Phenomenology of nitrogen oxides formation in a gas-diesel engine

O P Lopatin
Department of thermal engines, automobiles and tractors, Vyatka State Agricultural Academy, October prospect, 133, Kirov, 610017, Russian Federation

E-mail: nirs_vsaa@mail.ru

Abstract. A zone model of the process of nitrogen oxides formation in a gas diesel cylinder when working on natural gas with exhaust gas recirculation is considered. The presented phenomenology of combustion of diesel fuel injected through a nozzle with five holes in methane-air mixture with products of exhaust gas recirculation in the combustion chamber of a diesel engine running on natural gas with recirculation of exhaust gases, where the behavior of processes and components distribution of nitrogen oxides is significantly different. For clarity, the selected zones of nitric oxide formation are schematically presented in the work as a graphic image.

The formation of toxic substances-nitrogen oxides (NOx) and incomplete combustion products in the diesel cylinder during combustion occurs in fundamentally different ways. The first group of toxic substances is associated with chemical reactions of fuel oxidation that occur both during the pre-flame period and during the combustion process. The second group of toxic substances is formed when nitrogen and excess oxygen are combined in the combustion products. The reaction of formation of NOx are mostly thermal in nature but all are associated with oxidation reactions of the fuel. Therefore, consideration of the mechanism of formation of toxic substances, which are products of fuel combustion and toxic substances resulting from the incomplete combustion of the fuel, of course, need to explore separately [1-6].

Nitrogen oxides are the most toxic of all polluting chemical compounds found in diesel exhaust gases. They are formed during the combustion of fuel, mainly due to the chemical reactions of the two main components of air: nitrogen (N2) and oxygen (O2). NOx interacts with water vapor in the air to form acids that affect the human lungs, causing chronic diseases. In chronic poisoning, inflammatory diseases of the mucous membranes of the respiratory system, muscle and heart weakness, and nervous disorders are observed. By absorbing natural background radiation in the ultraviolet and visible parts of the spectrum, NOx reduces the transparency of atmospheric air and is involved in the formation of photochemical fog – smog consisting of photochemical oxidants and ozone [7-13].

Given the phenomenology of combustion of diesel fuel injected through a nozzle with five holes in methane-air mixture c products of combustion in the cylinder of a diesel engine, methane-fuel charge formed after fuel injection into the combustion chamber, in view of the involvement in the movement of the jet methane-air mixture from the environment, molecular and turbulent diffusion of the fuel in the torch and in the surrounding space of the combustion chamber in the axial and radial directions, taking into account the twisting of the flow methane-air vorticity, given, that there will also be
concentration heterogeneity, it is necessary to identify a number of zones in the combustion chamber, where the nature of the processes and the distribution of NOx components will differ significantly (figure 1) [14-18].

![Figure 1](image_url)

**Figure 1.** Phenomenological model of the process of NOx formation in a diesel cylinder when working on natural gas with recirculation: 1 – zone of formation of NO by bimolecular reaction; 2 - zone of rapid NO; 3 - zone of rapid and thermal NO; 4 - zone of thermal NO formed by the Zeldovich mechanism; 5 - zone of NO decomposition; 6 - zone with a predominance of fresh methane-air mixture and recirculation products; 7, 8 and 9 - zone of no oxidation in NO2.

The boundaries of these characteristic zones are conditional and in turbulent motion we can only talk about the stability of the time-average boundaries, but the instantaneous values of speeds and concentrations of nitrogen oxides are constantly changing.

The first zone (figure 1) is the zone of NO formation by a bimolecular reaction, which is the core of the fuel jet, determined by an excess of hydrocarbon fuel and a lack of oxidizer at a temperature level of more than 1000 K. the formation of nitrogen oxide (NO) occurs here as a result of the collision of nitrogen molecules of the methane – air mixture and recycled gases with oxygen molecules. The resulting nitric oxide is oxidized to NO. At the same time, the share of NO2 in zone 1 can reach 12% of the total amount of NOx.

As you move the fuel jet, the intensification of evaporation processes and burning, increasing the temperature and the excess air ratio increases the possibility of developing other mechanisms of formation of NOx, the more likely the closer the conditional boundary separating the kernel and shell torch [19-22].

The second zone is the rapid NO formation zone, which is a fuel torch shell that has the same characteristics as the first one, at a temperature level less than 1500 K, where there is a lack of air nitrogen oxidizer and recirculated gases. In zone 2, the formation and decomposition of nitrogen hemioxide N2O, as well as the formation of intermediate compounds CN, NH, involved in the subsequent mechanism of formation of rapid NO. Nitrogen dioxide NO2 formed in zone 1 is almost completely converted to NO.

So, in the initial region of the front combustion of methane-air mixture with the recycled products has place the formation of substantial quantities of NO. Here, nitrogen oxides NOx are formed at temperatures not exceeding 1500 K.

The third zone is the zone of rapid and thermal NO formation, which is a zone of deep pyrolysis of the methane molecule. In zone 3, the CN and NH radicals formed in zone 2 are oxidized. In the area of changes in the values of such indicators as pressure and temperature due to the large difference in the dissociation energy of oxygen and nitrogen, the oxygen molecule dissociates into atoms in the absence of a methane-air mixture with nitrogen atom recycling products. Further, the formation of thermal NO proceeds by the mechanism of Ya. B. Zeldovich and through the OH radicals.
The fourth zone is the formation of thermal NO mechanism Zeldovich, which is a zone of combustion of methane-air charge with the recycled products, located on either side of the zone of maximum temperature (T>1900 K), which is different from the third oxidizer excess. Under such conditions, the predominant reactions are the oxidation of CH₄ methane, which determine the thermal regime in the gas-diesel cylinder when working with recirculation. In the fourth zone, the formation of thermal NO occurs to a determining degree according to the mechanism Ya. B. Zeldovich. The local formation of NO in zones 3 and 4 is related to the concentration of oxygen atoms, which depends on the oxygen concentration in each local zone and the temperature in it.

The fifth zone is the zone of decomposition of NO, which is a zone of combustion of poor methane-air mixture with exhaust gases (with breaks and stopping the burning flame of the poor), which consumes nitric oxide.

The sixth zone is a zone with a predominance of methane-air mixture with the combustion products. In this area all completed the chemical reaction, and establishes a uniform concentration of products of complete combustion, where the nitrogen oxide, mainly, is not produced and not consumed [23-26].

In the combustion chamber of the diesel engine during the combustion of methane-air mixture with exhaust gases, ignited atomized diesel fuel, there are a number of characteristic zones of the joint effect of the neighboring torches fuel jets, which are observed mainly areas with a homogeneous methane-air mixture with the recycled products and a large number of local volumes. In zones 7, 8 and 9, during the expansion stroke, the combustion products are sharply cooled by the water-cooled cylinder walls. At temperatures below 970 K, nitric oxide NO is oxidized to nitrogen dioxide NO₂. At the same time, the share of NO₂ in zones 7, 8 and 9 can reach 18% of the total amount of nitrogen oxides.

These zones are in interaction with each other, which ensures stability of the process of nitrogen oxides formation during combustion of the methane-air mixture with recirculation products. These are turbulent heat exchange between zones, transfer of products of incomplete reactions and oxygen that contribute to the dehydrogenation of methane CH₄, purity, scale and speed of turbulent pulsations that determine the mixing time for the torch zones and the time of formation of nitrogen oxides [27-31].

During the compression cycle, no nitrogen oxide is formed in the combustion chamber of the gas diesel when working with exhaust gas recirculation due to the low temperature of the methane-air mixture with recirculation products. When burning fuel in the core of the torch (zone 1 in figure 1) and on the surface (zone 2 in figure 1) on the wall increases, the average temperature in the cylinder, which leads to increased concentrations of nitric oxide NO in the areas of lean methane-air mixture with the recycled products.

In turn, at a higher flame temperature (zones 3 and 4), the formation of nitric oxide NO depends on the local oxygen concentration. During the expansion process, when the temperature of the gases in the gas-diesel cylinder decreases, the NO content decreases, and only 60-70% of the formed NO remains at the time of opening the exhaust valve [32-36]. Therefore the release of nitric oxide NO in combustion of methane-air mixture with the recycled products in the cylinder of diesel engine, which determines the content of nitrogen oxides in the exhaust gas depends on the maximum temperature, the volume of products recirculated, the oxygen concentration in zone 4 and the duration of the zone 5, in which the nitrogen flow rate to 30-40%, resulting in the maximum temperature zone 4. In the combustion products, however, nitric oxide prevails, which is 82-88% of the total amount of nitrogen oxides.

References
[1] Semprini S, Sánchez D and De Pascale A 2016 Solar Energy 132 279-93
[2] Kozlov A N, Anfilatov A A and Chuvashov A N 2019 Journal of Physics: Conf. Series 1399 055051
[3] Osorio-Tejada J L, Llera-Sastresa E and Scarpellini S 2017 Renewable and Sustainable Energy Reviews 71 785-95
[4] Lopatin O P 2020 *IOP Conf. Series: Earth and Environmental Science* **421** 072019
[5] Chuvashev A N and Chuprakov A I 2019 *Journal of Physics: Conf. Series* **1399** 055085
[6] Starik A M, Savel'ev A M, Favorzkiii O N and Titova N S 2018 *International Journal of Green Energy* **15** 161-8
[7] Likhanov V A and Lopatin O P 2019 *Journal of Physics: Conf. Series* **1399** 055016
[8] Presser C, Nazarian A and Millo A 2018 *Fuel* **214** 656-66
[9] Skryabin M L 2020 *IOP Conf. Series: Earth and Environmental Science* **421** 072012
[10] Likhanov V A and Rossokhin A V 2018 *IOP Conf. Series: Materials Science and Engineering* **457** 012007
[11] Jeevahan J, Mageshwaran G, Joseph G B, Raj R B D and Kannan R T 2017 *Chemical Engineering Communications* **204** 1202-23
[12] Pérez J, Lumbraeras J, Rodriguez E and Vedrenne M. *Transportation Research Part D: Transport and Environment* **52** 156-71
[13] Likhanov V A and Lopatin O P 2019 *Journal of Physics: Conf. Series* **1399** 055020
[14] Wyser T, Hagen R, Foxx A and McCarthy G 2016 *Federal Register* **81(206)** 73478-4274
[15] Markov V A, Loboda S S and Kamaldinov V G *International Conference on Industrial Engineering “ICIE 2016”* 225-34
[16] Likhanov V A and Lopatin O P 2020 *IOP Conf. Series: Earth and Environmental Science* **421**
[17] Rodzkin A, Kundas S and Wichtmann W 2017 *Energy Procedia “International Scientific Conference “Environmental and Climate Technologies”, CONECT 2017”* 261-7
[18] Romanyuk V, Likhanov V A and Lopatin O P 2018 *Theoretical and Applied Ecology* **3** 27-32
[19] Jeevahan J, Mageshwaran G, Joseph G B, Raj R B D and Kannan R T 2017 *Chemical Engineering Communications* **204** 1202-23
[20] Likhanov V A and Lopatin O P 2018 *IOP Conf. Series: Materials Science and Engineering* **457** 012011
[21] Frances C 2009 *Sustainability* **1** 43-54
[22] Sikarwar V S, Zhao M, Fennell P S, Shah N and Anthony E J 2017 *Progress in Energy and Combustion Science* **61** 189-248
[23] Likhanov V A, Lopatin O P and Yurlov A S 2019 *Journal of Physics: Conf. Series* **1399** 055026 072018
[24] Sinyavski V V, Shatrov M G, Dunin A Y, Shishlov I G and Vakulenko A V 2019 *Periodicals of Engineering and Natural Sciences* **7** 281-6
[25] Yeo J, Rochussen J and Kirchen P 2016 *SAE Technical Papers* September
[26] Likhanov V A and Lopatin O P 2017 *Thermal Engineering* **64(12)** 935-44
[27] Khan M I, Yaseen T, Farooq M et al. 2016 *Renewable and Sustainable Energy Reviews* **66** 702-41
[28] Kozlov A V, Terenchenko A S, Luksho V A and Karpukhin K E 2017 *IOP Conference Series: Earth and Environmental Science “International Conference on Energy Engineering and Environmental Protection, EEEP 2016”* p 012096
[29] Likhanov V A and Lopatin O P 2018 *Ecology and Industry of Russia* **22(10)** 54-9
[30] Wang H, Sun J and Kolmanovsky I 2016 *Proceedings of the American Control Conference “2016 American Control Conference, ACC 2016”* 3298-303
[31] Khan M F, Latif M T, Dominick D, Mohd Nadzir M S, Lim C H, Amil N, Jaafer S A, Sahani M and Tahir N M 2015 *Atmospheric Environment* **106** 178-90
[32] Likhanov V A and Lopatin O P 2019 *Ecology and Industry of Russia* **23(9)** 60-5
[33] Mwangi J K, Lee W J, Chang Y C et al. 2015 *Applied Energy* **159** 214-36
[34] Xing Y, Song H, Yu M et al. 2016 *Atmosphere* **7(9)** 121
[35] Likhanov V A and Skryabin M L 2019 *IOP Conf. Series: Earth and Environmental Science* **315** 032045
[36] Khan R, Ahmad I, Ismail M et al. 2016 *Journal of Analytical and Applied Pyrolysis* **120** 493-500