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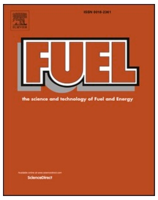

Full Length Article

External fuel reforming for compression-ignition engines

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ABSTRACT

This paper presents the results of a study on the reduction of toxic exhaust gas emissions from compression-ignition engines by applying a fuel pretreatment. This treatment consists of contacting the fuel with a heterogeneous catalyst in the form of a Cu-Ni alloy applied to the nozzle needle in the fuel injector body. In this case, the pre-treatment of the fuel allows the fuel to reform. As determined in laboratory tests, fuel reforming is presented by an increase in the proportion of the olefin group in the atomised fuel and a decrease in the proportion of the paraffin group, which may indicate the occurrence of a fuel dehydrogenation reaction and the release of free hydrogen on contact with the catalyst. To apply the heterogeneous catalyst by electrospray fusion, the passive part of the atomiser needle was used, connecting the needle's precision surfaces (its guide and firing cone). Laboratory tests of the atomiser modified in this way showed a change in the hydrocarbon groups of the fuel after contact with the catalyst. Results from bench tests of an experimental compression-ignition engine equipped with a pre-treated fuel injector showed a reduction in nitrogen oxide emissions of up to 30 %. Analysis of the engine process indicator diagrams shows that the achievement of such results is related to the reforming of the fuel, which leads to a reduction in the maximum pressure and heat release values, resulting in a reduction in the combustion temperature in the kinetic phase of the combustion process, responsible for the formation of nitrogen oxides in the engine cylinder. The applied electro-spark alloying method for the deposition of Cu-Ni catalysts on the passive part of the injector nozzle's needle does not cause thermal distortion of the precision pair of the fuel injector and can be recommended for use both in the production process of injection equipment for compression-ignition engines and during their operation.

1. Introduction

1.1. Pre-combustion processes in the engine

Achieving the technically best operational and environmental performance of internal combustion engines is primarily related to organising the combustion process in such a way as to both make efficient use of the energy contained in the fuel and reduce the potential for toxic compounds in the exhaust gas [1]. The phenomena occurring in the combustion chamber play a major role here, but the problem should be approached more broadly, taking into account both the possibilities for reducing the toxicity of the exhaust gases in the exhaust systems and the possible preparation of the fuel and air before they enter the combustion chamber. In this respect, the thermal processes occurring in an internal

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Abbreviations: ASTM, standardization organization, formerly known as the American Society for Testing and Materials; BASE, 4-hole spray nozzle in the factory version; BMEP, brake mean effective pressure; BTDC, angle before top dead center; DMA, Distillate Marine Fuel, the "D" stands for "distillate," and the "MA" refers to a specific category within distillate fuels. Categorisation comes from the International Organization for Standardization's ISO 8217 standard; dQ_k, rate of difusion combustion; dQ_k, rate of kinetic combustion; *FC*, fuel consumption; HCCI, homogeneous charge compression ignition; NO_x, nitrogen oxides emission; n_{Tmax}, engine speed at maximum torque; p_{cmax}, p_{cmax}, maximum combustion pressure, maximum combustion pressure; P_e, effective power; RCCI, reactivity controlled compression ignition; *T*, torque; T_c, combustion temperature; TEST, 4-hole spray nozzle with a catalytic layer; T_k, temperature in the kinetic phase of combustion; T_{max}, maximum torque; *WSD* 1.4, normalized wear scar diameter; *Ø*, injector hole diameter; λ, air excess ratio; η_o, overall engine efficiency; τ_c, fuel self-ignition delay.

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combustion engine should be considered in the following sequence of stages [2].

- preparation of the fuel and air before the combustion chamber;
- to carry out the effective processes taking place in the combustion chamber;
- reduction and oxidation of toxic exhaust components in the exhaust gas.

Among these stages, air coolers and turbochargers/superchargers or components for exhaust gas recirculation are used in the intake systems. Catalytic reactors and particulate filters are used in the exhaust systems. However, the processes taking place in the combustion chamber have the greatest influence on engine efficiency, and the course of phenomena during each of these stages is influenced by the course of the preceding stage[3].

It should be noted that in the first stage, in addition to the preparation of the air, there is also a suitably prepared fuel, and development work is currently focused on the use of petroleum-based fuels and their mixtures with renewable fuels, which primarily include methyl esters of oils derived from oilseed crops. However, the appropriate preparation of these fuels before they are delivered to the combustion chamber has not been widely used [4]. Striving to improve both the economic performance of the engine along with lowering the level of toxic emissions in the exhaust gases is a major challenge for designers of reciprocating internal combustion engines. One solution for changing the chemical composition of certain substances, such as fuel, is the use of catalysts, whose presence lowers the activation energy, which enables or facilitates certain chemical reactions to take place [1]. Fuel catalysts applied to the injector needle in compression ignition engines are designed to improve fuel combustion efficiency and reduce harmful emissions [5]. The mechanism of action of these catalysts is based on several basic theories. First, these catalysts operate on the principle of heterogeneous catalysis, where chemical reactions take place on the surface of a solid catalyst. In the case of catalysts applied to the injector needle, the catalyst is in direct contact with the fuel, which allows for more efficient conversion of harmful substances into less toxic products. Precious metals such as platinum, palladium and rhodium are often used as catalysts due to their ability to accelerate chemical reactions at high temperatures. Second, these catalysts support the oxidation and reduction processes that are crucial for converting harmful exhaust gases such as carbon monoxide (CO) and nitrogen oxides (NO_x) into less toxic gases such as carbon dioxide (CO_2) and water vapor (H_2O). As a result, harmful emissions are significantly reduced. Thirdly, applying catalysts to the injector needle allows for a more even distribution of the catalyst in the fuel, which increases the catalytically active surface and improves combustion efficiency [6].

Our goal was to determine the effect of the preliminary fuel treatment—fuel reforming using heterogeneous catalysts in the form of a Cu-Ni alloy, applied to the nozzle of the fuel injector—on the ecological and operational parameters of a compression ignition engine.

1.2. Preliminary fuel treatment

The desired simultaneous reduction in fuel consumption (increase in engine efficiency) along with a reduction in exhaust toxicity is contrary to the so far developed theory of internal combustion engines [1], and the explanation of the possibility of obtaining these dual effects should be sought with a careful analysis of the phenomena occurring in the organisation of the engine operating process as well as the appropriate preparation of the fuel. To such a “preparation” – pre-treatment of the fuel, we should refer to the application of the effect of catalytic materials on the fuel, which can be carried out during the fuel flow in the fuel injectors, that is, immediately before its atomisation in the combustion chamber [7].

The theoretical aspect of the influence of fuel pretreatment on the processes taking place in the combustion chamber of a compression-ignition engine is related, firstly, to the formation of a dehydrogenation reaction when the fuel comes into contact with a catalytic material, as a result of which the most abundant group of paraffinic hydrocarbons transforms into an olefinic one with the release of free hydrogen [8]:

$$C_nH_{2n+2} \Rightarrow^{cat} C_nH_{2n} + H_2 \tag{1}$$

The effect of increase of NOx emission during hydrogen combustion were observed by other researchers [9]. However, the amount of hydrogen produced in the combustion chamber in this experiment is possibly relatively small, as a high concentration of hydrogen would lead to an increase in combustion temperature, and consequently, a rise in NOx emissions [10], which was not observed in the presented.

Some of the hydrogen ions react with other substances, including fuel and lubricating oil. Intermediate compounds in the form of free radicals form further intermediate compounds and, under appropriate combustion conditions, undergo complete and total combustion. Hydrogen ions, however, being highly reactive, mostly undergo combustion in the reaction with oxygen [9,11]:

1 Initiating reactions:

$$H + H \rightarrow H_2 \tag{2}$$

$$H_2 + M \rightarrow H + H + M \tag{3}$$

$$O + O \rightarrow O_2 \tag{4}$$

$$O_2 + M \rightarrow O + O + M \tag{5}$$

$$H_2 + O_2 \rightarrow H + HO_2 \tag{6}$$

2 Chain-propagating reactions:

$$H + O_2 \rightarrow O + OH \tag{7}$$

$$H_2 + O \rightarrow H + OH \tag{8}$$

$$H_2 + OH \rightarrow H + H_2O \tag{9}$$

$$H + O_2 \rightarrow HO_2 \tag{10}$$

3 Final reactions:

$$H + H + M \rightarrow H_2 + M \tag{11}$$

$$O + O + M \rightarrow O_2 + M \tag{12}$$

$$H + OH + M \rightarrow H_2O + M \tag{13}$$

$$HO_2 + H_2 \rightarrow H_2O + OH \tag{14}$$

where: M – a molecule of an inert substance.

For practical reasons, the above equations are usually described using a simplified model in the form of:

$$2H_2 + O_2 \rightarrow 2H_2O. \tag{15}$$

Secondly, the same contact between the fuel and the catalyst promotes lower activation energy levels, and as is known[1], according to the Arrhenius equation, a reduction in this energy reduces the time of the initial physical and chemical processes during the first period of combustion. Olefin compounds have a double bond structure, which makes them more likely to participate in free radical reactions than saturated hydrocarbons, allowing them to decompose and release energy more quickly during combustion. These characteristics may have a positive effect on the fuel’s combustion rate. Increasing the effect of the catalyst on the flowing fuel is supposed to serve the high temperature of the atomiser elements, and it is in the atomiser – on the surface of the firing pin and body that the catalyst is applied [12].

In the operational practice of internal combustion engines, several methods of fuel reforming are encountered, aimed at improving combustion efficiency and reducing harmful emissions.

- Catalytic reforming: This process involves the use of catalysts to convert hydrocarbons into more reactive compounds, leading to better combustion. Catalysts can be placed in the exhaust system or in the combustion chamber [13–16]. The catalytic reforming processes are summarized in literature [17].
- Steam(−catalytic) reforming: In this method, fuel is mixed with steam in a high-temperature process, resulting in the production of syngas (H2,CO and CO_2). This gas can then be used as fuel or added to the fuel mixture [18–20]. This method is used in the production of hydrogen from fuels such as natural gas, methane, LPG, or gasoline. By exposing these raw materials to steam at elevated temperatures and in the presence of nickel catalysts, synthesis gas (syngas) is produced. The reactions occurring during the process include the conversion of sulfur compounds and olefins, hydrogen sulfide removal reactions, feedstock purification reactions, and primary reactions [21].
- Plasma(−catalytic) reforming: This technology utilises plasma to break down hydrocarbons into smaller molecules, which increases their reactivity and enhances the combustion process [22–24]. For example, the processes of plasma reforming of methane leading to hydrogen production occur in accordance with specific reactions [25].
- Thermal(−catalytic) reforming: In this method, fuel is heated to high temperatures, leading to its breakdown into simpler chemical compounds that are easier to combust [26–28]. For example, the thermal catalytic route utilizing a catalyst containing a high density of atomic Pt_1 and Ir_1 species supported on a reactive alpha-molybdenum carbide substrate is used for the partial reforming of ethanol into hydrogen and acetic acid with near-zero carbon dioxide emissions [29]. In the research literature reforming is presented as modifying the chemical structure of the fuel at high temperatures and refers to: endothermic steam reforming in the presence of oxygen-free steam [30], and exoenergetic decomposition of fuel into smaller molecules in the presence of oxygen[31].

Both of these phenomena take place in the combustion chamber at high temperatures and, in the first case, lead to the formation of hydrogen and carbon monoxide, the components of the synthetic gas, while in the second case, improve the reactivity of the mixture and consequently increase its self-ignition capacity and flammability range [32–34]. Both of these phenomena can take place separately or simultaneously, and their intensity depends on the availability of oxygen [35,36]. Fuel reforming carried out in this way takes place at temperatures of the order of 1000 K – the value at which spontaneous ignition of the fuel–air mixture occurs [37]. The presented issue of fuel reforming applies primarily to HCCI (homogeneous charge compression ignition) engines directly in the combustion chamber – internal reforming. External reforming can also be used by applying the energy of the recirculated exhaust gas, which flows through a separate catalytic reactor. Here, a specific dose of fuel is injected into the waste gas stream flowing through the extended surface of this secondary reactor. Steam reforming occurs, whereby the thermal energy of the exhaust gas is recovered, the calorific value of the mixture is increased, and in addition, hydrogen is produced, which, as mentioned earlier, due to its physical properties (volatility, high calorific value, etc.) allows the fuel to burn more completely [4].

Slightly different, but no less interesting, is the use of catalytic converters for fuel reforming while achieving reactivity stratification of the agent in an engine with RCCI (reactivity controlled compression ignition). In the paper of Cisek et al. [38]a catalytic diesel reformer is presented that produces a synthesis gas in the form of a mixture of carbon monoxide and hydrogen. This gas has a lower reactivity than diesel fuel, but it forms a homogeneous mixture in the cylinder and the remaining diesel fuel is injected directly into the cylinder, resulting in a highly reactive mixture zone.

It should be emphasised that fuel reforming, whether inside the combustion chamber or externally in catalytic reactors, involves the use of thermal processes that allow the fuel to be affected, leading to changes in its group composition. The group composition of hydrocarbons in fuel intended to power compression-ignition engines contains paraffinic (saturated), olefinic (unsaturated) and aromatic groups [4].

It should be noted that for multi-atomic systems (which include hydrocarbon fuels in the first instance), the activation energy is defined as the minimum kinetic energy by which the potential energy of the system should be greater for a chemical reaction to take place in the system.

Since the activation energy depends on the structure of the particles and their strength relationships in the research of Ambroziak [39] an example of the behaviour of paraffinic hydrocarbons C_nH_{n2n+2} is presented. In these hydrocarbons, the $C–H$ bond-breaking energy is higher than the $C–C$ bond-breaking energy, so with an increase in the number of carbon atoms a lower activation energy is needed to break the molecule. It is with this in mind that the high stability of isooctane C_8H_{18}, used as a reference fuel for the determination of the octane number of the fuel, can be explained. To facilitate overcoming the energy barrier associated with activation energy, we can either supply more energy to the reaction medium (e.g. heating) or use a substance that reacts readily with the substrate (low activation energy) and the resulting compound readily transforms into the final product (also low activation energy). A substance that facilitates the transition from substrates to products in this way is a catalyst that completely reconstitutes itself after the substrates have been converted to products. It follows that the presence of a catalyst and its contact with the fuel before it is injected into the combustion chamber is desirable.

The literature does not provide information on studies concerning the reforming of engine fuels using heterogeneous catalysts in the form of a Cu-Ni alloy, applied to the nozzle of the fuel injector. Based on previous studies by the authors [40–42], preliminary investigations were conducted in laboratory settings using a single fuel and employing the engine's load characteristics to determine the effect of fuel reforming on the ecological and operational parameters of a compression ignition engine. To this end, studies were carried out to assess the change in the proportions of hydrocarbon groups after the fuel passed along the surface with the catalytic coating, as well as tests on an engine dynamometer to determine the engine parameters. A comparison of the results from both tested injectors, Base and Test, allowed for the formulation of conclusions regarding the applicability of the reforming method for practical use.

2. Materials and methods

2.1. Preliminary assumptions

The catalysts used both in exhaust gas aftertreatment reactors and applied to engine internals are in the form of heterogeneous catalysts. The requirements placed on such materials, both in the chemical industry and in the automotive sector, are essentially the same. Desirable characteristics of catalytic converters are [43]:

- High activity ensuring a high degree of substrate conversion under the most economical conditions possible (low temperatures and pressures).
- High selectivity ensuring the desired direction of the chemical transformations taking place while minimising side reactions as much as possible.
- Longevity retention of properties such as activity and selectivity over a long lifetime.

- Poison resistance.
- Sufficiently high mechanical strength, and abrasion and compression resistance. Too little mechanical wear resistance would contribute to dusting of the catalysts and to a significant reduction in their service life.
- High thermal conductivity.
- Good reproducibility of the preparation

When considering the possibility of using catalytic converters in fuel injectors, it should be noted that, despite the simple geometric shapes, the injector nozzle consists of two elements fitted precisely to each other, and making any structural changes eliminates the use of high-temperature technologies, while the high fuel pressure values in the injector impose appropriate requirements for the bonding of the catalytic material to the substrate – the nozzle needle, made of high-alloy steel. Another condition for the choice of catalytic material is an atomiser operating temperature which does not exceed 500 K and implies the use of low-temperature catalysts. The above-mentioned conditions are met by heterogeneous catalysts in the form of metals – platinum group and cuprum group [43,44].

Platinum group metals are divided into two groups: light platinum and heavy platinum. The light platinides include ruthenium, rhodium and palladium. The heavy platinides, on the other hand, include osmium, iridium and platinum. All of these metals have similar chemical properties. They are low in activity and very difficult to oxidise. Platinides are catalysts for reactions such as oxidation (platinum), reduction of nitrogen oxides (rhodium), and also enable the dehydrogenation of paraffinic hydrocarbons, so they can be used both in catalytic exhaust gas cleaning reactors and in fuel system components or inside combustion chambers. Platinum catalysts are widely used not only in the automotive sector, but also in other areas, particularly in the petrochemical and refining industries.

When selecting a catalytic converter for compression-ignition engine nozzles, another limitation is the small surface area of the firing pin onto which the catalyst can be applied. Increasing the catalyst's contact area with the fuel can be achieved by choosing a catalyst application method that, in addition to adhering well to the substrate, also has a rough surface. One such method is electro-spark alloying, which does not result in high process temperatures, very good adhesion of the applied material to the substrate and increased roughness of the resulting coating.

The second group of low-temperature catalysts in the applications in question are the cuprates. This group includes copper, silver and gold – metals that are easy to process, have relatively high melting and boiling points, and are low-reactivity metals.

Metals from the cuprum group offer the possibility of producing low-temperature catalysts, i.e. catalysts that activate at much lower temperatures than, for example, catalysts composed of metals from the platinum group [45,46]. The use of low-temperature catalyst materials is particularly advisable in fuel system components, e.g. in injectors, due to the relatively low operating temperatures of these components. An example of a low-temperature catalyst in which a copper-group metal is used is an oxide-silver catalyst for the complete oxidation of organic compounds. Copper matrix bimetallic catalysts belong to this group [45].

Summarising the issue thus presented, it can be concluded that the most suitable catalysts to be used in the fuel injector body are platinum catalysts, which have the advantage of a low operating temperature, but the aforementioned electro-spark alloying method for catalyst application is expensive, not least because of the large dispersion (loss) of the catalyst during spark discharge. The operating temperature range of fuel injectors coincides with the operating temperatures of bimetallic catalysts of the Cu-Ni, Cu-Cr type – in the order of 500 K [47].

The choice of material for the catalyst was based on the high resistance of Cu-Ni alloys to external conditions. Cu-Ni alloys, or cupronickels, are valued for their durability and corrosion resistance [48,49], making them ideal for heavy-duty applications, such as marine environments. These materials also exhibit high resistance to fatigue wear and good thermal conductivity, which helps reduce the risk of internal stress that could lead to cracking [50]. For the same reasons, Ni-Cu alloys are used for protective coatings [51,52]. When applying the catalytic material, the electro-spark alloying [53] method was used. This method is characterized by very strong adhesion of the deposited material (in this case, the catalytic material) to the substrate (the nozzle needle) and is carried out without significant overheating of the substrate, which is the most important advantage of this method for alloying precision pairs – in this case, the nozzle needle.

With regard to the choice of location and method of catalyst application, including a copper-matrix bimetallic catalyst, a part of the nozzle needle of type D1LMK149/2 compression-ignition engine type SB3.1 was selected, connecting two precision surfaces – the guide and the stop cone. This element is passive (Fig. 1a), i.e. it only acts as a connector, and can be used to apply a bimetallic catalyst by electro-spark alloying (Fig. 1b). The method and the fabricated component are shown in Fig. 2. Using the EIL-8a device, this method allows up to four layers of anode material (Cu-Ni catalyst) to be deposited at spark discharge currents of up to 5A and a catalyst layer of up to 0.15 mm to be obtained [2].

The advantages of the chosen method of catalyst application include the low temperature of the surface to which the catalyst is applied and the achievement of a rough surface. It should be noted that these advantages make it possible to produce a needle with fuel pre-treatment for both newly built nozzles and those in service [2].

Experimental tests were carried out in two stages, the first of which determined the change in the proportions of hydrocarbon groups after the fuel passed along the catalytic coated surface, while the second stage was carried out on an engine dynamometer to determine the effect of fuel pretreatment – internal reforming on the environmental and operational parameters of the compression-ignition engine.

2.2. Laboratory tests

The catalyst material selection tests consisted of measuring the hydrocarbon composition of the fuel after passing through the injectors with the catalyst material applied to the passive part of the nozzle needle. For this purpose, a laboratory bench with a high-pressure pump was set up, together with the fuel supply and discharge system and sampling system components. Fuel drawn from the main tank was pumped with a four-section in-line injection pump to the injectors, which were installed to a common manifold. After passing through the injectors, on the needles of which the catalytic converter was applied, the fuel went to the manifold from which a fuel sample was taken through a valve. After passing through the manifold, the fuel went into the main tank.

In order to determine the hydrocarbon composition in the fuel according to the ASTM standard, a four-column device was used FIA D1319 (Lawler Manufacturing Corporation, Edison, NJ USA [46]), which uses a standard method for testing the types of hydrocarbons in liquid crude oil (according to ASTM test D1319 [46]) based on the adsorption of a fluorescent indicator.

In laboratory tests, hydrocarbon fuel was used, the parameters of which are shown in Table 1. All parameters were determined in the certified laboratory of the Maritime University of Technology in Szczecin in accordance with the standardised test methods indicated in Table 1.

The laboratory testing programme consisted of determining changes in the proportion of individual hydrocarbon groups – saturated (paraffins) and unsaturated (olefins) at measurement points corresponding to fuel sampling every 30 min. Three bimetallic heterogeneous catalysts were used:

- cat no. 1 – Cu-Ni;
- cat no. 2 – Cu-Cr;
- cat no. 3 – Cu-Ni + Pt.

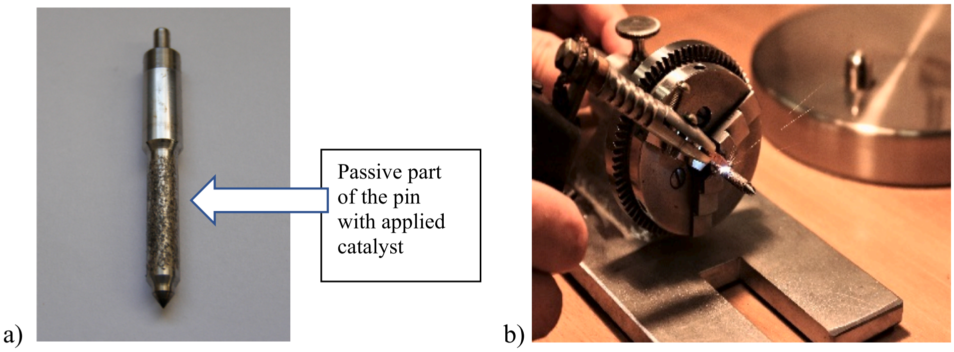

Fig. 1. Compression-ignition engine atomiser needle: a) passive parts of the needle with catalyst applied; b) needle during catalyst application process by electro-spark alloying.

Table 1
Physico-chemical parameters of petroleum hydrocarbon fuel.

Lp.	Test parameter	Research method	ON
1.	Density at 15 °C	PN-EN ISO 12185:2002 [22]	828.5 kg/m^3
2.	Viscosity at 40 °C	PN-EN ISO 3104:2004 [54]	2,456 mm/s^2
3.	Cetane number	PN-EN ISO 16715:2014–08 [55] ASTM D7668 [56]	54.0
4.	Flash point	PN-EN 2719:2016–08 [57]	60.5 ℃
5.	Cold filter blocking temperature	PN-EN 116:2015–09 [58] ASTM D[59]	−29 ℃
6.	Cloud point	PN-ISO 3015:2019–06 [60]	−8 ℃
7.	Water content	PN-EN ISO 12937:2005 [61]	0.003 %
8.	Coke residue (from 10 % distillation residue)	PN-EN ISO 10370:2014–12 [62]	0.09 %
9.	Contaminant content	PN-EN 12662:2014–05[63]	8 mg/kg
10.	Incineration residue	PN-EN ISO 6245:2008 [64]	0.005 %
11.	Lubricity. Corrected wear trace diameter WSD 1.4 at 60 °C	PN-EN ISO 12156–1:2024–02[65]	343 µm
12.	Corrosion test on copper plates	PN-EN ISO 2160:2004 [66] ASTM D130 [67]	1a
13.	Fractional composition (distillation)	PN-EN ISO 3405:2019–05 [68]	Up to 250 ℃ distils 49.1 %. Up to 350℃ distils 97.6 %. 95 % distils w 338.8℃

In the first two catalysts, the proportion of copper was 0.3, while catalyst No. 3 had traces of platinum due to the fact that in the electro-spark alloying process, a steel wire with a diameter of 0.08 mm was introduced into the spark discharge region with platinum deposited on its surface by ion implantation.

2.3. *Engine bench tests*

The experimental part of the research was carried out on a dynamometer bench in the internal combustion engine laboratories of the Cracow University of Technology. A diagram of this stand is shown in Fig. 2.

The stand consists of the following components: 1 – SB 3.1 test engine, 2 – KS 37A-1 alternator brake, 3 – AVL CA364 crankshaft angle transducer, 4 – piston injection pump type: P56-01A with regulator type R14V-20–110/12 M, 5 – W1B-01 injector with four-hole nozzle D1LMK14/2, 6 – AVL light source, 7 – AVL CCD digital camera PULNIX THC9700, 8 – AVL KARL STORZ endoscope diameter: 7 mm, 9 – AVL SMOKEMETER 401 filter opacimeter, 10 – AVL CEB II exhaust gas analyser, 11 – AVL INDIMETER 617D measurement of high-speed signals, 12 – AVL VIDEOSCOPE 513D digital filming of fuel injection and combustion in the engine cylinder, 13 – piezoelectric fuel pressure sensor upstream of the injector, 14 – injector needle displacement sensor, 15 – piezo-quartz cylinder pressure sensor, 16 – pressure equalization tank, 17 – laminar flow meter, 18 – Ascania micro-manometer, 19 – tunnel exhaust gas intake probe, 20 – endoscope cooling air compressor,21 – adjustable dilution air intake, 22 – dilution air dust filter, 23 – dilution air chemical filter, 24 – heat exchanger, 25 – tunnel flue gas inlet, 26 – flue gas mixing orifice, 27 – engine flue gas dilution tunnel, 28 – tunnel mixture intake probe, 29 – T60A20 PALL measuring filter assembly, 30 – rotameter, 31 – vacuum pump, 32 – laboratory gas meter, 33 – SARTORUS M3P electronic microbalance, 34 – fan, 35 – adjustable throttle valve, 36 – tunnel outlet pipe, 37 – flue gas mixture flow measuring orifice, 38 – main fuel tank, 39 – three-way valve 40 – mass fuel gauge.

A detailed description of the measurement modules and the methodology for calculating the heat rate $dQ/d\alpha$ and the combustion temperature $T_c\ (\alpha)$ was included in the authors' earlier articles [32,38,69]. The technical characteristics of this engine are given in Table 2.

The core component of this bench is a single-cylinder, research, undercharged compression-ignition engine equipped with a hydraulic injector with an interchangeable 4-hole nozzle in the factory version (BASE) and with a catalytic coating applied (TEST). As the injector opening pressure increases for a given nozzle, the number of droplets rises while their average size decreases. This effect is explained by the relationship between fuel discharge pressure at the nozzle and outflow velocity, as described by Bernoulli's equation. An appropriately selected injector opening pressure should ensure that the fuel velocity at the nozzle is high enough for the fuel jet to break up immediately upon exiting the nozzle. This engine is used in the laboratory as a measurement tool for cause-effect analysis, which not only allows the effect of introduced changes in structural (structural), control or fuel parameters on the efficiency of the combustion process and the composition of the exhaust gas to be determined, but also allows the causes of these changes to be identified. This is possible because the engine is richly equipped with specialised measuring equipment. In addition to the AVL Fuel Balance mass dynamic fuel consumption meter, the AVL Bench Emission System CEB II and the AVL Smoke Meter SM 401, the AVL Indimeter 617D (measurement of fast-variable pressure in the engine cylinder, fast-variable fuel pressure in the injector, fast-variable displacement of the injector needle) was installed, as well as the AVL VideoScope for recording and analysing fast-variable images in the engine cylinder (course of injection, self-ignition and fuel combustion).

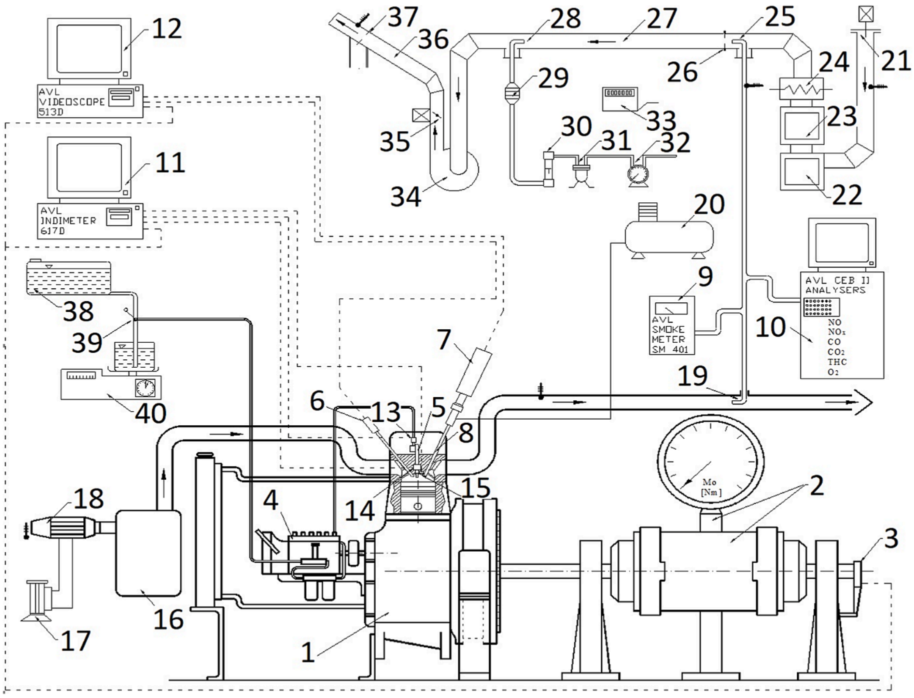

Fig. 2. Diagram of the test bench [32].

Table 2
Technical specification of the engine[32].

Type of Engine	**SB 3.1 (1-cylinder research engine)** **Primary unit: SW 680 (Leyland)**
combustion system	direct fuel injection to open combustion chamber in the piston
total cylinder volume	1.85 dm^3
number of cylinders	1
cylinder diameter	127 mm
piston stroke	146 mm
compression ratio	15.75
rated power P_e	23 kW
nominal speed	2200 rpm
maximum torque T_{max}	110 Nm
speed at maximum torque n_{Tmax}	1600 rpm
direction of rotation of the crankshaft	Left
lubricating system	circulating pressurised
cooling system	liquid, forced
geometric start of fuel injection	27°BTDC
static injector opening pressure	17 MPa
injection pump	piston type, P56-01A
speed governor	R 14 V-20–110/12 M
injector type	W1B-01
injection nozzle	4-hole, $\O$=0.35 mm

3. Results and discussion

3.1. Laboratory tests

The results obtained during the laboratory tests show the change in the proportions of the paraffinic and olefinic groups of the fuel after passing along the surface of the atomiser needle on the passive surface to which the catalyst was applied. In order to confirm the effect of the catalyst on the change in the proportion of individual hydrocarbon groups, Figs. 3 and 4 show graphs corresponding to measurements of fuel not affected by catalysts.

The results of these tests showed that the bimetallic catalysts interacted with the fuel practically equally and presented a reduction in the proportion of paraffins in favour of an increase in olefins in the samples tested. This may demonstrate the validity of the assumptions about the occurrence of dehydrogenation reactions in fuel exposed to catalysts. These assumptions are to be confirmed by bench tests on a compression-ignition engine equipped with an injector with a Cu-Ni alloy catalytic coating on the nozzle needle.

3.2. Engine bench tests

When investigating the effects of introduced changes to an internal combustion engine's design, control, fuel or post-process parameters on its performance, both basic operating properties (e.g. fuel consumption, overall efficiency, exhaust gas composition) and process parameters are analysed to determine the causes of the observed changes in performance (e.g. maximum combustion pressure and temperature, kinetic and diffusive combustion rate, auto-ignition delay, start and end of combustion, etc.). Since it is often the case that the changes introduced have a different or even opposite effect at different loads (or speeds), comparisons of the effects of the changes introduced (e.g. in relation to the base nozzle) should not be made for only one operating point of the engine. In the research presented here, determining the effect of a new type of catalytic fuel atomiser on the properties of the diesel engine, engine measurements were made at a constant speed (2000 *rpm* – maximum torque speed) and the load changed at 5 measurement points from 30 % to 90 % of the maximum torque of the test single-cylinder compression-ignition engine used.

The initial assumption of the developers of the catalytic atomiser under investigation is to achieve such an effect (by changing the chemical structure of the fuel) on the course of the heat release rate in the engine cylinder, so as to achieve lower concentrations and emissions of oxides of nitrogen (NO_X) in the engine exhaust. However, it was first necessary to check how the tested atomiser interacts with the basic engine energy parameters: hourly fuel consumption (*FC*) and overall engine efficiency (η_o).

For the different engine loads and the two tested atomisers, the TEST and BASE values are shown in Fig. 5. It can be seen that, for idle only, the *FC* fuel consumption is slightly higher (approx. 6 %) when using the catalytic atomiser (TEST) than for the factory atomiser (BASE). This situation can be linked to the low combustion temperature at that time and the low reactivity of the catalytic converter used in the atomiser

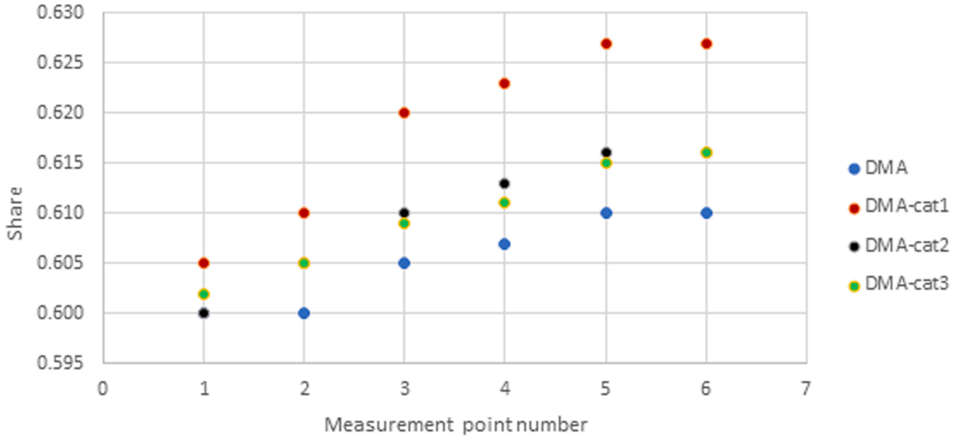

Fig. 3. Change in the proportion of unsaturated hydrocarbons after passing through bimetallic catalysts: cat 1 – Cu-Ni; cat 2 – Cu-Cr; cat 3 – Cu-Ni + Pt.

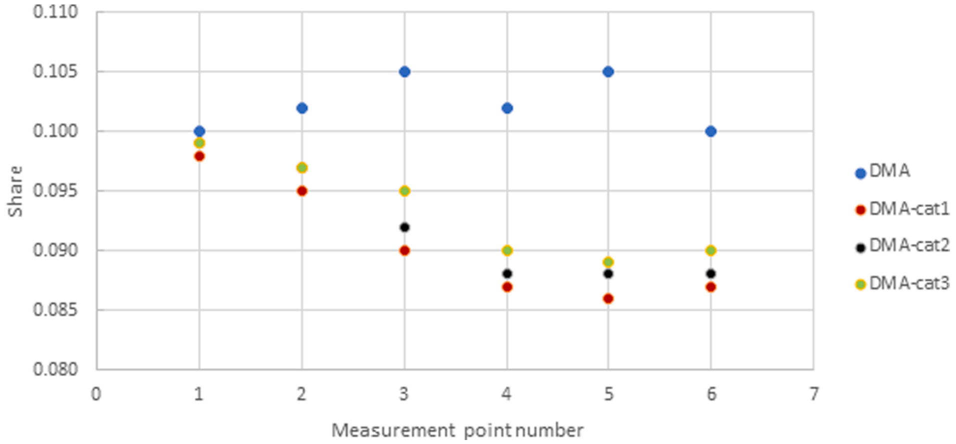

Fig. 4. Change in the proportion of saturated hydrocarbons after passing through bimetallic catalysts: cat 1 – Cu-Ni; cat 2 – Cu-Cr; cat 3 – Cu-Ni + Pt.

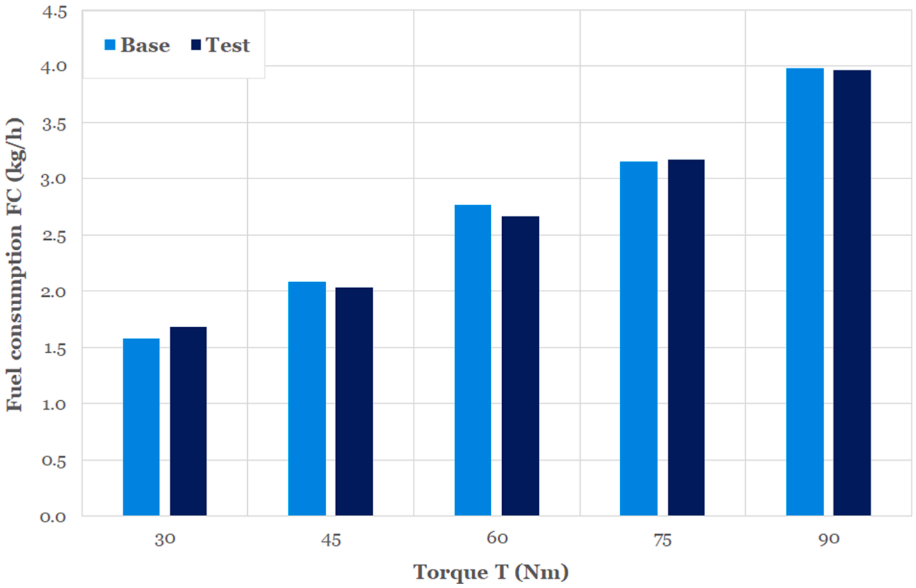

Fig. 5. Fuel consumption (*FC*) values for the tested fuel nozzles.

under these conditions. The situation is different at medium engine loads – fuel consumption is then 2 % to 4 % lower for the catalytic atomiser than for the base atomiser. By contrast, at very high engine loads (75 %-95 % BMEP), the differences in hourly fuel consumption for the TEST and BASE atomisers are negligibly small and within the limits of repeatable engine operation (less than 0.5 %).

Since hourly fuel consumption is not a comparative parameter for different engines and different fuels, the values for the overall efficiency (η_o) of the engine are additionally presented in Fig. 6. The percentage changes in η_o for TEST and BASE of the atomiser are in this case obviously the same as for hourly fuel consumption.

The results presented in Figs. 5 and 6 indicate that the effect of reforming on engine performance—expressed in terms of fuel mass consumption and overall efficiency—is significantly smaller than its impact on increasing ignition delay and the associated reduction in peak combustion pressure. A decrease in peak combustion pressure typically leads to lower engine efficiency. However, the further presented experimental results demonstrate that this effect was counteracted by a reduction in fuel dose due to improved combustion quality.

The key independent variable in this research is the concentration of oxides of nitrogen (NO_x) in the exhaust gas of the engine operating with a base atomiser and a catalytic atomiser. For different engine loads, this is shown in Fig. 7.

The results presented in Fig. 7 show that the catalytic atomiser under test (TEST) has a significant effect on the reduction of NO_x concentrations (relative to the factory atomiser) for all engine loads used. The comparison shows that the reduction in NO_x concentration ranges from a dozen to almost 30 %. The primary reason for these changes, according to the diagram in Fig. 8, is probably a reduction in the temperature at that time in the kinetic phase of the combustion process responsible for the formation of NO_x particles in the engine cylinder (among other things due to the large amount of oxygen still present at that time).

In order to confirm this, an indicator graph analysis was performed for the fuel nozzles tested and the heat release rate and combustion temperature waveform were calculated as a function of crankshaft rotation angle.

From Fig. 9, it can be clearly seen that, as in the case of the NO_x concentration in the engine exhaust, the values of the maximum combustion pressure (at the same points of engine operation) are also lower for the case of the catalytic atomiser than for the factory atomiser. Most often, the reduction in maximum combustion pressure, which is the reason for the then lower combustion temperature T_c, which in turn causes a reduction in the number of NO_x particles formed in the engine cylinder, is due to the then shorter fuel auto-ignition delay τ_c. During the shorter period τc, i.e. the shorter time between the start of fuel injection and the onset of auto-ignition, a smaller portion of the total fuel dose accumulates in the combustion chamber, resulting in a less dynamic first, kinetic phase of combustion, responsible for the reduced number of NO_x particles formed.

Fig. 10 shows the auto-ignition delay in the engine cylinder τ_c with the fuel atomisers tested. The results show that the use of a catalytic atomiser did not shorten the auto-ignition delay, so this is not the reason for the significant reduction in NO_x concentration observed in the engine exhaust at the time. The change in ignition delay time can be interpreted in a manner analogous to the influence of the catalytic material on the combustion process dynamics presented later, which results from the decrease in the maximum combustion pressure shown in Fig. 9.

Fig. 11 shows the combustion rate (dQ_k) in the kinetic phase of combustion, respectively. It can be stated that the catalysts on the tested fuel nozzles result in a more efficient distribution of fuel within the combustion chamber, leading to more uniform combustion. This contributes to a reduction in energy spikes and results in a lower heat release rate. By correlating this graph with the previous one (fuel consumption), it can be observed that the lower energy release rate in the variant with the catalyst does not impair engine efficiency, as it also leads to reduced fuel consumption. This indicates that the implemented changes may enhance the overall energy efficiency of the engine.

Fig. 12, on the other hand, shows the temperature in the kinetic phase of combustion (T_k) for the engine with the tested nozzles. The reduction in combustion temperature may result from the influence of the catalyst placed in the injector on the chemical structure of the hydrocarbons, which, in their altered form, have a lower combustion rate.

The reduction in the concentration of NO_x in the exhaust gas, for the case where a catalytic atomiser is used (Fig. 7), is accompanied, in addition to the then lower p_{cmax}, by a lower amount and rate of heat release in the kinetic phase of combustion (Fig. 11) and hence a lower temperature T_k in this phase of combustion (Fig. 12). This fully explains the first level of cause-and-effect events.

The results shown in Figs. 11 and 12 raise the question as to why the use of a catalytic atomiser (TEST) results in a reduction in kinetic combustion rate and temperature, if the auto-ignition delay is not then shortened. This is probably due to the effect of the catalyst placed in the atomiser on the chemical structure of the hydrocarbons, which in their altered form have a lower combustion rate only in the short-term kinetic phase.

Fig. 13 shows the diffusion combustion rate *(dQ_k)* for the engine with the tested fuel nozzles for the tested fuel nozzles, respectively.

The catalyst in the atomiser does not reduce the average combustion

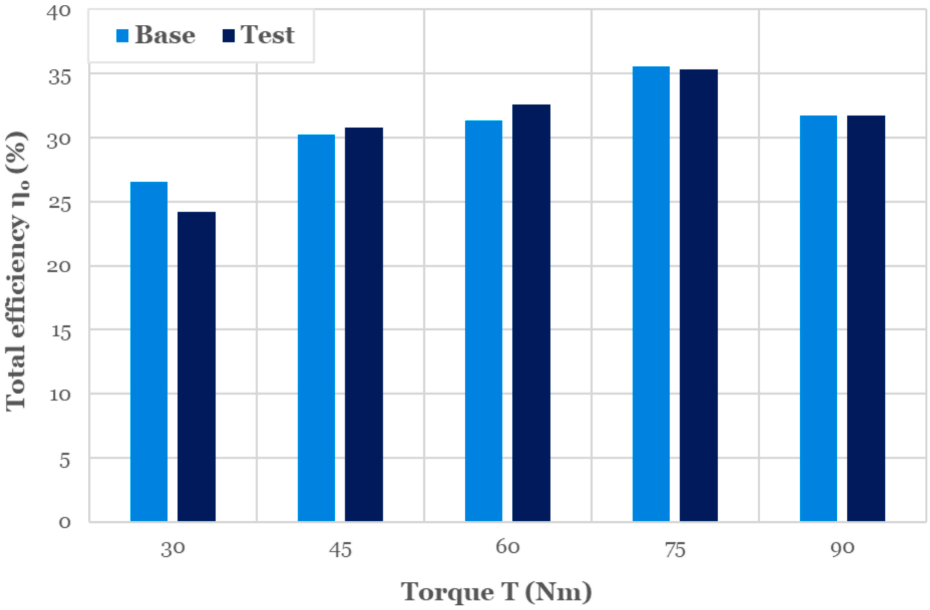

Fig. 6. Overall efficiency values (η_o) of the engine for the tested fuel nozzles.

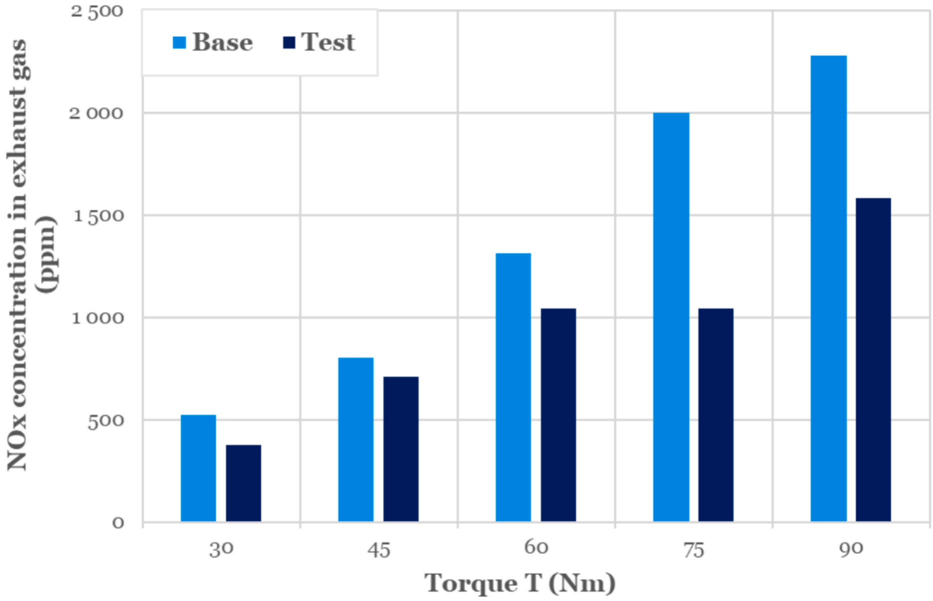

Fig. 7. NO_x concentration in the exhaust of the engine with the tested fuel nozzles.

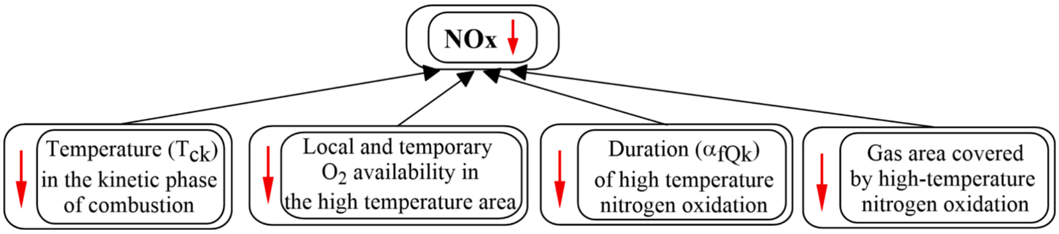

Fig. 8. Primary causes of NO_x particle formation in the engine cylinder [9].

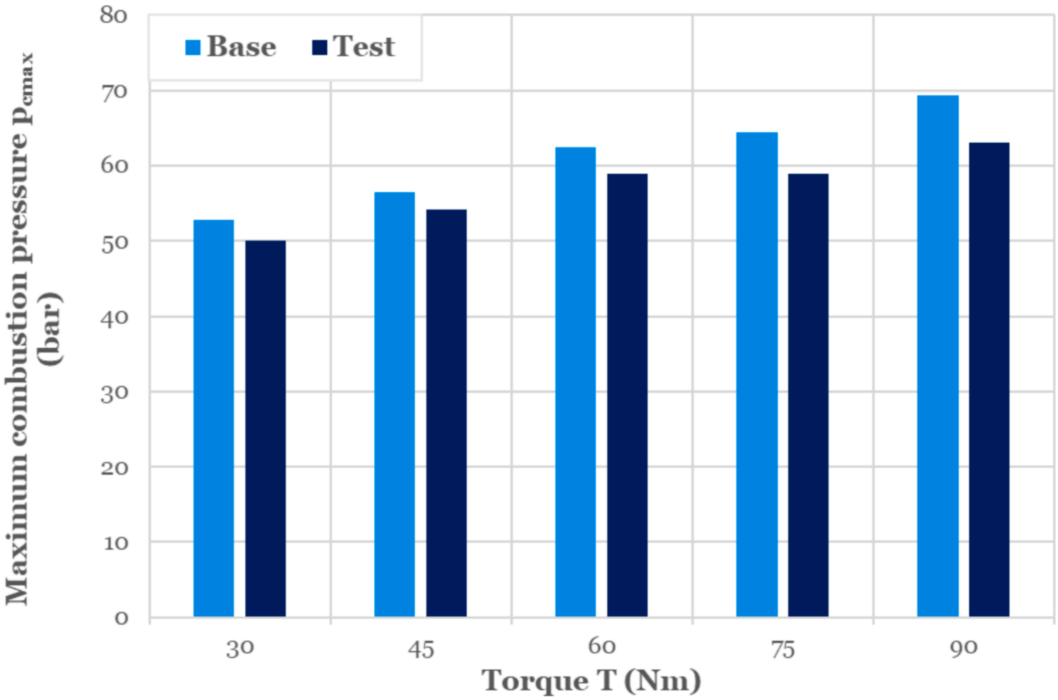

Fig. 9. Maximum combustion pressure (p_{cmax}) for the engine with the tested fuel nozzles.

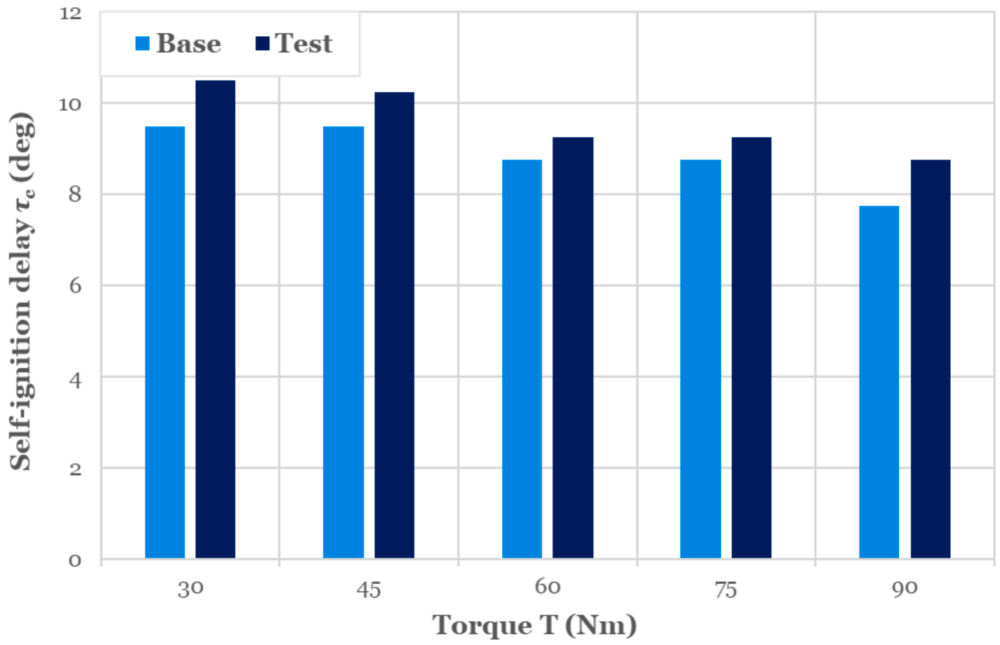

Fig. 10. The auto-ignition delay τ_c in the engine cylinder with the tested fuel nozzles.

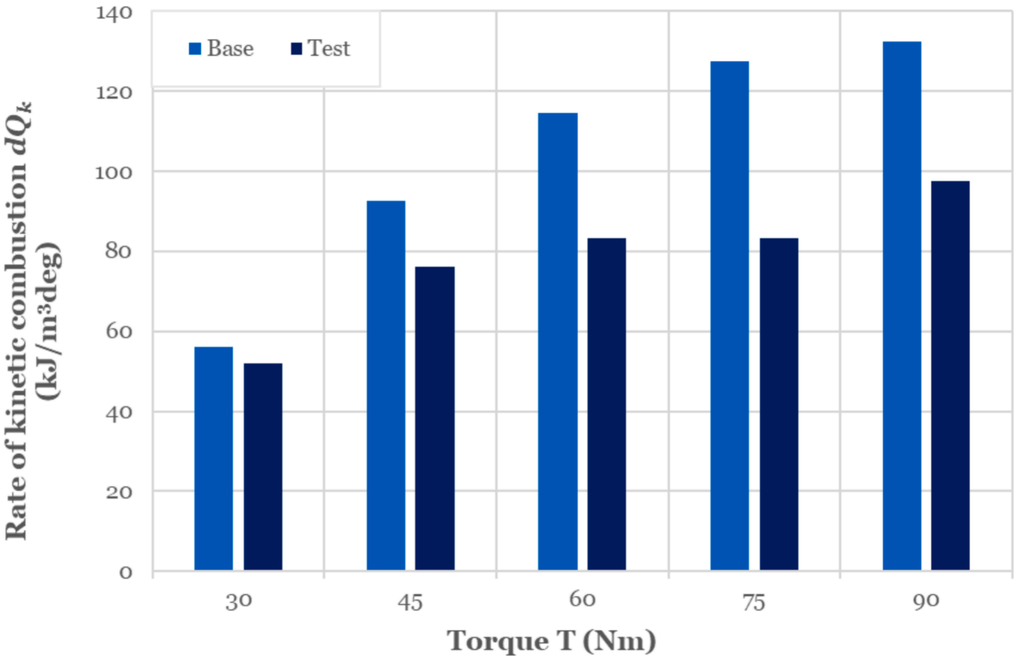

Fig. 11. Kinetic combustion rate (dQ_k) for the engine with the tested fuel nozzles.

rate due to the selective increase in the then diffusive combustion rate (dQ_k) – Fig. 13. Thanks to the higher combustion rate in the long diffusive combustion phase, the use of a catalytic atomiser is not associated with a delay in the end of combustion and an increase in combustion duration, which would then correlate with a reduction in the overall efficiency of the engine circuit.

It should therefore be assumed at this stage of the research that the use of a catalyst in the atomiser (TEST) probably leads to reforming – a change in the fuel structure (hydrocarbon bonds) that results in a selective effect on the rate of heat release in the engine cylinder, causing a reduction in the combustion rate in the kinetic phase of combustion (reducing the concentration of NO_x in the exhaust gas) and at the same time leading to an increase in the diffusive combustion rate, thus not significantly affecting the combustion duration and overall efficiency of the engine.

4. Conclusions

The research results confirm that the experiment successfully achieved its objective, which was to assess the impact of preliminary fuel treatment—specifically, fuel reforming using heterogeneous catalysts made of a Cu-Ni alloy applied to the fuel injector nozzle—on the environmental and operational performance of a compression ignition engine.

The laboratory and dynamometer tests carried out allow the following conclusions to be drawn:

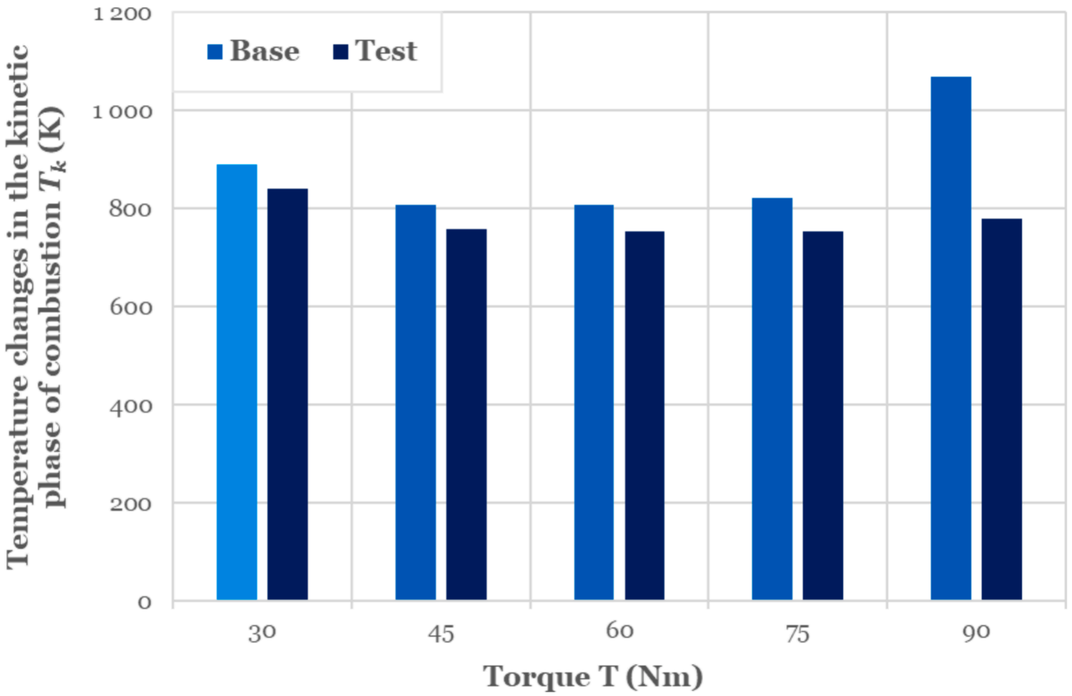

Fig. 12. Temperature variation in the kinetic combustion phase (T_k) for the engine with the tested nozzles.

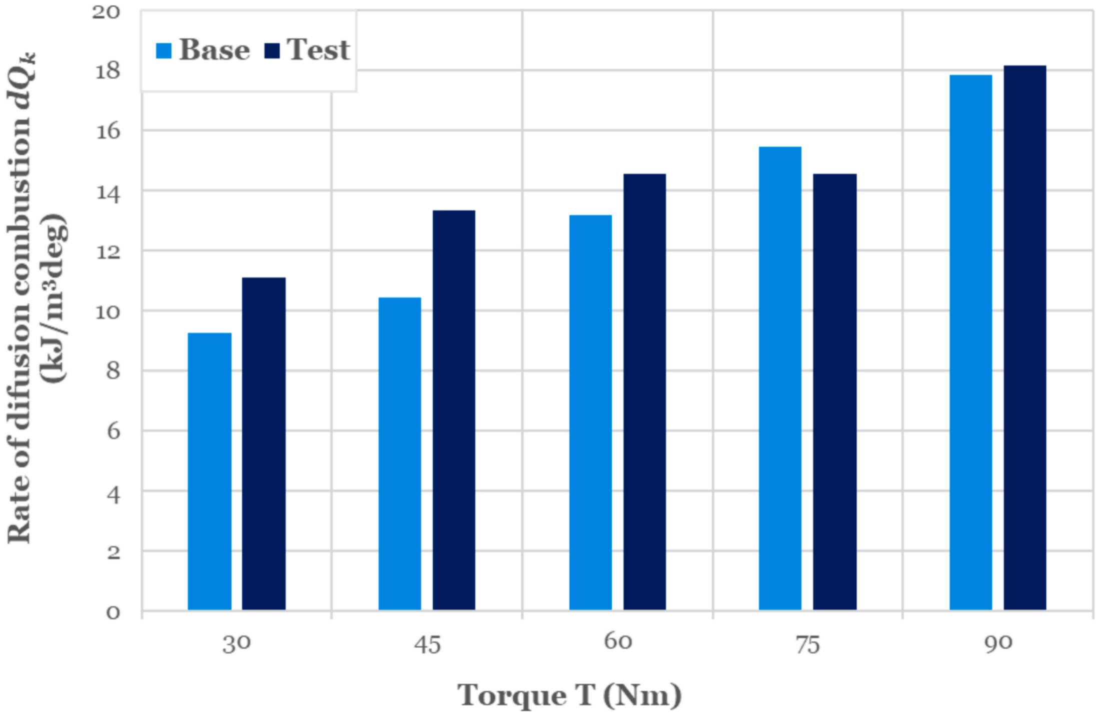

Fig. 13. Diffusive combustion rate *(dQ_k)* for the engine with the tested fuel nozzles.

- one way of reducing emissions of toxic compounds, including nitrogen oxides in the exhaust gas of compression-ignition engines may be through fuel pre-treatment – external reforming of the fuel using heterogeneous catalysts in the fuel injector;
- the catalytic material in this case may be copper matrix bimetals, which, when
- in contact with the fuel, contribute to a group change of the hydrocarbons in the fuel – a process that bears the hallmark of external fuel reforming;
- the method of applying the catalyst may be electro-spark fusion, which allows the catalyst to adhere well to the substrate – the nozzle needle – without causing thermal distortion and increasing the roughness of the catalyst surface, thus, it can be applied both to newly manufactured fuel nozzle components and to those already in service.;
- laboratory tests have shown that the use of a Cu-Ni bimetallic catalyst on the passive part of a compression-ignition engine's nozzle needle allows the formation of a dehydrogenation reaction during

which part of the paraffin group is converted into an olefin group, indirectly indicating fuel reforming and the formation of free hydrogen;

- dynamometer engine tests carried out on an experimental compression-ignition engine showed a reduction of up to 30 % in the level of nitrogen oxide emissions in the exhaust gas when using spray nozzles with fuel pre-treatment. It has been shown a reduction in NOx emissions, which, under the same engine load, indicates a decrease in the utilization of oxygen contained in the combustible mixture (Fig. 7). Similarly, at loads ranging from 45 Nm to 90 Nm, was observed an increase in overall engine efficiency (Fig. 6), which directly results from lower specific fuel consumption.
- the fuel mass consumption values obtained for all tested engine loads were lower for the modified injector compared to the standard injector (Fig. 7). The reduction in fuel consumption for petroleum-based fuels is directly linked to an increase in the air excess ratio λ, and a decrease in CO2 emissions. Under comparable cylinder filling conditions and engine load, this allows us to draw conclusions regarding the impact on CO2 emission reduction and the increase in oxygen (O2) content in the exhaust gases. This latter factor, in turn, is associated with the reduction of carbon monoxide (CO), soot (C), and unburned hydrocarbons (HC) emissions.
- during the inspection of the combustion chamber of the tested experimental engine, no coal deposits was found. This can be explained by the fact that the dehydrogenation reactions occur in the presence of the catalyst on the nozzle needle even before the fuel is sprayed into the combustion chamber. In turn, the free hydrogen generated (according to the dehydrogenation reaction) promotes better fuel combustion. In summary, the obtained results do not provide grounds to conclude that the use of reformed fuel would lead to an increase in carbon deposits inside the combustion chamber;
- analysis of the indicator diagrams of the test engine during operation with the fuel pre-treatment injector shows the effect of the catalyst on the speed of the kinetic phase of the combustion process;
- further direction of research in the field of external fuel reforming in compression-ignition engines should be pursued in the identification and application of catalysts that influence the speed of combustion in both its kinetic and diffusive phases, thus enabling improvements not only in the ecological but also in the economic performance of engines;
- this experiment can be further expanded to include studies on different types of fuels and various catalytic coatings. Moreover, the experiment can be conducted on different types of engines, including highly boosted ones, and the experimental design itself can follow a different approach than the one presented in the article—for example, by considering different preset engine speeds and torque loads set on the brake.

CRediT authorship contribution statement

Klyus Oleh: Writing – review & editing, Writing – original draft, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Szczepanek Marcin:** Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Resources, Methodology, Investigation, Formal analysis, Data curation. **Cisek Jerzy:** Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Resources, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Olszowski Sławomir:** Writing – review & editing, Visualization, Validation, Software, Resources, Methodology, Investigation, Formal analysis. **Behrendt Cezary:** Writing – review & editing, Validation, Software, Resources. **Chybowski Leszek:** Writing – review & editing, Validation, Supervision, Software, Resources, Methodology, Investigation, Funding acquisition, Formal analysis.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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