NITROGEN OXIDES FORMATION in combustion processes

NITROGEN OXIDES FORMED DURING COMBUSTION

N_2O - nitrous oxide

NO - nitric oxide

NO_2 - nitrogen dioxide

N = 14, O_2 =16, NO = 30, NO_2= 46

CONTRIBUTION OF PARTICULAR NITROGEN OXIDES IN TOTAL NO_X PRODUCTION

- the biggest contribution has nitric oxide (**NO**)
  - its content in flue gas is in the range of: 100 –1000 mg/m^3
- next is nitrogen dioxide **NO_2 in proportion** 5-10% of **NO**
  - its content in flue gas is in the range of: 10 –100 mg/m3
- N_2O has the least contribution:
  - its content in flue gas is in the range of: 1–10 mg/m^3

WHAT DOES NO_X MEAN ?

DEFINITION OF NO_X

NO_X means the sum of NO and NO_2 contents in flue gas recalculated on **NO_2**

$$NO_x = NO + NO_2$$

(expressed in NO_2)

UNITS OF NO_X

Units of NOx content in flue gas

- **mg/m^3**
- **ppm (emission)**
- **µg/m^3 (imission)**
- **g/GJ**

Remarks:

1. The NO_x content in flue gas is given for a certain content of oxygen (O_2) in flue gas.
2. The NO_x content in flue gas is given for normal conditions.
3. ppm - unite – part per million ($x10^{-6}$)

NO_X emissions conversion chart

ppm:

$$NO_x\ [ppm] = NO\ [ppm] + NO_2\ [ppm]$$

ppm → mg/m³

$$NO\ [mg/m^3] = 1.3387\ NO\ [ppm]$$

$$NO_x\ [mg/m^3] = 2.0525\ NO_x\ [ppm]$$

mg/m³ → GJ (dla NOx)

1 g/GJ = 2.7 [mg/m³] for bituminous coal

1 g/GJ = 2.35 [mg/m³] for lignite

NO_x emission units which are in use in the power generation industry

In Poland (and in EU) NO_x is expressed as follows:

$$[mg\ NO_2/m^3]$$

for 6% O_2 in dry flue gas

at normal conditions

NO_X FORMATION IN COMBUSTION PROCESSES

COMBUSTION CHEMISTRY OF NITROGEN OXIDES

The chemical mechanism of NO_x (NO and NO_2) formation during combustion obeys hundreds of elementary chemical reactions.

Depending on the temperature range, stoichiometric ratio and type of nitrous species present in the combustion zone, it is possible to distinguish predominant groups of chemical reactions, which are called the mechanisms of nitrogen oxides formation.

Usually the type of flame determines the conditions of the predominant mechanism of NO_x formation.

MAJOR SOURCES OF NO_X FORMATION DURING COMBUSTION

1. Air nitrogen (N_2)
   - *thermal NO_x*
   - *prompt NO_x*

2. Fuel nitrogen (N_F)
   - *fuel NO_x*

MAJOR MECHANISMS OF NITRIC OXIDE (NO) FORMATION DURING COMBUSTION

- **Thermal**
- **Prompt**
- **Fuel**

THERMAL NITRIC OXIDE MECHANISM

ZELDOVICH's MECHANISM OF NO FORMATION

$$O_2 + M = O + O + M \quad (3)$$ (dissociation)

Where M is stable molecule of high energy necessary to break the bounds of O_2 [10].

The „liberated" O atoms can react with N_2 through a relatively slow reaction:

$$O + N_2 \rightarrow NO + N, \quad (4)$$

the N atoms „liberated" in this reaction quickly react with O_2

$$N + O_2 \rightarrow NO + O \quad (5)$$

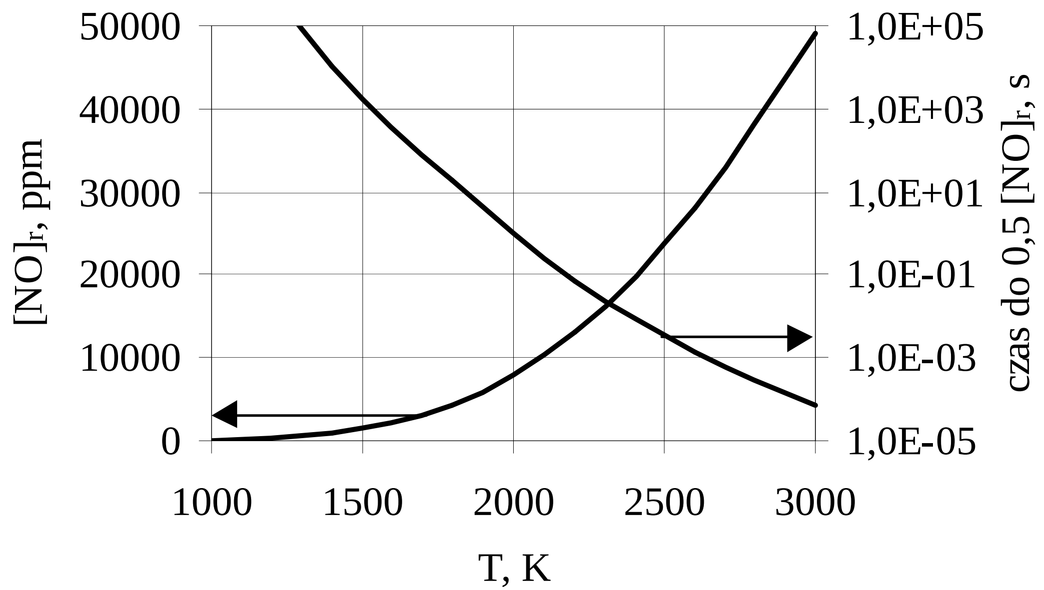
also giving NO.

RATE OF NO_X FORMATION via ZELDOVICH MECHANISM

Rate of NO_x formation by thermal mechanism

$$d[NO]/dt = k_p[O_2]^{1/2}[N_2]$$

where $k_p \cong 2K_3^{1/2}k_2$, which is in accord with the experimental.



Equilibrium concentration of NO, $[NO]_r$, and time to reach $0{,}5[NO]_r$ versus the temperature

It shows that the Zeldovich mechanism becomes important when the temperature reaches the range of 1600-1800 K.

PROMPT NITRIC OXIDE MECHANISM

REACTIONS OF HYDROCARBON RADICALS WITH N_2

There are many hydrocarbon radicals in flame (CH, CH_2, CH_3, C_2H_4, C_2H_5, C_3H_7, C, C_2...), which can react with molecular nitrogen (N_2).

$$CH_2 + N_2 \rightarrow HCN + NH$$

$$CH + N_2 \rightarrow HCN + N$$

$$C + N_2 \rightarrow CN + N$$

general

$$CH_x + N_2 \rightarrow HCN \text{ and other radicals (CN, NH, N...)}$$

As a result: HCN, NH i CN are easily oxidized to NO in flame.

FUEL NITRIC OXIDE MECHANISM

WHAT IS A SOURCE OF FUEL NITRIC OXIDE

1. The source of fuel NO are nitric compounds in fuel, often called *fuel nitrogen* (denoted $\boldsymbol{N_F}$).

2. **The content of *fuel nitrogen* in fuels is very different!!!!**

3. ***Fuel nitrogen* can be a very important source of nitric oxides.**

FUEL NITROGEN (NF) IN FUELS

FUEL NITROGEN IN GAS

Natural gas practically doesn't have *fuel nitrogen*.

FUEL NITROGEN IN LIQUID FUELS

Crude oil has *fuel nitrogen* in the range of

0.01 do 0.3% wt.

Only exceptionally N_F content excess 0.9%.

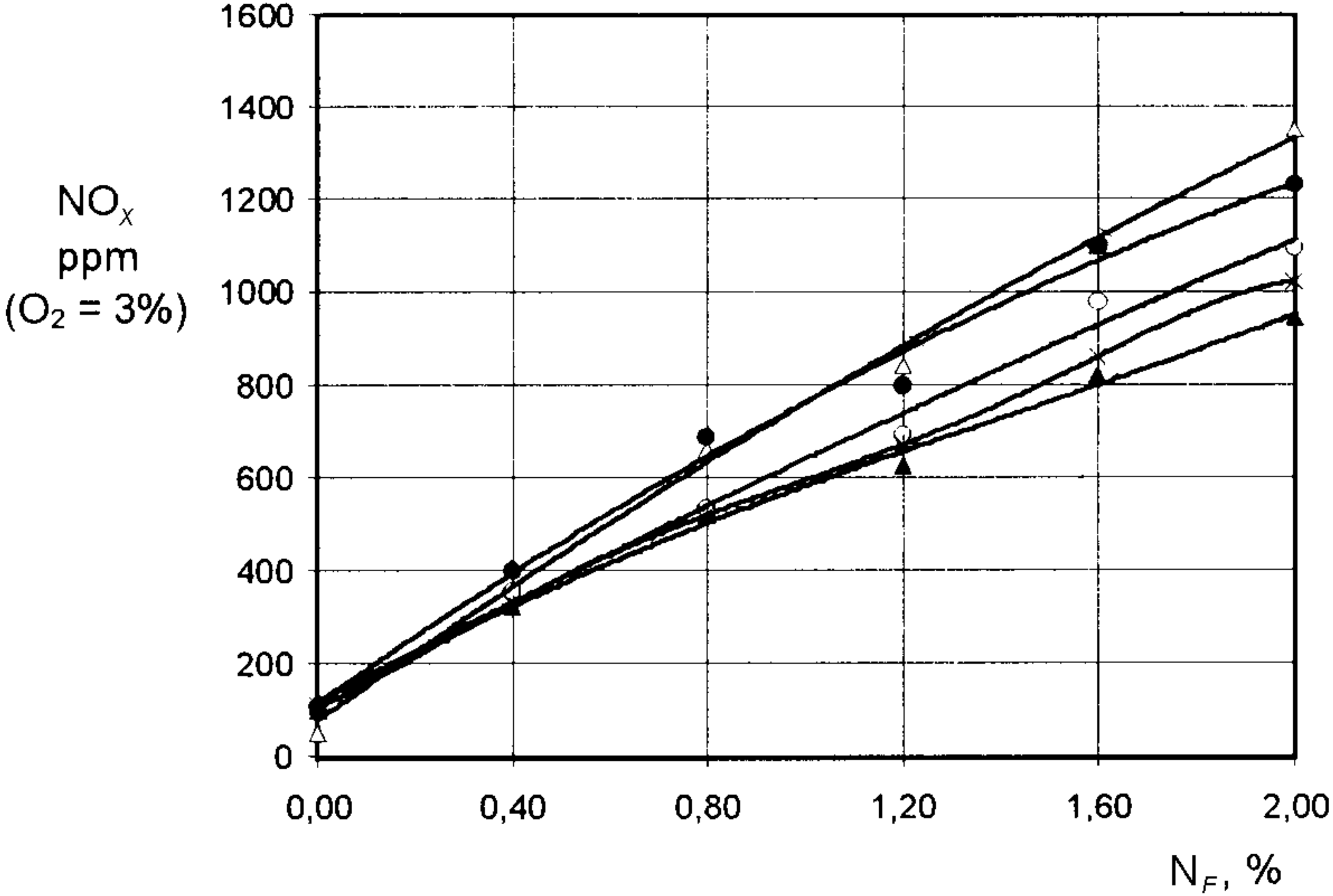
Major groups of nitric compounds are: pyridyne, indoles, chinolines, tetrahydrochinolines, carbazoles i pyroles.

Nitric compounds in oil are relatively stable in the elevated temperature, therefore during crude oil destillation they are cumulated in heavy fractions of oil. For example, the content of N_F in asphaltes reaches 1.5%.

FUEL NITROGEN IN HEATING OILS

Fuel	Content, %					W_d MJ/kg	$V_{a, min}$ m^3/kg	T_{comb} °C
	C	H	S	**N**	O			
Gas	85	15	–	–	–	47	11,57	2263
Heating oil 1	86,4	12,5	0,05	**0.05**	1	45,2	11,18	2258
Heating oil 2	85,5	13	0,4	**0.3**	0,8	43,6	11,96	2210
Heating oil 3	87	11,4	0,5	**0.6**	0,3	43,1	10,74	2262

THE INFLUENCE OF NF CONTENT ON NO_X EMISSION



FUEL NITROGEN IN COAL

The origin of *fuel nitrogen* in coal is organic material of coal, these are vegetables, bacteria and fungi containing amines, alkaloid and chlorophyll being source of nitrogen.

N_F in different coals:

Bituminous coal:	0.6 - 2.8% N (85% C)
Anthracite	<1% N
Lignite:	0.6 - 2% N.

SELECTED NITRIC COMPOUNDS IN COAL

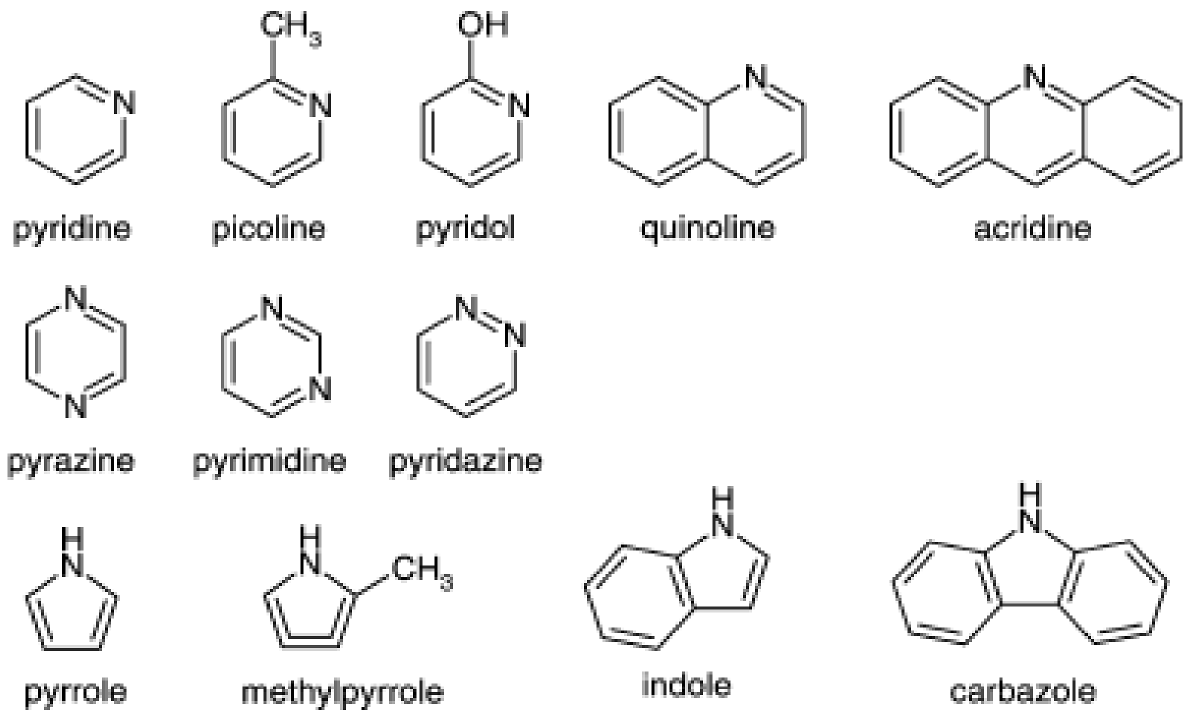
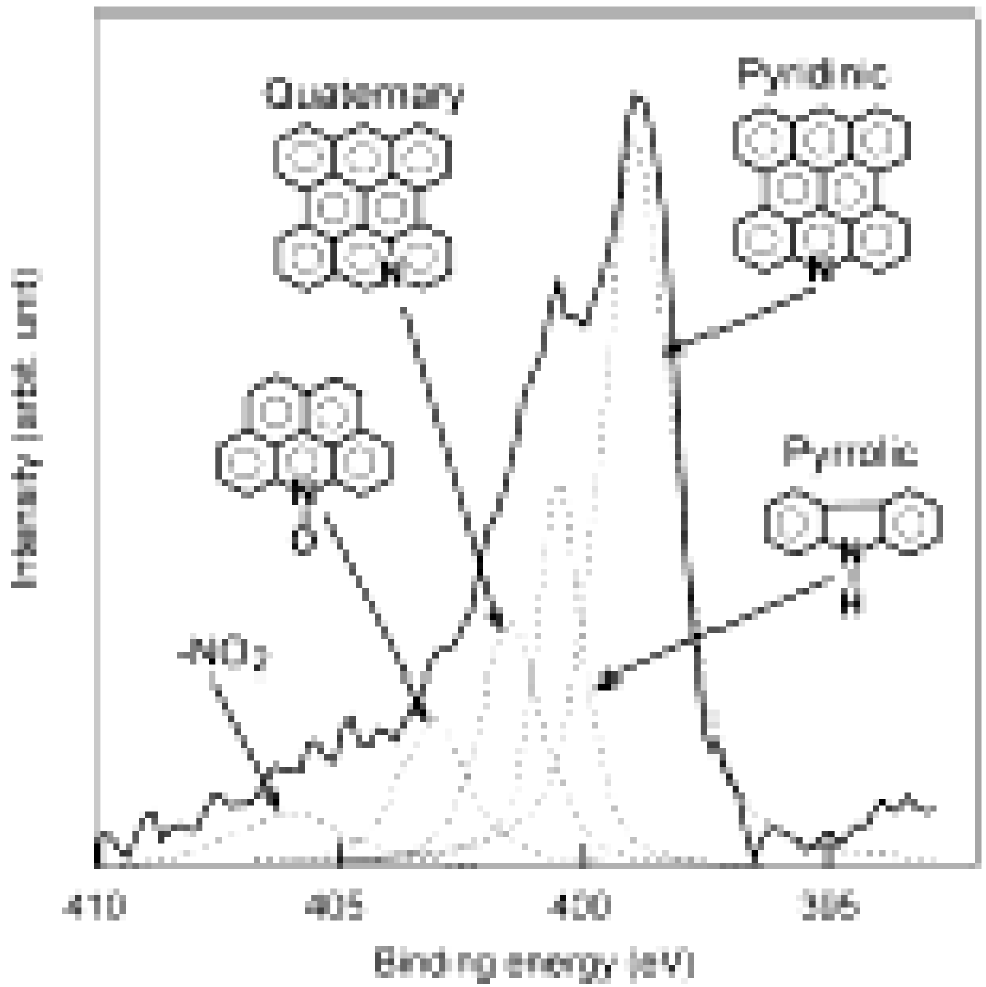


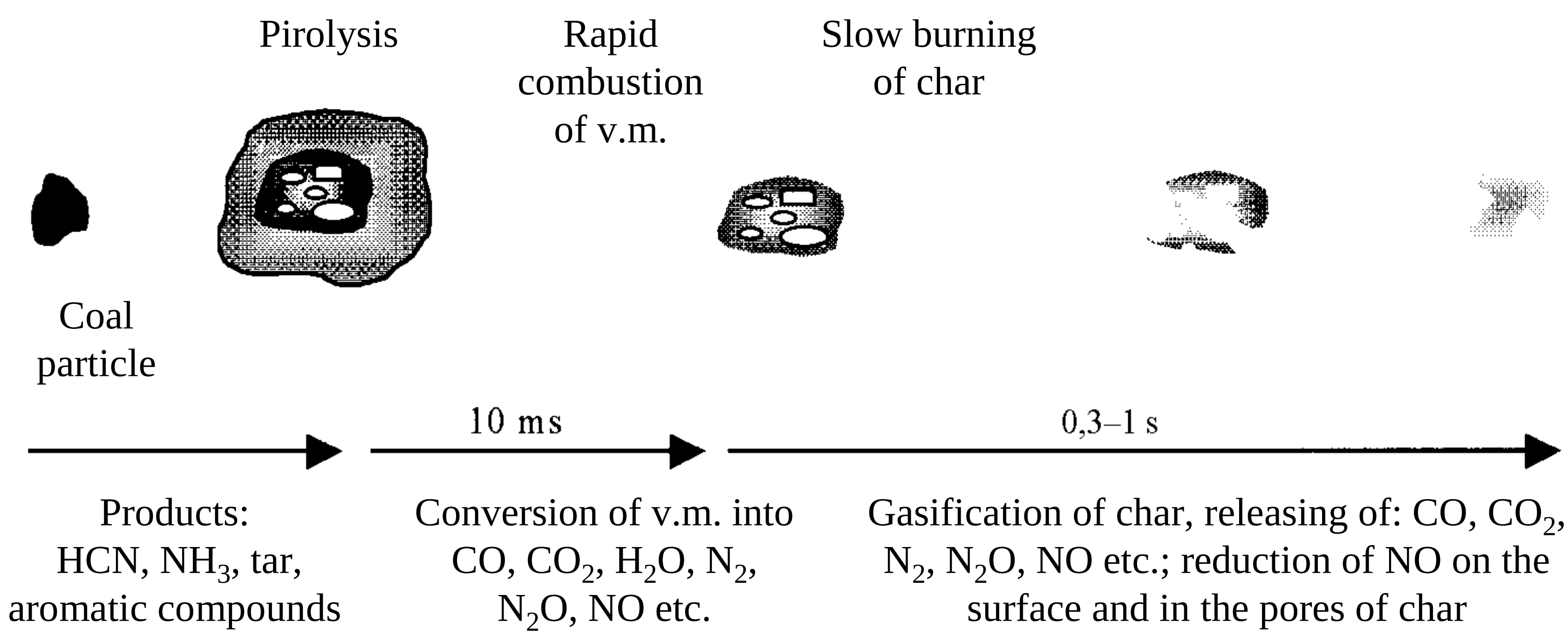
Fig. 4. Selected nitrogen containing cyclic compounds. Pyridinic structures include pyridine, picoline (a pyridine with a methyl group), pyridol (a pyridine with an OH-group), quinoline (pyridine ring fused to benzene), and acridine (dibenzo-derivative of pyridine). Related structures include pyrazine, pyrimidine, and pyridazine (six-membered rings with two nitrogen atoms). Pyrrolic compounds include pyrrole, methylpyrrole, indole (pyrrole ring fused to benzene), and carbazole (dibenzo-derivative of pyrrole).

Major nitric compounds in coal

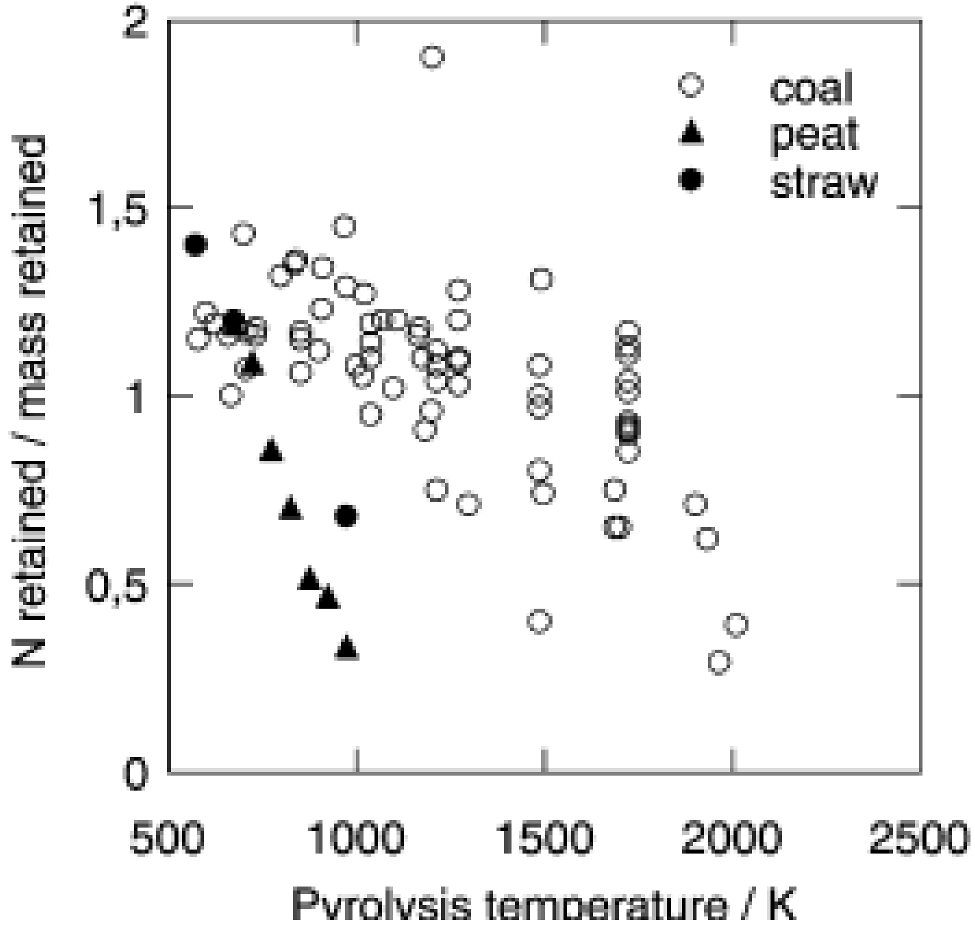


CONVERSION OF FUEL NITROGEN DURING COAL COMBUSTION

CONVERSION OF FUEL NITROGEN DURING COAL PARTICLE BURNING

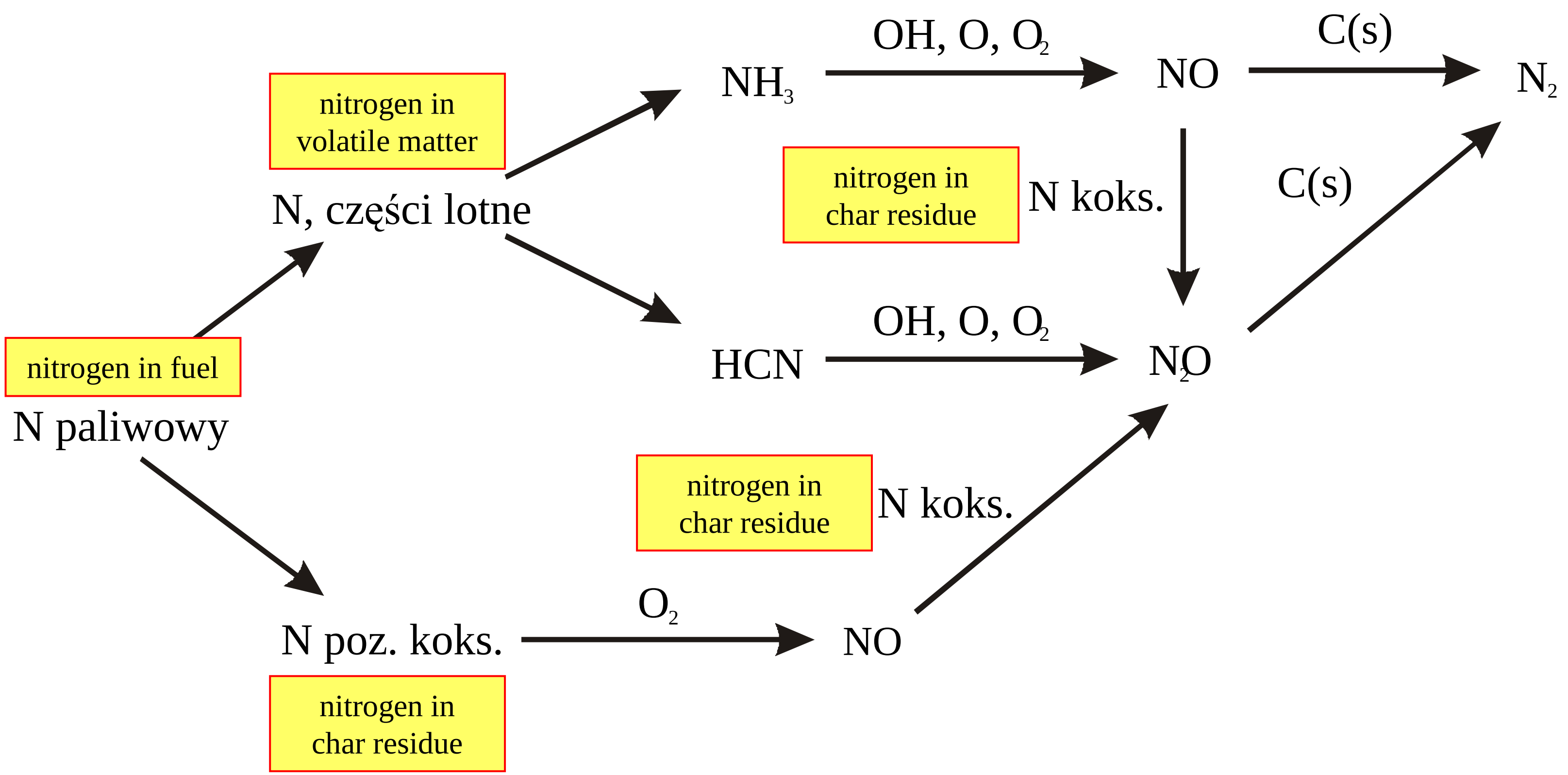


EVALUATION OF FUEL NITROGEN DURING COAL PYROLYSIS



NITRIC OXIDE FORMATION DURING COAL COMBUSTION

FUEL NITRIC OXIDE FORMATION DURING COAL COMBUSTION



CONVERSION OF GAS-PHASE **FUEL-N** TO NO

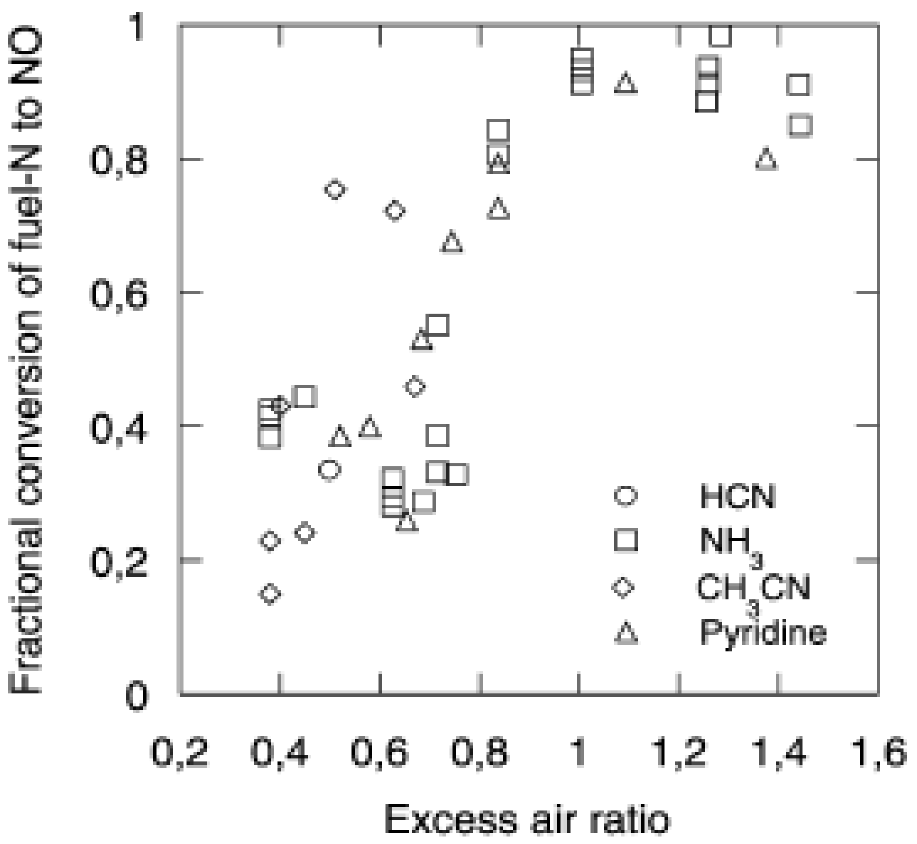


Fig. 6. Conversion of gas-phase fixed nitrogen to NO in premixed flames as function of excess air ratio (HCN [205], NH_3 [201,205, 206], CH_3CN [206], pyridine [207,208]).

CONVERSION OF CHAR **FUEL-N** TO NO

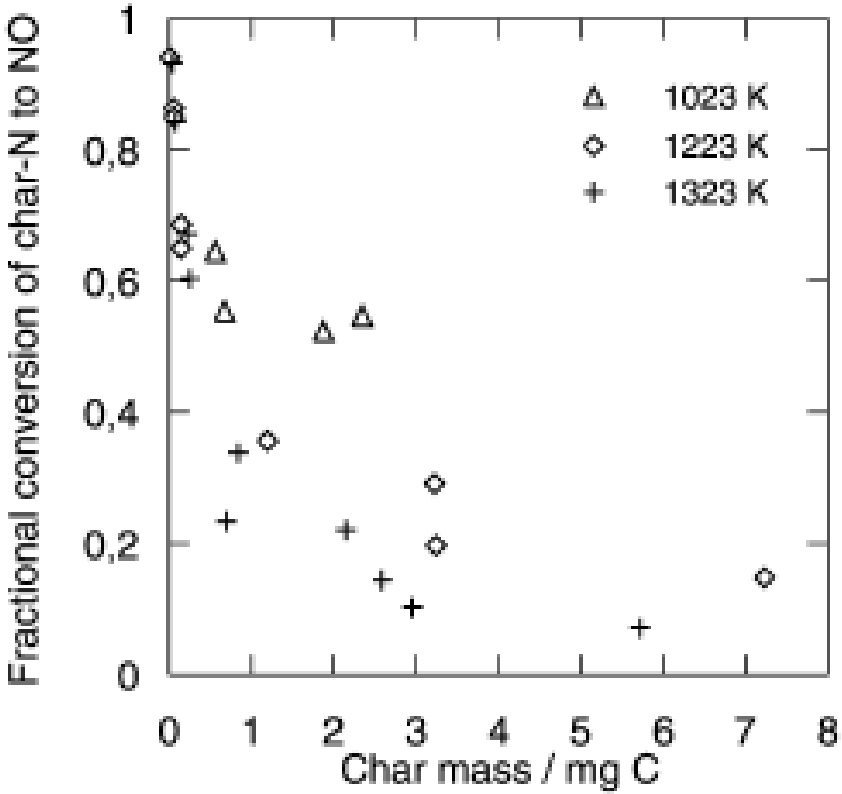


Fig. 11. Net NO formation selectivity from char combustion in a fixed bed as a function of initial char mass for a pulverized (10–20 μm) bituminous coal char [217].

NITRIC OXIDE REDUCTION ON CHAR

$$O_2 + 2\,(-C) \rightarrow 2\,(-CO) \qquad \text{(I)}$$

$$(-CO) \rightarrow CO + \text{free carbon site} \qquad \text{(II)}$$

$$2\,(-CO) \rightarrow CO_2 + (-C) + \text{free site} \qquad \text{(III)}$$

$$O_2 + (-C) + (-CN) \rightarrow (-CO) + (-CNO) \qquad \text{(IV)}$$

$$(-CNO) \rightarrow NO + (-C) \qquad \text{(V)}$$

$$NO + (-C) \rightarrow \tfrac{1}{2} N_2 + (-CO) \qquad \text{(VI)}$$

$$NO + (-CNO) \rightarrow N_2O + (-CO) \qquad \text{(VII)}$$

$$N_2O + (-C) \rightarrow N_2 + (-CO) \qquad \text{(VIII)}$$

NITROGEN DIOXIDE (NO_2) FORMATION IN FLAMES

CONDITIONS OF NITROGEN DIOXIDE (NO_2) FORMATION IN FLAMES

- NO_2 is a secondary product, and is formed by oxidation of NO in combustion processes.
- NO_2 is formed in cooler regions of flame, in the temperature range of:

$T < 800$ °C

- NO_2 undergoes destruction on tat higher temperatures:

$T > 1200$ °C

BASIC MECHANISM OF NITROGEN DIOXIDE (NO_2) FORMATION IN FLAMES

- The major reaction of NO_2 formation is with hydroperoxide radical HO_2 :

$$NO + HO_2 \rightarrow NO_2 + OH$$

(where from HO_2: $H + O_2 + M \rightarrow HO_2 + M$)

- The temperature range of this reaction:

$$\mathbf{T < 1000\ K}$$

ADDITIONAL MECHANISM OF NO_2 FORMATION

➢ Hydrocarbonperoxides RO_2 plays a considerable part in NO_2 formation:

$$NO + RO_2 \rightarrow NO_2 + RO$$

(where from RO_2: $R + O_2 + M \rightarrow ROO + M$)

where R are alkil radicals:

CH_3, C_2H_5 and higher

NITROGEN DIOXIDE FORMATION IN REACTION WITH ATOMIC OXYGEN

- The three body reaction:

$$NO + O + M \rightarrow NO_2 + M$$

NO_2 also is generated, but the contribution of this reaction is not important.

The temperature range: $T < 800$ K.

CONTRIBUTION OF NITROGEN DIOXIDE NO_2 TO THE TOTAL NO_X

- The NO_2 contribution to the total NO_x formation during pulverized coal combustion is minor:

$$[NO_2]/[NO_x]*100\% \approx 5\%$$

- More important contribution to the total production of NO_x NO_2 introduces during combustion in gas turbines:

$$[NO_2]/[NO_x]*100\% \approx 10\text{-}15\%$$

NITROUS OXIDE (N_2O) FORMATION IN FLAMES

CONDITIONS OF NITROUS OXIDE (N_2O) FORMATION

- NO_2 is produced in flames due to:

1. Oxidation of amine radicals (mainly Nhand less significant CN_2).
2. In lean regions of gas flames.
3. In fluidized bed furnaces (T approx. 850 °C)

MAJOR SOURCES OF NIROUS OXIDE N_2O IN FLAMES

Major reaction

$$NH + NO \rightarrow N_2O + H$$

- NH – amine radical
- Where is from NH? Mainly, from decomposition of ammonia (NH_3, perhaps also hydrogen cyjanide (HCN).

NIROUS OXIDE N_2O FORMATION IN LEAN FLAMES (λ<1)

$$O + N_2 + M \rightarrow N_2O + M$$

The temperature range of the chemical reaction:

T < 1500 °C

NIROUS OXIDE N_2O FORMATION IN FLUIDIZED BEDS

In catalytic reaction:

$$2NO \rightarrow N_2O + 0.5O_2$$

Catalysts in fluidized bed:

1. char
2. Limestone

HOW IMPORTANT IS NITROUS OXIDE N_2O?

- N_2O is known is the as laughing gas.
- N_2O has contribution to the stratospheric ozone destruction
- In combustion processes N_2O is formed mainly in fluidized beds (N_2O content in flue gas up to 50 ppm).
- N_2O has also some contribution to NO emission, by chemical reactions with radicals O i OH:

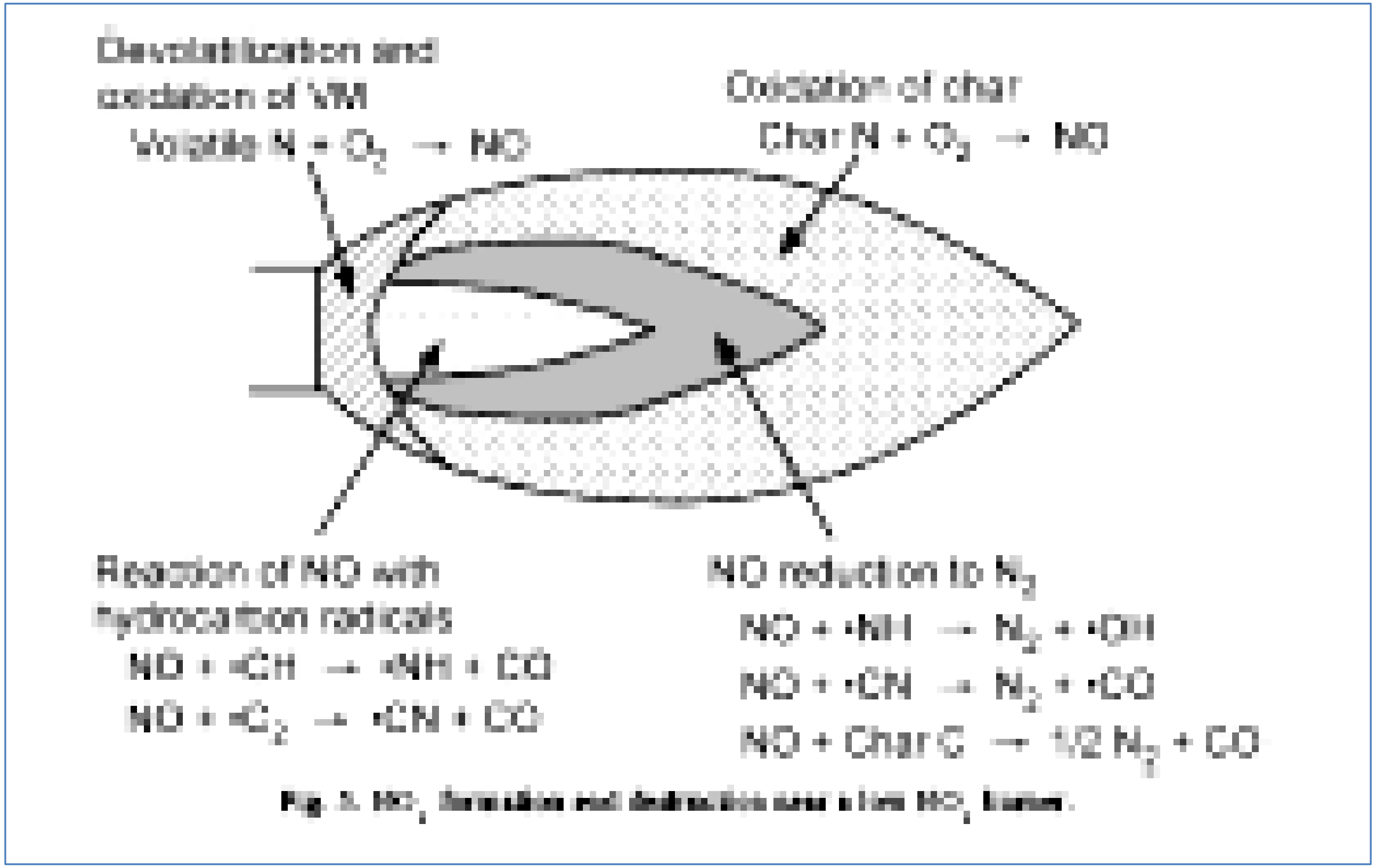
$$N_2O + O \rightarrow NO + NO$$

DOMINATING MECHANISMS OF NOx IN FLAMES

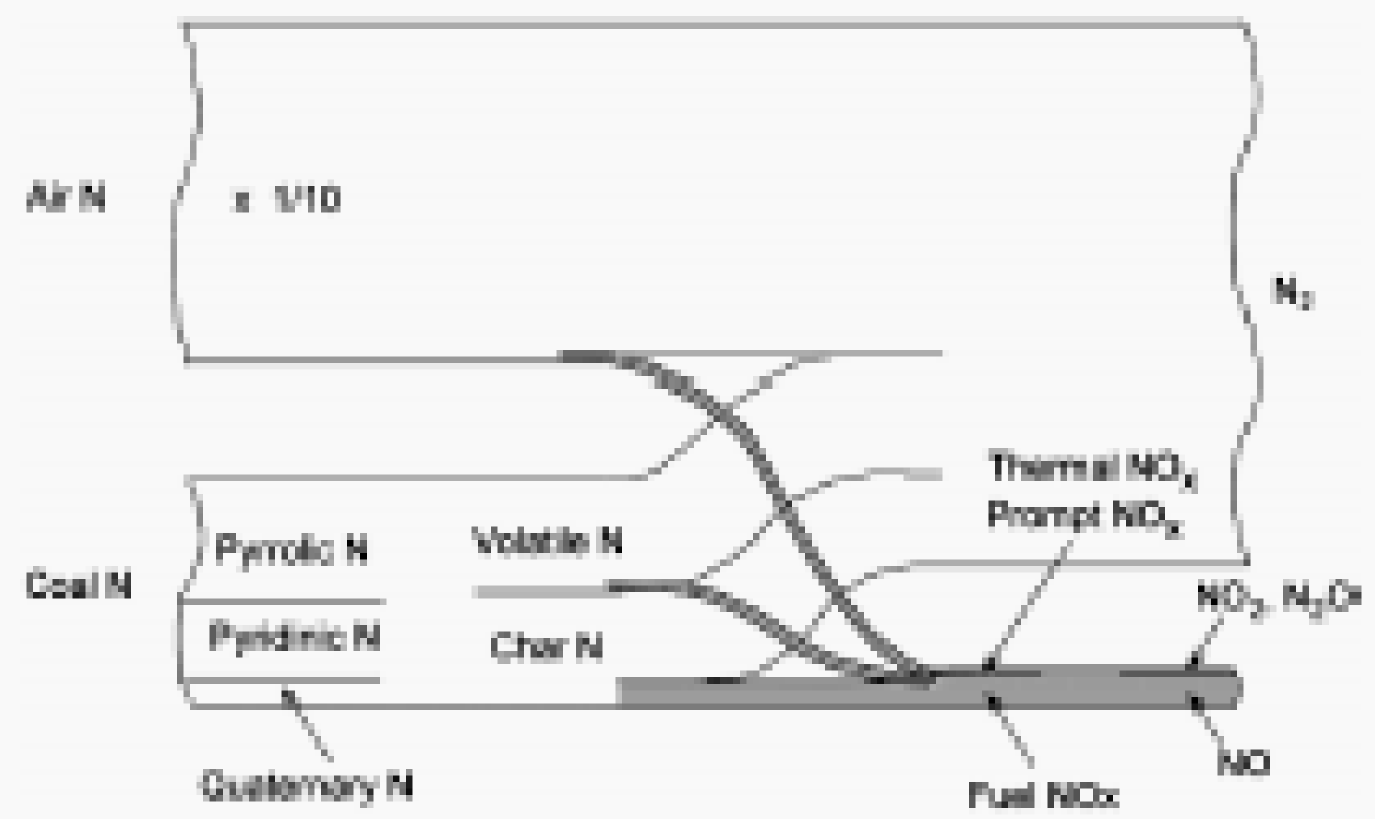
MAJOR FACTORS INFLUENCING NO_x FORMATION

- fuel nitrogen N_F
- flame temperature
- air excess (λ)
- residence time in flame

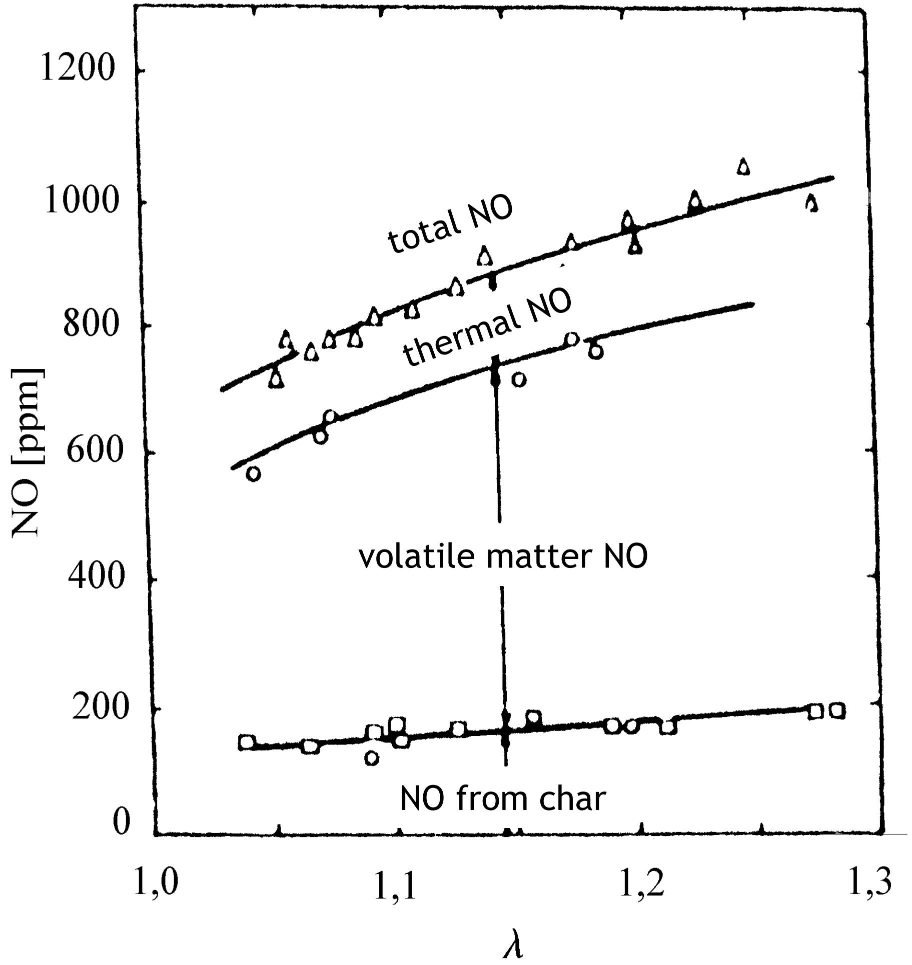
NO_X FORMATION IN PULVERIZED COAL FLAME



SOURCES OF NO_X EMISSION IN PULVERIZED COAL FLAME



CONTRIBUTION OF PARTICULAR NITRIC OXIDES IN TOTAL NOX EMISSION FROM PF



Fuel NO_x is dominating NO_x

Bituminous coal ($T_{pł}$ = 1650 °C)

Lignite (T_{flame} = 1250 °C): approx.95% of NO_x is fuel NO_x

NOx EMISSION vs. FURNACE TYPE (PF BOILERS)

Furnace type	Power MW_e	Coal type	NO_x mg/m^3
Tangencial	650–750	bituminous	710±60
Tangencial	465–490	bituminous	750–1000
Tangencial	200–360	bituminous	500–900
Wall fired	425–460	bituminous	1360±110
FBB	110	bituminous	400±80
FBB	160	bituminous	520±80
FBB	230	lignite	280 ±50

OIL FLAMES

Heavy heating oil has much of *fuel nitrogen* N_F > 0,5%.

NO_x emission from oil burners operating on heating oils nr 2 and 3 is in the range:

$300\text{-}700\ mg/m^3$

(mainly fuel NOx).

Fuel nitrogen N_F is a dominating factor.

Light heating oil has less *fuel nitrogen* N_F < 0,05%

NO_x emission form oil burners operating on light heating oil (nr 1) is in the range:

$180\text{-}220\ mg/m^3$

(mainly thermal NO_x).

GAS FLAMES

No *fuel nitrogen* N_F in gas.

Industrial gas burners (flames).

Range of NOx emission: **100-300 mg/m^3**

Dominating mechanism: thermal

Small gas burners (flames):

Range of NOx emission: **10-100 mg/m^3**

Dominating mechanism: thermal + prompt (20%)