \sqrt{P_{O_2}}}$	$\frac{P_{CO_2}}{P_{CO} \sqrt{P_{O_2}}}$	$\frac{(P_{H_2O})(P_{CO})}{(P_{H_2})(P_{CO_2})}$	$\frac{P_{H_2O}}{P_{OH} \sqrt{P_{H_2}}}$	$\frac{P_{H_2O}}{\sqrt{P_{O_2} \sqrt{P_{N_2}}}}$	$\frac{P_{H_2}}{(P_H)^2}$	$\frac{P_{O_2}}{(P_O)^2}$	$\frac{P_{N_2}}{(P_N)^2}$
298	40,048	45,066	-5,018	46,181	-15,171	71,232	81,202	159,600
300	39,786	44,760	-4,974	45,876	-15,073	70,762	80,664	158,578
400	29,240	32,431	-3,191	33,600	-11,142	51,758	58,944	117,408
600	18,633	20,087	-1,454	21,264	-7,210	32,676	37,146	76,162
800	13,289	13,916	-0,627	15,060	-5,243	23,082	26,202	55,488
1000	10,062	10,221	-0,159	11,322	-4,062	17,294	19,612	43,056
1200	7,899	7,764	0,135	8,822	-3,275	13,416	15,208	34,754
1400	6,347	6,014	0,333	7,030	-2,712	10,632	12,054	28,812
1600	5,180	4,706	0,474	5,686	-2,290	8,534	9,684	24,350
1800	4,270	3,693	0,577	4,638	-1,962	6,896	7,836	20,874
2000	3,540	2,884	0,656	3,799	-1,699	5,582	6,356	18,092
2200	2,942	2,226	0,716	3,113	-1,484	4,504	5,142	15,810
2400	2,443	1,679	0,764	2,541	-1,305	3,602	4,130	13,908

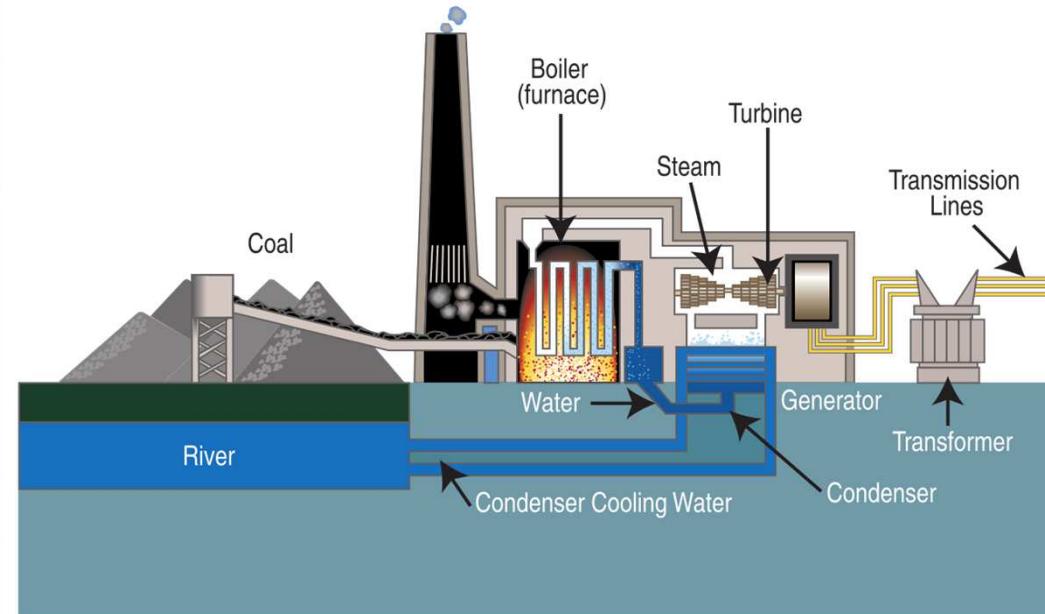
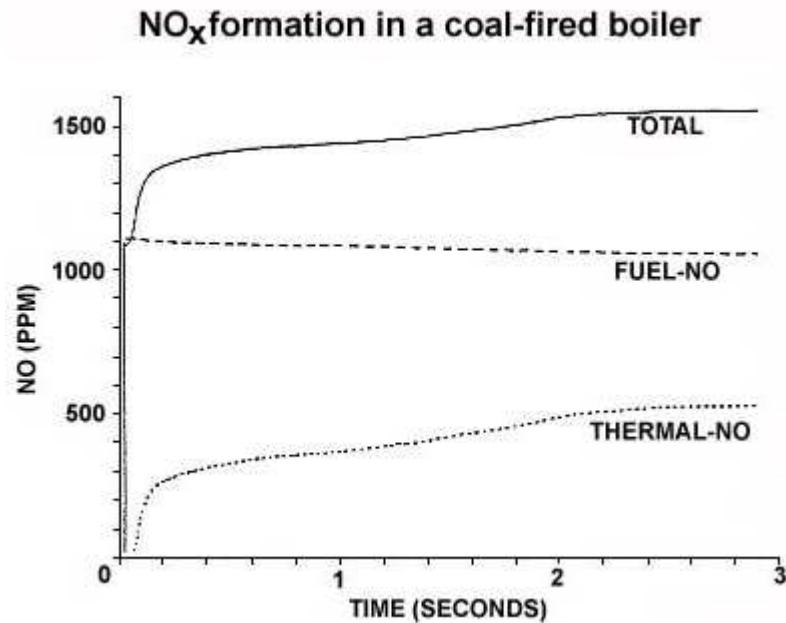
Tabela A4.1

Constantes de equilíbrio. (Dados extraídos de Rogers e Mayhew, 1994.) (continua)



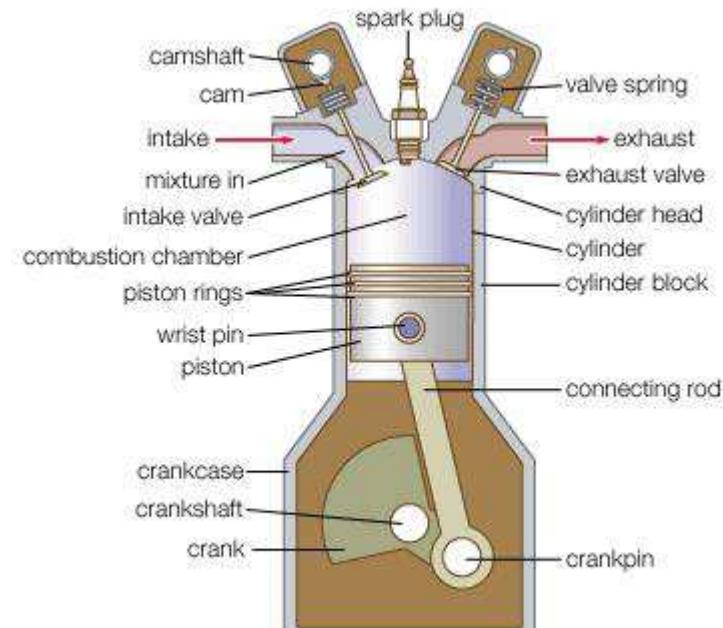
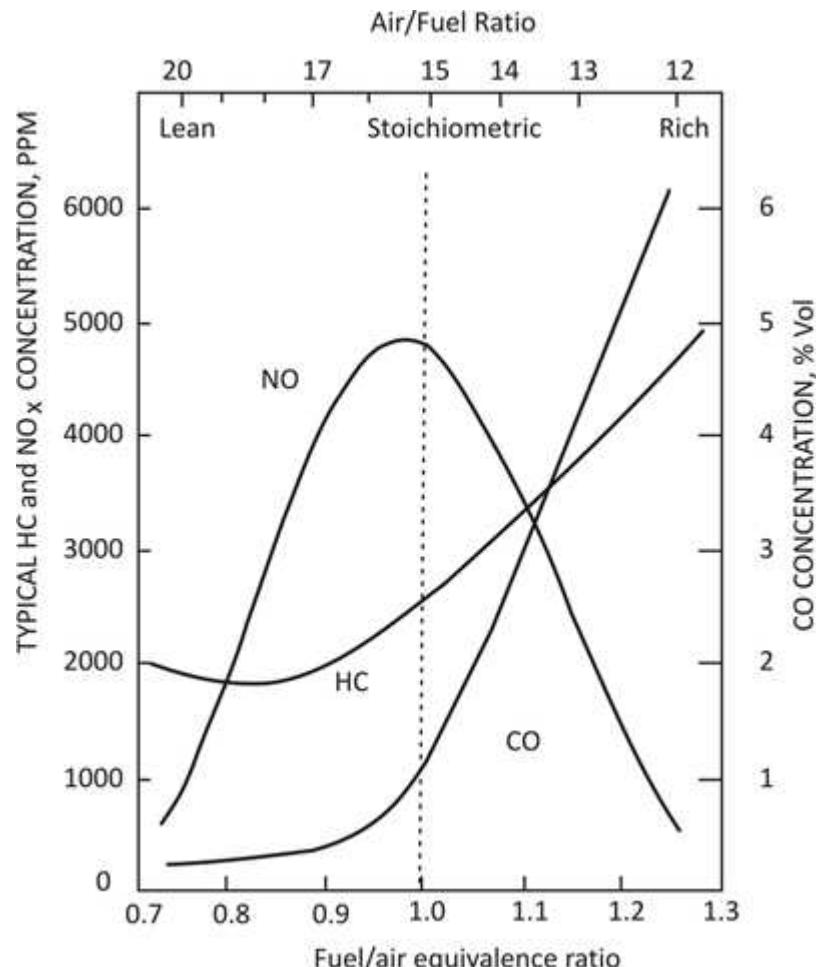
More rpm, less combustion time!!!





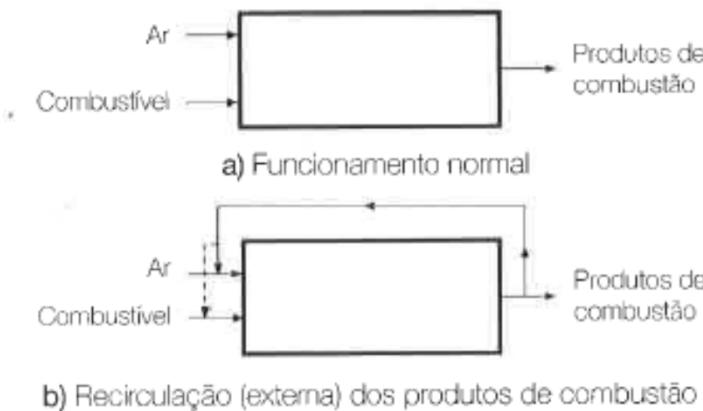
ppm ☺ !!!

Emissions



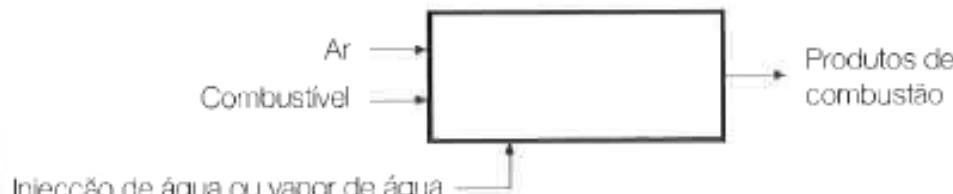
$$\phi = \frac{1}{\lambda}$$

How to control combustion to lower at least NOx emissions?

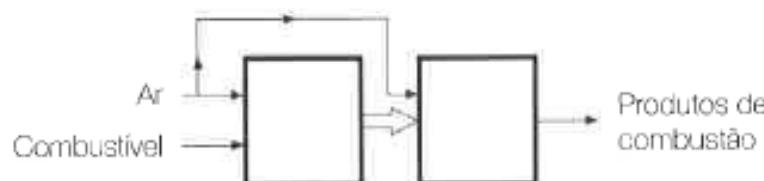


EGR-Exhaust gas recirculation

Water injection

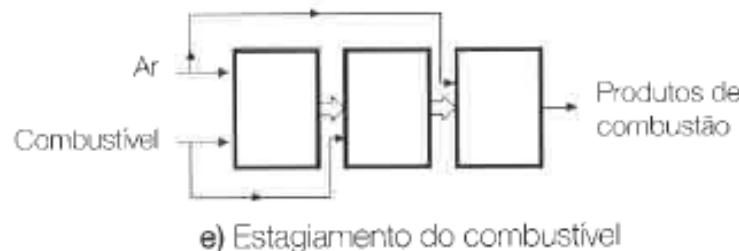


c) Injecção de água ou vapor de água

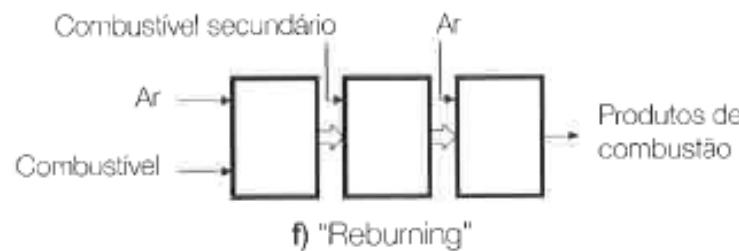


d) Estagiamento do ar de combustão

Air introduction in 2 stages

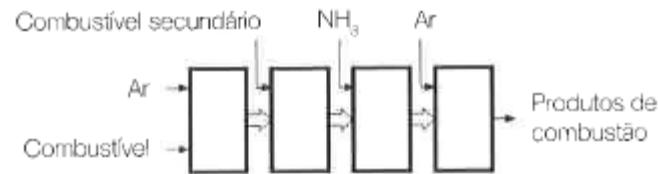


Air introduction in 2 stages
+fuel introduction in 2 stages

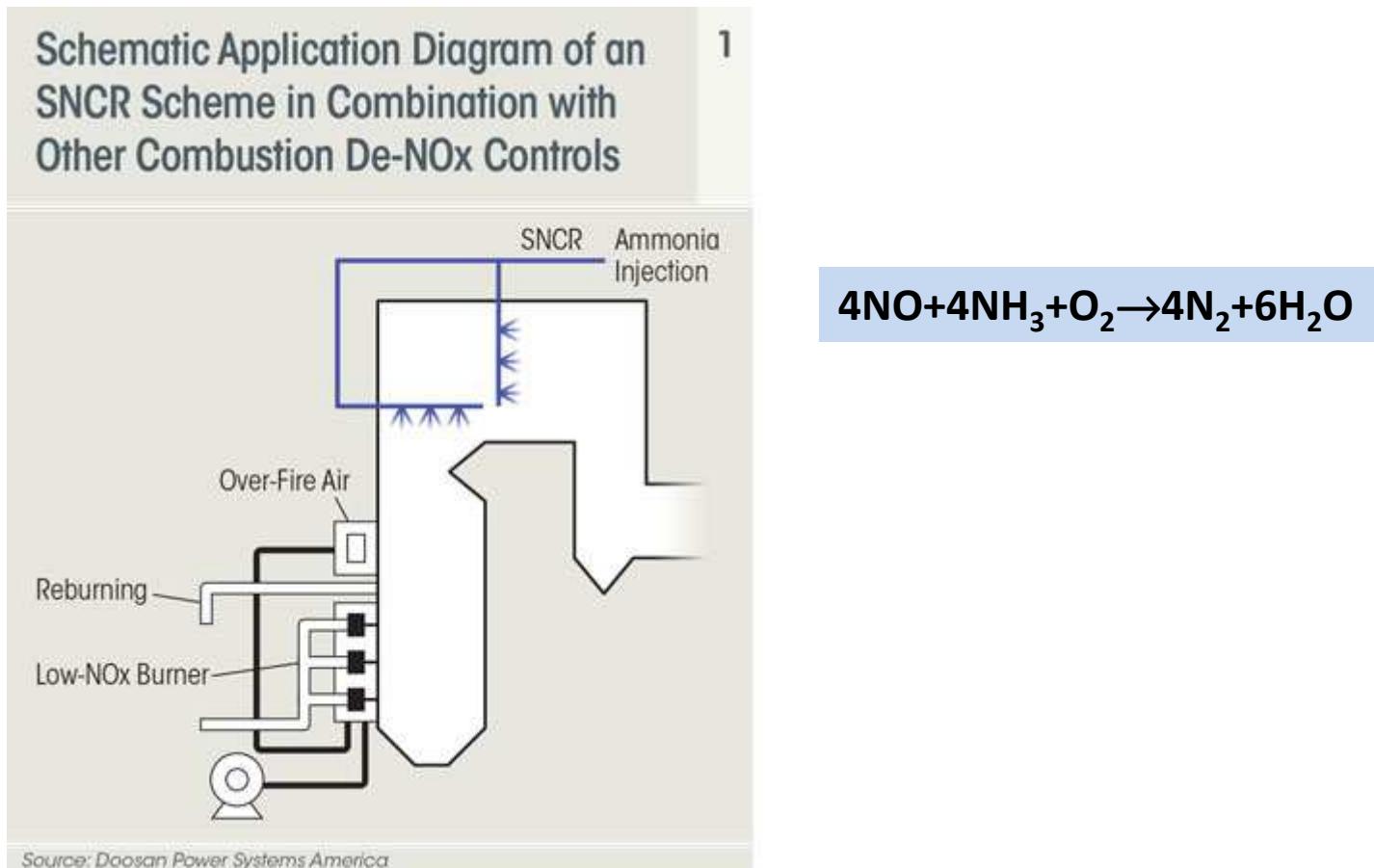


"Reburning"
+Non-catalytic Selective NOx reduction

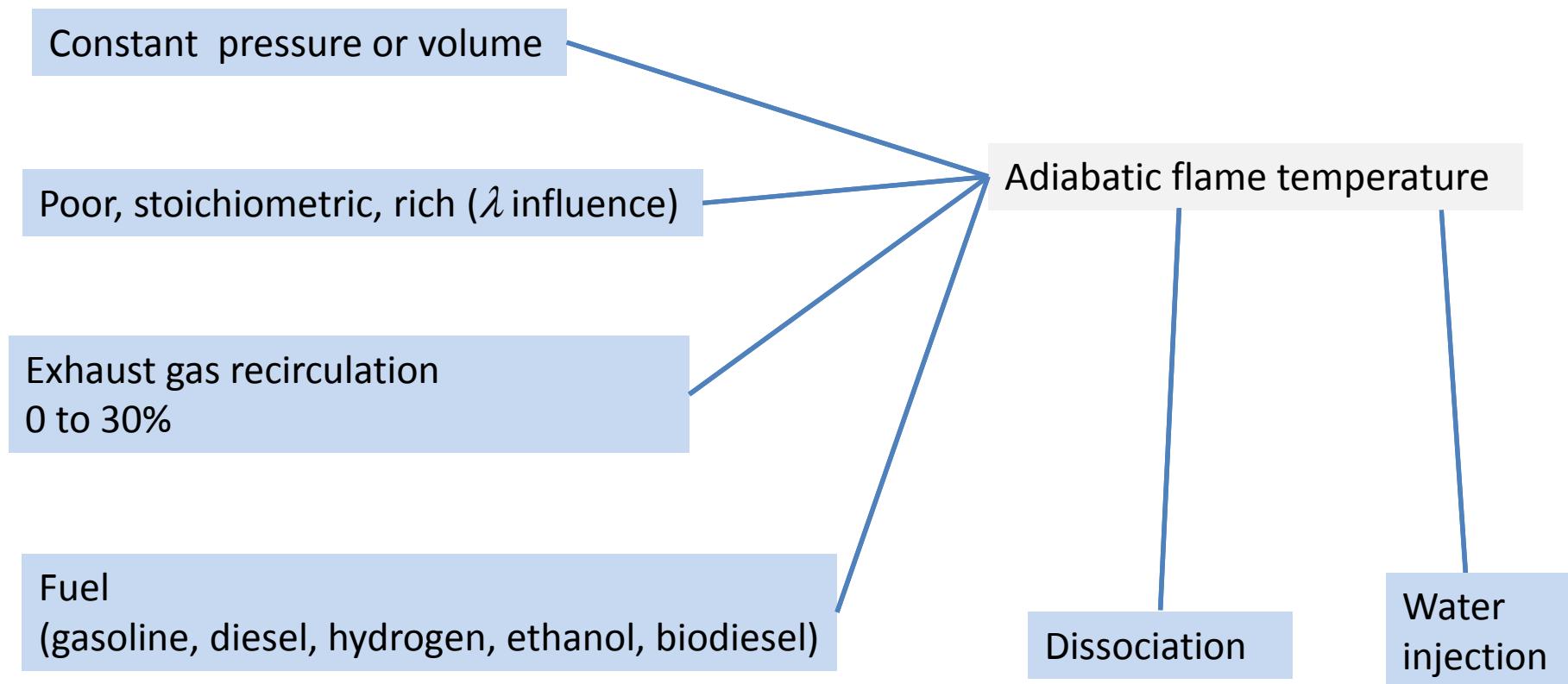
Poor pre-mixtures



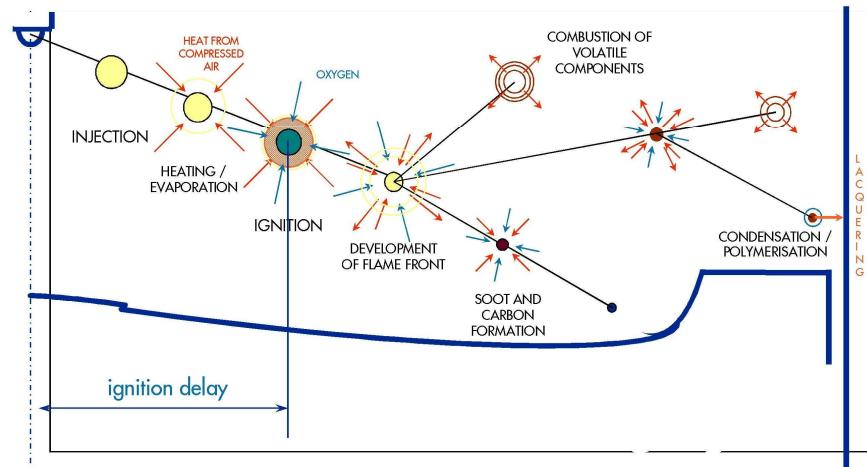
Coal fire power-plants – NOx control- SNCR- Selective non Catalytic Reduction



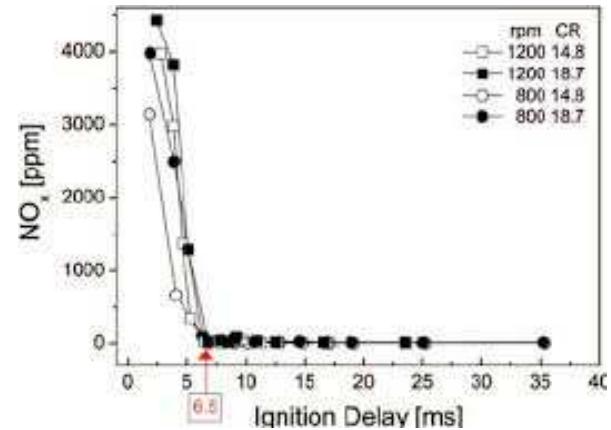
Adiabatic Flame Temperature



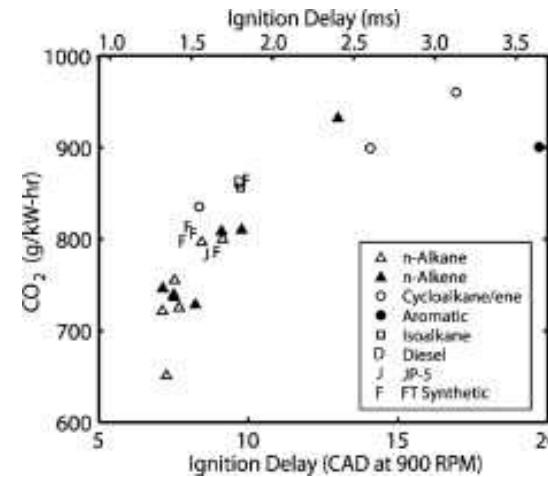
Diesel Combustion Process

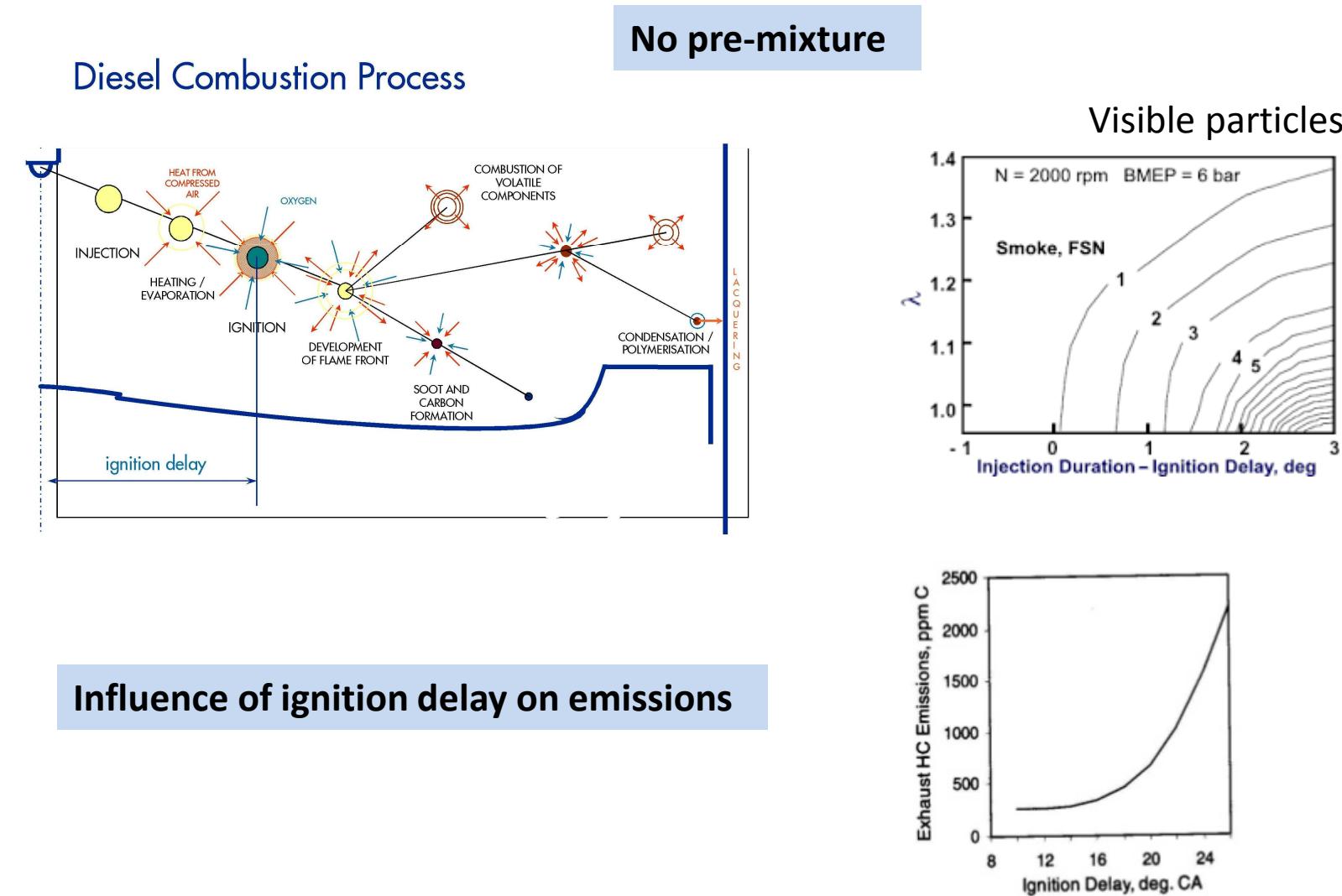


No pre-mixture

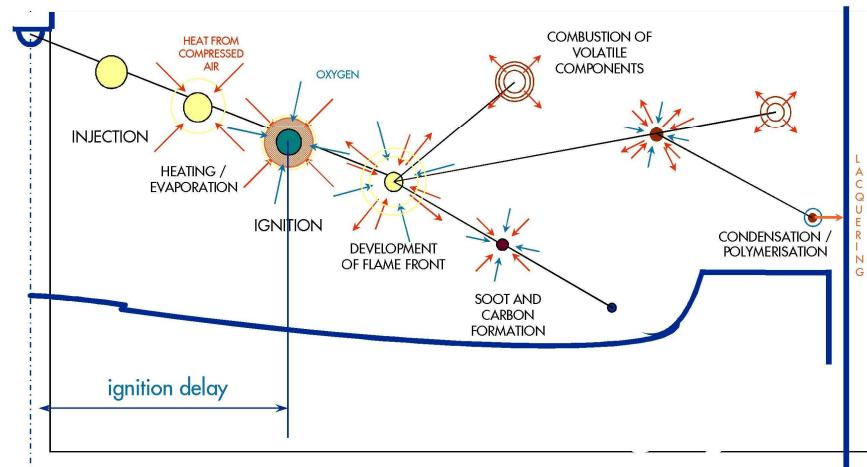


Influence of ignition delay on emissions

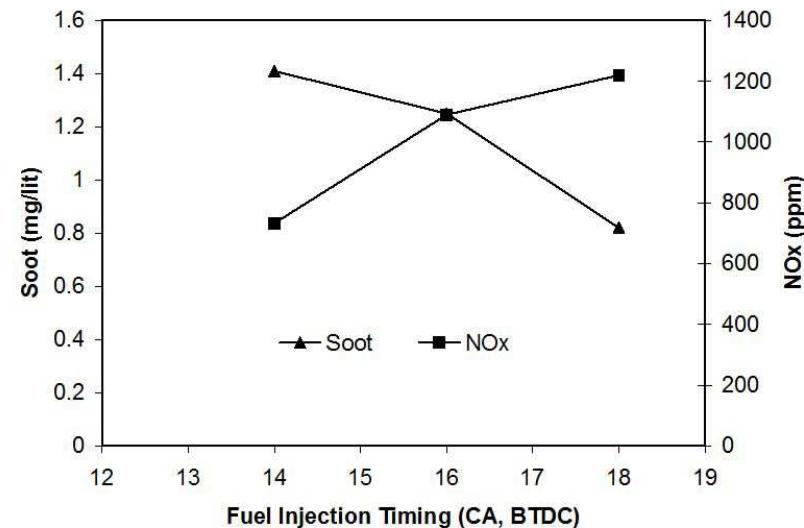




Diesel Combustion Process



No pre-mixture



Influence of ignition delay on emissions

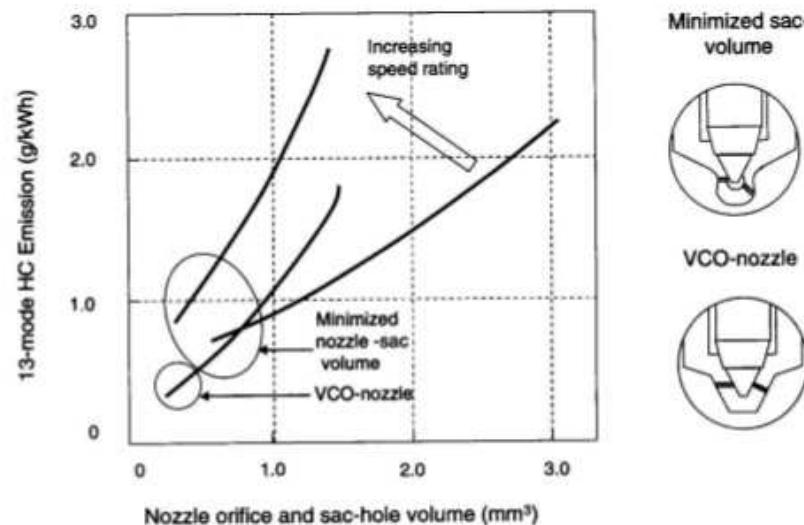
CA-Crank angle (angulos de cambota)

BTDC-Before Top dead centre (antes do ponto morto superior)

Diesel Engine Emissions : formation, effect of variables and their control

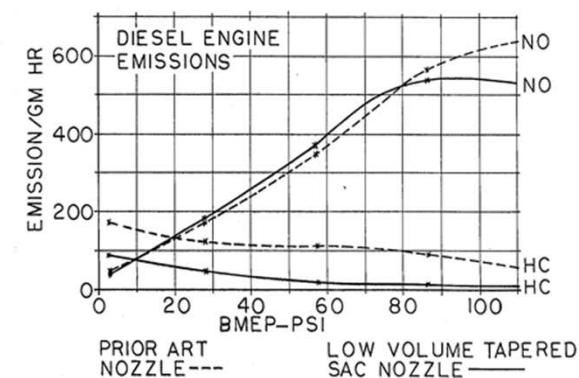
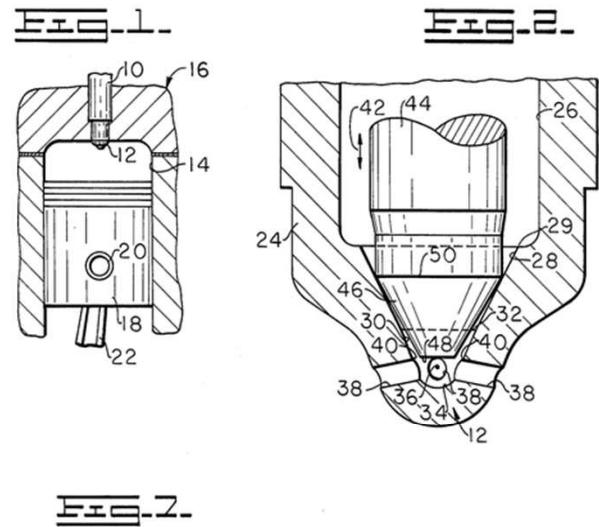
HC emission from CI Engines

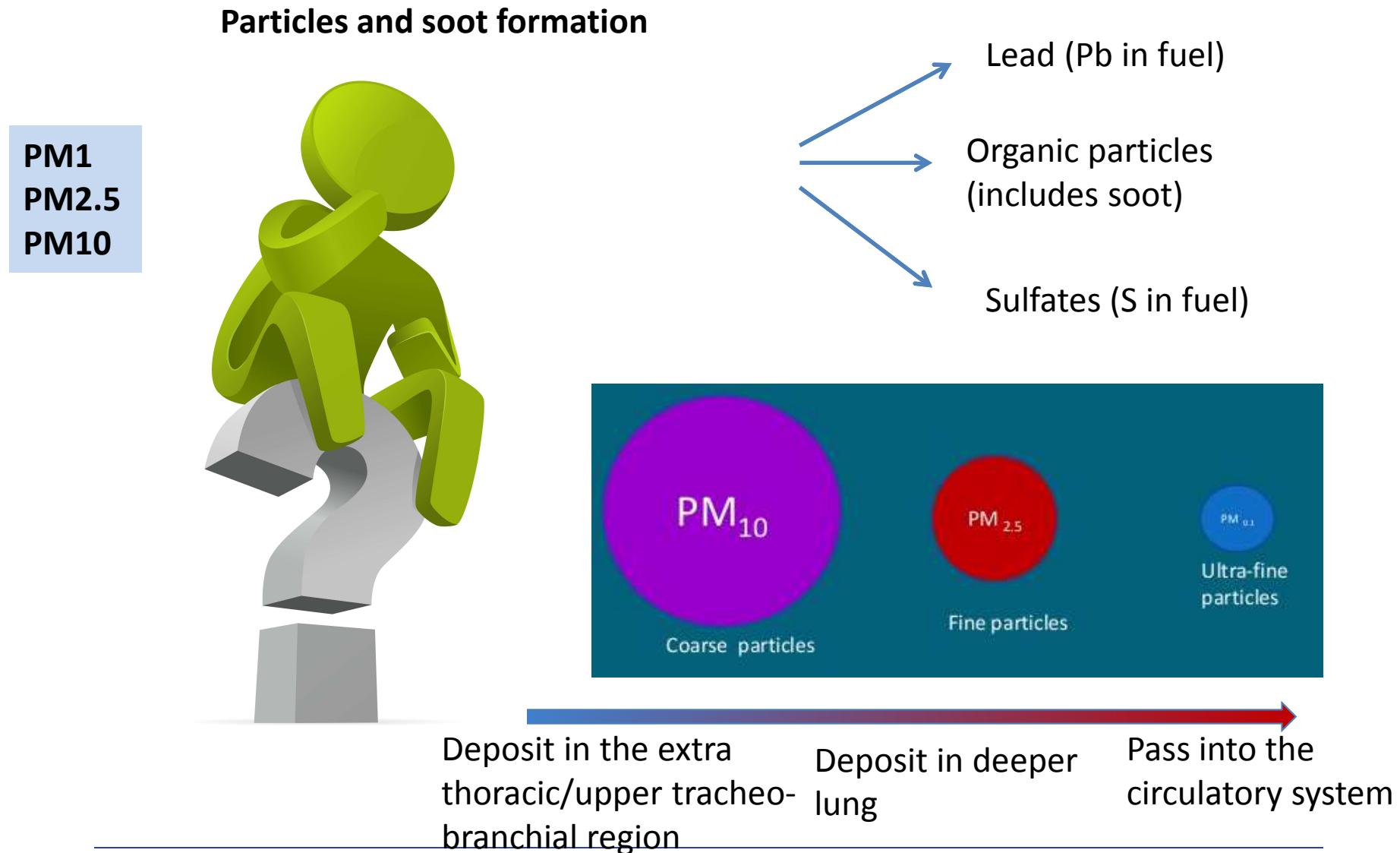
- Effect of nozzle sac volume and hole type



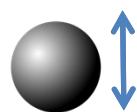
Influence of injector nozzle

U.S. Patent Aug. 15, 1978 Sheet 1 of 2 4,106,702





Organic particles (includes soot- carbonaceous material) H, C, O



15 nm < Spherule diameters < 30 nm



Nucleation mode



Accumulation mode

Solids – dry carbon particles, commonly known as soot,

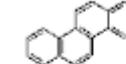
SOF – heavy hydrocarbons adsorbed and condensed on the carbon particles, called Soluble Organic Fraction,

SO₄ – sulfate fraction, hydrated sulfuric acid H₂SO₄.

Polycyclic Aromatic Hydrocarbons



Naphthalene
C₁₀H₈



Chrysene
C₁₈H₁₂



Pyrene
C₁₆H₁₀



Coronene
C₂₄H₁₂



Ovalene
C₃₂H₁₄

SOF-Polynuclear Aromatic Hydrocarbons (PAH) are hydrocarbons containing two or more benzene rings

2012

- Emissões atmosféricas específicas e resíduos radioativos associados à produção de energia

emissões	
CO2 (g/kWh)	279,13
SO2 (g/kWh)	2,56
NOX (g/kWh)	1,04
Resíduos Radioativos ($\mu\text{g}/\text{kWh}$)	18,75



[all in mg/km]

RENAULT Clio 1.2 16V 75	M5 1149	Petrol	CO 269	HC 49	NOx 28
RENAULT Clio 1.5 dCi 88	M5 1461	Diesel	CO 298	HC 23	NOx 155 PM 0.1

low emission zones and the raising of air-quality target



particulate matter (PM)
ozone (O_3)
nitrogen dioxide (NO_2)
sulfur dioxide (SO_2)

Ambient (outdoor air pollution) in both cities and rural areas was estimated to cause **3 million** premature deaths worldwide in 2012

Ambient Air Quality Directive 2008/50/EC

Mean	Limit PM ₁₀ (Particulate Matter)	Limit NO ₂ (Nitrogen Dioxide)
24 h (PM ₁₀) 1 h (NO ₂)	50 µg/m ³ not more than 35 violations /year	200 µg/m ³ not more than 18 violations/year
1 year	40 µg/m ³	40 µg/m ³

PM10 and PM2.5 particulates are easily breathed in (causing lung cancer).

low emission zones and the raising of air-quality target

Avenida da Liberdade

■ Dados da Estação	
Código:	3075
Data de início:	1994-01-01
Tipo de Ambiente:	Urbana
Tipo de Influência:	Tráfego
Zona:	Área Metropolitana de Lisboa Norte (a)
Rua:	Avenida da Liberdade
Freguesia:	Santo António
Concelho:	Lisboa
Coordenadas Gauss Militar (m)	Latitude: 195336 Longitude: 111902
Coordenadas Geográficas WGS84	Latitude: 38°43'13" Longitude: -9°08'45"
Altitude (m):	44
Rede:	Rede de Qualidade do Ar de Lisboa e Vale do Tejo
Instituição:	Comissão de Coordenação e Desenvolvimento Regional de Lisboa e Vale do Tejo
Contacto:	21 0101 300

(a) a zona é uma aglomeração

■ Poluentes

Poluente	Símbolo	Data de Início	Data de Fim
Monóxido de Azoto	NO	1994-01-01	
Dióxido de Azoto	NO ₂	1994-01-01	
Óxidos de Azoto	NO _x	1994-01-01	
Partículas < 10 µm	PM ₁₀	1998-02-01	
Monóxido de Carbono	CO	1994-01-01	



■ Escolha uma outra estação:

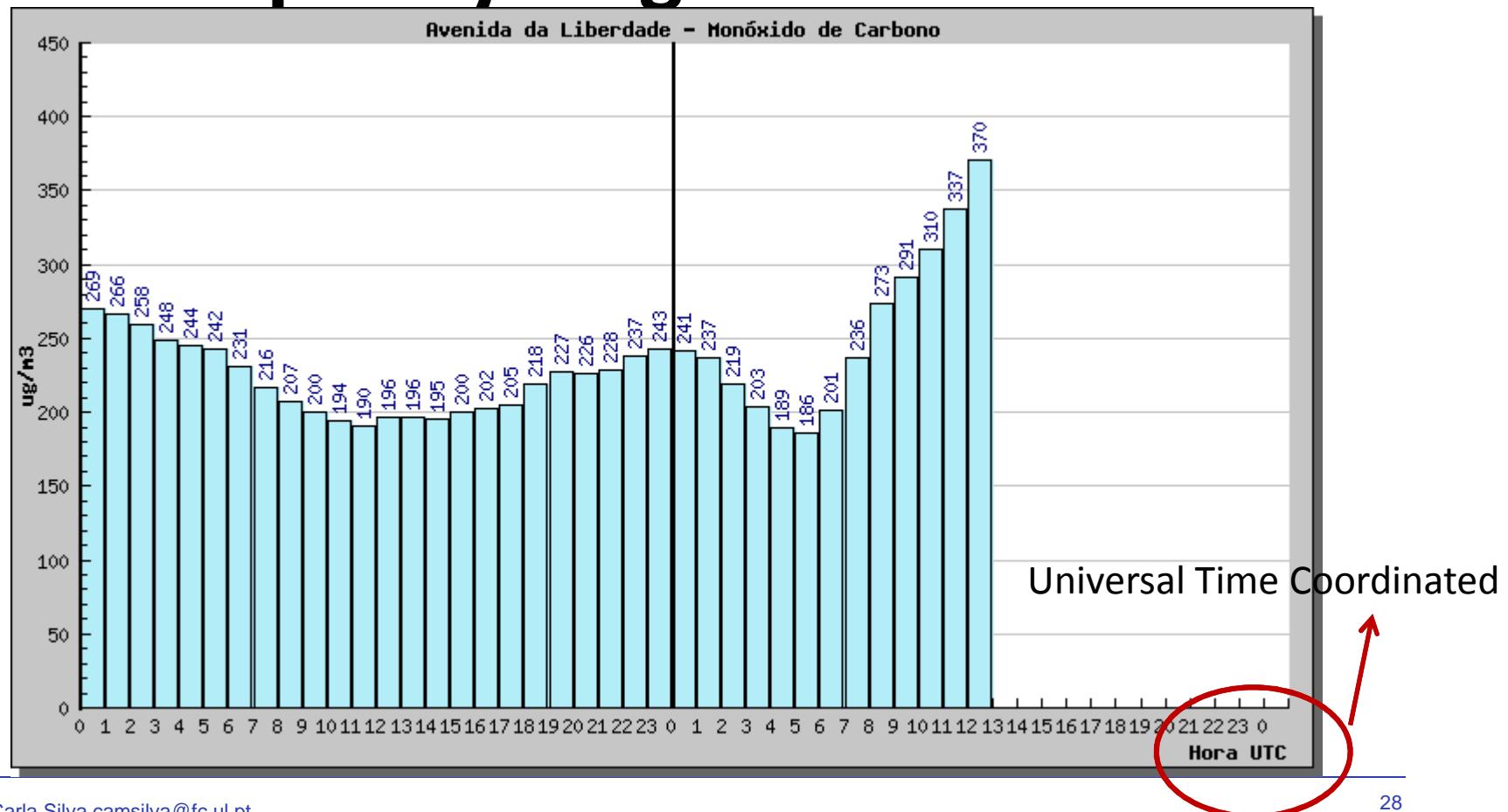
Escolha uma estação ▾ OK >

■ Estatísticas:

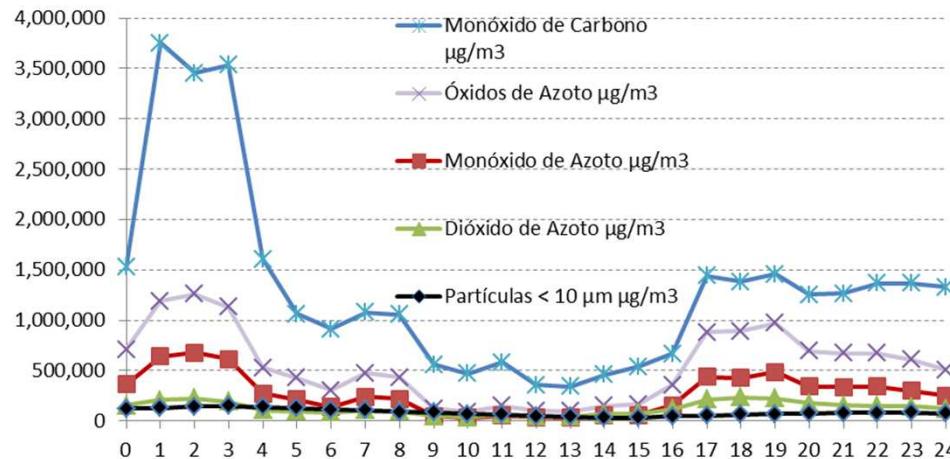
Escolha um poluente ▾

▼ OK >

low emission zones and the raising of air-quality target



Air-quality av. Liberdade



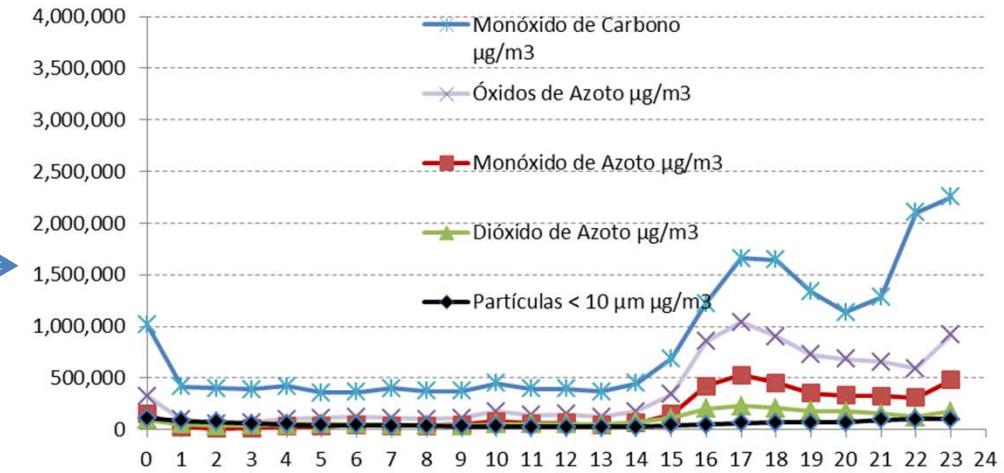
1-1-2015
(Thursday)

QualAr

Base de Dados Online sobre a Qualidade do Ar



3-1-2015
(Saturday)



low emission zones and the raising of air-quality target

Estação	Avenida da Liberdade
Infléncia	Tráfego
Ambiente	Urbana
Poluente	Dióxido de Azoto (NO ₂)
Ano	2015

Dados Estatísticos

Parâmetro	Valor Anual (base horária)	Valor Anual (base diária)
Eficiência (%)	98,7%	98,4%
Dados Validados (n.º)	8.644	359
Média (µg/m ³)	58,6	58,5
Máximo (µg/m ³)	247,3	128,8

Limiar de Alerta

(Decreto-lei n.º 102/2010)

Designação	Valor (µg/m ³)	Nº. de Excedencias
Limiar de Alerta (medido em três horas consecutivas)	400	0

Protecção da Saúde Humana: Base Horária

(Decreto-lei n.º 102/2010)

Designação	Valor (µg/m ³)	Excedências Permitidas (horas)	N.º Excedências (horas)
VL	200	18	20

Legenda:

VL - Valor limite: 200 µg/m³.

Protecção da Saúde Humana: Base Anual

(Decreto-lei n.º 102/2010)

Designação	Valor (µg/m ³)	Valor Obtido (µg/m ³)
VL	40	58,6

low emission zones and the raising of air-quality target

■ Critérios

Estação:	Avenida da Liberdade
Poluente:	Partículas < 10 µm (PM10)
Ano:	2015

■ Dados Estatísticos

Parâmetro:	Valor Anual (base horária)	Valor Anual (base diária)
Eficiência (%)	94,3%	93,7%
Dados Validados (n.º)	8.263	342
Média (µg/m³):	36,0	36,0
Máximo (µg/m³):	219,5	118,9

■ Protecção da Saúde Humana: Base Diária
(Decreto-lei n.º 102/2010)

Designação:	Valor (µg/m³)	Excedências Permitidas (dias)	N.º Excedências (dias)
VL	50	35	<u>66</u>

Legenda:
VL - Valor limite: 50 µg/m3.

■ Protecção da Saúde Humana: Base Anual
(Decreto-lei n.º 102/2010)

Designação:	Valor (µg/m³)	Valor obtido (µg/m³)
VL	40	36,0

Legenda:
VL - Valor limite: 40 µg/m3.



Stationary combustion
(limits in mg/m³)



Mobile combustion
(limits in g/km)

EN

Official Journal of the European Communities

L 309/17

ANNEX VII

EMISSION LIMIT VALUES FOR DUST

- A. Dust emission limit values expressed in mg/Nm³ (O₂ content 6 % for solid fuels, 3 % for liquid and gaseous fuels) to be applied by new and existing plants pursuant to Article 4(1) and 4(3), respectively:

Type of fuel	Rated thermal input (MW)	Emission limit values (mg/Nm ³)
Solid	≥ 500	50 ⁽²⁾
	< 500	100
Liquid ⁽¹⁾	all plants	50
Gaseous	all plants	5 as a rule 10 for blast furnace gas 50 for gases produced by the steel industry which can be used elsewhere

(1) A limit value of 100 mg/Nm³ may be applied to plants with a rated thermal input of less than 500 MWth burning liquid fuel with an ash content of more than 0.06 %.

(2) A limit value of 100 mg/Nm³ may be applied to plants licensed pursuant to Article 4(3) with a rated thermal input greater than or equal to 500 MWth burning solid fuel with a heat content of less than 5 800 kJ/kg (net calorific value), a moisture content greater than 45 % by weight, a combined moisture and ash content greater than 60 % by weight and a calcium oxide content greater than 10 %.

- B. Dust emission limit values expressed in mg/Nm³ to be applied by new plants, pursuant to Article 4(2) with the exception of gas turbines:

 Solid fuels (O₂ content 6 %)

50 to 100 MWth	> 100 MWth
50	30


 mg/Nm³

- A. NO_x emission limit values expressed in mg/Nm³ (O₂ content 6 % for solid fuels, 3 % for liquid and gaseous fuels) to be applied by new and existing plants pursuant to Article 4(1) and 4(3), respectively:

Type of fuel:	Limit values ⁽¹⁾ (mg/Nm ³)
Solid ⁽²⁾ , ⁽³⁾ :	
50 to 500 MWth:	600
>500 MWth:	500
From 1 January 2016	
50 to 500 MWth:	600
>500 MWth:	200
Liquid:	
50 to 500 MWth:	450
>500 MWth:	400
Gaseous:	
50 to 500 MWth:	300
>500 MWth:	200

mg/Nm³

N=normal /standard pressure and temperature

$$\text{Conversion NO/NO}_2 \\ = (14+16)/(14+32) \sim 1.53$$

⁽¹⁾ Except in the case of the 'Outermost Regions' where the following values shall apply:

Solid in general: 650

Solid with < 10 % vol comps: 1 300

Liquid: 450

Gaseous: 350

⁽²⁾ Until 31 December 2015 plants of a rated thermal input greater than 500 MW, which from 2008 onwards do not operate more than 2 000 hours a year (rolling average over a period of five years), shall:

- in the case of plant licensed in accordance with Article 4(3)(a), be subject to a limit value for nitrogen oxide emissions (measured as NO_x) of 600 mg/Nm³;
- in the case of plant subject to a national plan under Article 4(6), have their contribution to the national plan assessed on the basis of a limit value of 600 mg/Nm³.

From 1 January 2016 such plants, which do not operate more than 1 500 hours a year (rolling average over a period of five years), shall be subject to a limit value for nitrogen oxide emissions (measured as NO_x) of 450 mg/Nm³.

⁽³⁾ Until 1 January 2018 in the case of plants that in the 12 month period ending on 1 January 2001 operated on, and continue to operate on, solid fuels whose volatile content is less than 10 %, 1 200 mg/Nm³ shall apply.

- A. NO_x emission limit values expressed in mg/Nm³ (O₂ content 6 % for solid fuels, 3 % for liquid and gaseous fuels) to be applied by new and existing plants pursuant to Article 4(1) and 4(3), respectively:

Type of fuel:	Limit values ⁽¹⁾ (mg/Nm ³)
Solid ^{(2), (3)} :	
50 to 500 MWth:	600
>500 MWth:	500
From 1 January 2016	
50 to 500 MWth:	600
>500 MWth:	200
Liquid:	
50 to 500 MWth:	450
>500 MWth:	400
Gaseous:	
50 to 500 MWth:	300
>500 MWth:	200

(¹) Except in the case of the 'Outermost Regions' where the following values shall apply:

Solid in general: 650

Solid with < 10 % vol comp: 1 300

Liquid: 450

Gaseous: 350

(²) Until 31 December 2015 plants of a rated thermal input greater than 500 MW, which from 2008 onwards do not operate more than 2 000 hours a year (rolling average over a period of five years), shall:

- in the case of plant licensed in accordance with Article 4(3)(a), be subject to a limit value for nitrogen oxide emissions (measured as NO_x) of 600 mg/Nm³;

- In the case of plant subject to a national plan under Article 4(6), have their contribution to the national plan assessed on the basis of a limit value of 600 mg/Nm³.

From 1 January 2016 such plants, which do not operate more than 1 500 hours a year (rolling average over a period of five years), shall be subject to a limit value for nitrogen oxide emissions (measured as NO_x) of 450 mg/Nm³.

(³) Until 1 January 2018 in the case of plants that in the 12 month period ending on 1 January 2001 operated on, and continue to operate on, solid fuels whose volatile content is less than 10 %, 1 200 mg/Nm³ shall apply.

NO_x@6%O₂

Convert for the same %O₂:

$$xi_{6\%} = xi * \frac{n}{n_{6\%}}$$

Fuel CxHy

$$n_{xO2} = 4.76 * \left[\frac{x + (1+xO2)\frac{y}{4}}{1 - 4.76xO2} \right] + \frac{y}{4} \quad (\text{wet})$$

$$n_{xO2} = 4.76 * \left[\frac{x + (1-xO2)\frac{y}{4}}{1 - 4.76xO2} \right] - \frac{y}{4} \quad (\text{dry})$$

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EMISSION LIMIT VALUES FOR DUST

- A. Dust emission limit values expressed in mg/Nm³ (O₂ content 6 % for solid fuels, 3 % for liquid and gaseous fuels) to be applied by new and existing plants pursuant to Article 4(1) and 4(3), respectively:

Type of fuel	Rated thermal input (MW)	Emission limit values (mg/Nm ³)
Solid	≥ 500 < 500	50 ⁽²⁾ 100
Liquid ⁽¹⁾	all plants	50
Gaseous	all plants	5 as a rule 10 for blast furnace gas 50 for gases produced by the steel industry which can be used elsewhere

(1) A limit value of 100 mg/Nm³ may be applied to plants with a rated thermal input of less than 500 MWth burning liquid fuel with an ash content of more than 0.06 %.

(2) A limit value of 100 mg/Nm³ may be applied to plants licensed pursuant to Article 4(3) with a rated thermal input greater than or equal to 500 MWth burning solid fuel with a heat content of less than 5 800 kJ/kg (net calorific value), a moisture content greater than 45 % by weight, a combined moisture and ash content greater than 60 % by weight and a calcium oxide content greater than 10 %.

- B. Dust emission limit values expressed in mg/Nm³ to be applied by new plants, pursuant to Article 4(2) with the exception of gas turbines:

 Solid fuels (O₂ content 6 %)

50 to 100 MWth	> 100 MWth
50	30

 NO₂@6%O₂

 Convert kmol/kmol in mg/Nm³

$$X = \text{fraction} = \frac{n_{NO}}{n_{Total}} * M_{NO} * \frac{1}{V_{Total}} * 10^3$$

$$X = \text{mg/m3} = \frac{\text{kmol}}{\text{kmol}} * \frac{\text{kg}}{\text{kmol}} * \frac{1}{\text{m3}} * \frac{10^3}{\text{kmol}}$$

$$\begin{aligned} \frac{V}{n} &= \frac{RT}{p} = \frac{8.314 \frac{kJ}{kmol} * 298K}{100 kPa} = \\ &\frac{8.314 \frac{kJ}{kmol} * 298K}{100 kNm/m3} = 24.8 m3/kmol \end{aligned}$$

Table 1

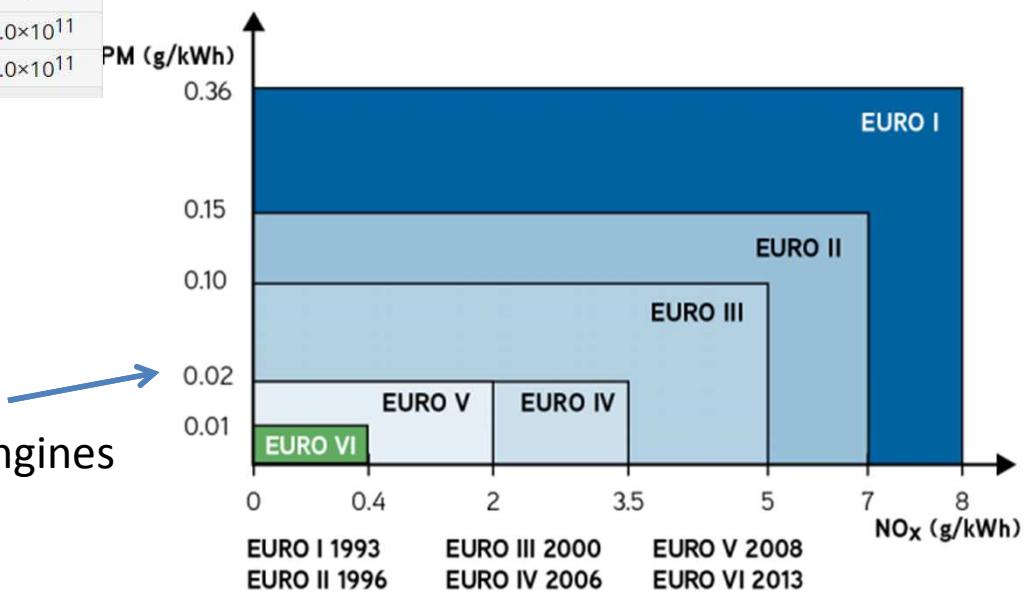
 EU Emission Standards for Passenger Cars (Category M₁*)

Stage	Date	CO	HC	HC+NOx	NOx	PM	PN
		g/km					#/km
Compression Ignition (Diesel)							
Euro 1†	1992.07	2.72 (3.16)	-	0.97 (1.13)	-	0.14 (0.18)	-
Euro 2, IDI	1996.01	1.0	-	0.7	-	0.08	-
Euro 2, DI	1996.01 ^a	1.0	-	0.9	-	0.10	-
Euro 3	2000.01	0.64	-	0.56	0.50	0.05	-
Euro 4	2005.01	0.50	-	0.30	0.25	0.025	-
Euro 5a	2009.09 ^b	0.50	-	0.23	0.18	0.005 ^f	-
Euro 5b	2011.09 ^c	0.50	-	0.23	0.18	0.005 ^f	6.0×10^{11}
Euro 6	2014.09	0.50	-	0.17	0.08	0.005 ^f	6.0×10^{11}

Passenger cars



Truck/bus engines



low emission zones and the raising of air-quality target

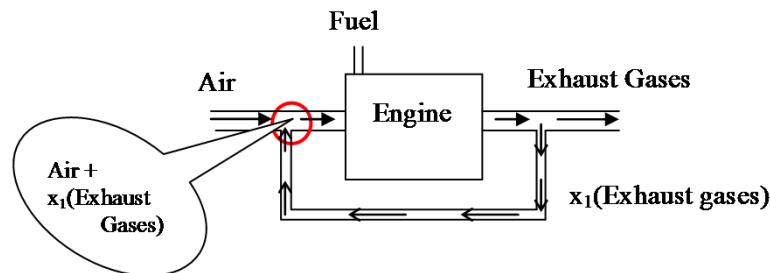
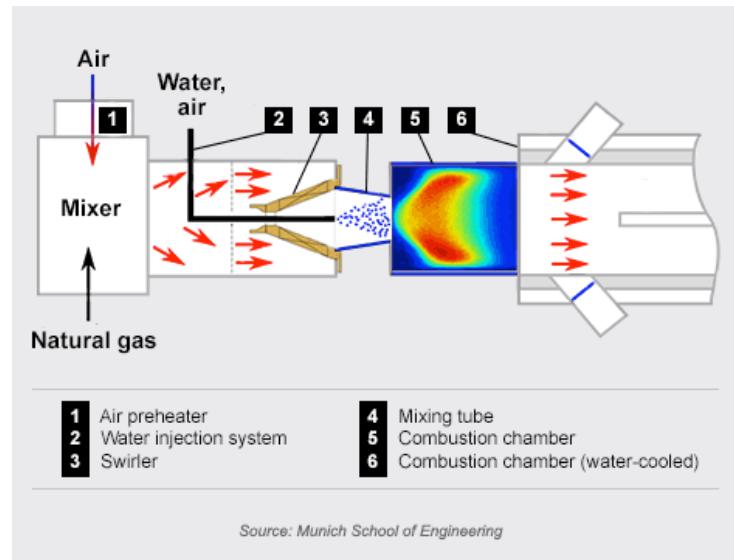
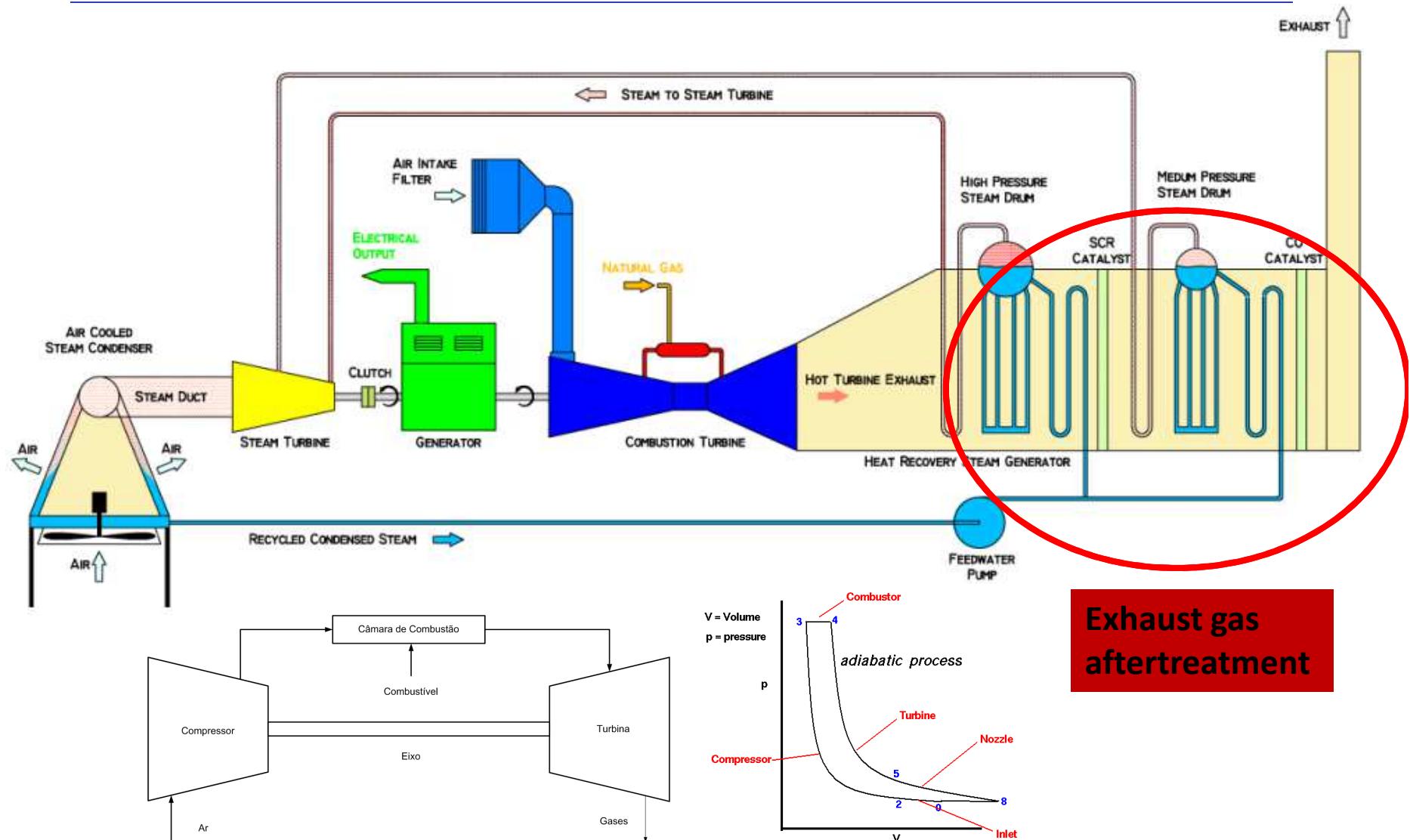


Figure 2: Exhaust Gas Re-circulation

Combustion alteration not enough!!!!!!



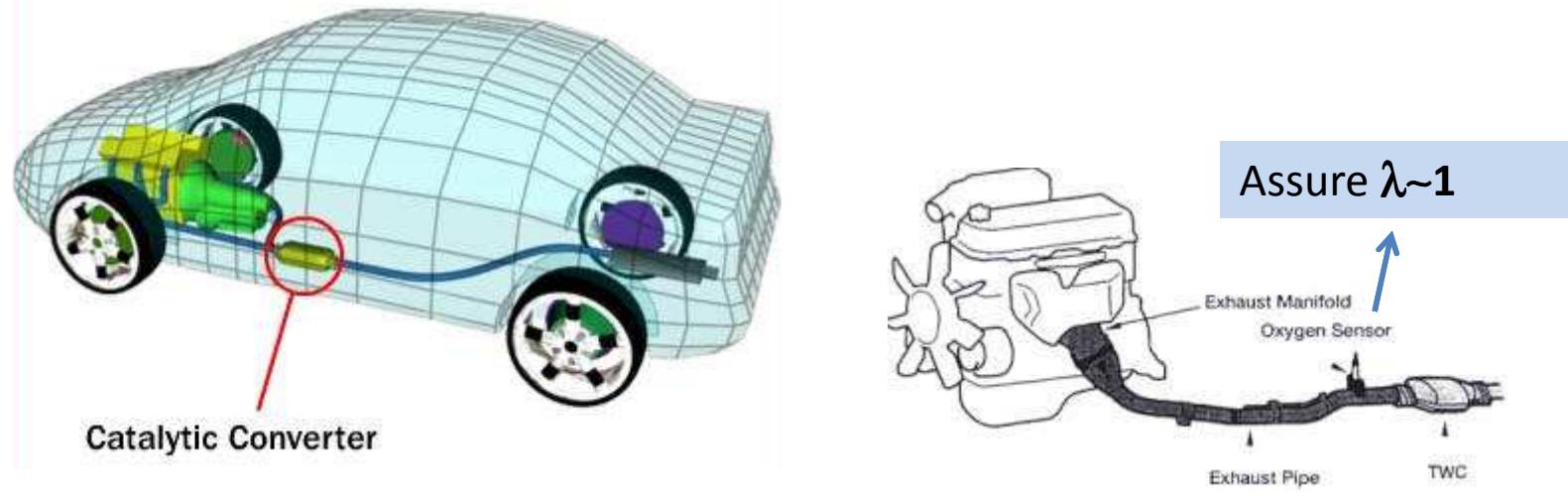


low emission zones and the raising of air-quality target



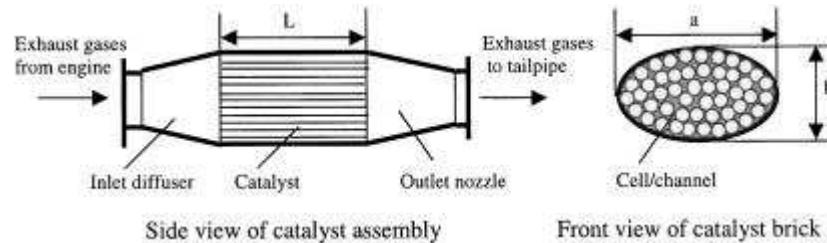
Exhaust gas
aftertreatment

Exhaust gas aftertreatment gasoline

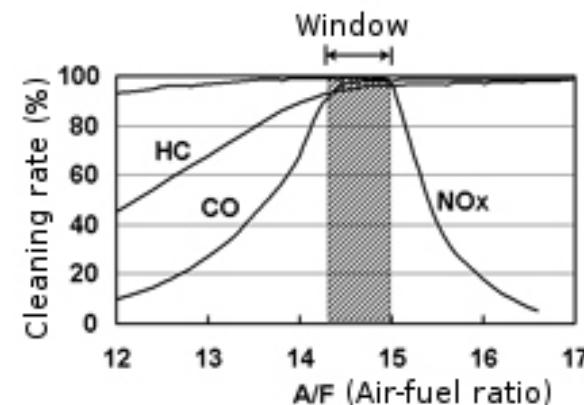


Gasoline engines (spark-ignition) → TWC-Three Way catalytic converter

Exhaust gas aftertreatment



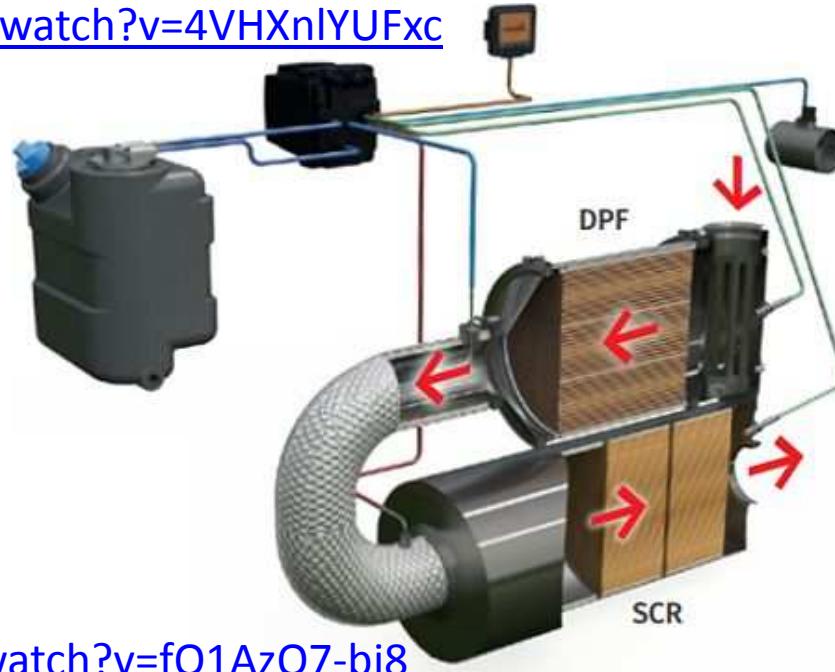
Cleaning rate or catalytic converter efficiency,
e.g.,



$$\frac{NOx_{in} - NOx_{out}}{NOx_{in}} \times 100\%$$

Exhaust gas aftertreatment Diesel

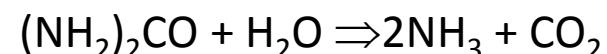
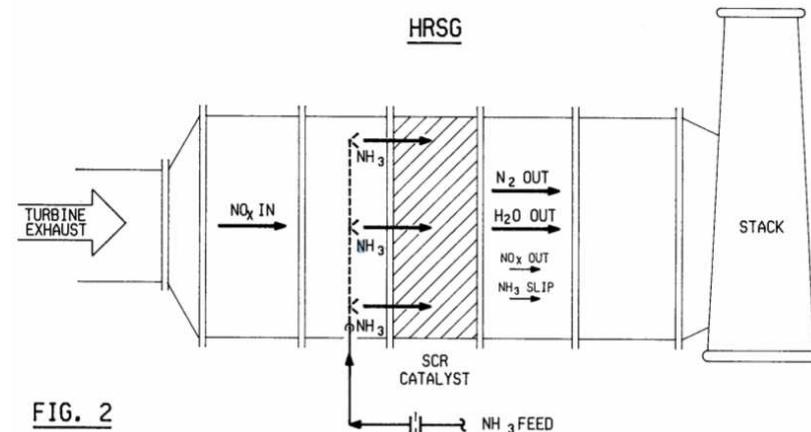
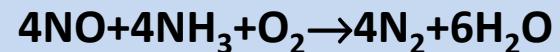
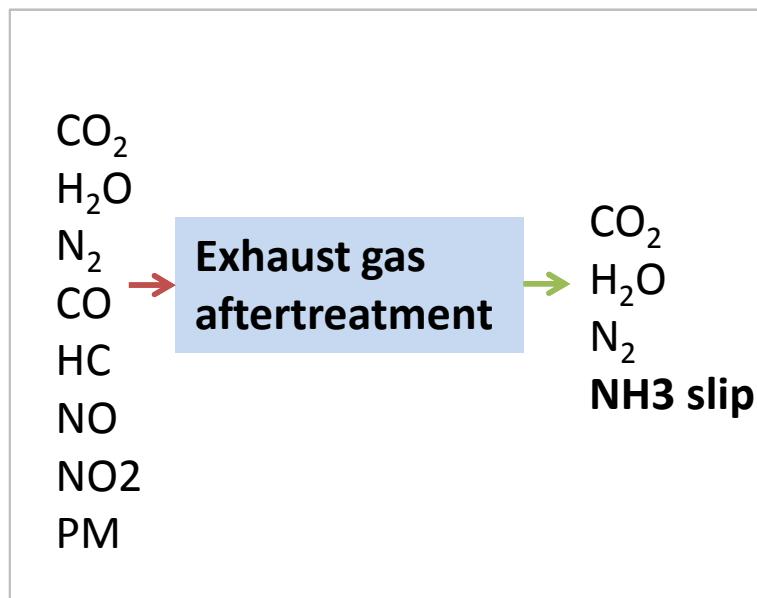
<https://www.youtube.com/watch?v=4VHXnIYUFxc>



<https://www.youtube.com/watch?v=fO1AzO7-bj8>

Rudolf Diesel engines (compression-ignition) → Oxidation catalyst
Particle filter
Selective catalytic reduction

Exhaust gas aftertreatment (with SCR)



Urea solution (~ 5% fuel consumption)
 Urea 32.5% wt ($\pm 0.7\%$), density of 1.09 g/cm³

Exhaust gas aftertreatment (with SCR)



Central Coal Sines >= 2011

P#11 Consider the molar composition (kmol) of flue gas of a coal furnace with a coal consumption of 90 tonne/h. (power plant with installed power > 500 MW).

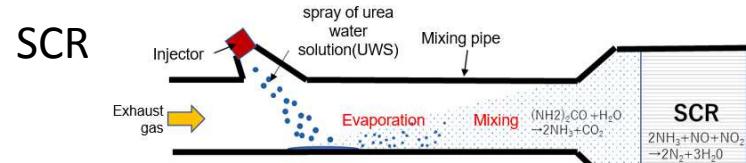
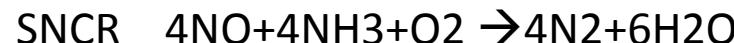
$$\text{CO}_2 = 0.052769348$$

$$\text{H}_2\text{O} = 0.028669893$$

$$\text{N}_2 = 0.271015989$$

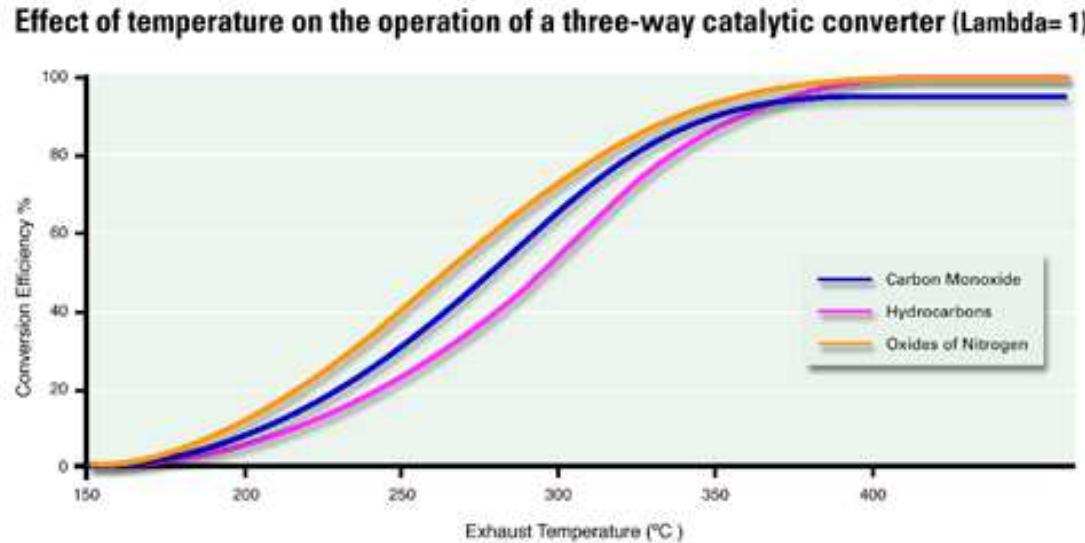
$$\text{NO} = 8.20116 \times 10^{-5}$$

$$\text{O}_2 = 0.015955756$$



- Calculate the NO emissions and compare with the limit value imposed by legislation.
- If you use SNCR (selective non catalytic reduction, 80% conversion efficiency), how much NH₃ would you add, and what would be your new NO emissions? Compare with the limit.
- If you use SCR (selective catalytic reduction, 80% conversion efficiency), how much urea would you add, and what would be your new NO emissions? Compare with the limit.
- Discuss on weather to use SNCR or SCR.

P#12 A mixture of methane gas and air at 25°C and 1 atm is burned in a water heater at 100% theoretical air. The mass flow rate of methane is 1.15 kg/h. The exhaust gas temperature was measured to be 500 °C and approximately 1 atm and is subjected to exhaust aftertreatment. The volumetric flow rate of cold water (at 22 °C) to the heater is 4 L/min.



- (a) Determine the combustion efficiency.
- (b) Calculate the temperature of the hot water if the heat exchanger were to have an efficiency of 1.0, i.e., perfect heat transfer.
- (c) Consider the following concentrations of emissions at the combustion products:
5000 ppm NO. Estimate the NO exhaust gas emissions in g/h.

Table: Air pollutant emission standards for coal-fired power plants in China, European Union and the United States (mg/m^3)

		China	EU	US
SO ₂	New	100	200	160
	Existing	200/400 ¹	400	160/640 ³
NOx	New	100	500/200 ²	117
	Existing	100/200 ⁴	500/200 ²	117/160/640 ⁵
PM	New & existing	30	50	22.5
Mercury	New	0.03	-	0.001
	Existing	0.03	-	0.002

1) 400 for four provinces with high-sulphur coal

2) 500 until end 2015; 200 as from 2016

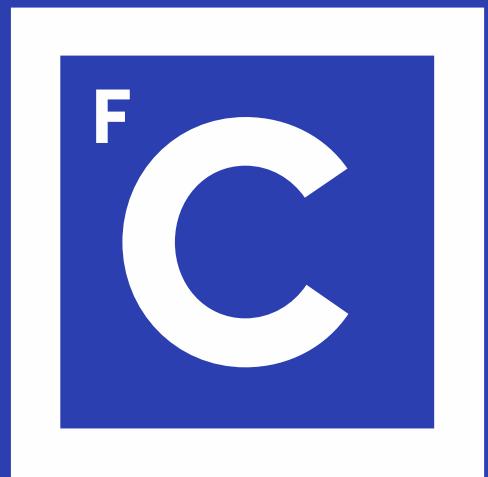
3) 160 for plants built 1997-2005; 640 for plants built 1978-1996

4) 100 for plants built 2004-2011; 200 for plants built before 2004

5) 117 for plants built after 2005; 160 for plants built 1997-2005; 640 for plants built 1978-1996

Source: WRI (2012)

Obrigado



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