Study on the Treatment of Exhaust Gases at Diesel Engines with the Purpose of Reducing the Emissions of Nitrogen Oxides

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The paper presents the possibility of chemically treating the gases resulted from the burning process at Diesel engines. The importance of this issue resides in the fact that the pollution norms are very restrictive especially in the case of nitrogen oxides. The aspects highlighted by the authors achieve a connection between the chemical processes taking part after the combustion and the beneficial effects as regards the environment. The tests performed comparatively on engines equipping high-capacity motor vehicles endowed or not with the technology of chemical treatment with the purpose of reducing the nitrogen compounds validate the imposed desiderata. The mechanism of nitrogen oxides formation is influenced by the high temperature necessary to a complete combustion and the excess of air in the combustion chamber. The emissions were established according to the ESC testing norms for high-capacity engines. At present the chemical treatment of exhaust gases with urea solution and water represents the most viable solution both from the viewpoint of the technology applied and of the afferent costs.

Key words: AdBlue, Diesel engine, exhaust gases, emission of nitrogen oxides, ESC, SCR.

The pollution of the atmosphere with gases and particles triggers important concentration modifications, not only locally but also with risk of planetary manifestation. The incidences of certain typical pulmonary diseases, climate alterations which in the long run may have extremely serious consequences, are caused by the action of certain polluting agents.

One of the negative aspects of the motor vehicles industry is represented by the environment pollution. In the case of engines with internal combustion, the chemical polluters are determined by the process of fuel oxidation, a complex process generating, beside carbon dioxide, water, nitrogen and oxygen in excess, a series of chemical substances, products of the incomplete combustion, which are found in small quantities in the exhaust gases (2% of volume).

An interesting element is represented by the figures characterizing the emissions of the main polluting substances produced in Europe, both in absolute values and as values compared to the world emission; an important part of these emissions are caused by transports, among which 61% are represent by the nitrogen oxides. If we consider only the pollution produced by transports we remark that the emission of nitrogen oxides is relatively equally divided between the engines with spark ignition 44.6%, and the engines with compression 12.2% [4].

It is known that in the exhaust gases there are: carbon monoxides, unburned or partially oxidised hydrocarbons, nitrogen oxides, smoke and lead products from the gasoline additives under the form of aerosols and vapours. The accumulation of carbon dioxide and other greenhouse effect gases lead to the rapid warming of the planet, which would trigger the increase of the sea levels, floods, storms and other climatic catastrophes.

Experimental part

Technologies for the decrease of the polluting emissions contained in engines combustion gases

In order to limit the pollution of the atmosphere with lead compounds one renounces more and more to the additivation of gasoline with lead based anti-detonants. The most frequently used and most efficient passive solution is the using of catalysis and catalysts. There were conceived catalytic systems called catalytic reactors and catalytic converters where the oxidation and/or reduction reactions may take place with the help of certain chemical promoting substances.

The action of catalysts is based on their property to substantially reduce the energetic threshold for the triggering of oxidation and reduction reactions and to accelerate the reaction speed of these processes.

By means of applying the EURO 4 and EURO 5 norms (fig. 1), which impose a quantity of emissions for:

EURO 4: 1.5 CO g/kWh; 0.46 HC g/kWh; 3.5 NO_x g/kWh; 0.02 PM g/kWh
EURO 5: 1.5 CO g/kWh; 0.46 HC g/kWh; 2.0 NO_x g/kWh; 0.02 PM g/kWh [5], one adopts the installation of certain control devices attached to motor vehicles in order to limit the emission of polluting substances. The delay between the introduction of EURO 4 and EURO 5 is relatively short, i.e. 3 years (1 October 2005 for EURO 4 and 1 October 2008 for EURO 5).

Key words: AdBlue, Diesel engine, exhaust gases, emission of nitrogen oxides, ESC, SCR.

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Fig. 1. The NO_x and PM emissions limits
The mechanism of nitrogen oxides forming

The nitrogen oxides exist in reduced proportion (2000-4000)ppm in the gases emitted by spark ignition engines, nevertheless enough to be categorised as noxious elements [1]. According to Zeldovici, the formation of thermal nitrogen oxides takes place in the flame and is developed according the reactions below:

a) in the case of oxygen excess, the molecules of nitrogen react with the oxygen radicals resulted from the thermal decomposition of oxygen, at very high temperatures:

\[ O + N_2 \rightarrow NO + N \]  

The nitrogen radical resulted from this reaction and/or from the thermal decomposition of molecular nitrogen reacts with the molecule of oxygen:

\[ N + O_2 \rightarrow NO + G \]  

The sum reaction of the two reactions above is:

\[ N_2 + O_2 \rightarrow 2NO \]  

b) in the case of fuel excess, the hydroxyl (OH) radicals, produced through combustion, react with the nitrogen radicals, resulted from the thermal decomposition:

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

The main factors influencing the formation of thermal nitrogen oxides are:

- the concentration of the atomic oxygen \( O_1 \), formed as a result of the thermal dissociation of the molecules of oxygen \( O_2 \);
- the high temperature, above 1300°C;
- the time of the reaction.

The increase of these parameters' value generally triggers the increase of the quantity of thermal nitrogen monoxides produced.

The thermal mechanism is due to the reaction of the molecular nitrogen and of the following reactions with the molecular oxygen, based on the atomic nitrogen thus formed. In the case of the areas rich in fuel, the mechanism should be completed by the oxidation reaction of the elementary nitrogen by means of the OH radicals.

The selective catalytic reduction

In order to reduce polluting emissions, in the case of Diesel engines one uses a solution of urea and demineralised water (32.5%), commercially called AUS32 or AdBlue which observes the DIN V 70070 standard [7].

The AdBlue chemical process is:

\[ NH_2CO (urea) + H_2O (water) \]

The heat from the exhaust system and water are necessary for the decomposition of the urea into ammoniac and carbon dioxide:

\[ NH_2CO + H_2O \Rightarrow 2NH_3 + CO_2 \]  

The reduction of the nitrogen oxide by the ammoniac, in the presence of oxygen:

\[ NO_x + NH_3 + O_2 \Rightarrow \text{(catalytic reaction)} \]  

The SCR technology (Selective catalytic reduction) is based on the optimised combustion at the engine level and a system of gases treatment at the converter exit in order to reduce the level of the nitrogen oxides (NO\(_x\)) and turn them into nitrogen (harmless for the environment) and water. This system of gas treatment at the converter exit is made by mounting a separate tank containing AdBlue.

**Results and discussions**

*Results obtained in the operation of engines of the OM 501 LA range with and without SCR*

The emissions are established based on the ESC tests using conventional Diesel engines, including the ones with electronic equipment of fuel injection, exhaust gases recirculation (EGR) and/or oxidation catalysts [3].

The "testing cycle" represents a sequence of testing points with set number of revolutions and couple, which must be reached on its track by the engine in the stabilised mode (ESC test) or under transitory operation conditions (fig.3). The ESC test represents a test made of 13 stabilised modes.

The testing sequence is started. The test should be performed in the order of the mode numbers.

The engine must operate during the time delay prescribed for each mode, so that the change in number of revolutions or load of the engine should not exceed 20 s. The specified number is maintained in the range of ±50rpm, and the specific couple is maintained in the range of ±2% of the maximum couple at the number of revolutions of the test.

Following the ESC tests performed on the OM 501 LA engine (fig.4) with the following general characteristics:

- cylindrical capacity: 11946 cm\(^3\),
- bore: 130 mm,
- stroke: 150 mm,
- maximum output power: 300 kW,
- maximum torque: 2000 Nm.

We fond a significant reduction of the main polluting substances: NO\(_x\), CO, HC and PM, compared to the engines not equipped with this system.

The comparative values of the emissions concentrations resulted after the tests performed on the OM 501 LA engine in the two cases (with and without SCR) are presented in figures 5, 6 and 7.

Following the ESC tests performed on the OM 501 LA engine without SCR, the measured values of the concentrations of NO\(_x\) are high, being at the maximum limit admitted by the EURO 3 pollution norms.
The ESC tests performed on the same type of OM 501 LA engine with SCR indicate a significant reduction of the NOx concentrations compared to the pollution norms imposed by EURO 4.

In the case of the EURO 5 engine, more AdBlue is injected in order to reduce even more the level of the nitrogen oxide. In the case of the EURO 4 standards, the additive corresponds to a percentage of 3-4% of the fuel quantity, and in the case of the EURO 5 standards, the percentage is around 5-7%. The solution for observing the requirements of EURO 4 and EURO 5 is to manufacture Diesel engines with more efficient combustion and a technology of gas treatment at the catalyst exit, using the AdBlue additive and the SCR technology (Selective Catalytic Reduction).

**Conclusions**

AdBlue represents a corrosive solution, with the crystallisation point at the temperature of -11.5°C, and its chemical stability is not constant.

The SCR technology requires a permanent feeding, AdBlue being stocked in a supplemental tank, and if the latter is not permanently supplied, this will lead to an increase of the level of polluting emissions. It is not possible to upgrade from EURO 3 to EURO 4, as the engine configuration is completely different.

The SCR technology has efficiently proved its reliability, has enough potential to correspond to the EURO 5 norms, being a safe investment at present and in the future. It functions throughout Europe with gas oils of different qualities, does not require upkeep and is conceived for the entire life duration of the vehicle. This technology does not affect the intervals of service or the intervals of engine oil changes, significantly reduces the engine fuel consumption (5-7)% and provides the most efficient solution in terms of costs, environment protection and performances.

**References**

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