NITROGEN OXIDES FORMATION
in combustion processes
NITROGEN OXIDES FORMED DURING COMBUSTION

N₂O - nitrous oxide
NO - nitric oxide
NO₂ - nitrogen dioxide

N = 14, O₂ = 16, NO = 30, NO₂ = 46
CONTRIBUTION OF PARTICULAR NITROGEN OXIDES IN TOTAL NO\textsubscript{X} PRODUCTION

- the biggest contribution has nitric oxide (NO)
  - its content in flue gas is in the range of: 100 - 1000 mg/m\textsuperscript{3}
- next is nitrogen dioxide NO\textsubscript{2} in proportion 5-10% of NO
  - its content in flue gas is in the range of: 10 - 100 mg/m\textsuperscript{3}
- N\textsubscript{2}O has the least contribution:
  - its content in flue gas is in the range of: 1-10 mg/m\textsuperscript{3}
WHAT DOES $\text{NO}_x$ MEAN?
DEFINITION OF NO\textsubscript{X}

NO\textsubscript{X} means the sum of NO and NO\textsubscript{2} contents in flue gas recalculated on NO\textsubscript{2}

\[ \text{NO}\textsubscript{X} = \text{NO} + \text{NO}\textsubscript{2} \]

(expressed in NO\textsubscript{2})
UNITS OF NO$_{X}$
Units of NOx content in flue gas

- mg/m³
- ppm (emission)
- µg/m³ (imission)
- g/GJ

Remarks:

1. The NOₓ content in flue gas is given for a certain content of oxygen (O₂) in flue gas.
2. The NOₓ content in flue gas is given for normal conditions.
3. ppm - unite - part per million (x10⁻⁶)
**NO\textsubscript{x} emissions conversion chart**

**ppm:**

\[ \text{NO}_x \text{ [ppm]} = \text{NO} \text{ [ppm]} + \text{NO}_2 \text{ [ppm]} \]

**ppm \rightarrow mg/m\textsuperscript{3}**

\[ \text{NO} \text{ [mg/m}\textsuperscript{3}] = 1.3387 \text{ NO} \text{ [ppm]} \]

\[ \text{NO}_x \text{ [mg/m}\textsuperscript{3}] = 2.0525 \text{ NO}_x \text{ [ppm]} \]

**mg/m\textsuperscript{3} \rightarrow GJ (dla NOx)**

1 g/GJ = 2.7 [mg/m\textsuperscript{3}] for bituminous coal

1 g/GJ = 2.35 [mg/m\textsuperscript{3}] for lignite
\( \text{NO}_x \) emission units which are in use in the power generation industry

In Poland (and in EU) \( \text{NO}_x \) is expressed as follows:

\[
\text{[mg NO}_2/\text{m}^3]\]

for 6\% \( \text{O}_2 \) in dry flue gas

at normal conditions
NO$_X$ FORMATION IN COMBUSTION PROCESSES
COMBUSTION CHEMISTRY OF NITROGEN OXIDES

The chemical mechanism of NO\textsubscript{x} (NO and NO\textsubscript{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\textsubscript{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

\[ O_2 + M = O + O + M \] (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:

\[ O + N_2 \rightarrow NO + N, \] (4)

the \( N \) atoms „liberated” in this reaction quickly react with \( O_2 \)

\[ N + O_2 \rightarrow NO + O \] (5)

also giving NO.
It shows that the Zeldovich mechanism becomes important when the temperature reaches the range of 1600-1800 K.
PROMPT NITRIC OXIDE MECHANISM
REATIONS OF HYDROCARBON RADICALS WITH $N_2$

There are many hydrocarbon radicals in flame (CH, CH$_2$, CH$_3$, C$_2$H$_4$, C$_2$H$_5$, C$_3$H$_7$, C, C$_2$...), which can react with molecular nitrogen ($N_2$).

\[
\begin{align*}
\text{CH}_2 + N_2 & \rightarrow \text{HCN} + \text{NH} \\
\text{CH} + N_2 & \rightarrow \text{HCN} + N \\
C + N_2 & \rightarrow \text{CN} + N
\end{align*}
\]

general

\[
\text{CH}_x + N_2 \rightarrow \text{HCN} \text{ and other radicals (CN, NH, N...)}
\]

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 $N_F$).

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
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 exceed 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 distillation 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

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Content, %</th>
<th>$W_d$ MJ/kg</th>
<th>$V_{a, \text{min}}$ m$^3$/kg</th>
<th>$T_{\text{comb}}$ °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
<td>S</td>
<td>N</td>
</tr>
<tr>
<td>Gas</td>
<td>85</td>
<td>15</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Heating oil 1</td>
<td>86,4</td>
<td>12,5</td>
<td>0,05</td>
<td><strong>0.05</strong></td>
</tr>
<tr>
<td>Heating oil 2</td>
<td>85,5</td>
<td>13</td>
<td>0,4</td>
<td><strong>0.3</strong></td>
</tr>
<tr>
<td>Heating oil 3</td>
<td>87</td>
<td>11,4</td>
<td>0,5</td>
<td><strong>0.6</strong></td>
</tr>
</tbody>
</table>

**Note:** The values in **red** indicate the presence of nitrogen in the fuels.
THE INFLUENCE OF NF CONTENT ON NO\textsubscript{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

**Pirolysis**
- Coal particle
- Products: HCN, NH₃, tar, aromatic compounds

**Rapid combustion of v.m.**
- 10 ms
- Conversion of v.m. into CO, CO₂, H₂O, N₂, N₂O, NO etc.

**Slow burning of char**
- 0.3–1 s
- Gasification of char, releasing of: CO, CO₂, N₂, N₂O, NO etc.; reduction of NO on the surface and in the pores of char
EVALUATION OF FUEL NITROGEN DURING COAL PYROLYSIS
NITRIC OXIDE FORMATION DURING COAL COMBUSTION
FUEL NITRIC OXIDE FORMATION DURING COAL COMBUSTION

N, części lotne

NH₃ → NO

OH, O, O₂

C(s) → N₂

HCN → NO

OH, O, O₂

N koks.

C(s)

N poz. koks.

O₂ → NO

N koks.
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$_3$CN [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

\[
\begin{align*}
O_2 + 2 (-C) & \rightarrow 2 (-CO) \quad \text{(I)} \\
(-CO) & \rightarrow CO + \text{free carbon site} \quad \text{(II)} \\
2 (-CO) & \rightarrow CO_2 + (-C) + \text{free site} \quad \text{(III)} \\
O_2 + (-C) + (-CN) & \rightarrow (-CO) + (-CNO) \quad \text{(IV)} \\
(-CNO) & \rightarrow NO + (-C) \quad \text{(V)} \\
NO + (-C) & \rightarrow \frac{1}{2} N_2 + (-CO) \quad \text{(VI)} \\
NO + (-CNO) & \rightarrow N_2O + (-CO) \quad \text{(VII)} \\
N_2O + (-C) & \rightarrow N_2 + (-CO) \quad \text{(VIII)}
\end{align*}
\]
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:

  \[ T < 800 \, ^\circ C \]

- NO$_2$ undergoes destruction on higher temperatures:

  \[ T > 1200 \, ^\circ C \]
BASIC MECHANISM OF NITROGEN DIOXIDE (NO$_2$) FORMATION IN FLAMES

- The major reaction of NO$_2$ formation is with hydroperoxide radical HO$_2$:

\[
\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}
\]

(where from HO$_2$: H + O$_2$ + M → HO$_2$ + M)

- The temperature range of this reaction:

\[T < 1000 \text{ K}\]
ADDITIONAL MECHANISM OF NO$_2$ FORMATION

- Hydrocarbonperoxides RO$_2$ plays a considerable part in NO$_2$ formation:

\[
\text{NO} + \text{RO}_2 \rightarrow \text{NO}_2 + \text{RO}
\]

(where from RO$_2$: \[ \text{R} + \text{O}_2 + \text{M} \rightarrow \text{ROO} + \text{M}\])

where R are alkyl radicals:

\[
\text{CH}_3, \text{C}_2\text{H}_5 \text{ and higher}
\]
NITROGEN DIOXIDE FORMATION IN REACTION WITH ATOMIC OXYGEN

- The three body reaction:

\[ \text{NO} + \text{O} + \text{M} \rightarrow \text{NO}_2 + \text{M} \]

\(\text{NO}_2\) also is generated, but the contribution of this reaction is not important.

The temperature range: \(T < 800\ \text{K}\).
CONTRIBUTION OF NITROGEN DIOXIDE NO₂ TO THE TOTAL NOₓ

➤ The NO₂ contribution to the total NOₓ formation during pulverized coal combustion is minor:

\[
\frac{[\text{NO}_2]}{[\text{NO}_x]} \times 100\% \approx 5\%
\]

➤ More important contribution to the total production of NOₓ NO₂ introduces during combustion in gas turbines:

\[
\frac{[\text{NO}_2]}{[\text{NO}_x]} \times 100\% \approx 10\text{-}15\%
\]
NITROUS OXIDE (N\textsubscript{2}O) FORMATION IN FLAMES
CONDITIONS OF NITROUS OXIDE (N\textsubscript{2}O) FORMATION

- NO\textsubscript{2} is produced in flames due to:
  1. Oxidation of amine radicals (mainly N and less significant CN\textsubscript{2}).
  2. In lean regions of gas flames.
  3. In fluidized bed furnaces (T approx. 850 °C)
**MAJOR SOURCES OF NIROUS OXIDE N$_2$O IN FLAMES**

**Major reaction**

\[ \text{NH} + \text{NO} \rightarrow \text{N}_2\text{O} + \text{H} \]

- 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 ($\lambda<1$)

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

The temperature range of the chemical reaction:

$$T < 1500 \, ^\circ C$$
NIROUS OXIDE N₂O FORMATION IN FLUIDIZED BEDS

In catalytic reaction:

\[ 2\text{NO} \rightarrow \text{N}_2\text{O} + 0.5\text{O}_2 \]

Catalysts in fluidized bed:

1. char
2. Limestone
HOW IMPORTANT IS NITROUS OXIDE N\textsubscript{2}O?

- N\textsubscript{2}O is known as laughing gas.
- N\textsubscript{2}O has contribution to the stratospheric ozone destruction.
- In combustion processes N\textsubscript{2}O is formed mainly in fluidized beds (N\textsubscript{2}O content in flue gas up to 50 ppm).
- N\textsubscript{2}O has also some contribution to NO emission, by chemical reactions with radicals O and OH:

\[ \text{N}_2\text{O} + \text{O} \rightarrow \text{NO} + \text{NO} \]
DOMINATING MECHANISMS
OF NO\textsubscript{x} IN FLAMES
MAJOR FACTORS INFLUENCING $\text{NO}_x$ FORMATION

- fuel nitrogen $N_F$
- flame temperature
- air excess ($\lambda$)
- residence time in flame
$\text{NO}_x$ FORMATION IN PULVERIZED COAL FLAME

Fig. 5. $\text{NO}_x$ formation and destruction over a low $\text{NO}_x$ burner.
SOURCES OF NO\textsubscript{X} EMISSION IN PULVERIZED COAL FLAME

Fig. 3. Nitrogen flow pattern in advanced pulverized coal combustion system.
CONTRIBUTION OF PARTICULAR NITRIC OXIDES IN TOTAL NOX EMISSION FROM PF

**Fuel NO\textsubscript{x} is dominating NO\textsubscript{x}**

**Bituminous coal (T\textsubscript{pt} = 1650 °C)**

**Lignite (T\textsubscript{flame} = 1250 °C):**
approx. 95% of NO\textsubscript{x} is fuel NO\textsubscript{x}
<table>
<thead>
<tr>
<th>Furnace type</th>
<th>Power $\text{MW}_e$</th>
<th>Coal type</th>
<th>$\text{NO}_x$ $\text{mg/m}^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tangential</td>
<td>650–750</td>
<td>bituminous</td>
<td>710±60</td>
</tr>
<tr>
<td>Tangential</td>
<td>465–490</td>
<td>bituminous</td>
<td>750–1000</td>
</tr>
<tr>
<td>Tangential</td>
<td>200–360</td>
<td>bituminous</td>
<td>500–900</td>
</tr>
<tr>
<td>Wall fired</td>
<td>425–460</td>
<td>bituminous</td>
<td>1360±110</td>
</tr>
<tr>
<td>FBB</td>
<td>110</td>
<td>bituminous</td>
<td>400±80</td>
</tr>
<tr>
<td>FBB</td>
<td>160</td>
<td>bituminous</td>
<td>520±80</td>
</tr>
<tr>
<td>FBB</td>
<td>230</td>
<td>lignite</td>
<td>280 ±50</td>
</tr>
</tbody>
</table>
OIL FLAMES

Heavy heating oil has much of fuel nitrogen $N_F > 0.5\%$.

$\text{NO}_x$ emission from oil burners operating on heating oils nr 2 and 3 is in the range:

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

(mainly fuel $\text{NO}_x$).

Light heating oil has less fuel nitrogen $N_F < 0.05\%$

$\text{NO}_x$ emission form oil burners operating on light heating oil (nr 1) is in the range:

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

(mainly thermal $\text{NO}_x$).
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%)**