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DODATOČNÉ VSTREKOVANIE PALIVA DO VALCA VZNETOVÉHO MOTORA AKO METÓDA ZNIŽOVANIA NO_x

THE DIESEL FUEL POST-INJECTION INTO ENGINE CYLINDER AS METHOD OF NO_x REDUCTION

Možnosti obmedzovania emisií NO_x *vo valci vznetového motora pri jeho konštrukcii alebo prostredníctvom prevádzkových parametrov sú limitované. Preto sa robia štúdie efektívnosti rôznych metód znižovania* NO_x *vo výfukových plynoch. Metóda, ktorú použili autori, využíva redukčného činiteľa vo forme chemicky aktívnych uhľovodíkov (radikálov) z paliva. Aby sa získali čiastočne oxidované a tepelne rozložené uhľovodíky, aplikoval sa dodatočný vstrek (vstreknutie ďalšej časti paliva) do valca vznetového motora v priebehu expanzie. Na vykonanie tejto funkcie sa skonštruoval špeciálny systém na dodávku paliva skladajúci sa z dvoch vstrekovacích čerpadiel. Jedno z čerpadiel vstrekovalo hlavnú (primárnu) dávku paliva, druhé vstrekovalo dodatočnú dávku paliva. Vstrekovanie oboch dávok paliva bolo realizované rovnakým vstrekovačom. Vo výfukovom systéme jednovalcového testovacieho motora sa použil katalytický konvertor a všetky výfukové plyny vytvorené spaľovaním hlavnej dávky paliva a chemicky aktivované uhľovodíky pochádzajúce z dodatočnej dávky paliva prechádzali cez konvertor. Na vyhodnotenie dosiahnutých výsledkov sa definovali rôzne postupy zamerané na efektívne znižovanie* NO_x*. Počas testov sa menil uhol vstreku hlavnej i dodatočnej dávky paliva (vzhľadom na hornú úvrať) ako aj teplota, priestorová rýchlosť výfukových plynov prechádzajúcich cez konvertor a druh paliva.*

Zistilo sa, že ak sa použije metóda redukčného činiteľa, je celkový efekt redukcie NO_x *kombináciou efektov získaných vo valci selektívnou nekatalytickou redukciou a účinkov v katalytickom konvertore získaných selektívnou katalytickou redukciou.*

The possibilities of limiting the emission of nitrogen oxides in the cylinder of the diesel engine by means of its design and operating parameters are limited. This is why studies of the effectiveness of various methods for NO_x *reduction in exhaust gases are being undertaken. The method used by the authors involves the utilization of a reducing agent in the form of chemically active hydrocarbons (radicals) from the fuel. In order to obtain partially oxidized and thermally decomposed hydrocarbons, the post-injection of fuel (the injection of an additional portion of fuel) into the diesel engine cylinder during the expansion stroke was implemented. To perform this function, a special fuel supply system consisting of two injection pumps was designed. One of the pumps was injecting the main (primary) fuel dose, and the other one – the additional fuel dose. Injection of both fuel doses was accomplished by the same injector. A catalytic converter was used in the exhaust system of the one-cylinder test engine, and all the exhaust gases produced in the combustion of the main diesel fuel dose and chemically activated hydrocarbons coming from the fuel post-injection (additional fuel dose) were passing through the converter. Various* NO_x *reduction efficiency measures were defined to evaluate the results obtained. During the tests, the additional diesel fuel dose and post-injection angle (relative to the TDC), as well as temperature, space velocity of exhaust gases through converter and sort of diesel fuel were changed.*

It was found that using that method of the reducing agent dosage, the total effect of nitrogen oxide reduction was a combination of the effects obtained in the engine cylinder by Selective Non-Catalytic Reduction (SNR) and the effects obtained in the catalytic converter by Selective Catalytic Reduction (SCR).

1. Introduction

The issue of NO_x emission reduction pertains not only to diesel engine exhaust gases, but also to the spark ignition, petrol-fuelled engine. However, in the conventional spark-ignition engine, the problem of particulates emission is not so important as in the diesel engine, where particulates are produced during the combustion of heterogeneous mixtures, specific to the diesel engine. Nitrogen oxide emission in petrol engines has been limited to the level imposed by the relevant standards by the common use of three-way catalytic converters, reducing also other toxic constituents of the exhaust gases (CO, HC). This concept is not useful in the diesel engine whose exhaust gases contain a significant amount of oxygen [4]. For this reason, research projects initiated currently aim to develop efficient NO_x emission reduction methods, based on the proven technologies for NO_x elimination from exhaust gases typical for the chemical industry and power industry.

According to the results of tests [19, 22, 23], nitrogen oxides generated in the process of burning diesel fuel in the diesel engine can be reduced by two methods: Selective Non-Catalytic Reduction (SNR) and Selective Catalytic Reduction (SCR). The former

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one is a thermal method, and it can be employed in the processes of reduction taking place in the engine cylinder and partially in the exhaust system owing to a relatively high temperature of exhaust gases to which the reducing agent is added. However, outside the cylinder, the effectiveness of this method is low because of a rapid drop in the exhaust gas temperature. This temperature depends on the diesel engine operating conditions and, in the exhaust systems, ranges from 373 to 423K when the engine is idling, from 423 to 623K in urban traffic (low and medium loads and engine speeds), and from 623 to 1023K on a highway. In order to employ the SNR method to reduce nitrogen oxides it would be necessary to heat up exhaust gases, which involves energy losses.

In the engine exhaust system it is more favourable to use a catalytic converter which reduces NO_x emissions by means of the SCR method. An extensive development of this method, with an application to engine exhaust gases, started in the eighties. Similarly as in the chemical industry and stationary power plants, nitrogen-containing compounds, such as ammonia or urea, are usually considered as nitrogen oxide reducing agents. Various test results indicate that ammonia used in a catalytic converter to reduce the concentration of nitrogen oxides in the diesel engine exhaust gases provides high reduction efficiency exceeding 90%. The use of this reducing agent is, however, not practical owing to its toxicity, explosiveness in a mixture with air, and also by a sharp and unpleasant odour. Additionally, it would be necessary to use pressure vessels for the transportation of ammonia. Consequently, urea as an indirect source of ammonia seems to be more useful in this application.

Urea used as a non-toxic source of ammonia is a safe reducing agent. Additionally, its good solubility in water facilitates transportation in diluted form. As a result of injecting urea into hot exhaust gases (having a temperature above 430K) before the catalytic converter, the first reaction taking place is the hydrolysis of urea, during which ammonia and other compounds such as NH_2 are produced (one kilogram of urea yields 0.566 kg of ammonia). Assuming the NO to NO_2 ratio of 9:1, which is valid for the diesel engine exhaust gases, it can be calculated that to reduce 1 kg of NO_x, about 0.67 kg of urea is needed [9]. The efficiency of NO_x reduction depends both on the reduction process conditions and on the amount of urea used.

It must be emphasised that in order to use urea and/or ammonia in traction engines it would be necessary to employ a costly system dosing these reducing agents adequately to engine operating conditions (NO_x content of exhaust gases), and periodically replenishing the tank with the reducing agent. It would be also necessary to build a complete distribution system for ammonia or urea, and to take protective measures against the effects caused by a potential escape of toxic ammonia to the atmosphere from the engine exhaust system. Thus the use of the selective catalytic reduction of nitrogen oxides by means of nitrogen-based compounds is better justified in industrial diesel engines or in engines installed on ships, while for traction diesel engines powering motor vehicles it is more appropriate to focus research activities on the use of other reducing agents, such as hydrocarbons.

2. Studies of NO_x Reduction with Hydrocarbons

Publications on that subject usually describe the results of tests conducted in laboratory conditions. Such tests usually involve the reduction of nitrogen oxides contained in a mixture prepared from gases stored in pressure gas vessels and having similar composition to that of the actual diesel engine exhaust gases. To investigate the effects of NO_x reduction by the SCR method, hydrocarbons (also from a pressure gas vessel) were introduced into such gaseous mixtures flowing through a catalytic reactor. Less results of tests conducted with actual diesel engine exhaust gases are available. In such tests, the following substances were used to reduce nitrogen oxides: hydrogen H_2, gaseous hydrocarbons CH_4, C2H_4, C_3H_6, etc. [7, 10, 12, 13], alcohols [4, 7, 14, 15] and hydrocarbons contained in diesel fuel. Diesel fuel was usually injected into the exhaust system, before the catalytic reactor [5, 10, 12, 13, 17, 18].

Because of its temperature, the location where hydrocarbons are added to exhaust gases has a considerable influence on the process of nitrogen oxide reduction, as it is related to the amount and chemical activity of radicals generated during the initial decomposition of hydrocarbon molecules. The most favourable solution seems to be the injection of an additional hydrocarbons directly into the cylinder, where they would be subjected to the initial decomposition. High temperature of the working medium and longer time of the initial decomposition of hydrocarbon molecules would be the advantages of such a solution. Considering possible engineering applications, the method of dosing the reducing agent into the cylinder has more advantages. This method was used in the tests described here, where additional hydrocarbons (contained in diesel fuel) were introduced directly into the engine cylinder, as a result of the post-injection of an additional, small portion of fuel, during the expansion stroke. Contrary to the main fuel dose injected during the compression stroke, the additional fuel dose did not have any influence on the engine output power.

In order to chemically activate the hydrocarbons, the additional fuel dose injected into the cylinder should undergo a similar physical and chemical transformation as in the autoignition delay period, i.e. it should produce the so-called cool flame, without reaching the hot flame state (i.e. autoignition and combustion). In such conditions, as a result of thermal decomposition of hydrocarbon molecules and their initial reactions with oxygen contained in the exhaust gases, chemically active molecules of hydrogen H_2, radicals $R^\bullet$ (hydrocarbon molecule after loosing one hydrogen atom), $HO_2^\bullet$, $ROO^\bullet$ and atomic hydrogen $H^\bullet$ are produced, demonstrating strong NO_x-reducing properties. This method of injecting additional fuel dose into the cylinder causes some portion of the products of partial oxidation of hydrocarbons to react with nitrogen oxides yet in the engine cylinder (because of high temperature inside it). Consequently, a part of nitrogen oxides is subjected to thermal reduction. It must be noted that the radicals taking part in the process of nitrogen oxide reduction may be also contained in the products of water, carbon monoxide, and carbon dioxide dissociation, generated by burning the main fuel dose [19, 22, 23].

Reactions of NO_x reduction taking place in a catalytic reactor have different course than thermal reactions, and their mechanism depends not only on the reducing agent type, but also on the reactor type used. Iwamoto, who first started to use hydrocarbons for NO_x reduction in the diesel engine exhaust gases by the SCR method, proved that in the Cu/ZSM-5 zeolitic reactor, reducing agents such as C_2H_4, C_3H_6, C_4H_8 and alcohols demonstrate selective reducing capability, while H_2, CO and CH_4 are non-selective reducing agents with respect to nitrogen oxides [11]. This indicates that the level of NO_x reduction depends on the selective capability of particular reducing agents. In the case when diesel fuel is used as the reducing agent source it is difficult to determine its selective capability, because it depends on the percentage of particular hydrocarbons or hydrocarbon groups in the fuel. According to [6, 14], aromatic hydrocarbons are the best reducing agents, followed by olefins, paraffins, and aldehydes. It must be remembered that depending on the engine operating conditions, the composition and amount of unburned hydrocarbons change continuously. Apart from the selective capability of the reducing agent and the exhaust gas temperature, at the same relative volumetric flow rate of exhaust gases SV, the efficiency of NO_x reduction is influenced also by H_20, SO_2, and O_2 [13]. The mechanisms of NO_x reduction in a catalytic converter have been investigated in many papers summarized in [23], especially interesting being the model presented by Hamada, proposing two ways of NO_x reduction [8].

In view of the above, it may be stated that the final effect of NO_x reduction in the diesel engine exhaust gases combines the results of both thermal (SNR) and catalytic (SCR) reduction. Partial effects depend not only on the volume of the additional injection of fuel being the source of the reducing agent, but also on the time and temperature at which hydrocarbons are present in the cylinder before the exhaust valve opens. In order not to burn the hydrocarbons additionally introduced into the cylinder, the fuel post-injection (effected during the expansion stroke) must not be too early in relation to the injection and combustion of the main fuel dose. It cannot be effected too late, either, since the temperature in the cylinder may be too low and the time mentioned above may be too short. Thus the total NO_x reduction efficiency may be influenced by the following factors: volume of the additional fuel dose, timing of fuel post-injection (relative to the expansion stroke), engine speed and engine load, exhaust gas temperature, oxygen concentration in the exhaust gases, etc. Diesel fuel composition, i.e. the content of hydrocarbon groups influencing thermal decomposition of molecules, may also have a significant effect on the reduction efficiency.

The idea presented in the paper is based on the simultaneous implementation of diesel fuel post-injection and a catalytic converter. It does not require any additional dosing system for injecting hydrocarbons before the converter. The method could be implemented quite easily in widely used common-rail injection systems which allow the fuel dose injected to be divided into freely adjusted portions. Such a system of hydrocarbon dosage has been already indicated in [16], but without any detailed information.

The possibility of using fuel-contained hydrocarbons in the process of thermal and catalytic reduction of NO_x in the diesel engine exhaust gases has been investigated in the Cracow University of Technology [3, 19, 20, 21, 22, 23]. Tests were done on the single-cylinder test engine. For the purpose of tests, a special fuel supply system was built, consisting of two injection pumps: a main injection pump delivering fuel necessary for engine operation, and an additional injection pump delivering additional amount of fuel (hydrocarbons) used for NO_x reduction. The pumps were connected in a row by means of a clutch providing continuous change of angle between injection the main fuel dose and the additional fuel dose. Fuel from both pumps was delivered to the engine cylinder through the same injector. To eliminate unnecessary interaction between fuel pressures generated by both pumps, a double check valve was installed before the injector. A catalytic converter was installed in the exhaust system. Exhaust gas samples were taken for analysis before and after the catalytic converter. Temperature was measured at the points where samples were taken.

3. NO_x reduction efficiency definitions

As it has been mentioned before, owing to a high temperature in the cylinder and a longer time of initial decomposition of molecules, first effects of radicals and hydrogen reducing action may be observed yet in the engine cylinder, and also in the exhaust manifold between the cylinder and the catalytic converter. The resultant NOx reduction has the form of Selective Non-Catalytic Reduction (SNR). In the catalytic converter, however, NO_x reduction is accomplished by Selective Catalytic Reduction (SCR). To evaluate the effects of both NO_x reduction methods, and to evaluate the total effect, three definitions of NO_x reduction efficiency have been introduced. Auxiliary quantities used for calculations, together with the points where the exhaust gases were sampled for analysis, are shown in Fig. 1.

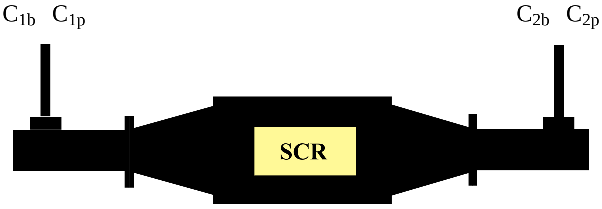

Fig. 1. Quantities used for the calculation of NO_x reduction efficiency

where:

C1b – NO_x concentration before the catalytic converter, the engine being supplied only with the main fuel dose (without fuel post-injection),

C1p – NO_x concentration before the catalytic converter, the engine being supplied with the main and additional fuel dose (with fuel post-injection),

C2b – NO_x concentration after the catalytic converter, the engine being supplied only with the main fuel dose (without fuel post-injection),

C2p – NO^x concentration after the catalytic converter, the engine being supplied with the main and additional fuel dose (with fuel post-injection).

For the purpose of a test results analysis, several definitions of NO_x reduction efficiency can be applied:

η_{SNR} – the efficiency of thermal Selective Non-Catalytic Reduction between the cylinder and the catalytic converter.

$$\eta_{SNR} = \frac{C_{1b} - C_{1p}}{C_{1b}}$$

η_{SCR} – the efficiency of Selective Catalytic Reduction in the catalytic converter.

$$\eta_{SCR} = \frac{C_{1p} - C_{2p}}{C_{1p}}$$

η_T – the total efficiency of NO_x reduction, combining the effects of both Selective Non-Catalytic Reduction (SNR) before the catalytic converter and Selective Catalytic Reduction (SCR) in the catalytic converter.

$$\eta_T = \frac{C_{1b} - C_{2p}}{C_{1b}}$$

4. Results and discussion

4.1. The influence of fuel post-injection timing during the expansion stroke

Efficiency of NO_x reduction measurements were made at two engine speeds: at 1600 r.p.m., and 2000 r.p.m. The torque developed by engine was constant ($T = 60$ Nm) in both cases. The main fuel dose was adjusted so as to obtain the assumed operating parameters of the engine, and its volume was $q_1 = 60$ mm^3/cycle at 1600 r.p.m., and $q_1 = 63$ mm^3/cycle at 2000 r.p.m. The ratio of the reducing agent to nitrogen oxides before catalytic reactor was kept at a constant level ($HC_1/NO_x = 3$). This value was determined by analyzing the results of tests conducted in other research centres. These results were obtained for direct introduction of hydrocarbons before the catalytic converter, and the optimum HC_1/NO_x ratio in terms of NO_x reduction efficiency and reducing agent utilization was determined at a level of 3 [1, 2, 4].

The start angle of fuel post-injection (injection of additional fuel dose) (was varied from 60 to 200° ATDC – after the top dead centre (the exhaust valve of the test engine starts to open at 140 ° ATDC). It was not possible to use smaller angle values because, in spite of considerably increased additional fuel dose, it was impossible to obtain the assumed ratio $HC_1/NO_x = 3$. It is generally known that the amount of nitrogen oxides produced in the combustion chamber is constant at constant engine speeds and constant engine loads. However, when the start angle of fuel post-injection was changed, the concentration of hydrocarbons before the converter also changed, and it was necessary to adjust the additional injection fuel dose in order to maintain a constant HC_1/NO_x ratio. Changes in the concentration of hydrocarbons were mainly due to the utilization of some hydrocarbons in the process of NO_x reduction between the cylinder and the converter (Selective Non-Catalytic Reduction, SNR), and due to the fact that some hydrocarbons from the additional injection fuel dose were burnt in the engine cylinder, when the fuel post-injection took place too early after the TDC.

Fig. 2 shows the influence of the fuel post-injection angle on the efficiency of NOx reduction between the engine cylinder and the catalytic converter. The highest value of $\eta_{SNR} = 24\%$ was obtained for 1600 r.p.m. and $\alpha = 60°$ ATDC. For $\alpha > 140°$ ATDC, the efficiency was around 10%. At 2000 r.p.m., for $\alpha = 80°$ ATDC, η_{SNR} was 22%, and for $\alpha > 120°$ ATDC, (SNR was about 4%. It is clear that the efficiency of NO_x reduction depends on the fuel post-injection angle only for low values of this angle.

A drop in the efficiency of NO_x reduction by the SNR method for the increasing values of the fuel post-injection angle α (valid for low α values only) can be explained by the fact that less reducing agent was delivered to the cylinder when the delay of fuel post-injection relative to the TDC was longer. In such conditions the amount of chemically activated hydrocarbons decreased as well, also as a result of decreasing temperature inside the cylinder. At higher α values the efficiency of thermal NO_x reduction did not change, which may be explained by a stable amount of chemically activated hydrocarbons, although the total amount of hydrocarbons was different.

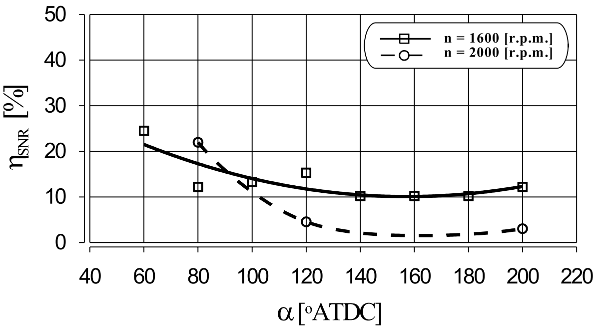

Fig. 2. The influence of the fuel post-injection angle on the efficiency of thermal NO_x reduction

The total efficiency of NO_x reduction η_T, combining all processes of NO_x reduction before and after the catalytic converter as a function of the fuel post-injection angle, is presented in Fig. 3. The functions showing this relationship are increasing for both engine speeds. A stronger influence of the fuel post-injection angle is visible at 2000 r.p.m. and for $\alpha < 120°$ ATDC. At 1600 r.p.m. similar values of η_T (about 20%) were obtained in the whole range of variability of the fuel post-injection angle. At 2000 r.p.m., η_T was around 18% in the α range from 120 to 200 oATDC, but when the start of fuel post-injection was closer to the TDC, the values of η_T decreased, reaching 10% for $\alpha = 80$ oATDC. This decrease in the total conversion efficiency was caused by lower NO_x reduction efficiency in the converter, dropping down to even negative values (the amount of nitrogen oxides in the converter increased) – see Fig. 4.

Fig. 4 shows an increase in the NO_x reduction efficiency in the catalytic converter along with the increasing fuel post-injection angle, mainly for low values of that angle ($\alpha < 120°$ ATDC), and for both engine speeds. For higher values of α, a stabilization of NO_x reduction efficiency can be observed. It should be noted that for the lowest α values the efficiency η_{SCR} drops below zero. Positive aspects of catalytic converter utilization can be noticed only for α exceeding 80° ATDC at 1600 r.p.m., and for α exceeding 120° ATDC at 2000 r.p.m., because in that range the NO_x reduction efficiency is greater than zero.

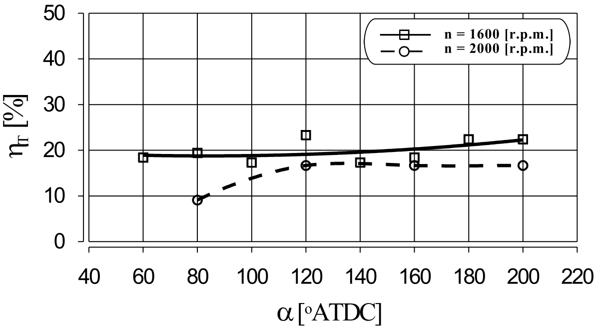

Fig. 3. The influence of the fuel post-injection angle on the total efficiency of NO_x reduction

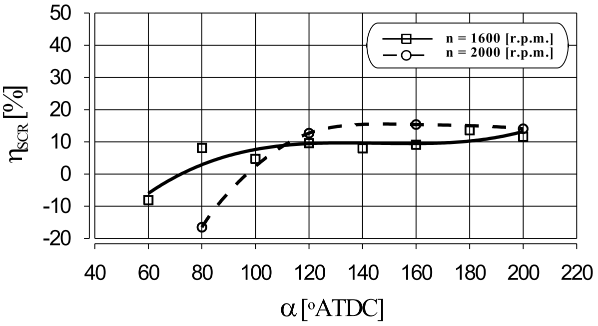

Fig. 4. The influence of the fuel post-injection angle on the efficiency of catalytic NO_x reduction

Negative values describing NO_x reduction efficiency demonstrate that the catalytic converter does not reduce nitrogen oxides effectively. This is caused by the fact that at high exhaust gas temperatures (exceeding the activation temperature of the converter by 200 K) the converter becomes inactive and loses its selective capability including the capability of NO_x reduction. Probably because of high exhaust gas temperatures and an excess of oxygen, further reactions of nitrogen oxidation take place in the converter (the exhaust gas temperature after the converter is lower, and the reaction of nitrogen oxidation is endothermic), and the concentration of nitrogen oxides inside the converter increases.

4.2. The influence of the additional diesel fuel dose

Tests were conducted at two engine speeds: 1600 and 2000 r.p.m., with two constant parameters: the engine torque ($T = 60$ Nm), and the fuel post-injection angle ($\alpha = 100°$ ATDC). The volumes of additional fuel dose were relatively high, reaching 26% of the main fuel dose at 1600 r.p.m. and 33% of the main dose at 2000 r.p.m. Such volumes were necessary to obtain the required maximum HC_1/NO_x ratio of 10 before the converter. It was expected that by using diesel fuel as a reducing agent source (diesel fuel is a mixture of hydrocarbons having various selectivity in terms of NO_x reduction), the optimum level of that ratio in terms of NO_x reduction efficiency would be much higher than 3.

The curves shown in Fig. 5 prove that with higher volumes of additional fuel dose, the efficiency of NO_x reduction in the SNR process increased. This increase was, however, not uniform, being higher for 1600 r.p.m. and lower for 2000 r.p.m. One can suspect that at 1600 r.p.m. more chemically active hydrocarbons were used in the SNR reactions. The volumes of fuel injected as the additional dose were smaller, but most of the hydrocarbons were not burnt. Initially decomposed and partially oxidized (chemically activated) hydrocarbons acted as an effective NO_x reducing agent. The maximum efficiency (SNR in test conditions reached about 34% at 1600 r.p.m. and about 10% at 2000 r.p.m.

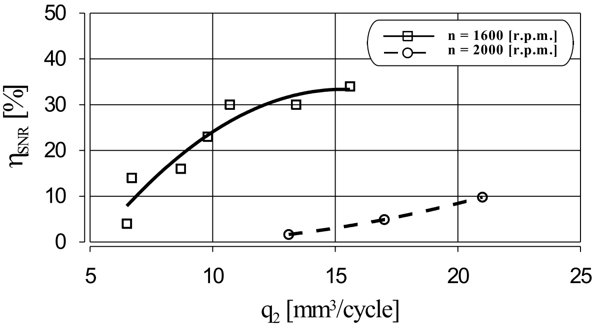

Fig. 5. The influence of the additional fuel dose on the efficiency of thermal reduction of nitrogen oxides

The total efficiency of NO_x reduction η_T as a function of the additional fuel dose volume is presented in Fig. 6.

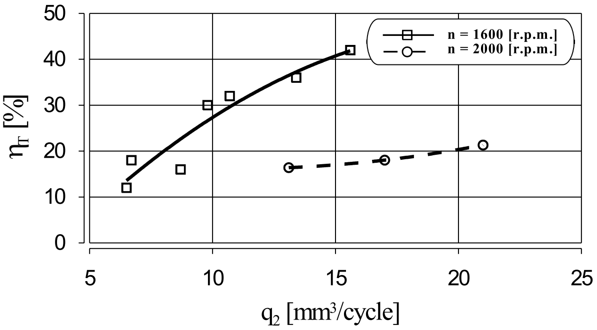

Fig. 6. The influence of the additional fuel dose on the total efficiency of NO_x reduction

The shape of both curves (for both engine speeds) is identical as those of the SNR process efficiency curves. The reason for higher η_T values for the corresponding volumes of the additional fuel dose are additional processes of NO_x reduction taking place in the catalytic converter. For the maximum volume of the additional fuel dose, the efficiency η_T reached about 42% at 1600 r.p.m. and about 21% at 2000 r.p.m. From the comparison with the results of the SNR process (Fig. 5) it is clear that the gain is relatively small. This is caused by low conversion efficiency in the catalytic converter.

Fig. 7 shows the influence of the additional fuel dose volume on the efficiency of NO_x reduction in the catalytic converter (η_{SCR}). Attention must be drawn to the small influence of the additional fuel dose volume on the efficiency of the SCR process in the catalytic converter. The fuel post-injection results in a slight tendency towards higher efficiency numbers only at 1600 r.p.m. A reason for this insignificant sensitivity of the NO_x reduction efficiency to the additional fuel dose volume may be the fact that, irrespective of the variation in the amount of hydrocarbons introduced into the converter, only a constant portion of hydrocarbons demonstrate selective reducing capability suitable for the converter being used. With the fuel post-injection, slightly better average efficiency of the SCR process in the converter (about 13%) was reached at 2000 r.p.m., while at 1600 r.p.m. the efficiency was about 8%. The reason for this may be higher exhaust gas temperature before the converter at 2000 r.p.m. resulting in gaining selective capabilities by more hydrocarbons contained in exhaust gases.

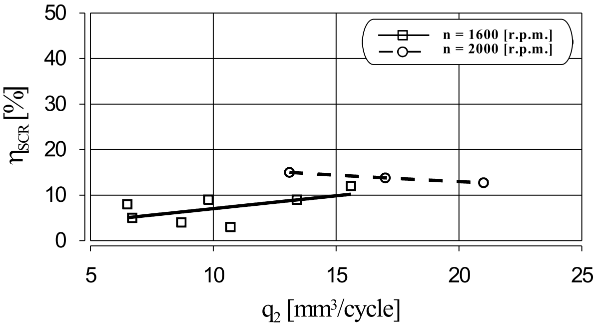

Fig. 7. The influence of the additional fuel dose on the efficiency of NO_x reduction in the catalytic converter

4.3. The influence of the space velocity of exhaust gas flowing through the converter

The space velocity of exhaust gas SV is defined as the ratio of volumetric flow rate of exhaust gas flowing through the converter to the converter volume. As it can be seen in Fig. 8, the influence of this parameter on the efficiency of NO_x selective catalytic reduction turned out to be very strong. While at the highest SV of 78×10^3 h^{-1} the NO_x reduction efficiency of 22% was obtained, at SV = 30×10^3 h^{-1} even 68% reduction efficiency was found. As during the tests the proportion of the reducing agent to the NO_x volume did not change ($HC_1/NO_x = 5$), it must be stated that the reduction of NO_x concentration after the converter was caused by better conditions for the adsorption of nitrogen oxides and the reducing agent in the active cells of the converter due to prolonged contact time. Because of lower velocity of exhaust gas flowing through the converter, particles of nitrogen oxides and those of the reducing agent, due to their low kinetic energy, were deposited easier, increasing the level of adsorption in the active cells of the converter.

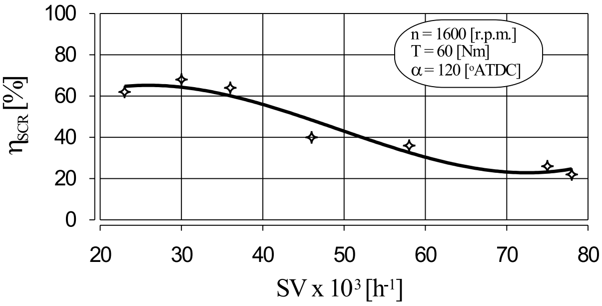

Fig. 8. The influence of space velocity SV on the efficiency of catalytic NO_x reduction

Fig. 9 shows the total efficiency of NO_x reduction as a function of the space velocity of exhaust gas flowing through the converter. This includes NO_x reduction accomplished by selective non-catalytic (thermal) method (SNR) and by selective catalytic reduction (SCR).

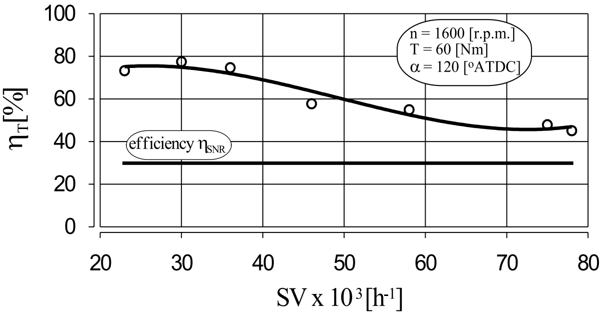

Fig. 9. The influence of space velocity SV on the total efficiency of NO_x reduction

The concentration of nitrogen oxides in the natural exhaust gas was 710 ppm. As a result of thermal reduction between the engine cylinder and the converter it decreased to 500 ppm. Consequently, (SNR was 29.5% and this value did not change during the investigation of the influence of SV on the NO_x reduction efficiency in the converter. The total efficiency of NOx reduction was determined assuming the concentration of nitrogen oxides in natural exhaust gas, i.e. 710 ppm, as a reference value. With this assumption it was possible to determine the efficiency of NO_x reduction from the whole volume of nitrogen oxides contained in the natural exhaust gas of the engine. As it can be seen, the minimum reduction efficiency of 42% was registered at the highest SV of exhaust gas flowing through the converter, namely at 78 × × 10^3 h^{-1}. The total efficiency of NO_x reduction was higher at lower SV values, and at SV of 30 × 10^3 h^{-1} an efficiency of 77,5% was obtained.

The results obtained lead to a conclusion that both methods implemented, i.e. the SNR and the SCR have a significant influence on the total efficiency of NO_x reduction in the exhaust gas of the engine. As at certain conditions of NO_x reduction process (with the post-injection of diesel fuel into the engine cylinder) there are some limitations affecting the possibility of influencing the efficiency of thermal reduction, the development work on the optimisation of catalytic converters, and consequently on the improvement of the SCR process, should be intensified.

4.4. The influence of exhaust gas temperature at the converter

The investigation of the influence of exhaust gas temperature on the efficiency of NO_x reduction was conducted at a constant engine velocity $n = 1600$ r.p.m., and at a constant engine torque $T = 80$ Nm. The following parameters were also fixed: static injection timing of main fuel dose (27° BTDC), start angle of fuel post-injection $\alpha = 100°$ ATDC), the main fuel dose $q_1 = 76$ mm^3/cycle, and the additional fuel dose $q_2 = 20$ mm^3/cycle. The test stand was equipped with an exhaust gas cooler to adjust the temperature of exhaust gas before the converter in the range of 260 to 460 °C.

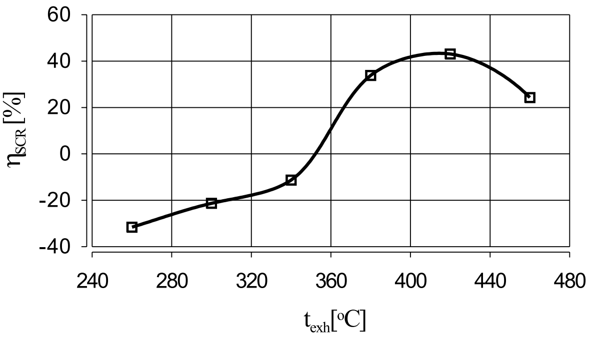

Fig. 10. The influence of exhaust gas temperature before the converter on the efficiency of NO_x catalytic reduction in a Cu/ZSM-5 converter

Fig. 10 shows that the converter used in the investigation featured the highest catalytic activity in terms of NO_x reduction at exhaust temperatures approximately between 380 °C and 460 °C, providing the highest NO_x reduction efficiency ranging from 25% to 44%. At temperatures between 260 °C and 360 °C, however, the efficiency of NO_x reduction in the converter was negative, which means that the converter lost its catalytic function in the NO_x reduction process and became an NO_x "generator". This was caused by reactions opposite to the NO_x reduction, intensified at lower exhaust gas temperature. Nitrogen oxides were produced mainly from diesel fuel constituents containing nitrogen (additives augmenting the cetane number) and from radicals such as, for example, $CH_2^{\bullet}$, $CNO^{\bullet}$, $HCN^{\bullet}$.

4.5. The influence of diesel fuel group composition

Three diesel fuel grades differing in chemical composition were analysed. The properties of the fuels are collected in Table 1. Three main groups of hydrocarbons were distinguished in the diesel fuel: aromatic hydrocarbons, ethylenic hydrocarbons (olefins), and saturated hydrocarbons (paraffins and naphtenes).

An investigation of the influence of diesel fuel group composition on the NO_x reduction in the exhaust gas was conducted at a constant engine velocity $n = 1600$ r.p.m. and a constant torque $T = 60$ Nm. The main fuel dose $q_1 = 60$ mm^3/cycle, the post-injection fuel dose $q_2 = 20$ mm^3/cycle, the static injection timing of main fuel dose was 27° BTDC, and the start angle of fuel post-injection $\alpha = 100°$ ATDC.

Fig. 11 shows percentages of these hydrocarbons in the fuels used. The highest value of the total efficiency of NO_x reduction $\eta_C = 54$ % was obtained for fuel "3", and the lowest value (48%) was obtained for fuel "1" (Fig. 12). The reason was a high NO_x reduction efficiency achieved in the converter for fuel "3" due to NOx selective catalytic reduction, as shown in Fig. 13.

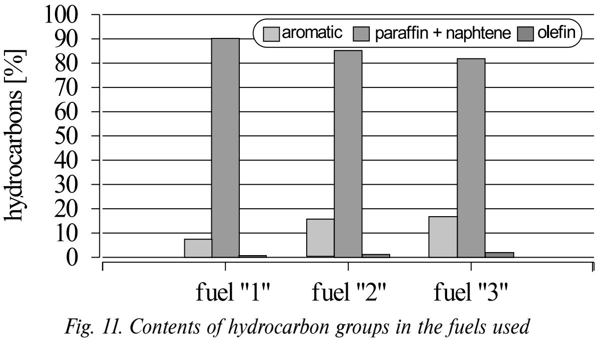

Fig. 11. Contents of hydrocarbon groups in the fuels used

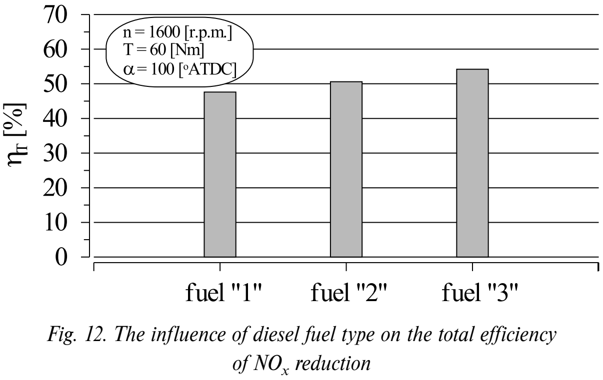

Fig. 12. The influence of diesel fuel type on the total efficiency of NO_x reduction

The highest efficiency of NO_x reduction in the catalytic converter $\eta_{SCR} = 42\%$ was obtained for fuel "3" (Fig. 13).

Table 1

	Parameter	Unit		Fuel	
			"1"	"2"	"3"
1.	**Composition:**	[% vol.]			
	aromatic hydrocarbons (arenes)		8.75	13.64	16.23
	ethylenic hydrocarbons (olefins)		1.08	1.19	1.96
	saturated hydrocarbons (paraffins + naphtenes)		90.17	85.17	81.81
2.	**Aromatic hydrocarbons**	[% mass]	9.85	14.96	17.68
3.	**Average molecular weight**		254	189	214
4.	**Structural composition:**				
	Carbon content of:				
	aromatic structures C_A	[%]	5.63	11.20	12.34
	naphtene structures C_N		33.21	24.93	25.26
	paraffin structures C_P		61.16	63.87	62.40
	contents of rings in an average molecule:				
	total P		1.24	0.86	1.01
	aromatic hydrocarbons P_A		0.17	0.26	0.32
	naphtene hydrocarbons P_N		1.07	0.60	0.69
5.	**Density at 20 °C**	[kg/m^3]	0.837	0.8165	0.8305
6.	**Sulphur content**	[% mass]	< 0.001	< 0.001	0.07
7.	**Normal distillation:**	[°C]			
	Start of distillation:		140	85	111
	5		190	120	155
	10		224	149	179
	20		250	176	202
	30		268	194	220
	40		282	210	239
	50		297	228	257
	60		309	249	273
	70		320	273	294
	80		331	296	314
	90		350	330	337
	95		356	355	359
	97		359	370	367
8.	**Mass balance of distillation process:**				
	distillation below 250 °C	[% mass]	13.11	51.6	39.3
	distillation 250 – 300 °C		31.73	22.3	24.6
	distillation 300 – 350 °C		35.77	20.5	24.1
	distillation residue		19.29	5.4	11.9
	distillation losses		0.1	0.2	0.1
9.	**Cetane number**		58.078	47.713	50.151

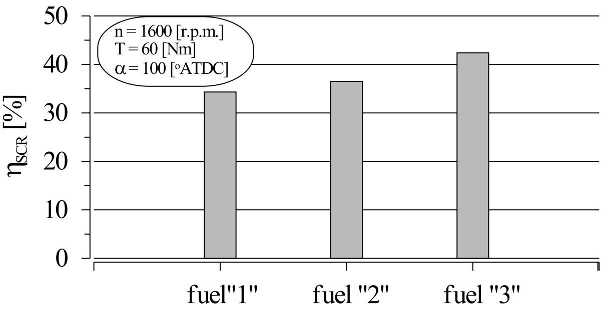

Fig. 13. The influence of diesel fuel type on the efficiency of NO_x reduction in a catalytic converter

The η_{SCR} was 34% and 36% for fuels "1" and "2" respectively. Taking into account the properties of fuels collected in Tables 1, it may be concluded that the efficiency of selective catalytic reduction of nitrogen oxides in the catalytic converter depends on the aromatic hydrocarbon content of the fuel used. This is caused by the fact that aromatic hydrocarbons feature better selective properties in the NO_x reduction process taking place in the converter used in the experiment than other hydrocarbons contained in diesel fuel. Such dependencies are also described in the literature on the subject discussed [6, 11, 14]. For example, according to [6], hydrocarbon groups can be ordered according to their selectivity as follows: arenes > olefins > paraffins, while according to [14] the order is: arenes > olefins > n-paraffins > aldehydes. This explains why the η_{SCR} was the lowest for fuel "1" containing 9.85% of aromatic hydrocarbons by weight (the lowest content), and the highest for fuel "3" containing 17.68% of aromatic hydrocarbons by weight (the highest content).

5. Conclusions

It has been found that, as a result of fuel post-injection in the engine cylinder, nitrogen oxides are reduced not only in the catalytic converter, but also in the exhaust manifold between the cylinder and the converter. Two methods of NOx reductions were isolated: the SNR process (Selective Non-Catalytic Reduction) taking place outside the converter, and the SCR process (Selective Catalytic Reduction) in the catalytic converter. To evaluate the effects of NOx reductions, several definitions of various NO$_x$ reduction efficiency measures have been introduced. The main conclusions drawn from the experiments are as follows:

1. The results indicate that the total efficiency of the NO$_x$ reduction depended mainly on the efficiency of Selective Non-Catalytic Reduction (SNR). The additional fuel dose volume, engine speed and engine load were influential factors. Better effects were observed at lower engine speeds.
2. The influence of the fuel post-injection angle on the NO$_x$ reduction efficiency was the strongest when the additional fuel dose was injected close to the TDC. In such a case better effects were obtained from the SNR process, but with a negative effect in the converter. As a result, the total effect of the reduction practically did not depend on the fuel post-injection angle. Injection of the additional portion of fuel too close to the TDC is, however, not allowed because of the possible autoignition of diesel fuel. This would lead to a rapid increase in the exhaust gas temperature and possible damage to the converter. In view of the above, and considering also an effective use of the reducing agent (which has an effect on diesel fuel consumption), it would be more advantageous to inject the additional fuel dose at crank angles between 120 and 160 ° ATDC. These values do not have to be the optimum values for different operating conditions of the engine (engine load and engine speed), and for other engines.
3. The tests conducted at two different engine speeds and constant engine load showed that the influence of the additional fuel dose volume, and the HC$_1$/NO$_x$ ratio before the converter, on the efficiency of NO$_x$ reduction in the catalytic converter η_{SCR} is rather small. This influence could be, however, more visible in different operating conditions of the test engine. The resultts obtained from the study justify the conclusion that there is a need for further research into a catalytic system which would feature higher activity and better selectivity, and could be used in the converter. Some parameters, such as the reaction time, may be also optimized by adjusting the volume of the converter to the volume and rate of flow.
4. A strong influence of the space velocity of exhaust gas flowing through the converter on the efficiency of selective catalytic reduction of nitrogen oxides taking place inside the converter was found. By reducing this velocity, the efficiency of NOx catalytic reduction was raised.
5. In order to optimize the efficiency of NO$_x$ reduction, the temperature of exhaust gas before the converter should be maintained in a strictly defined range.
6. The influence of fuel composition on the efficiency of selective non-catalytic reduction of nitrogen oxides turned out to be rather low. However, a stronger influence of fuel type on the efficiency of catalytic reduction taking place in the converter was observed. It was determined that fuels containing more aromatic hydrocarbons provide better opportunities in terms of the effectiveness of selective catalytic reduction of nitrogen oxides.

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