OVERVIEW OF NITROGEN OXIDE REACTIONS DURING FOSSIL FUEL COMBUSTION IN THE ATMOSPHERE

Abstract: This paper discusses the reactions of formation and decomposition of nitrogen oxides during fossil fuel combustion and in the atmosphere. Information about the chemical processes of pollutant formation and decomposition is the basis for the development of theoretical models of pollutant emissions. The information also provides a clearer picture about the primary factors influencing emissions. Nitrogen oxides are pollutants that damage human health, living and nonliving nature, and material property.

Keywords: nitrogen oxides, chemical reaction, fossil fuels, combustion, atmosphere.

INTRODUCTION

It is well-known that global ecological awareness began to develop in the second half of the 20th century. The consequences of various events on the environment and human health became evident at that point [1]. Mass construction of power plants has led to the emission of pollutants in concentrations above the prescribed limit values. One of the biggest problems that humanity faces is global warming, which is a direct consequence of the greenhouse effect. In recent decades, there has been an increase in the emission of toxic gases, therefore, respiratory diseases, carcinogens and other diseases became more frequent. All this has led to the fact that in the modern world there is increased awareness of the need for renewable energy sources and the improvement of various technologies in order to make energy use as accessible, economical and environmentally friendly as possible. Energy efficiency policy is gaining in importance and more and more attention is being paid to it. The goal is to reduce energy consumption, while keeping the level of comfort and quality of life unchanged. This goal is not easy to achieve, but a significant resource in this regard are legal regulations on energy efficiency. In order to use energy rationally and efficiently in Serbia, a number of laws and bylaws that thoroughly regulate energy efficiency have been introduced. Legal regulation of this issue is important in order to clearly establish a system in which its subjects, their rights and obligations, as well as sanctions in case of non-compliance, are clearly defined.

Air is usually polluted by various systems through the emission of pollutants, which are generated by fossil fuel combustion. Pollutants are generated during the combustion of oil-based fuels, coal, and gas, both from the burners of power plants or industrial facilities and from transport. In areas with large industrial complexes and in denser urban areas, air pollution has reached the levels that pose a serious threat to large world cities. In addition to direct effects of pollution, there are also many indirect ones, such as formation of smog due to photochemical reactions and increased formation of fog, as well as absence of rain due to increase particulate presence. When heat is accumulated in large quantities, it can produce a “heat island”, which alters the local temperature gradients, thus causing the inversion of layers of air in cities. It is well known that relatively minor temperature changes in the air and water can be detrimental to certain living systems sensitive to temperature.

Five principally different types of pollutants are generated inside combustion chambers: nitrogen oxides, carbon monoxide, organic components (unburned and incompletely burned hydrocarbons), sulfur oxides, and solid particles (including aerosols). The level of pollutant emission from a specific burner device depends on the interaction between physical and chemical processes within the device. Concentrations of different pollutants usually differ from the values calculated from chemical balance, which highlights the role of chemical kinetics in pollutant generating processes.

For a number of pollutants, such as carbon monoxide, organic compounds, and particulate matter, the reactions of their formation and decomposition constitute the initial stage of their combustion. To understand the chemical aspects of their formation, one must be familiar with the mechanisms of combustion. For other pollutants, such as nitrogen or sulfur oxides, formation and decomposition reactions do not constitute any stage of combustion. However, the reactions that include those components proceed under conditions that create burning reactions, which is why the chemistry of their formation is directly associated with their combustion. Combustion produces nitrogen oxides, whereby nitrogen, which is contained both in the fuel and in the air that participate in the combustion, participates in the oxidizing reaction.
NITROGEN OXIDES

The most important nitrogen oxide pollutants found in the atmosphere include nitrogen monoxide [NO], nitrogen dioxide [NO2], and nitrous oxide [N2O]. Other well-known nitrogen oxides, which occur in the atmosphere only in small concentrations, include nitrogen trioxide [N2O3], nitrogen tetroxide [N2O4], and nitrogen pentoxide [N2O5]. All of these oxides are gases at room temperature, with the exception of N2O5, which is a solid.

Nitrous oxide, N2O, is a colorless and odorless gas with a slightly sweet taste; it boils at -88.5 °C, freezes at -102.4 °C, and has a density of 1.53 g cm⁻³. It is soluble in water (at 0 °C, 1 cm³ of H2O dissolves 1.3052 cm³ of N2O). While at 25 °C, it dissolves 0.5962 cm³ of N2O. It is far more soluble in ethanol. It is non-reactive with water, bases, or acids. It is formed naturally in the soil, in the amount that far exceeds its anthropogenic emissions [1]. It is naturally emitted from seas and oceans. The total global emission of nitrous oxide is somewhere around 50 Tg year⁻¹ [2], whereas global anthropogenic emission amounts to ca. 20 Tg year⁻¹ [3].

The primary anthropogenic emitters of N2O include coal- or other fuel-fired power plants, biomass combustion, use of nitrogen-based artificial fertilizers, waste disposal, manufacture of adipic acid, water pollution, etc. N2O concentrations in the atmosphere are around 310 ppbv, with a relatively slow increase of about 0.3% year⁻¹ (0.8 ppbv year⁻¹) [4]. In the prehistoric period, concentrations of N2O were approximately 285 ppbv [3]. The data suggest that the trend of atmospheric N2O increase between 1960 and 1976 was 0.4±0.5 ppbv year⁻¹, while in the 1976-1988 period it was 0.8±0.02 ppbv year⁻¹. Nitrous oxide can cause the thinning of stratospheric ozone as well as the greenhouse effect. It is stable in the atmosphere and can remain there from 100 to 150 years [2, 3].

Nitrogen monoxide (NO) is a colorless and odorless gas with the density of 1.0367 g cm⁻³; it condenses at -151.8 °C, freezes at -163.6 °C, and is poorly soluble in water (1 cm³ of H2O at 0 °C dissolves 0.07 cm³ of NO). It does not react with water. It is formed during fossil fuel combustion at high temperatures.

Nitrogen trioxide (N2O3) is the anhydride of nitrous acid (HNO2). It is stable only at low temperatures as a dark blue liquid; it crystalizes to blue crystals at -103 °C and boils at 3.5 °C. At 25 °C there is only 10% of N2O3 left, while the remaining portion comprises NO and NO2. It forms nitrates with bases.

Nitrogen dioxide (NO2) and nitrogen tetroxide (N2O4) are toxic gases in equilibrium mixture. NO2 is a toxic gas with a specific smell and reddish-brown color. Below 150 °C it loses color, as the two NO2 molecules associate to form the colorless N2O3 (2NO2 ⇄ N2O3). At 25 °C, the N2O3 molecules prevail; with further cooling, it condenses to a liquid (boiling point at 21.5 °C), while at -11.20 °C, it forms solid colorless crystals. It begins to decompose above 150 °C and completely decomposes at 600 °C (2NO2 ⇄ 2NO + O2). It is in a gaseous state under normal atmospheric conditions.

Nitrogen pentoxide (N2O5) is the anhydride of nitric acid (HNO3). It is a colorless crystal substance that melts at 30 °C and boils at 47 °C. It is a volatile compound that decomposes when slightly heated (2N2O5 = 4NO2 + O2). At regular temperature, it decomposes by an explosion.

REATIONS OF NITROGEN OXIDES DURING COMBUSTION

The biggest amount of nitrogen oxides that occur in urban and industrial environments is generated from the combustion of solid, liquid, and gaseous fuels. Nitrogen monoxide is formed from nitrogen and oxygen during combustion.

N2 + O2 ⇄ 2NO

The balance of the reaction depends on flame temperature, pressure, oxygen and nitrogen concentration, retention time of gases in flame zones with different temperatures, and the cooling rate of generated gases. Formation of nitrogen monoxide is more intensive at higher flame temperatures, while its oxidation to nitrogen dioxide, as an exothermic reaction, is more intensive at lower temperatures.

Therefore, it is crucial to control the conditions of fossil fuel combustion in order to control the generation of nitrogen oxides. Nitrogen oxides can be generated in certain industrial processes, such as manufacture of nitric acid and explosives, metal cleaning, and various organic syntheses.

During specific fires, such as biomass burning in tropical or subtropical regions, nitrogen oxides are formed in the soil as the result of the microbiological processes of nitrification and denitrification, which depend upon soil temperature and humidity, ground vegetation, and the amount of nitrate fertilizers used.

The total global emission of nitrogen oxides on this basis is 12 Tg (N) per year [5]. A small amount of oxides formed in the stratosphere reach the troposphere.

For instance, nitrogen monoxide is formed due to high temperatures resulting from atmospheric electric discharges. On this basis, the global emission amounts to approximately 8 Tg (N) per year [6].

There are two principally different sources of NO generation during the combustion of traditional fuels. These are the oxidation of atmospheric (molecular) nitrogen and the oxidation of fuel components that contain nitrogen (nitrogen-based fuels). In most burner devices, the initial process is the primary source of NO. However, nitrogen-based fuels are the primary source of NO in combustion chambers that utilize crude oil or coal and that often contain a significant amount of organic nitrogen compounds.

It is well known that the combustion of lean and near-stoichiometric air/fuel mixtures has the following
primary reactions that govern the formation of NO from molecular nitrogen:

\[ O + N_2 \rightleftharpoons NO + N \]
\[ N + O_2 \rightleftharpoons NO + O \]

It is assumed that the reaction

\[ N + OH \rightleftharpoons NO + H \]

can also contribute to the formation of NO, especially in near-stoichiometric and rich air/fuel mixtures.

Combustion chambers usually release NO and NO\(_2\). These oxides react in the presence of hydrocarbons under the influence of sunlight and accompanied by the formation of smog. As a rule, concentration of NO\(_2\) is significantly lower than that of NO, yet in the exhausts from gas turbine engines, NO\(_2\) concentration reaches a considerably high level. According to its manner of generation, there are three types of NO: thermal, fuel, and primary nitrogen monoxide.

At high flame temperatures, \(N_2\) reacts with oxygen, forming the thermal nitrogen monoxide. If a fuel contains compounds containing nitrogen, the nitrogen is released at lower temperatures, forming the fuel nitrogen monoxide. Primary nitrogen monoxide is not formed from atmospheric \(N_2\) and \(O_2\).

In most combustion chambers, thermal NO is the dominant component among nitrogen oxides. Crude oil and coal often contain a significant amount of organic nitrogen compounds, so the nitrogen contained in the fuel can be an important source of fuel NO.

During fluidized bed combustion of coal at relatively low temperatures (ca. 1,275 K), the fuel NO constitute the basic portion of NO. Primary NO is formed in a turbulent diffusion gas flame, where maximum temperature can go below 1,575 K. Primary NO is formed due to reactions between radicals, generated from the fuel, and \(N_2\); the resulting materials react with oxygen-containing compounds and thus form NO.

### REACTIONS OF NITROGEN OXIDES IN THE ATMOSPHERE

Content and distribution of nitrogen oxides in the atmosphere depends on the sources of the same processes of transfer and removal from the atmosphere. This means that the content of such pollutants varies temporally and geographically, with an added influence of weather conditions. The concentration of atmospheric nitrogen oxides in urban and industrial areas is higher than in non-urban environments. It can change over a day as well as over a year, which is mainly due to emissions and weather conditions.

The concentration is also higher during the fall, winter, and early spring due to higher energy consumption. Concentrations in non-urban areas are considerably lower, approximately 1 parts per billion by volume (ppbv). This was confirmed by the measurements conducted in the pure troposphere, the results of which are shown in Table 1 [7].

<table>
<thead>
<tr>
<th>Latitude</th>
<th>Altitude (km)</th>
<th>NO (ppbv)</th>
<th>NO(_x) (ppbv)</th>
<th>Measurement period</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°S-50°N</td>
<td>0-10</td>
<td>≤0.1</td>
<td>0.2-0.6</td>
<td>December 1982</td>
</tr>
<tr>
<td>51-87°N</td>
<td>0.2-12</td>
<td>≤0.01</td>
<td>&lt;0.6</td>
<td>March 1982</td>
</tr>
<tr>
<td>30-35°N</td>
<td>3-8</td>
<td>0.015-0.035</td>
<td>0.2</td>
<td>February 1983</td>
</tr>
<tr>
<td>40-8°N</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
<td>January-February 1984</td>
</tr>
<tr>
<td>3°S-360°N</td>
<td>5</td>
<td>0.014-0.2</td>
<td>-</td>
<td>July-August 1985</td>
</tr>
<tr>
<td>15-42°N</td>
<td>-</td>
<td>0.001</td>
<td>-</td>
<td>October-November 1983</td>
</tr>
<tr>
<td>37-38°N</td>
<td>8-15</td>
<td>0.04-0.25</td>
<td>-</td>
<td>June 1987</td>
</tr>
</tbody>
</table>

There are two main sources of nitrogen oxides (NO, NO\(_2\)) in the air: natural sources, whose global emission is estimated at approx. 450 x 10\(^6\) t/year, and anthropogenic sources, whose global emission is estimated at 45 x 10\(^6\) t/year. Even though anthropogenic emission constitutes only 1/10 of the total emission, it significantly impacts air quality, especially in urban and industrial areas, where nitrogen oxides mostly occur. Consequently, concentrations of nitrogen oxides are 10 to 100 times higher in urban and industrial than in non-urban areas.

Influenced by solar radiation, atmospheric NO is converted into NO\(_2\) through a series of reactions. The process unfolds via the so-called photolytic cycle of NO\(_2\) [8], resulting in rapid NO and NO\(_2\) transformations. If there are no particular influences in the air, the cycle leads to a NO/NO\(_2\) state of balance. However, sources of nitrogen oxides are also most often volatile organic compounds that participate in the photolytic cycle and thus increase NO\(_2\) generation.

Nitrogen monoxide, which is anthropogenically formed mostly from fossil fuel combustion, is converted into NO\(_2\) via different chemical processes, producing nitric acid. Nitrogen monoxide can also form in the upper layers of the atmosphere, where cosmic radiation causes the nitrogen molecules to split, producing metastable nitrogen atoms, which in turn react with oxygen, ozone, or a hydroxyl group, yielding NO [9] [19].

\[ N + O_3 \rightarrow NO + O_2 \]
\[ N + OH \rightarrow NO + H^+ \]
\[ N + O_2 \rightarrow NO + O^- \]
\[ O_3 + NO \rightarrow NO_2 + O_2 \]
\[ NO_2 \rightarrow NO + O^- \]
\[ N + NO_2 \rightarrow 2NO \]
\[ O^- + NO_2 \rightarrow NO + O_2 \]

In the troposphere and lower stratosphere, the following processes can be expected:

\[ O^- + N_2O \rightarrow 2NO \]
\[ N_2O \rightarrow NO + N^- \]
By reacting with atomic oxygen or ozone, atmospheric NO is converted into NO₂ via the following reactions:
\[ \text{NO} + \text{O} \rightarrow \text{NO}_2 + \text{M} \]
\[ \text{NO} + \text{O}_2 \rightarrow \text{NO}_2 + \text{O} \]
Nitrogen monoxide oxidizes by means of the hydroperoxide group, alkyl peroxides (AO₃), methyl peroxides (CH₃C(O)O), hydroxalkyl peroxides (R-OH-O₂), and peroxy acetyl radical (CH₂C(O)O₂). Some inorganic reactions oxidize NO to NO₂.
The resulting NO₂ in the atmosphere is converted into nitrous and nitric acid, nitrites, and nitrates.
Nitrous acid (HONO) in the atmosphere is generated via the following reactions [10]:
\[ \text{HO}^- + \text{NO} \rightarrow \text{HONO} \]
\[ \text{HOO}^- + \text{NO}_2 \rightarrow \text{HO}_2\text{NO}_2 \]
\[ \text{RO}^- + \text{NO}_2 \rightarrow \text{R'CHO}^- + \text{HONO} \]
\[ \text{NO} + \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HONO} \]
\[ \text{NO} + \text{HONO}_2 \rightarrow \text{NO}_2 + \text{HONO} \]
During daytime, nitrous acid is generated to the greatest extent through a reaction between a hydroxyl group and NO:
\[ \text{OH}^- + \text{NO} \rightarrow \text{HONO} \]
Under normal conditions, there is a concentration balance between the hydroxyl group and the nitrous acid in the atmosphere. However, if the nitrous acid was formed by a non-photolytic reaction, it will become the source of the hydroxyl group, especially in the period around sunrise [11].
Another source of nitrous acid is the reaction of NO₂ with water vapor in the atmosphere:
\[ 2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HONO} + \text{HNO}_3 \]
It has been established that nitrous acid concentrations increase during the night, so it can be assumed with a high degree of probability that the acid is formed via a non-photolytic reaction, with a low NO content and a high humidity is greater than during the summer. Reactions of these molecules, proceed in the atmosphere on a wider scope.
Aldehydes and alkenes react with the nitro group in the atmosphere as follows:
\[ \text{NO}_3^- + \text{CH}_2\text{O} \rightarrow \text{HNO}_2 + \text{HCO} \]
\[ \text{NO}_3^- + \text{CH}_3\text{CHO} \rightarrow \text{HNO}_2 + \text{CH}_3\text{CO} \]
\[ \text{NO}_3^- + \text{C}_3\text{H}_6 \rightarrow \text{CH}_3\text{CH}_2\text{ONO}_2 \]
\[ \text{NO}_3^- + \text{C}_3\text{H}_6 \rightarrow \text{CH}_3\text{CH}(_2\text{ONO}_2)\text{CH}_2 \]
Organic nitrate compounds are formed at high hydrocarbons/NOₓ ratios, whereby up to 24% of nitrogen compounds can be converted into organic nitrate compounds [14].
A reaction between NO₂ and the nitrate group in the atmosphere yields N₂O₅. The reaction proceeds during the night, when the N₂O₅ concentration can be considerably high. On the other hand, when exposed to heat, N₂O₅ decomposes as follows:
\[ \text{N}_2\text{O}_5 + \text{M} \rightarrow \text{NO}_2 + \text{NO}_3^- + \text{M} \]
and it also reacts with water, yielding nitric acid:
\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 \]
Nitrogen pentoxide can play a significant part in atmospheric chemical processes considering that it is formed in colder areas but it decomposes and reacts in warmer areas, i.e. with solar radiation present.
Experimental studies [15] have shown that solar radiation influences the photolysis of N₂O₅, which generates several compounds:
\[ \text{N}_2\text{O}_5 + \text{h} \gamma (\lambda = 254 \text{ nm}) \rightarrow \text{NO}_2 + \text{NO}_3^- \rightarrow \text{O}^- + \text{NO}_2 + \text{NO}_2 \rightarrow \text{NO} + \text{NO}_2 + \text{O}_2 \]
The photolysis predominantly produces NO₂ and nitrate ion. The chlorine present in smoke gases reacts with hydroxyl radicals yielding atomic chlorine. The chlorine molecule in the atmosphere is also split into atoms before reacting. Chlorine is important for the activation of inactive components and their subsequent reactions in the atmosphere. Some of the more relevant reactions between chlorine and nitrogen oxides to be found in the atmosphere include the following [16]:

\[
\begin{align*}
Cl_2 + h\gamma &\rightarrow Cl' + Cl' \\
Cl + Cl' + M &\rightarrow Cl_2 + M \\
Cl' + O_2 + M &\rightarrow ClOO' + M \\
ClOO' + NO &\rightarrow ClO' + NO_2 \\
ClOO' + NO &\rightarrow ClO + ClNO \\
ClO + NO + M &\rightarrow ClO' + M \\
ClNO + O_2 &\rightarrow NO + Cl_2 \\
ClNO + O_2 &\rightarrow Cl + NO_2 \\
ClO + NO + M &\rightarrow ClO' + M \\
ClO + NO &\rightarrow NO_2 + Cl \\
\end{align*}
\]

Chlorine atoms attack less reactive compounds, such as methane and NO, which allows the monoxide to oxidize:

\[
\begin{align*}
Cl' + RH &\rightarrow HCl + R' \\
R' + O_2 &\rightarrow RO_2 \\
RO_2' + NO &\rightarrow RO' + NO_2 \\
RO' + NO &\rightarrow RONO \\
RO' + NO_2 &\rightarrow RONO_2 \\
\end{align*}
\]

A reaction between sodium chloride and nitrogen oxides, releasing active chlorine, occurs in the tropospheric layers above seas and oceans, which contain sodium chloride particles [17]:

\[
\begin{align*}
NO_2' + NO_2 &\rightarrow N_2O_5 \\
N_2O_5 + NaCl &\rightarrow ClNO_2 + NaNO_3 \\
ClNO_2 + h\gamma &\rightarrow Cl' + NO_2 \\
\end{align*}
\]

The ammonia found in the atmosphere is generated from nitrogen compounds, from the decomposition of nitrogen-based fertilizers in the soil, or from anthropogenic emissions from specific industrial processes.

When it reaches the atmosphere, ammonia is converted into NO via the following reactions [18]:

\[
\begin{align*}
NH_4^+ + OH' &\rightarrow NH_3 + H_2O \\
NH_3 + HO' &\rightarrow NH_3 + O_2 \\
NH_4^+ + NO &\rightarrow N_2 + H_2O \\
NH_2' + NO_2 &\rightarrow N_2O + H_2O \\
NH_2' + O_3 &\rightarrow NH_2O + O_2 &\rightarrow HNO' + NO_x \\
\end{align*}
\]

**CONCLUSION**

The studies conducted so far, both theoretical and experimental, have shown that the reconstruction of combustion chambers and meticulous control of pollutant generation in their flaming chemical reactions can significantly reduce pollutant emissions from furnaces, combustion chambers, gas turbulent flow engines, and internal combustion engines.

At temperatures that in most cases lead to combustion, the presence of fuel and oxidizer inevitably produces pollutants. High concentrations of such pollutants can be lowered via subsequent chemical reactions at lower temperatures, but stopping the reaction will result in a high emission level. Therefore, the generation, decomposition, and change in the concentration of pollutants are in opposition, because the maximum combustion efficiency is reached with a stoichiometric or near-stoichiometric composition of the mixture, which results in the highest attained temperatures. The high temperatures in turn lead to the generation of large amounts of pollutants, which is why the process can be optimized through the regulation of mixture quality and temperature in the entire system.

**REFERENCES**


**BIOGRAPHY**

Sveta Cvetanović was born in Donje Dragovlje, in Serbia in 1961. He graduated from the Faculty of Occupational Safety in Niš. He was employed in occupational safety and fire safety sector in AIK bank in Sabac. He has been working at Faculty of Occupational Safety since 1990. His research interest include risk management, fire and explosion risk assessment, fire safety systems and remediation of accidents.

**PREGLED REAKCIJA AZOTNIH OKSIDA PRI SAGOREVANJU FOSILNIH GORIVA U ATMOSFERI**

_Sveta Cvetanović_

**Rezime:** U radu je dat pregled reakcija formiranja i razlaganja azotnih oksida pri sagorevanju fosilnih goriva i u atmosferi. Informacije o hemijskim procesima stvaranja i razlaganja zagađujućih materija su osnova za razvoj teorijskih modela njihove emisije, a takođe omogućavaju da se stvari kvalitetna predstava o osnovnim faktorima koji utiču na emisiju. Azotni oksidi su zagađujuće materije koje oštećuju zdravlje čoveka, živu i neživu prirodu i materijalna dobra.

**Ključne reči:** azotni oksidi, fosilna goriva, sagorevanje, atmosfera.