

OXIDES OF NITROGEN IN DIESEL ENGINES: FORMATION, EFFECTS AND CONTROL

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Diesel engines are used in heavy duty applications because of their high efficiency and reliability. However, oxides of nitrogen emissions remain a major concern. In diesel engines, fuel combustion is responsible for a major proportion of oxides of nitrogen emissions. Four sources of the oxides have been identified. The range of possible types of damage to environment and health, as well as effective methods for reduction of oxides of nitrogen, have been analysed.

1 INTRODUCTION

Despite their reputation for being dirty and noisy power plants, modern diesel engines (also called compression ignition engines) offer high fuel efficiency and low noise. However, they inherently produce higher oxides of nitrogen emissions, commonly referred to as NO_x, than spark ignition engines. These, together with particulate emissions, have become the major environmental concern and has become an important theme of study. During the past few decades, increasing attention, as a result of the ever growing stringent regulations on emissions, is being given to improve design and after treatment systems to ensure that the NO_x levels in particular conform with acceptable standards. The reduction in emissions also will be complimented by improvement in diesel fuel improvement [1]. Liotta and Montalvo studied the effect of Oxygenated Fuels on emissions from a Heavy-Duty Diesel engine. They increased the cetane number of oxygenated fuel and achieved some reduction in NO_x emissions. They further observed that addition of oxygenated additives to diesel fuel caused a small increase in NO_x emissions [2]. Ryan and Erwin also achieved lower NO_x emissions with increase in cetane number [3]. Mc Carthy et al. studied the cost effectiveness of reducing emissions and concluded that it is much cheaper to reduce NO_x emissions by increasing cetane number rather than by reducing the aromatic content [4].

In this field it is very useful to be aware of the origins of this pollutant substance. Four mechanisms of formation of oxides of nitrogen in combustion processes are: thermal, prompt, N₂O and fuel. It is important to point out that emissions of NO_x in diesel engines are exclusively generated through thermal and prompt mechanisms [5-8].

In this work, the formation, of oxides of nitrogen have been studied, through the most important and best known mechanisms. By analysing separate effects of these oxides, some contribution to the

comprehension of the source of NO emissions to the environment is intended. Furthermore, some means of control of nitrous oxides are summarised. This kind of study, jointly with similar studies could provide awareness of cleaner diesel engines, with regard to the two emissions, nitric oxide (NO) and nitric dioxide (NO₂), currently most restricted worldwide.

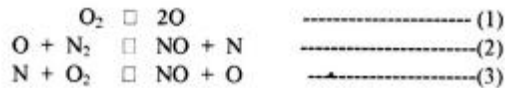
2 ORIGINS OF OXIDES OF NITROGEN

The formation of oxides of nitrogen is a highly temperature-dependent phenomenon and occurs because the equilibrium concentrations of the various NO_x compounds formed when oxygen and nitrogen are mixed at high temperatures and as a result of combustion of the fuel-bound nitrogen. Primarily nitrogen monoxide NO is formed, whereas the more poisonous nitrogen dioxide is formed only after the combustion when there is the exhaust gases and subsequently in the atmosphere. In diesel engines with low load, considerable NO₂ emissions must be expected due to the fact that the combustion process involves high air excess. As all NO is ultimately transformed into NO₂, NO_x emissions (NO + NO₂) are indicated as NO₂, threshold values are also listed as NO₂.

Four pathways are generally recognised as being responsible for nitric oxides formations in the combustion process of diesel engines depending on the particular engine operating conditions of temperature and concentration, on the residence time and the type of fuel: thermal mechanism; prompt mechanism; fuel mechanism (by direct reaction between oxygen from the air and nitrogen from fuel) and N₂O mechanism.

2.1 Thermal NO

It is fairly well established that NO formation in combustion process proceeds by Zel'dovich chain mechanism [9-11]:



The concentration of oxygen atoms available is responsible during or after combustion for this type of NO formation. At over 300°C and with rising temperatures the O concentration increases considerably as a result of the equilibrium dissociation of unburned oxygen molecules, O₂. Consequently, the NO formation speed also increases. A nitrogen atom is liberated, and it reacts with oxygen to form NO.

The above reactions (equations 1 and 2) take place in high oxygen areas (excess O₂) of the flame or in the post reaction zone [12]. In fuel – rich zones of the flame, the following reaction takes place mainly at temperatures over 1300°C:



The thermal nitric oxide formation depends on the following factors:

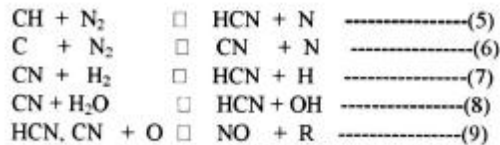
- Temperature in the reaction zone: apart from O₂ dissociation the reaction itself (equation 2) is highly temperature-dependent, so that both influences lead to a clear increase in NO formation with rising temperatures [13].
- Equivalence ratio or air-fuel ratio in the reaction zone which influences the concentration of atomic oxygen. NO emissions, generally, decrease with decrease air-fuel ratio.
- The gases residence time in the reaction zone at a maximum temperature or mixing speed after the reaction with cooler reaction products: the shorter the residence time, the smaller the NO formation.

The Zel'dovich mechanism can be taken as controlling the emission of nitric oxide from diesel engines. Consequently, nitric oxide is mostly produced early in the combustion process [14].

2.2 Prompt NO

The 'prompt' mechanism occurs in the low-oxygen area of flames. This phenomenon involves the reaction of hydrocarbon fragment (e.g. CH) with molecular nitrogen-so-called prompt. It is only weakly temperature dependent and accounts for only a relatively small proportion of the NO emission

from fuel lean combustion encountered in a diesel engine. Though the mechanisms involved are not fully understood, it is believed that the following reactions lead to the formation of NO:



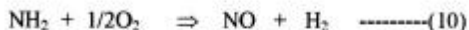
Where **R** is an organic residue.

The CN radical arising from fuel-nitrogen compounds is transformed further into HCN. Furthermore, atomic nitrogen is released. The cyanogen compounds and nitrogen atoms can then be oxidized to NO. Figure 1 illustrates the influence of the combustion temperature of NO formation according to different formation mechanism. It can be seen that the prompt NO formations are much less temperature-dependent than thermal NO formation.

2.3 Fuel NO

If fuels contain organically bonded nitrogen (organic nitrogenous compounds) then some of this nitrogen will eventually form the so-called fuel NO. The percentage of nitrogen undergoing this change depends on the nature of combustion process. Light distillate fuels contain small amounts of organic nitrogen, less than 0.06 percent, but heavy distillates may contain as much as 1.5 percent. Thus, depending on the degree of nitrogen conversion, the fuel NO can represent a considerable portion of the total NO [15,16].

Oxidation of these nitrogenous compounds is less temperature-dependent occurring even at lower temperatures and increasing with higher excess air Fig. 1:



However, during combustion only part of the fuel nitrogen is transformed into NO. In fuel-rich areas of the flame, not only fuel nitrogen but also thermally formed NO can be reduced to molecular nitrogen:

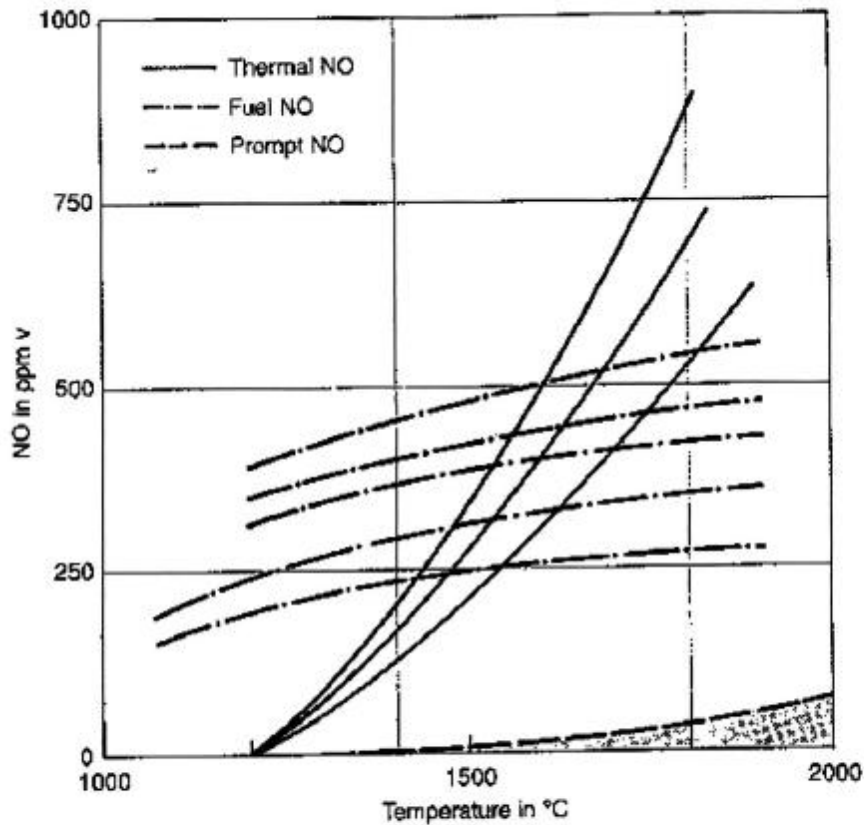


Fig. 1 Diagram of NO formation versus combustion temperature; parameter for thermal NO: O₂ excess

The lower the fuel's bound nitrogen content, the higher the transformation rate to NO as seen in

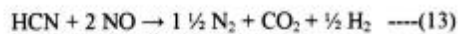
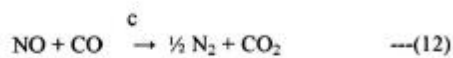
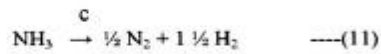


Fig. 2. Nevertheless, fuels with high nitrogen contents have higher NO_x emissions than those with low ones.

In Diesel engines, NO formation from fuel nitrogen is strongly overlapped by thermal NO formation. Even with a low fuel nitrogen content, high NO emission can occur.

The available evidence on the mechanism of NO formation from fuel-bound nitrogen suggests the following [17]:

- (a) Conversion of fuel-based nitrogen to NO is practically complete for fuel-lean flames operating on low

3 EFFECTS OF OXIDES OF NITROGEN

Oxides of nitrogen emissions have negative effects on environment and health, and the extent of the damage vary greatly. Their presence in the atmosphere, adversely affect the

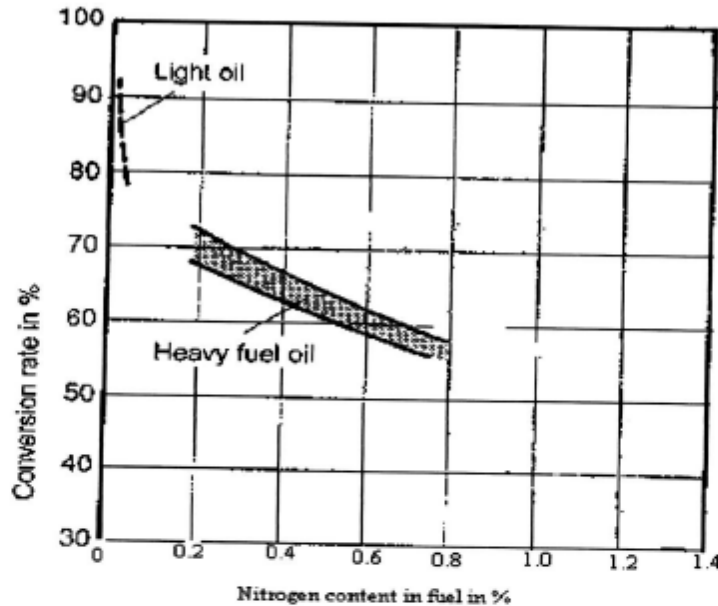


Fig.2 Transformation of fuel nitrogen into NO, showing three fuels as example

nitrogen concentrations (less than 0.5 percent by weight).

- (b) Conversion decreases with increasing concentration of fuel nitrogen (Fig. 2).
 (c) Conversion increases slowly with increasing flame temperature.
 (d) The composition of the nitrogen-bearing compound does not affect the conversion rate.

The temperature range where fuel NO sets in, (Fig.1), are generally higher than 'prompt' NO formation but less than thermal NO formation at temperatures exceeding 1800° C.

2.4 N₂O Mechanism

N₂O mechanism is the most characteristic intermediate compound, and therefore its kinetic mechanism is far less dominant over that of NO or NO₂ in diesel engines.

health of humans, animals, or microbial life and

materials goods. The disorders resulting from NO_x effects do not usually occur immediately on exposure, but rather after prolonged exposure, often after enrichment, i.e. accumulation, that chronic ailments become visible. Nitrogen oxides also contribute significantly to acid rain, formation of atmospheric ozone, global warming of the earth's surface and general air pollution, all of which have serious repercussions on well-being of millions of people and global ecosystems.

3.1 Acid Rain

The damage caused by acid deposition is worldwide problems that tends to destabilize an ecosystem.

Acid precipitation is a result of some reactions in air. Nitrogen dioxide react with water and atmospheric oxygen to produce nitric acid, which dissolve in water to produce acid rain. Uncontaminated rain water has a pH of about

5.6, but the oxides of nitrogen can reduce the pH to less than 2.

The foremost among damages of acid deposition is a significant loss of forests; resulting in either decline in trees growth (including deformation) or productivity.

Acidification seriously impair the survival of high-tropical-level-animals such as fish. Low pH not only affects fish directly, but contributes to labilization of metals, such as manganese, cadmium, and aluminum, potentially toxic to fish. Furthermore, precipitation of aluminum phosphates reduces the primary production of plants and phytoplankton so limiting the food supply, thus even magnifying the acid rain problem.

3.2 Global Warming

The effects of oxides of nitrogen, though not the only ones, can lead to a global warming of the earth's surface. Increased radiation of sunlight on the earth's surface, especially of high-energy ultra violet (UV) light, warms the surface of the earth as also decreased reflection from the area of the lower atmospheric layers. This results in the destruction of the stratospheric ozone layer as well as the increase of the so-called greenhouse gases. A rise in temperature would have numerous, fearsome consequences, among them the shifting of climatic zones, and with them the shifting of the inhabitable regions of the earth, the expansion of the deserts, as well as the flooding of larger areas of land due to the melting of the polar ice masses.

3.3 Ozone

In the preceding paragraphs, it has been stated that consequences of anthropogenic pollutants such as NO_x are warming the earth's surface, a decreased stability of the thermal layering of the stratosphere and increased UV radiation in the troposphere. Humans, many animals and plants are highly sensitively to hard UV-B and UV-C radiation which are even richer in energy.

Ozone and photochemical oxidants are highly irritating and oxidizing gases. Concentrations of a few parts per million can produce pulmonary congestion, edema, and pulmonary haemorrhage. A one-hour exposure on human to 2500 µg/m³ can decrease effective lung volume and decrease maximum breathing capacity [18]. Symptoms of ozone and oxidant exposure are a dry throat, followed by a headache disorientation, and altered breathing patterns.

Adequate control of ozone and photochemical smog production depends on control of all primary pollutants that contribute to ozone formation.

3.4 Smog

Coined by a combination of smoke and fog, smog represents a cloudy formation resulting from photochemical reaction of sunlight on the oxides of nitrogen and hydrocarbon emitted from automobiles. Smog causes irritation of eyes and throat, impairs lung function, damages plants and crops and makes rubber-like products crack and cause visibility problems (see also section 3.5).

3.5 Visibility

The ugly haze in our skies commonly known as smog contributes to the low visibility. Since NO₂ absorbs the full visible spectrum of light energy, it can reduce visibility even in the absence of particulate matter, resulting in scattering of light off very fine particles: 0.3 µm to 0.6 µm in diameter.

3.6 Toxicity

Nitrogen dioxide, a highly toxic gas, is a pulmonary irritant. Although little is known of the specific toxic mechanisms, high concentrations of NO₂ can produce pulmonary edema, an abnormally high accumulation of fluid in the lung tissue. NO₂ has never been found in such high concentrations in ambient air; as an air pollutant. Nitric oxide may have a combined (synergistic) effect on blood system with carbon monoxide, inhibiting further the capacity of blood to carry oxygen round the body. Among other effects include bronchitis, pneumonia, irritation of nose and eyes.

4 CONTROL OF NO_x EMISSIONS

The emission of nitric oxides from diesel engines is one of the more difficult ones to control, since control techniques normally tend to increase other emissions or fuel consumption. It follows, from the preceding sections that good control of NO_x emission can be obtained by careful consideration of air-fuel ratios, combustion and exhaust temperatures and design features to reduce the quench zones in a diesel engine. Other further factors that have to be considered include: injection rate, injection timing, compression ratio, used of catalytic converters and exhaust gas recirculation.

4.1 Exhaust Gas Recirculation

Exhaust gas recirculation (EGR) recycled exhaust is an effective method which can be used to reduce the NO formation rate and therefore the NOx emissions. The effect is primarily one of reducing the burned gas temperature for a given mass of fuel and oxygen burned.

Figure 3. illustrates the effects of dilution of intake air with exhaust gas on NOx exhaust levels [19-20].

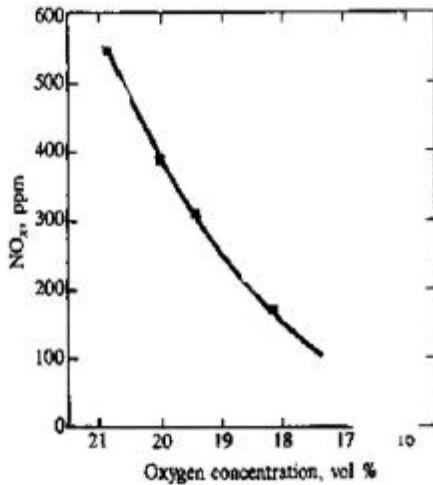


Fig. 3. Effect of reduction in oxygen concentration exhaust gas on NOx emissions in DI diesel Bore = 140 mm, stroke = 152 mm, $r_c = 14.3$. Speed = 1300 rev/min, fuel rate = 142 mm/stroke, injection timing at 4° Before Top Dead Centre

EGR method is becoming commonly used an indirect injection engines operated in areas where emission controls are strict. An increase in its use on automotive direct injection engines would be expected as legislation applying to these engines become more severe. Unfortunately the use of exhaust gas recirculation does tend to increase particulate emissions. This limits the extent of the EGR which can be applied to about 15 percent. This limit of recycle will reduce NOx emissions by about 80 percent.

4.2 Injection Timing

Injection timing is one of the most influential factors in nitric oxides emissions. By retarding the injection timing, useful reductions in nitric oxides emissions can be achieved for all diesel engines.

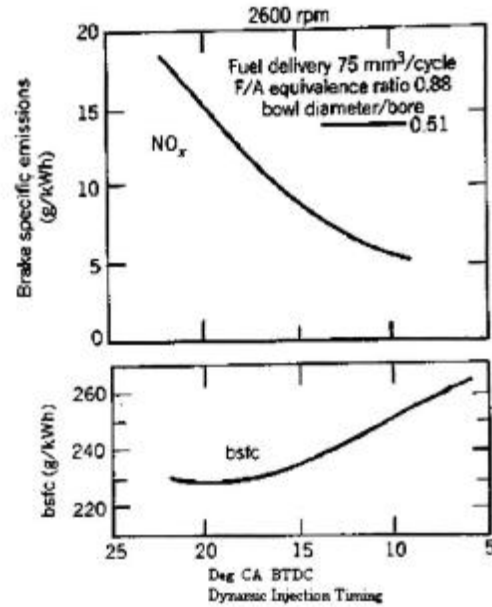


Fig. 4. Effect of injection timing on NOx emissions and fuel consumption.

Figure 4 shows NOx emission and fuel consumption as a function of injection timing for a direct injection engines [21].

The curves clearly indicates that as the injection is retarded from 22 to 15 degrees before top dead centre, the nitric oxide drop by a factor of 2, whereas the fuel consumption increases only by about 3 percent. For this reason, diesel engines are usually operated at injection timings slightly retarded from that which produces best fuel economy.

Indirect injection engines tend to produce lower NOx emissions because of the more retarded timings which are normally used. An indirect injection engine's start of combustion can be retarded from the common 2° Before Top Dead Centre (BTDC) to as late as 5° After Top Dead Centre (ATDC) without a serious penalty in economy. Further retard continues to reduce nitrogen oxides emissions but also gives a rapid increase in hydrocarbon emissions.

4.3 Injection Rate

Injection rate affects nitric oxides emissions, an increased rate giving increased emissions. This is because of increased mixing during the delivery period which gives a very hot flame when combustion occurs leading to the generation of larger quantities of NO. Increased injection rate can be useful at retarded timings when trading off smoke, brake specific fuel consumption and nitrogen oxides emissions. Changing the nozzle hole size can have a

similar effect where a decreased size can produce smaller droplets which give an increase in premixed burning yielding higher nitric oxide emissions.

4.4 Air-Fuel Ratio

Any change which gives higher combustion temperatures gives increased emissions of NO_x. Therefore increasing the air-fuel ratio (decreasing the fuel-air ratio) gives increased nitrogen oxides.

At high fuel-air ratio the additional fuel tends to cool the charge, so the localised peak temperatures are lowered resulting in drop in NO_x concentration, especially in direct injection engines. With indirect injection diesel engines, the conditions in the prechamber tend to be fuel rich and therefore less NO_x is produced.

4.5 Compression Ratio

Increasing the compression ratio similarly increases NO_x emissions since it increases the cycle temperature. At the same time however the decrease

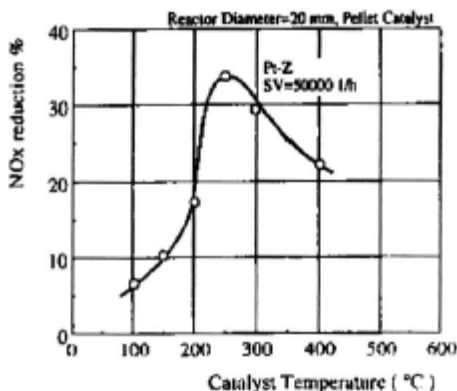


Fig. 5 Temperature dependence of the NO_x reduction efficiency

in the delay period associated with the increase in compression ratio allows more retarded timings to be employed.

The overall result in practice is thus small. Turbo-charging has a similar effect but inter-cooling can be used to control NO_x at high loads since the reduced inlet air temperature leads to reduced cycle temperature.

4.6 Catalyst

In the last few years, several kinds of catalysts have been developed to reduce NO_x in the presence of oxygen under the operating conditions of the diesel engines, and a good NO_x reduction has been achieved. Currently, three-way catalysts are

commercially used on gasoline engines as a means of reducing nitric oxide in an oxidizing environment. To effect this the engine has to be operate at a normally stoichiometric air-fuel ratio. However, diesel engines are operated under oxygen rich conditions and not stoichiometric. Recently, a platinum ion-exchanged ZSM - 5 Zeolite catalyst (Pt - Z) has been developed and found to be effective in reducing NO_x in diesel engine exhaust with high oxygen content [22].

The NO_x reduction efficiency of 33 percent has been achieved in normal engine operation at a maximum activation temperature of 250° C with this catalyst [23]. Figure 5 shows the temperature dependence of the NO_x reduction efficiency of a direct injection, 4 cycle, water cooled diesel engine operating at a compression ratio of 18.5.

5 CONCLUSIONS

The major man-made source of nitrogen oxides is the combustion of fossil fuel in power generation and road vehicles. Of all the oxides of nitrogen, the significant ones in the context of air pollution are nitric oxide and nitrogen dioxide.

While the effects of air pollution on materials, vegetation, and animals can be measured, health effects on humans and animals can only be estimated from epidemiological evidence which comes from occupational exposure to much higher NO_x concentrations than that is exposed to the general public. All the evidence available suggests that air pollution, by virtue of high NO_x concentrations, threaten environment, human health and well-being to an extent that strict control of these pollutants is necessary.

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