Reduction of NO$_x$ emission from diesel engines by the application of ceramic oxygen conductors

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Abstract

One of the major problems related to compression ignition engines is the emission of particulate mater and nitrogen oxides NO$_x$. Aftertreatment devices (e.g. DeNOx catalysts), exhaust gas recirculation (EGR) or common rail high pressure injection systems have been commonly used to reduce these emissions. However, the optimisation of the burning process is now considered to have the potential to reduce the emission of toxic compounds of exhaust gases and this seems to be the major direction of development for compression ignition engines. The present paper discusses a concept of reducing the NO$_x$ emission in exhaust gases from a compression ignition engine by eliminating nitrogen from the engine charge delivered to the cylinder. Since a dynamic development of ceramic oxygen conductors has recently been observed, it could be predicted that the application of these conductors in combustion engines might become possible in years to come. The present work offers results of research tests of an engine supplied with oxygen and with a mixture of oxygen and exhaust gases (EGR). It presents an analysis of the burning process and results of research tests on emission of toxic compounds of exhaust gases. Measurement of cylinder pressure and photographs from research tests with endoscopic video recording were used in the analysis.

Keywords: compression ignition engine, NO$_x$ emission, ionic conductor.

1   Introduction

At the present stage of compression ignition engine development, one of the main challenges is lowering PM and nitrogen oxide NO_x emission. The implementation of more and more rigorous standards limiting the emission level and the growing social ecological awareness faced the designers and manufacturers to undertake actions aiming to limit the emission of toxic exhaust gas compounds. Thereby it involved the necessity for using complex solutions, which can be divided into three main groups:

- A direct treatment of the combustion process, which is a source of forming the toxic compounds. The example action of such type is, among others, combustion of a homogeneous charge.
- Affecting the exhaust gas after the engine cylinder, i.e. exhaust aftertreatment. Such action as, among others, the selective catalytic reduction, using the Diesel Particulate Filters should be included in this group.
- The use of suitable fuels with lower sulphur content, for example.

   Only the combined use of solutions included in the groups stated above and their continuous development will ensure the compression ignition engines to be successful in the market. Some time ago the engine designers had already observed the potential possibilities of the widely understood conception of the fuel injection (i.e. fuel injection system design solution, injection characteristics). These observations resulted in a very dynamic development of the injection systems being noticed during several last years, mainly the Common Rail ones, which are dominant in case of the compression ignition engines.

2   Ionic conductor

As already mentioned, the base of the oxygen separator's construction constitutes a ceramic conductor of oxygen ions [2]. Electrochemical oxygen separation (EOS) from air using a ceramic membrane is an important economical challenge. Extensive research is being conducted for developing an optimized highly efficient device that could realize, in an economic way, the oxygen gas separation. Generally, the device (fig. 1) consists of a gas-tight membrane made of an ionic conductor with both active surfaces covered with oxygen-ion reversible electrodes in accordance with the following reaction:

$$O_2 + 4 \text{ e} = 2 \text{ O}^2 \qquad (1)$$
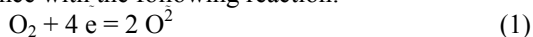
   Dissociation of an oxygen molecule must occur at the cathodic side of the cell. After migration of these anions through the electrolyte, the reverse reaction must occur at the opposite (anodic) side in order to reconstitute the O_2 molecule and release it into the surrounding gas phase. According to the redox reaction, it is clear that, in addition to the oxide ion migration through the membrane, four electrons must be simultaneously transferred from the cathode to the anode for each transported oxygen molecule.

   The electrons flow exclusively through the external circuit and the electronic current is under control of an external power source. This system implies a
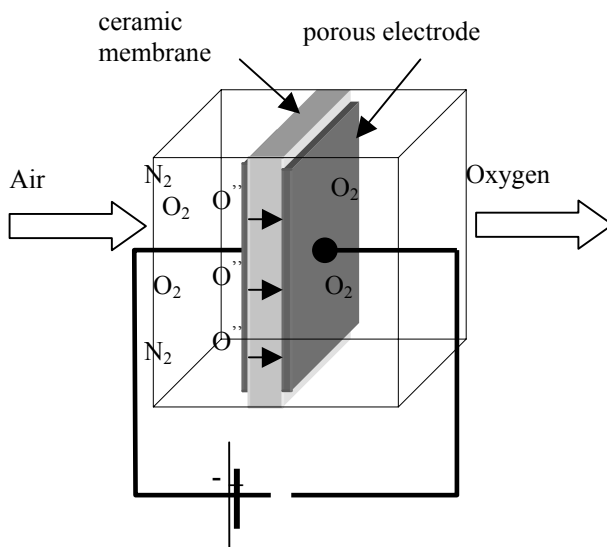
Figure 1:   Scheme of the electrochemical oxygen separator EOS.

negligible electronic contribution of conductivity of the electrolyte itself, whose oxygen transference number must be equal or very close to unity. The main advantage of this concept is that the oxygen flux is fully adjustable by varying the intensity through the membrane. In such a system oxygen can be transferred from the low oxygen partial pressure side towards the high pressure compartment. It can even act as a compressor without any mobile component.

For these applications, typical membrane materials include compounds of the structure of fluorite (solid solutions of zirconium or cerium dioxide), of perovskite (zirconates, cerates, gallates) and also of layered structures (apatites and bimevoxes). From an historical point of view, stabilized zirconia based electrolytes are the most commonly used oxide conductors. Zirconia ZrO_2 based membrane materials are suitable because of their relatively superior thermal and mechanical properties, availability of raw materials and ease of fabrication into different shapes. However, they exhibit lower ionic conductivity than ceria CeO_2 or Bi_2O_3 based systems at moderate temperature. Applications developed using zirconia materials imply to operate at temperature frequently close to 1000°C and even under these temperatures the oxygen fluxes remain relatively low.

The perovskite oxides are very interesting because there are two cation sites upon which to substitute lower valence cations, leading to a much wider range of possible oxygen ion conducting materials. A number of perovskite oxides are purely oxide ion conductors and, as such, have been used as electrolytes in the intermediate temperature range (650-800°C). Of the perovskites investigated to date, only the lanthanum gallate ($LaGaO_3$) based material has been found to be suitable for ionic applications. The performance of $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ at

intermediate temperatures was found to be higher than some of the existing fluorite-type oxides and, indeed, would enable a lowering of the operating temperature of devices when compared with the traditional zirconia-based devices.

The *BIMEVOX* family of oxide ion conductors are based on the well-known fluorite-related oxide Bi_2O_3 where $Bi_4V_2O_{11}$ is the solid solution series end member and a typical composition would be – $Bi_2V_{1x}Me_xO_{5.53x/2-\delta}$, where Me: Cu, Co, Zn *etc.*. These materials have proven to be highly effective as oxygen separation membranes with ionic conductivity of the order of 0.1 S·cm[1] at 600°C. A recent discovery in the field of ionic conductors has been the apatite-structured oxides based on lanthanum compositions, notably germanates and silicates of composition $La_{10x}Ge_6O_{26+y}$ and $La_{10x}Si_6O_{26+y}$. These materials have been identified as having relatively high levels of oxide ion mobility with Sr-doped material, $La_9SrGe_6O_{26.5}$ achieving 0.14 S·cm[1] at 950°C. At lower temperatures, this composition has higher levels of ionic conductivity than zirconia based materials by half an order of magnitude.

Table 1 lists key parameters of ionic conductors which may be found applicable in the proposed solution. Considerations presented imply that criteria such as electrical conductivity σ_{el} connected with power losses and the limiting current density ζ_g at which no degradation of material yet occurs will be crucial in deciding how useful these materials can be. Parameters gathered in Table 1 indicate explicitly that, given the adopted assumptions, all materials feature limiting current density ζ_g, higher than the required 0.38 A·cm[1]. In this case the decisive criterion of the material's usefulness becomes its demand for power necessary to run the device. According to calculations the minimum energy requirements should have the separator built with the use of some *BIMEVOX* materials.

The two most appropriate designs of oxygen separators under development are planar and tubular. The planar design offers higher oxygen production capacity per unit volume but requires interconnect materials and cumbersome seals, which have to be stable during thermal cycling. However, the technology can be easily scaled-up for large volume production of oxygen. The tubular design offers much better thermal cycling capability and no sealing may be necessary.

Figure 2 presents the schematic diagram of the combined EOS-TEG unit with the tubular design of elements and the corresponding electrical circuit. In this concept exhaust gases, which consist mainly of CO_2 and H_2O, flow by interior of the tubular separator EOS and there are enriched in oxygen transported by the membrane of the separator. The separator is supplied by TEG module which utilizes waste heat of gases. The mixture of gases containing necessary amounts of oxygen is transported to intake manifold of the engine.

Taking into account technical parameters of both EOS and TEG modules it seems to be possible to develop a compact construction which does not involve an additional current-voltage converter. The typical EOS element requires low voltage (1–2V) and high current density source of supply (of about 0.1-0.5 Acm[-2]). These requirements can be easily satisfied by conventional TEG modules.

Table 1:   Some material properties of selected ionic conductors [3–7].

Membrane material	Electrical conductivity at 700ºC S_{el} [S·cm^{-1}]	Limited current density ζ_g [A·cm^{-2}]	Power* P_R [kW]
$Zr_{0.92}Y_{0.08}O_2$	$2 \cdot 10^{-2}$	0.45	13.5
$LaGaO_3$	$6 \cdot 10^{-2}$	1.18	4.5
$Ce_{0.8}Sm_{0.2}O_2$	$8 \cdot 10^{-2}$	0.88	3.4
BIMEVOX	$2 \cdot 10^{-1}$	1.25	1.35

* The power corresponding to the electrical Joule heat generated
in the electrolyte material for assumed technical conditions.
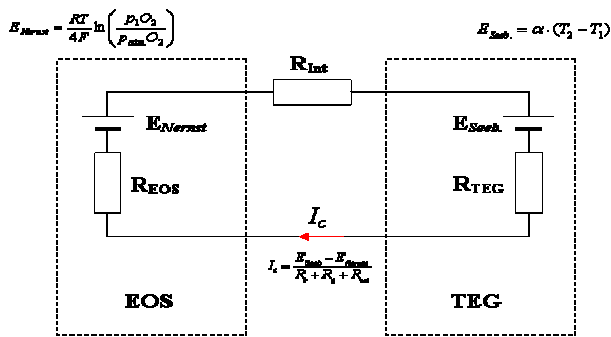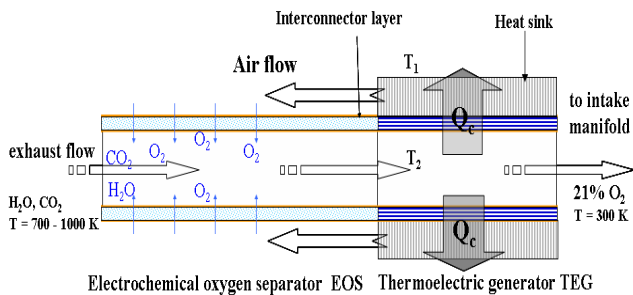

Figure 2:   Schematic diagram of the EOS-TEG unit and corresponding
simplified electrical circuit.

The assumptions presented allow for preliminary assessment of the extent of
the device's power demand. Assuming, as key components the P_{EOS} power
representing that corresponding to the amount of heat released on the separator's
resistance (Joule heat), and the P_{Nernst} power connected with change of the

thermodynamic potential (Nernst potential) of oxygen, the following can be obtained:

$$P = P_R + P_T = \frac{\zeta^2 \cdot d \cdot S_{el}}{\sigma_{el}} + \frac{\zeta \cdot S_{el} \cdot 8,314 \cdot T}{4 \cdot 96500} \cdot \ln\left(\frac{p_1}{p_2}\right)$$

(2)

where: S_{el} – electrical conductivity of the oxygen conducting material, T – absolute temperature, p_1 and p_2 – partial oxygen pressures on both sides of the oxygen membrane. Table 1 presents the calculation results for a variety of materials and one specific technical solution for which $p_1 = p_2 = 0.21$ atm. was assumed (equal partial pressures of oxygen on both sides of the membrane).

Having considered other factors such as e.g.: connections resistance, thermoelectric effects or diffusion potentials it can be assessed that an oxygen separator in which presently known materials of lowest specific resistance were applied, needs from 3 to 6 kW electric energy to assure required efficiency. This amount of energy can obviously be supplied by the electric system of the car with the use of the alternator of adequately higher parameters. Effectively such solution, however, is subject to an inevitable loss of mechanical power of the driving system even by 10kW, which is completely unprofitable in terms of the engine energy balance.

The application of thermoelectric generators harnessing the waste heat created during the engine operation may prove an alternative solution. The energy efficiency of presently constructed combustion engines with the spark or compression ignition ranges, on average, between 35% and 40%, which means that an engine of mechanical power of 66kW generates about 120kW of waste heat. At the same time, it can be evaluated that approximately half of the unused energy is being discharged through the engine's exhaust system, whereas the remaining part discharges through the body and the cooling system [8].

Considering thermodynamic limitations exclusively it is possible in theory to recover from 50 to 75% of waste energy, which means that the generator's efficiency of the 10% order is sufficient to obtain the 5kW power. Researches on the use of waste heat from the engines' exhaust are being carried out by many research centers. The very first thermoelectric generators built in industrial laboratories (e.g. Toyota, General Motors) were of a quite low power of several dozens watts [9–12]. In the prototypes installed on compression ignition engines (Cummins NTC-325, NTC-350) the above 1kW power was achieved at approximately 2.6% generator's efficiency [13–15]. In the generators the bismuth telluride commercial modules with efficiency of about 4.5% were applied. However, significant progress in the field of new thermoelectric materials (e.g. skutterudites, superlattices) provides chances to reach the efficiency larger then 15% [16–17].

3 Engine investigation

The tests were performed on an AVL 5804 0.5 dm^3 single cylinder CI engine fuelled with commercial diesel oil. The engine was fitted with a common rail injection system allowing a free adjustment of the course of the injection

i.e. number of injection phases, size of the doses and their timing. The article presents the results of the tests performed at 1200 rpm, which are representative at the selected loads. The oxygen was supplied from a pressurized cylinder through an expansion system to avoid gas pulsation in the intake manifold. The engine's air demand at 1200 rpm amounted to 16.5 kg/h.

The following were performed:
-    engine indicating,
-    NO_x concentration measurement for different O_2 flow intensities and different mixtures of fuel-air, fuel-oxygen and fuel –oxygen-exhaust gas,
-    video feed analysis of the combustion process for conventional engine fuelling and that of oxygen fuel mixture and oxygen-exhaust gas-fuel mixture (63% EGR).

Within the scope of the research, an indication of an engine fuelled with fuel-air, fuel-oxygen and fuel-oxygen-exhaust gas (60% EGR) mixtures was performed. The obtained results were compared to the results of conventional fuelling (fuel-air mixture). The tests were performed for various engine speeds and loads. Example results are presented in fig. 3. Additionally, in order to identify the onset of the injection, fuel pressures, taken in the fuel feed between the common rail and the injector were shown. The presented graphs show that the combustion process for the fuel-oxygen mixture is characterized by a higher maximum pressure compared to the fuel-air mixture. Another observation from the analysis of the combustion process are noticeable differences in the length of the self-ignition delay times. The process of combustion of the fuel-oxygen mixture is characterized by a significant shortening of the self-ignition delay time. The analysis of the course of pressure in the fuel feed between the common rail and the injector shows that the self-ignition of the oxygen-fuel mixture occurs immediately after the onset of the injection of the fuel dose into the cylinder. Consequently, a lower pressure increment in the cylinder results, resulting in a lower NO_x concentration. While performing the tests, a significant engine noise reduction was observed as well, yet this parameter had not been measured. A smooth passage of the curve of charge compression in the cylinder into a curve of pressure during the combustion makes it difficult to clearly determine the point of initiation of the combustion which is easy to notice for engines with conventional charge (fuel-air). A reduction of oxygen level in the charge for the benefit of the exhaust gases (63% EGR) resulted in an effect similar to the combustion of fuel-oxygen mixture. In this case the maximum pressure in the cylinder is comparable to that of the fuel-air mixture only the self-ignition delay time is shorter and the pressure increment is lower.

Since the oxygen content in the air amounts to 21%, in theory, the test engine of the assumed operating parameters needs 3.5 kg/h of oxygen. A test has been performed aiming at the determining the oxygen flow intensity supplied with the exhaust gases to the intake manifold in order to determine the necessary amount of oxygen supplied to the combustion chamber while keeping the NO_x concentration at a low level (fig. 4).

A low NO_x concentration was obtained at O_2 flow intensity up to 7.04 kg/h which is 37% of the oxygen-exhaust gas mixture supplied to the cylinder. This
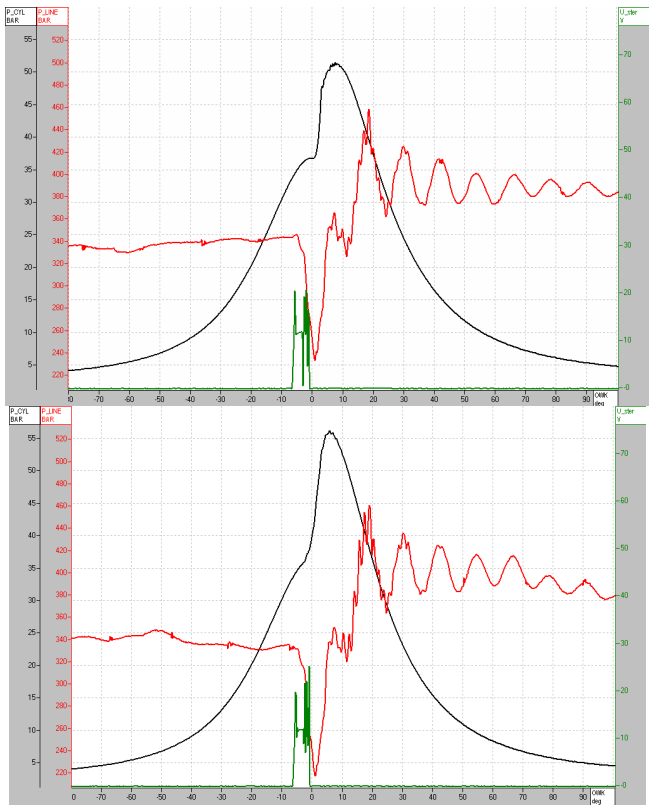
Figure 3:   Pressure in the engine cylinder and fuel pressure in the line
             between the common rail and the injector; engine supplied with
             the air-fuel mixture (diagram above) and the oxygen-fuel mixture
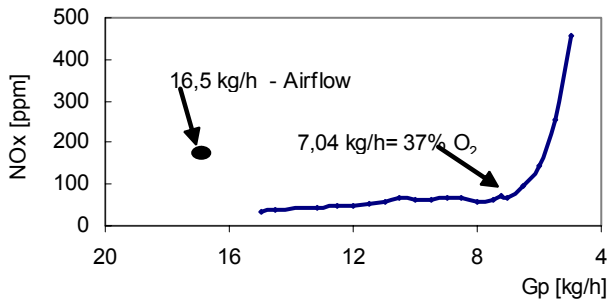   (bottom diagram).

Figure 4: NO_x concentration at different O_2 flow intensities. The engine was
             exclusively supplied with the oxygen-exhaust gas mixture.

value is almost twice as high as the theoretical one. A further drop in the O_2 flow intensity resulted in the increase in the NO_x concentration. The demand for 37% of oxygen as compared to the theoretical value of 21% results probably from the leakage in the intake manifold.

As a supplementary investigation, an endoscopic observation of the combustion process in an engine charged with oxygen and exhaust-oxygen mixture have been carried out. The results of these observations were compared to the results of the combustion of a conventional fuel-air mixture. Engine Video System 513D has been used for the investigation. The device records stroboscopic images – in this case – with a frequency of 0.5 ^{o}CA. Example images recorded during the said investigation are presented in fig. 5. When comparing the courses of the combustion for different mixtures, the largest differences were observed in the initial phase of the process. In the case of combustion of the fuel-oxygen mixture the first spots of self-ignition appear much earlier and their number is higher in comparison to the fuel-air mixture combustion. The combustion of oxygen-exhaust gas mixture was of similar nature. In the initial phase of the combustion of the fuel-oxygen mixture the flame penetrates the combustion chamber much more quickly and occupies a larger part of the chamber. Another observed difference is the intensity of the flame glow. The intensity is higher for the combustion of oxygen-air mixture as compared to the fuel-air mixture. This difference, however, may not necessarily result from the course of combustion itself but from the residual soot on the glass bulb protecting the endoscope. The smoke level measurements confirm that in the case of fuel-air mixture combustion the smoke level was much higher than in the case the engine was charged with oxygen and the oxygen-exhaust mixture.
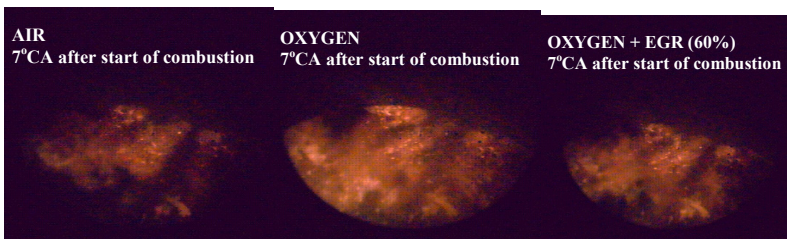

AIR
7°CA after start of combustion

OXYGEN
7°CA after start of combustion

OXYGEN + EGR (60%)
7°CA after start of combustion

Figure 5:   Picture of the combustion process inside the combustion chamber.

4   Conclusions

The performed research indicates that supplying oxygen to the combustion chamber rather than air has a positive impact on the thermal processes of a combustion engine. A slower pressure increment and the increase of maximum pressure in the cylinder have been observed. This indicates an increase in the overall engine efficiency. Any significant changes in the concentration of HC and CO have not been observed. The authors are planning to develop a model fitted with an oxygen separator applied in the intake manifold.

The through analysis of technical solution based on the presented idea should contain estimation of efficiency of penalty due to implementation of this technology. However, such detailed analysis is difficult to perform on the current stage of our work. It can be estimated that the total cost and weight of the oxygen separator combine with thermoelectric generator would be essentially lower when compare to cost and weight of fuel cell system proposed for electrically supplied cars.

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