Methods of pollution control and waste management

Lecture 7

The Earth's atmosphere and air pollution

Part 3

Nitrogen oxides: pollution prevention and control

- Adversely affect human health
- Precursors to ozone formation
- Contribute to acid deposition which damages vegetation and aquatic ecosystems
- Photochemical smog formation

Specific sources of NO_x

Typically 95% NO/5% NO_2

Stationary sources

- Electric Power Plants (20%)
- Nitric acid manufacturing plants
- Munufactures of nitrated materials

(fertilizer, explosives)

- Glass manufactures
- Cement manufacturers

Mobile sources: automobiles (50%)

Control of Nitrogen oxides emission

Nitrogen oxides are produced in the combustion processes by two mechanisms:

a) burning the nitrogen in the fuel - fuel NO_x (coal or heavy oil)

b) high-temperature oxidation of the molecular nitrogen in the air used for combustion – thermal NO_x

NO_x production is favored by high temperature and high excess oxygen concentrations. These factors must be considered in reducing NO_x emissions from stationary sources.

Control of Nitrogen oxides emission

- Alter combustion conditions to emit less NOx
  - Reduce peak temperatures of the flame zone
  - Reduce gas residence time in the flame zone
  - Reduce O_2 concentrations in the flame zone
- Treat the flue gas
  - Catalytic reduction
- **Choice of Fuel** – coals and residual fuel oils containing organically bound nitrogen contribute to over 50% of total emissions of NO_x (coal 0.5 – 2%, fuel oil 0.1- 0.5%). Natural gas used as a fuel can emit 60% less NO_x than coal.

Control of Nitrogen Oxides Emission

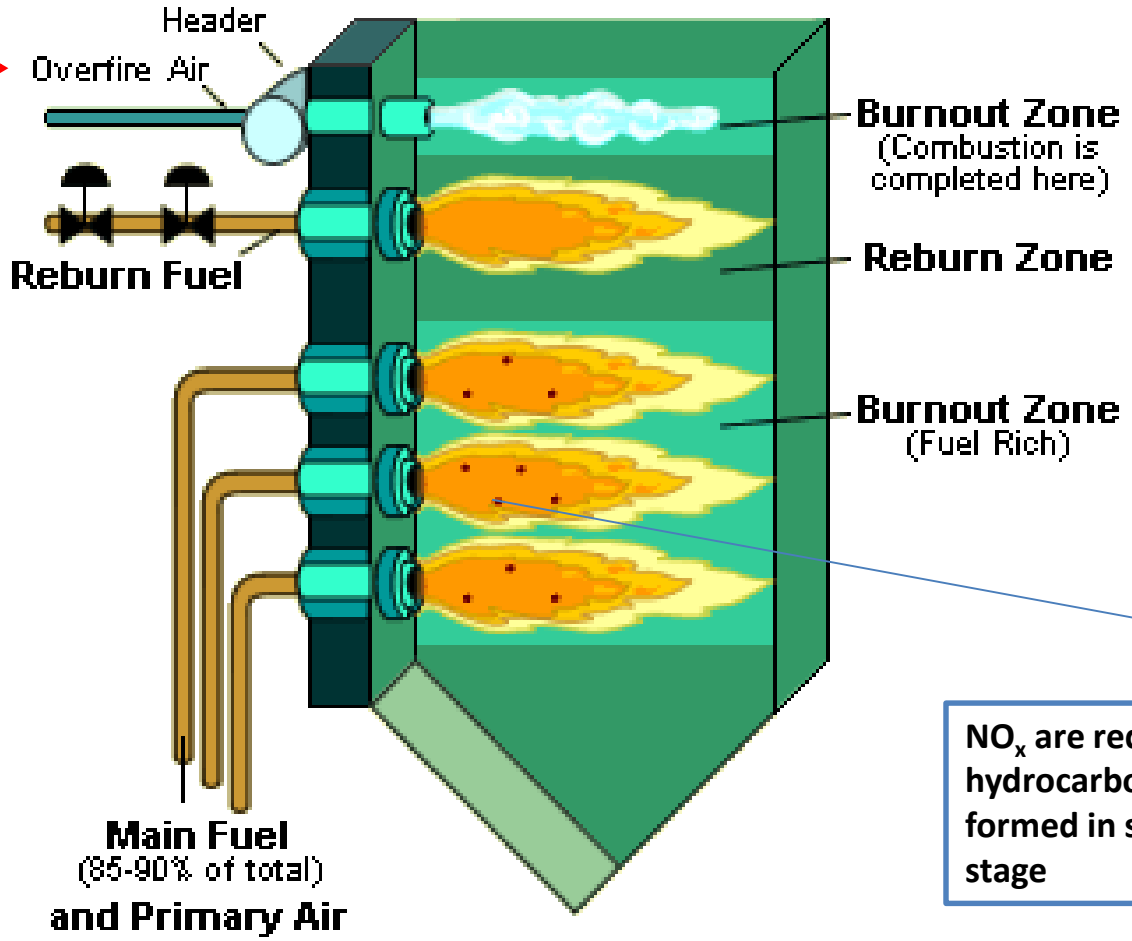
- **New low-NO_x burners** (limit the formation of nitrogen oxides by controlling the mixing of fuel and air) reduce emissions of NO_x by 40-60%.

- **Reburning (cyclone furnaces) staged combustion**

  75-80% of the furnace fuel input is burned in the furnace with minimum excess air. The remaining fuel is added to the furnace above the primary combustion zone. The secondary combustion is operated to generate hydrocarbon radicals that reduce to nitrogen the nitrogen oxides that are formed.

3 Stage combustion
OFA furnace

The relatively low-temperature secondary-stage limits the production of thermal NOx



NO_x

NO_x are reduced by hydrocarbon radicals formed in secondary stage

Control of Nitrogen Oxides

- **Flue gas recirculation** – rerouting of some of the flue gases back to the furnace (furnace air temperature and oxygen concentration can be reduced)

- **Low excess air firing –** the **minimum** amount of **excess air** (but incomplete fuel burnout is connected with emission of hydrocarbons, soot and CO)

- **Water or steam injection** – reduces flame temperature and thus thermal NO_x

Table 1. NO_x Removal Efficiencies for Combustion Modifications and Flue Gas Treatment
(percentage reduction in NO_x)

NO_x reduction technique	*Coal*	*Oil*	*Gas*
Combustion modification			
Low-excess-air firing	10–30	10–30	10–30
Staged combustion	20–50	20–50	20–50
Flue gas recirculation	n.a.	20–50	20–50
Water/steam injection	n.a.	10–50	n.a.
Low-NO_x burners	30–40	30–40	30–40
Flue gas treatment			
Selective catalytic reduction	60–90	60–90	60–90
Selective noncatalytic reduction	n.a.	30–70	30–70

n.a. Not applicable.

Pollution prevention and Abatement Handbook, World Bank Group, 1998

Flue Gas Treatment (FGT)

- **Selective Noncatalytic Reduction (SNCR)**

  Ammonia is used as reducing agent to convert NO_x to nitrogen. Instead ammonia urea compounds can be used.

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$$

Above 800 °C

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

at temperatures >1090°C
unfavorable side reaction!

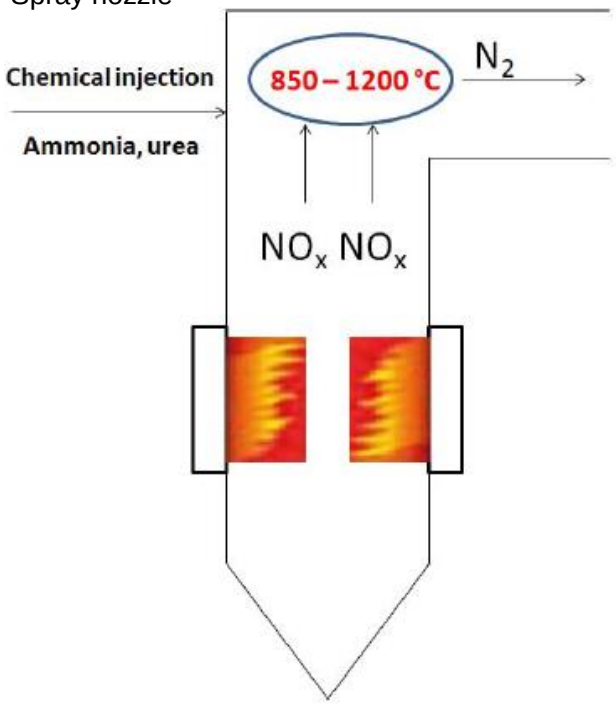
The equation for the reaction of urea is:

$$CO(NH_2)_2 + 2NO + 0.5O_2 = 2N_2 + CO_2 + 2H_2O$$

SNCR can remove 30-70% of NO_x from flue gases.

Selective Noncatalytic Reduction

Spray nozzle



Schematic of SNCR process. Adapted from [10].

The major drawbacks of SNCR:

- relatively limited removal level (up to 70%)
- requires high temperature
- ammonia slip (ammonia that has not reacted) and as a consequence ammonium salt formation that can cause plugging and corrosion
- at temperatures >1090°C ammonia decomposes and NO is created

$4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H_2O$

SNCR is not desirable in high-dust applications, because of the adsorption of ammonia on fly ash.

Flue Gas Treatment (FGT)

- **Selective Catalytic Reduction (SCR)**

  Ammonia is used as reducing agent to convert NO_x to nitrogen in the presence of a catalyst in convert upstream of the air heated.

$$4NO + 4NH_3 + O_2 \xrightarrow{TiO_2 \text{ or } V_2O_5 \text{ supported catalyst}} 4N_2 + 6H_2O$$

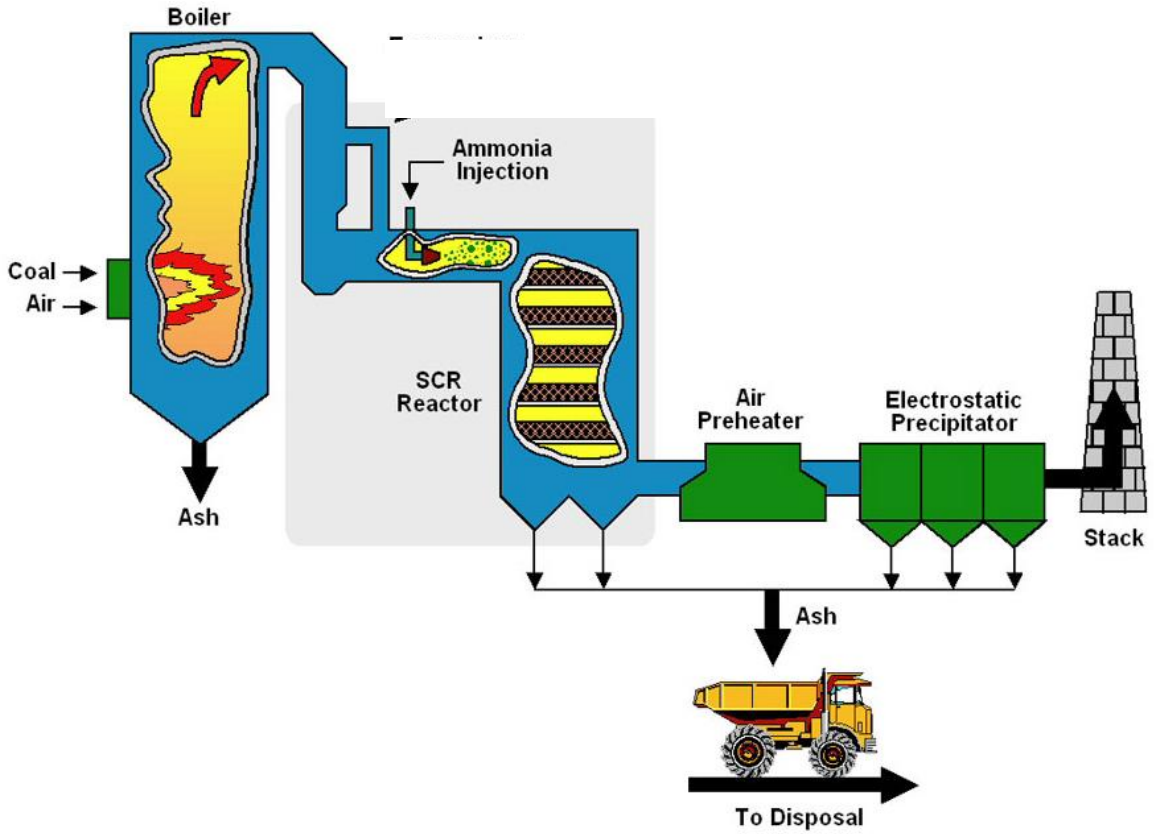
$$2NO_2 + 4NH_3 + O_2 \xrightarrow{TiO_2 \text{ or } V_2O_5 \text{ supported catalyst}} 3N_2 + 6H_2O$$

Mixture of TiO_2, V_2O_5, WO_3 as catalyst

Temperature ~ 300 - 400 ^oC

SCR can remove 60-90% of NO_x from flue gases but very expensive method, anhydrous ammonia is needed (problem with storage)

Selective Catalytic Reduction (SCR)



http://www.lanl.gov/projects/cctc/factsheets/scr/selcatreddemo.htm

Selective Catalytic Reduction (SCR)

- Capital costs are significantly higher than other types of NOx controls due to the large volume of catalyst that is required. The cost of catalyst is approximately 10,000 $/m^3

Btu=British thermal unit ≅ 1055 J
MMBtu = 1 million Btu

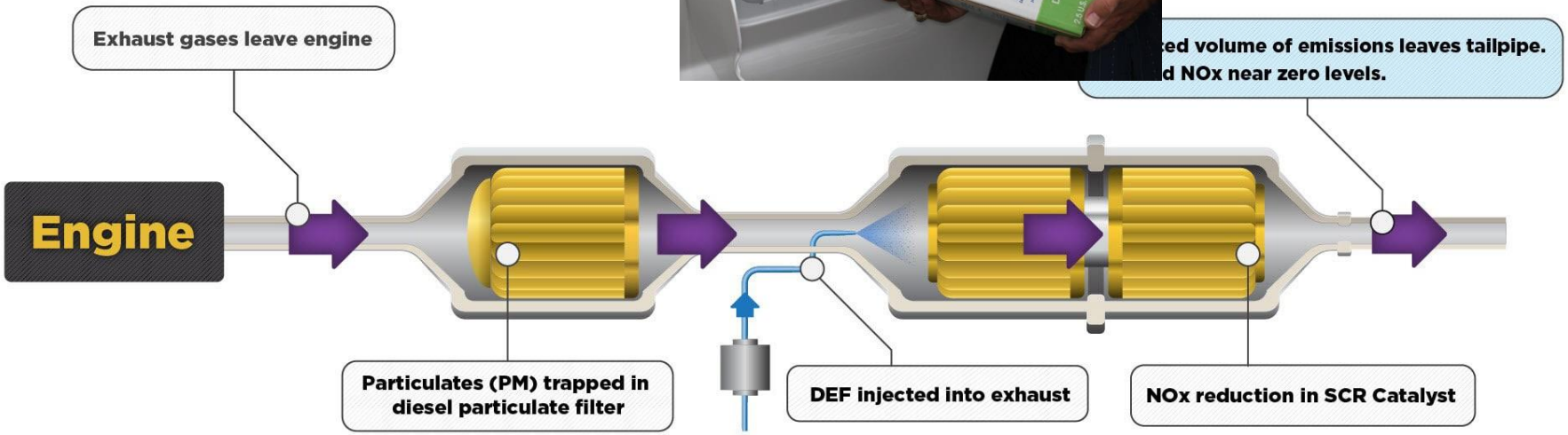
Table 1a: Summary of Cost Information in $/MMBtu/hr (1999 Dollars) [a, b]

Unit Type	Capital Cost ($/MMBtu)	O&M Cost [d] ($/MMBtu)	Annual Cost [d] ($/MMBtu)	Cost per Ton of Pollutant Removed ($/ton)
Industrial Coal Boiler	10,000 - 15,000	300	1,600	2,000 - 5,000
Industrial Oil, Gas, Wood [c]	4,000 - 6,000	450	700	1,000 - 3,000
Large Gas Turbine	5,000 - 7,500	3,500	8,500	3,000 - 6,000
Small Gas Turbine	17,000 - 35,000	1,500	3,000	2,000 - 10,000

Capital costs are fixed, one-time expenses incurred on the purchase of land, buildings, construction, and equipment. O&M = operations and maintenance

SCR and Diesel Emissions Control

Diesel Emissions Control System



Diesel exhaust fluid (**DEF**) is an aqueous urea solution made with 32.5% urea and 67.5% deionized water.

DEF is stored in a tank on board the vehicle, and injected into the exhaust stream by a metering system

Flue Gas Treatment (FGT)

- **Dry Adsorption**

  Activated carbon (220 ~ 230 ^{o}C) with ammonia injection to reduce NO_x to nitrogen and simultaneously SO_2 is oxidized to copper sulphate, if there is no sulfur in the fuel the carbon acts as a catalyst for NO_x reduction only. CuO, $CuSO_4$ can be used as calysts for the selective reduction of NO_x with NH_3

$$CuO + 0.5O_2 + SO_2 \rightarrow CuSO_4$$

$$4NO + 4NH_3 + O_2 \xrightarrow{\text{CuO or } CuSO_4 \text{ as catalysts}} 4N_2 + 6H_2O$$

$$CuSO_4 + 2H_2 \rightarrow Cu + SO_2 + 2H_2O$$

$$Cu + 0.5O_2 \rightarrow CuO$$

Wet methods for nitrogen oxide removal

- Generally for NO_2 because NO is insoluble. Need to oxidize NO first.

Scrubbing solutions containing **H_2O_2 and HNO_3**

$$2NO + HNO_3 + H_2O \rightarrow 3\ HNO_2$$

$$HNO_2 + H_2O_2 \rightarrow\ HNO_3 + H_2O$$

$$3NO_2 + H_2O \leftrightarrow 2HNO_3 + NO$$

30 – 80^{0}C
10 % HNO_3, 0.2% H_2O_2
or 10% NaOH, 3.5% H_2O_2

Carbon monoxide CO

Earth's atmosphere has a burden of approximately 530 million metric tons of CO (0.1 ppm) with average residence time ranging from 36-110 days.

Natural sources:

- Oxidation of methane and other hydrocarbons by hydroxyl radical
- Forest fires
- Degradation of chlorophyll during the autumn months (20%)
- Decay of plant matter other than chlorophyll

Anthropogenic sources (6%)

0.1% of CO in air
66% conversion O_2Hb to COHb
and rapid death

S. E. Manahan „Environmental Chemistry" Brooks/Cole Publishing Company , 1984

Fate of atmospheric CO

- Almost all of CO emitted into atmosphere is removed by reactions with hydroxyl radicals (80%), by soils (10%) and diffusion into the stratosphere

$HO\cdot + CO \longrightarrow CO_2 + H\cdot$

$H\cdot + O_2 \longrightarrow HOO\cdot$

$HOO\cdot + CO \longrightarrow HO\cdot + CO_2$

$HOO\cdot + HOO\cdot \longrightarrow H_2O_2 + O_2$

$H_2O_2 + h\nu \longrightarrow 2\ HO\cdot$

CO is removed from atmosphere primarily by reactions with hydroxyl and hydroperoxyl radicals

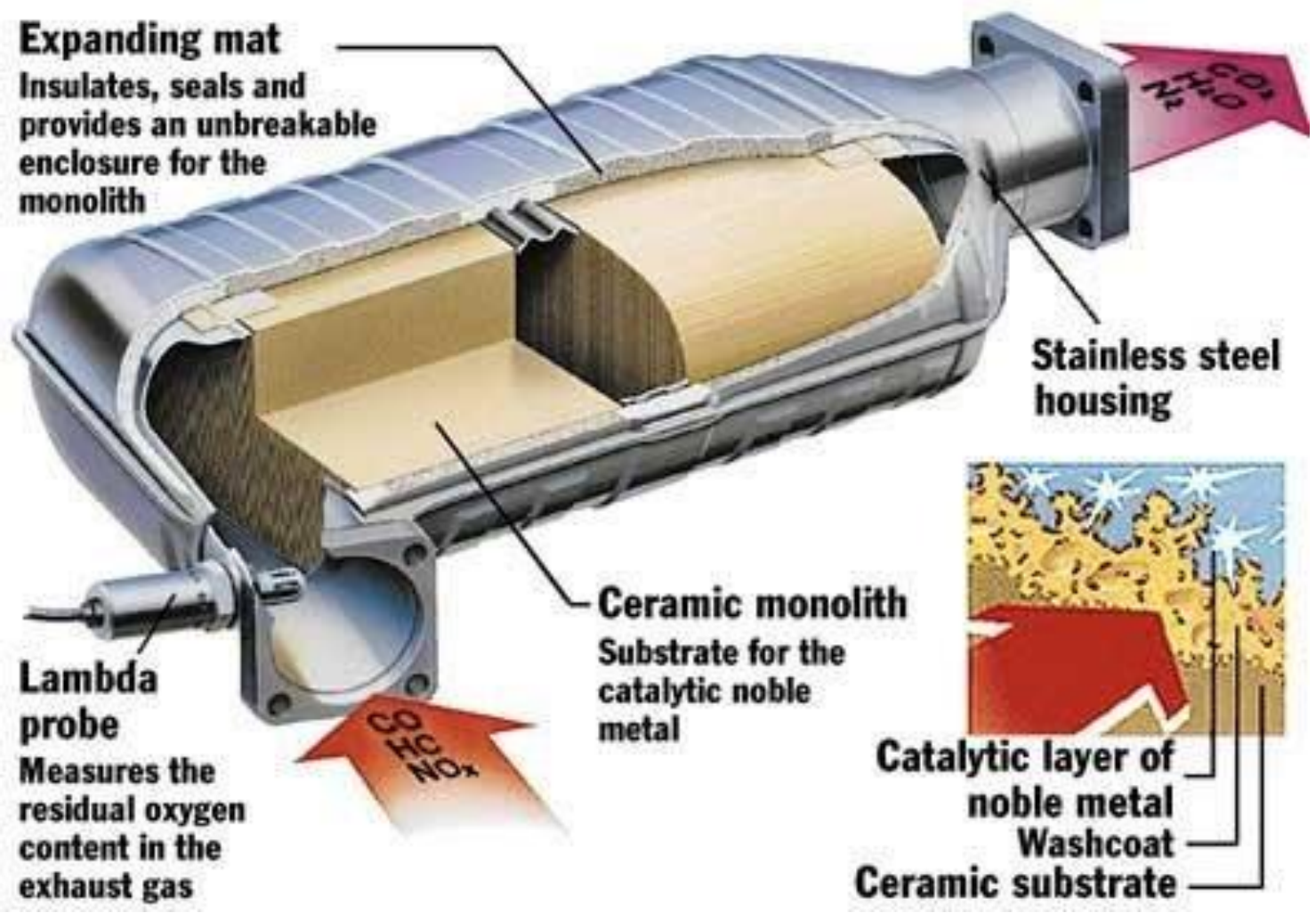
Control of carbon monoxide emissions

The internal combustion engines are primary source of localized carbon monoxide thus emissions control measures have been concentrated on the automobiles. There are two ways for emission reduction:

1) using of air-fuel mixture in which the weight ratio of air to fuel is relatively high,

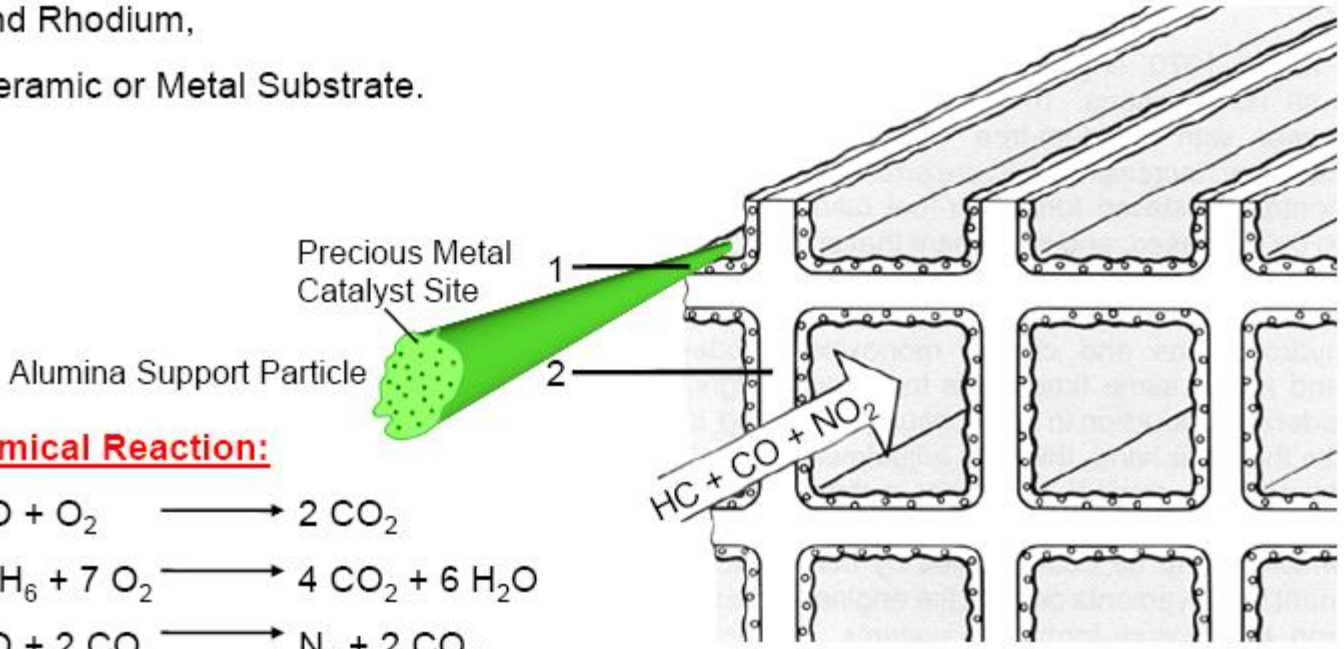
2) using of catalytic exhaust converters

Automotive exhaust converter



1 Catalyst Layer Containing Platinum and Rhodium,

2 Ceramic or Metal Substrate.



Chemical Reaction:

$2\ CO + O_2 \longrightarrow 2\ CO_2$

$2\ C_2H_6 + 7\ O_2 \longrightarrow 4\ CO_2 + 6\ H_2O$

$2\ NO + 2\ CO \longrightarrow N_2 + 2\ CO_2$

Automotive exhaust converter

- The catalytic converter was first invented by Eugene Houdry in 1950's
- Tetraethyl lead present earlier in gasoline „poisoned"the converter by forming a coating on the catalyst's surface, effectively disabling it, unleaded gasoline must be used
- First production of catalytic converter in 1973 in the USA

Automotive exhaust converter

- Products of incomplete combustion: CO and unburned hydrocarbons (UHCs), thermal and fuel NO_X

  100 ppm = 0.01% (volume percent)

  CO range: 1~2%

  UHCs range: 500~1000 ppm

  NO_X range: 100~3000 ppm

  The exhaust gases also contain approximately 0.3 moles of H_2 per mole of CO.

Automotive exhaust converter

- I step: Reduction of NO/NO_2 to N_2 (Rh as catalyst):

TWC -Three Way Catalytic Converter (CO, NO_x, C_xH_y)

$$NO(or NO_2) + CO \rightarrow \frac{1}{2} N_2 + CO_2$$

$$NO(or NO_2) + H_2 \rightarrow \frac{1}{2} N_2 + H_2O$$

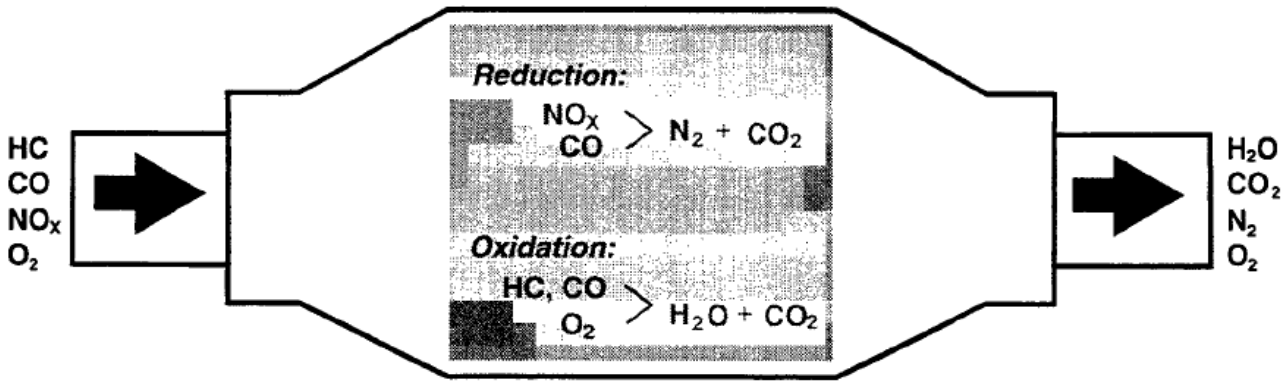
$$(2 + \frac{n}{2}) NO(or NO_2) + C_y H_n \rightarrow (1 + \frac{n}{4}) N_2 + yCO_2 + \frac{n}{2} H_2O$$

Automotive exhaust converter

- **Platinum/Palladium**; Oxidizing catalysts for HC and CO
- **Rhodium**; Reducing catalyst for NOx
- **Cerium**; Promotes oxygen storage to improve oxidation efficiency The diagram below shows the chemical reaction that takes place inside the converter.

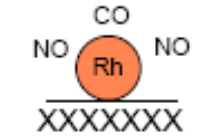
TWC Operation

As shown, the TWC reduces and oxidizes harmful engine-out gases; thereby, lowering the level of harmful gases emitted from the tailpipe.

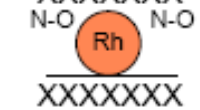


3-Way Catalytic Converter

Automotive exhaust converter

1. 

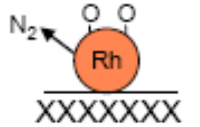
Clean Rh Surface

2. 

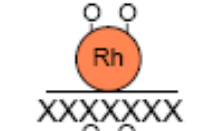
NO Molecules Attracted to Rh – Electron Bond Stretch

3. 

N Atoms and O Atoms Share Electron Bond With Rh

4. 

N Atoms Combine and Desorb as N_2 Molecules

5. 

Oxygen Atoms Remain

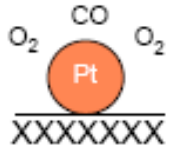
6. 

CO Molecules React With Oxygen Atoms to Form CO_2

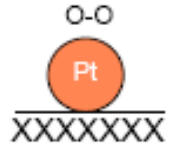
7. 

CO_2 Desorbs Leaving a Clean Rh Surface

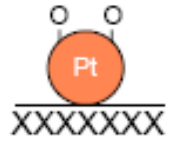
Automotive exhaust converter

1. 

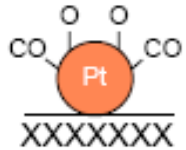
Clean Pt Surface

2. 

O_2 Molecule Attracted – Electron Bond Stretch

3. 

O Atoms Share Electron With Pt

4. 

CO Reacts With O Atoms to Form CO_2

5. 

CO_2 Desorbs, Leaving a Clean Pt Surface

Lean $\quad \overset{(+3)}{Ce_2O_3} + 1/2\ O_2 \longrightarrow (2)\ \overset{(+4)}{CeO_2}$

Rich $\quad (2)\ \overset{(+4)}{CeO_2} + CO \longrightarrow CO_2 + \overset{(+3)}{Ce_2O_3}$

Ce_2O_3 Captures Excess O_2 That Would Escape the Tailpipe and Saves it for CO Oxidation When in Short Supply. The Act of O_2 Storage Enhances NO Reduction.

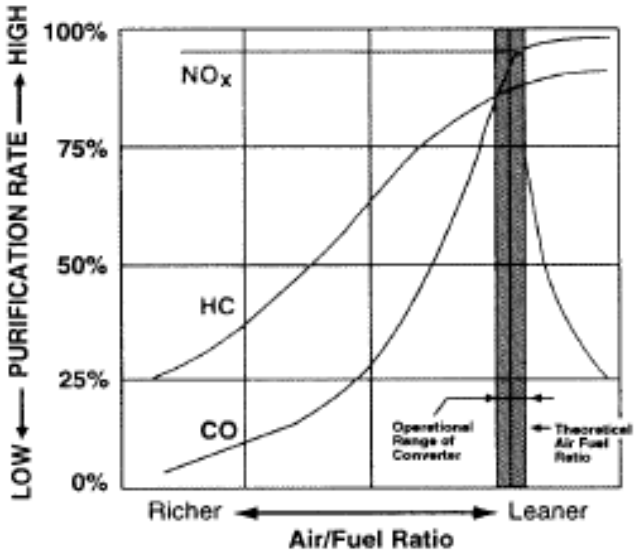
Air-fuel ratio AFR = mass ratio of air to fuel
The lower AFR = „richer” mixture

$$\lambda = \frac{m_{pow}}{m_c L_t}$$

m_{pow} mass of air
m_c mass of fuel
L_t stechiometric requirement (14.7 for gasoline)

Catalyst Efficiency

Efficient catalyst purification relies on the Closed Loop Control system to maintain a very narrow A/F mixture range around the "ideal" 14.7/1 ratio.

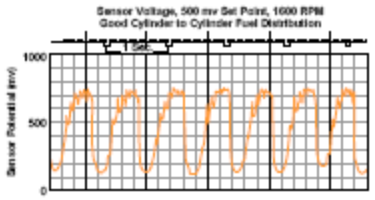


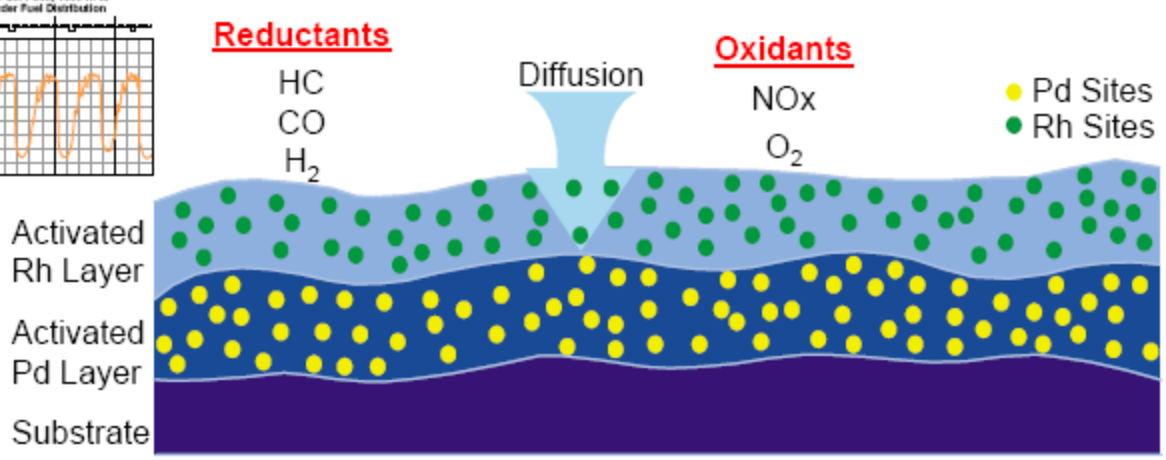
Air/Fuel Ratio

"stoichiometric" fuel mixture of 14.7 parts of air to 1 part of fuel

If exactly enough air is provided to completely burn all of the fuel, the ratio is known as the stoichiometric mixture

Automotive exhaust converter





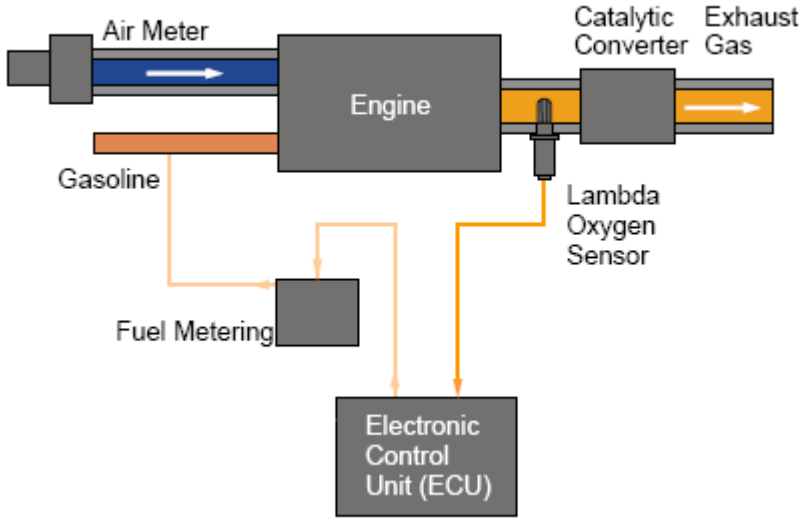
Competitive Reactions:

$HC, CO, H_2 + O_2 \longrightarrow CO_2 + H_2O$

$NO + Reductant \longrightarrow N_2 + CO_2, H_2O$

A Separate Rh Layer Promotes the Interaction of NO With the Reductant.

Automotive exhaust converter



Rys. 4. Sonda lambda

Pt electrode

Rys. 5. Budowa sondy lambda - przekrój

Lambda oxygen sensor