

Ozone Effects on the Emissions of Pollutants Coming from Natural Gas Combustion

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Abstract

The effects of ozone additions to natural gas/air mixtures on emissions of CO, C_nH_m, NO, and NO₂ were studied. The investigations have been realized in the stage composed of an ozone generator, the combustion chamber with a modified Mecker burner and gas composition, and flow rate and temperature measurement instrumentation. Comparisons were made of combustion with and without ozone additions. The tests were performed for 1.25 to 14.02 mg O₃/dm³(O₃+N₂) additions at 260, 330, and 390 W thermal powers and the air excess ratio of 0.8 to 1.4 using synthetic air. The investigations demanded the application of synthetic air. In experimental work a decrease of CO and C_nH_m concentrations with the ozone concentration in air and an increase in thermal power were confirmed and a slight increase of NO was observed. No effects of ozone on NO₂ concentrations have been detected.

Keywords: natural gas, combustion, ozone, CO, NO_x, C_nH_m

Introduction

Combustion of fuels is the main source of primary energy and, unfortunately, of air pollution. Our research concerns the reduction in emissions of pollutants and the improvement of energy efficiency in combustion [1]. Promoters of combustion are being searched to accelerate autoignition and to improve the combustion process [2-5]. Chemical additives added to natural gas used to be nitrates, peroxides, and many other reacting particles [6]. Therefore, ozone as a promotor is interesting, especially because of its oxidizing properties.

Ozone can act as an initiator in oxidation, even a very small concentration of ozone promotes aliphatic hydrocarbon oxidation. Ozone accelerates oxidation, proceeding in the lower range of temperature, when used in ozonized-air mixtures [7]. It decomposes very quickly when heated,

releasing O· radicals and initiating the oxidation chain reaction, which can also influence combustion products and decrease fuel consumption [8]. Ozone can initiate oxidation reactions of the simplest alkanes in the lower range of temperature than in the case of using oxygen. A wide review indicates that ozone effects in combustion were investigated in the course of the chemical reaction [9-12]. The mechanism of the reaction of methane with ozonized oxygen was investigated by Rotzoll [13]. Seo and Amano [7] focused on the enhancement of ozone concerning methane oxidation up to 750°C. The numerical simulations were in qualitative agreement with experiments emphasizing the role of ozone in methane oxidation. The initial temperature of oxidation reaction was reduced by about 100°C. Ozone effects on autoignition in engines were dealt with by Tachibana [14]. The effect of the addition of ozone to the intake air on combustion in a compression ignition engine was studied using a diesel CFR engine. Experimental results show that the addition of ozone improves autoignition characteristics. Regarding the changes in the exhaust emissions when

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ozone is added, a small decrease of CO, hydrocarbons, and particulates, and a small increase of NO_x have been observed. More recent investigations of ozone effects on the operation of engines were performed by Nasser et al. [15]. The investigations involved the generation of corona discharges within the engine's precombustion air stream. In spite of the low ozone concentration, a substantial reduction of specific fuel consumption, unburned hydrocarbon emissions, and CO emissions was achieved concerning both diesel and gasoline engines. The effects of ozone on the spark ignition of methane and methanol-air mixtures were investigated by Nomaguchi and Koda [16]. The inspection of the calculated evolution of species concentrations indicates that the acceleration effect is caused by the very rapid decomposition of ozone-producing oxygen atoms that attack parent fuel molecules and induce a radical chain reaction. The above statement was confirmed by numerical studies of the autoignition of lean CH₄/O₂/Ar by Golovitchev and Chomiak [10], who compared the effects of small additions of ozone and hydrogen peroxide (H₂O₂) in the high-pressure, high-temperature range. This assessment confirms the data provided by Tachibana and Nishida, who controlled the ignition and combustion of an HCCI engine by partially ozonizing the intake gas in a natural gas premixed compression engine. It was found, using numerical analysis, that controlling the HCCI operation with the addition of ozone to the ignition angle of direct injection of an O· radical becomes more effective than the addition of an OH· radical from H₂O₂ decomposition [17]. As shown by Rotzoll and Caprio et al. [13, 9], it is far more complicated at lower temperatures, when radical-radical reactions of peroxy radicals and partly their decomposition appear to dominate. The investigation on the effect of ozone injection to the internal-combustion engine was analyzed by Yagyu et al. [18]. The composition of vaporized hydrocarbon compounds was chemically changed with

even a slight ozone addition generating by-products detected by FTIR technology.

The effect of ozone on different fuels were investigated. The catalytic combustion of carbon black was studied by Bokova et al. [19, 20]. The catalytic combustion of carbon black in the presence of Cu-Ce-Al oxide was investigated by means of thermal analysis and EPR spectroscopy. Due to ozone the catalytic combustion of carbon black passes to lower temperatures, but does not change the catalytic properties of solids. We found that ozonation influences the nature of carbon black, increasing the concentration and stability of free radicals interacting with carbon particulate.

To conclude, it is evident that ozone is effective in strongly promoting hydrocarbon oxidation at temperatures far below those at which oxidation by oxygen alone occurs.

The effects of ozone additions to combustion substrates on emissions of CO, C_nH_m, NO, and NO₂ were investigated. The experimental apparatus consisted of an ozone generator, a combustion chamber with a modified Mecker burner, and measurement instrumentation. The scale and organization of the combustion process was determined by the selection of the ozone generator. The investigations and measurement methods for flow rates of combustion substrates, temperature, chemical composition of exhaust, wet methods for NO and NO₂, and ozone concentrations detection (to verify Infracal EL indications) were worked out.

Experimental Procedures

The experimental apparatus was composed of an ozone generator, the combustion chamber with a modified Mecker burner and gas composition, and flow rate and temperature measurement instrumentation. The experimental apparatus is shown in Fig. 1.

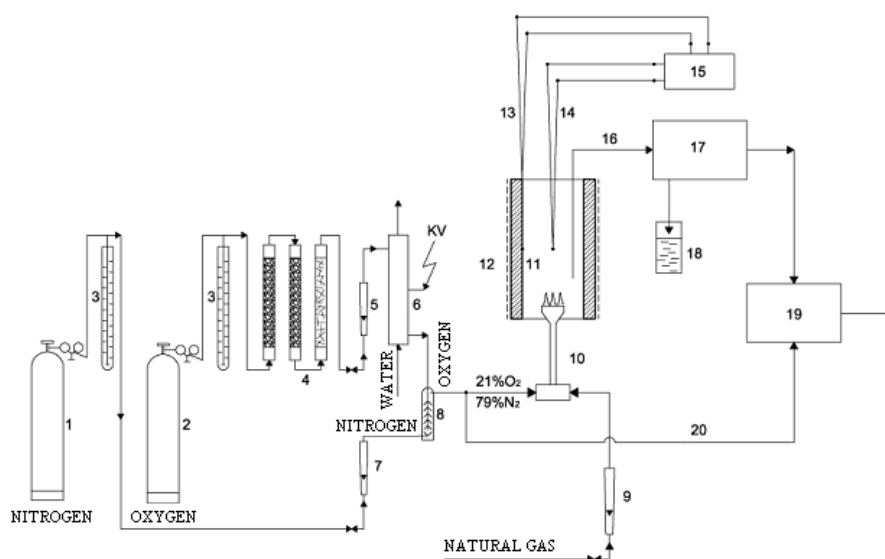


Fig. 1. The experimental apparatus.

1, 2 – nitrogen and oxygen cylinders, 3 – manostat, 4 – oxygen purifying system, 5, 7, 9 – rotameters, 6 – ozone generator, 8 – oxygen and nitrogen mixer, 10 – Mecker burner, 11 – combustion chamber, 12 – combustion chamber with heat insulation, 13, 14 – thermocouples in the wall and on the central axis in the reactor, 15 – milivoltmeter, 16 – exhaust sonde, 17 – water vapour cold trap, 18 – condensate vessel, 19 – exhaust analyzer, 20 – chemical composition controlling system of synthetic air.

Ozone Generating System

Ozone was generated from oxygen in a tubular ozone generator (maximum capacity up to 1.5 g/h). The gas flow rates of the facility were 40 to 60 dm³/h, and 180 to 200 dm³/h [21].

Combustion Reactor

The combustion reactor was composed of a Mecker burner and the combustion chamber. The possibility of the measurement instrumentation, and especially, the capacity of the ozone generator was determined by the power and construction of the reactor. The combustion chamber, made of heat-resistant steel, had a length of 180 mm and a diameter of 65 mm. Thermocouples were fitted at five different places along the chamber wall (Fig. 2). The thermal insulation of the combustion chamber was made of ceramic fibre 45 mm thick. The metallic heat shield (6) protected the combustion chamber. Plate (4) with a metallic ring (2) was the base of the reactor fitted to the burner. The bottom (3) and top (7) of the chamber were thermally insulated. Three holes at the top of the chamber served as exhaust sonde (8), thermocouple and exhaust outlet (9).

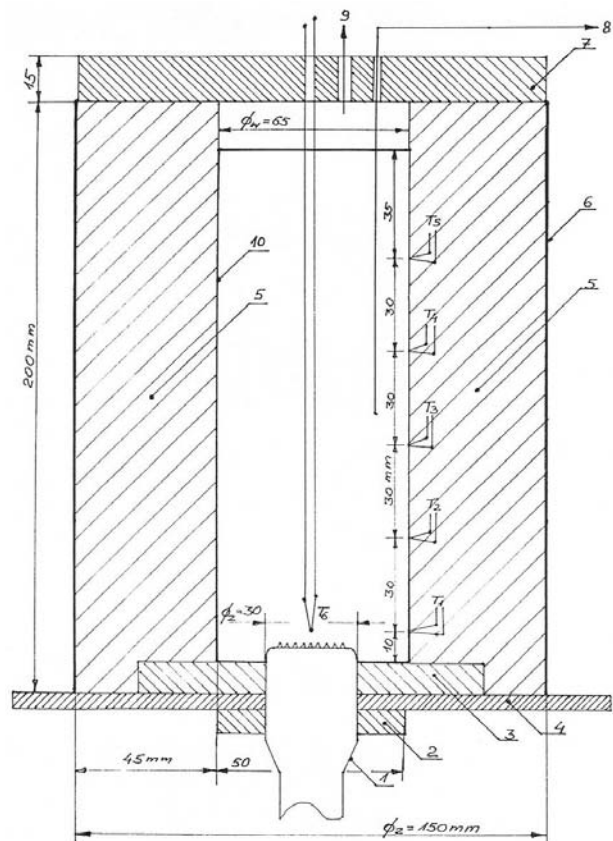


Fig. 2. The combustion reactor. 1 – Mecker burner, 2 – metallic ring, 3 – thermal insulation of the bottom of the combustion chamber, 4 – insulation board, 5 – thermal insulation made of ceramic fibre, 6 – metallic heat shield, 7 – thermal insulation of the top of the combustion chamber, 8 – exhaust sonde, 9 – exhaust outlet, 10 – heat-resisting sheet, T₁, T₂, T₃, T₄, T₅ – thermocouples in the wall, T₆ – thermocouple on the central axis in the reactor.

Table 1. GZ-50 natural gas parameters.

Quantity	Unit	Average value
Methane	%	95.844
Ethane	%	1.177
Propane	%	0.271
N – butane	%	0.045
I – butane	%	0.004
N – pentane	%	0.041
I – pentane	%	0.011
C ₆	%	0.014
Carbon dioxide CO	%	0.208
Nitrogen N ₂	%	2.314
Oxygen O ₂	%	0.068
Heat of combustion (p ₀ = 0.101325 MPa, T ₀ = 273.15 K)	kJ/m ³	39,472
Net heat of combustion (p ₀ = 0.101325 MPa, T ₀ = 273.15 K)	kJ/m ³	35,556
Density (p ₀ = 0.101325 MPa, T ₀ = 273.15 K)	kg/m ³	0.746
Humidity (p ₀ = 0.101325 MPa, T ₀ = 273.15 K)	g H ₂ O/m ³ gas	0.35

The investigated fuel was natural gas (GZ-50 with a high content of methane) taken from the city gas system. The average parameters of natural gas are shown in Table 1.

Oxidizer Conditioning System

The oxidizer conditioning system was composed of nitrogen and oxygen cylinders, an oxygen purifying system (from ozone generating system) and gas mixer, made of glass, with Raschig’s rings. Synthetic air was composed of 21% oxygen and 79% nitrogen (as in atmospheric air). Its chemical composition was checked in the controlling system by means of Infralyt EL.

Flow Rate Measurement Instrumentation

The flow system comprised oxygen, nitrogen, and natural gas rotameters. In order to equalize the pressure behind oxygen and nitrogen cylinders, manostates were installed.

Temperature Measurement Instrumentation

The temperature system was composed of a PtRh10-Pt-coated (S type) thermocouple 1 mm in diameter whose end was not shielded, and a digital multimeter MY-68 for con-

Table 2. Range of the investigations.

Fuel	Thermal power, W	Oxidizer	Ozone concentration, mgO ₃ /dm ³	Air excess ratio λ
GZ-50	260	Synthetic air Synthetic air + ozone	– 1.45 ÷ 14.02	0.8 ÷ 1.4
GZ-50	330	Synthetic air Synthetic air + ozone	– 1.41 ÷ 13.22	0.8 ÷ 1.4
GZ-50	390	Synthetic air Synthetic air + ozone	– 1.25 ÷ 12.01	0.8 ÷ 1.4

tinuous voltage measuring [22, 23]. The range of temperature was taken from its characteristics [24]. The temperature profile on the central axis in the reactor was measured every 10 mm till 150 mm along the combustion chamber. The wall temperature profile was measured by five NiCr – NiAl coated (K type) thermocouples fitted along the chamber wall.

Gas Composition Measurement Instrumentation

The gas composition system was composed of an exhaust sonde with an internal diameter of 3 mm, made of heat-resistant steel, a water vapour cold trap, condensate vessel, exhaust conditioning system, and Infracal EL analyzer (NO and NO₂ indications were verified by wet methods).

Range of the Investigations

The investigations have been performed in the combustion reactor in a wide range of the air excess ratio $\lambda=0.8\div 1.4$. Ozone generated from oxygen provided a three-times-larger quantity than air, which allowed us to obtain five different amounts of ozone in the investigations. The concentration of ozone was from 1.25 up to 14.02 mg O₃/dm³(N₂+O₂). Three thermal powers were carried out as 260, 330, and 390 W. The range of the investigations is shown in Table 2.

Results

Experimental results, conducted for both conditions with and without an addition of ozone, are presented in graph form (Figs. 3-6).

The flow rates of natural gas were measured at a rate of 26.6, 33.76, and 39.35 dm³/h corresponding to thermal powers at values 260, 330, and 390 W. The changes of NO_x and CO concentrations and maximum temperature profiles were similar in the total range of thermal powers; so the results for 390 W are presented only in this work.

The effect of the ozone concentration and air excess ratio on changes of NO_x and CO concentrations, and also on the maximum flame temperature profiles measured 5 mm above the burner nozzle, are shown in Fig. 3. The effect of ozone on the concentrations and E_{CO} emissions of carbon

oxide in a wide range of the air excess ratio are presented in Fig. 4. The effect of ozone on the concentrations and E_{NO} emissions of nitrogen oxide in a wide range of the air excess ratio are presented in Fig. 5, whereas the effect of the ozone concentration on the concentrations and E_{CnHm} emissions of hydrocarbons (and also on the thermal powers) are described in Fig. 6.

Discussion of Results

Fig. 3 generally presents the relationship between the air excess ratio and ozone concentration. The maximum temperature profile versus air excess ratio are also shown in the same diagram. The effect of ozone on the temperature level is not significant, although the maximum temperature profile slightly increases. The effect of ozone on CO is essential, even though the concentration of CO decreases. In the case of NO, the effect of ozone is evidently visible (NO concentration slightly increases).

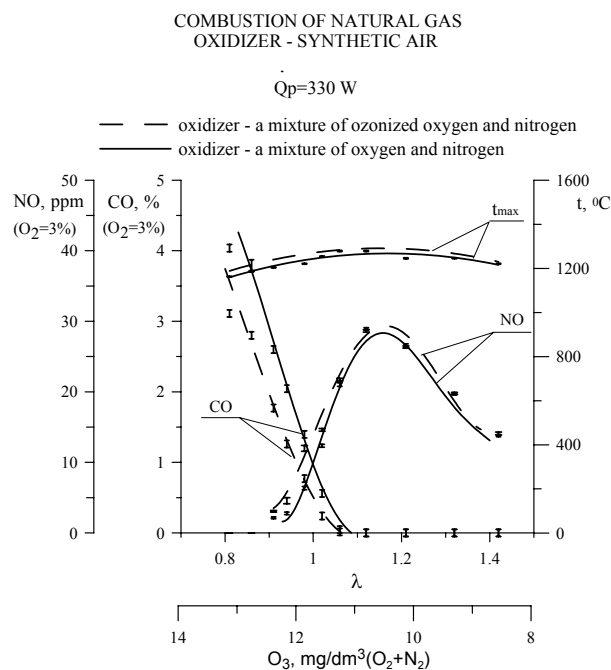


Fig. 3. The effect of the ozone concentration and air excess ratio on NO and CO concentrations, and also on the maximum flame temperature profiles, $\dot{Q}_p=330\text{kW}$.

Fig. 4 presents decreasing CO concentrations when the ozone concentration and air excess ratio increase for five amounts of ozone from 1.41 up to 13.22 mgO₃/dm³(N₂+O₂). The same trends of the performed investigation were observed concerning the air excess ratio in the range 0.8 to 1.07. The maximum CO emission, ca. 16 gCO/h, for 0.8 of air excess ratio was obtained. CO emissions decrease when

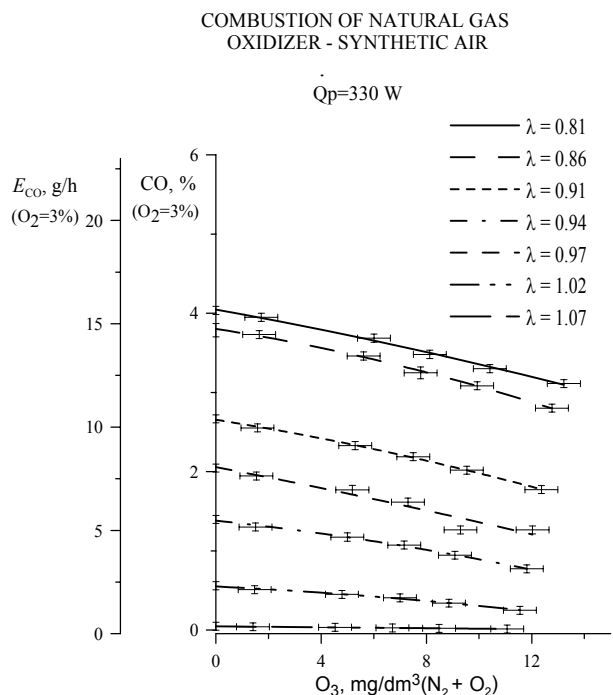


Fig. 4. The effect of ozone on the concentrations and E_{CO} emissions of CO in a wide range of the air excess ratio λ, Q_p=330kW.

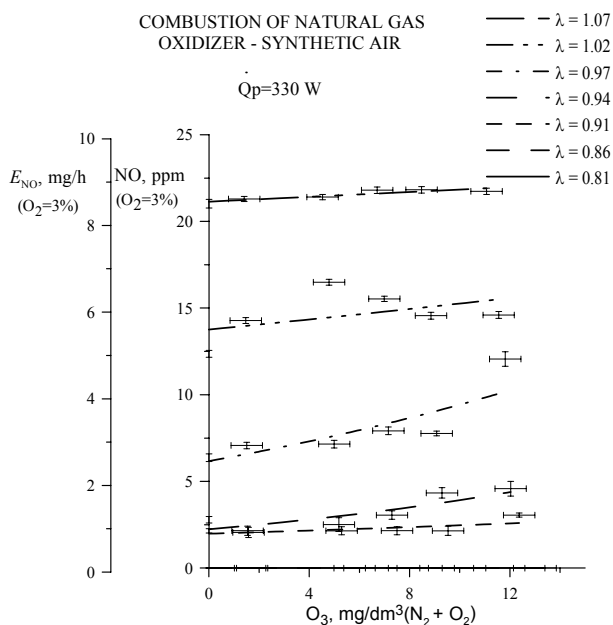


Fig. 5. The effect of ozone on the concentrations and E_{NO} emissions of NO in a wide range of the air excess ratio λ, Q_p=330kW.

the air excess ratio and ozone concentration increase. The character and rate of change of the CO emissions at the same excess air ratio is similar.

Fig. 5 shows the effect of ozone and air excess ratio on the concentration and emission of NO. While ozone concentration increases, the concentration and emission of NO also increases in the case of five different amounts of ozone. The increase of the NO concentration is connected with an increase of the temperature level in the ozonized oxidizer (Fig. 3).

The NO₂ concentration was measured below 1 ppm. Neither any effect of ozone on NO₂, nor NO₂ increase versus NO in the combustion products was to be observed.

The effect of ozone on the concentrations and E_{CnHm} emissions of hydrocarbons was estimated in combustion with air depletion. The hydrocarbon concentrations at 0.8 air excess ratio were measured. In the upper range of the air excess ratio hydrocarbons were not observed, the measuring error of the facility was about the same level as the NO concentration.

Fig. 6 present a strong decrease of concentration and emission of hydrocarbon. The maximum of concentration at 190 ppm (and emission at 100 mgC_nH_m/h) was measured at 330 W of thermal power. Such a dependence can be approximated by a second-degree polynomial.

Conclusions

In conclusion:

- The concentration and emission of CO decrease with increasing air excess ratio and ozone concentration in air, but also increases when the thermal power of the combustion chamber is enlarged.

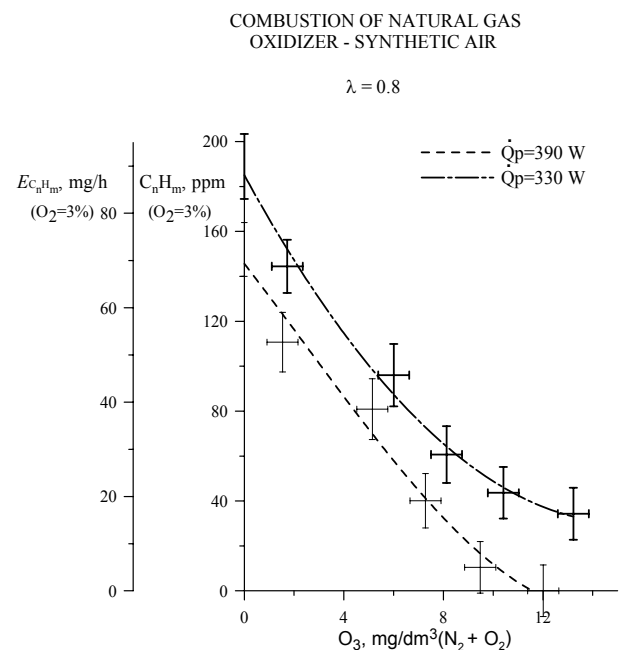


Fig. 6. The effect of ozone on the concentrations and on E_{CnHm} emissions of hydrocarbon and on thermal powers.

- The maximum of the concentration and emission of NO at an air excess ratio of about 1.2 was found, but the ozone concentration in air was slightly influenced. The thermal power of the combustion chamber increased the concentration and emission of NO.
- Because of the low NO₂ concentration in the combustion product, close to the measuring error, no effect of ozone on NO₂ was observed.
- The observed concentration and emission of hydrocarbons amounted only to an air excess ratio of 0.8. Moreover, it decreased by adding ozone. Its maximum for 330 W was found. It can be approximated by means of a second-degree polynomial.

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