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The effect of adding CO_2 to the axis of natural gas combustion flames on CO and NO_x concentrations in the combustion chamber

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Abstract

The paper presents the results of experiments on the effect of carbon dioxide addition during natural gas air combustion on the concentrations of CO and NO_x in the combustion chamber. Numerical simulations were also performed using the Chemkin-Pro program. As part of the presented experiments, an innovative method of introducing carbon dioxide through the central nozzle of a kinetic burner was tested. This technique allows CO_2 to be fed directly into the high-temperature zone, thus not hindering the mixing of the fuel with the oxidizer. The tests were carried out for an excess combustion air ratio of λ=1.1, 1.15 and 1.2, respectively, during the addition of CO_2 to 15% vol. of oxidizing mixture (air + carbon dioxide). From combustion gas analyses made at a distance of 740mm from the burner outlet in the furnace axis and 20 and 40 mm from the axis, it was found that combustion chamber CO concentrations depended on the amount of CO_2 introduced, the distribution of CO_2 in the combustion chamber cross-section associated with the CO_2 addition method and the excess air ratio. The highest CO concentrations were only noted in the combustion chamber axis with a considerable fraction of added CO_2. Based on the computations and experiments it has been confirmed that diluting combustion gas with CO_2 delivers a reduction in NO_x concentrations.

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Keywords: Natural gas, CO_2 additives, CO emission, NO_x emission

1. Introduction

Analysis of natural gas combustion in atmospheres modified by oxygen, carbon dioxide or water vapour is the subject of current studies [1–3]. The purpose of decreasing the fraction of air-derived nitrogen or substituting it with CO_2 is to reduce the flame temperature, to facilitate the combustion gas CO_2 capturing process and to reduce the NO_x. Nitrogen oxides contribute to the formation of toxic ozone and are jointly responsible for acid rain. The explanation of the lower flame temperature is the greater heat capacity of CO_2 than that of N_2. Adding CO_2 to the combustion substrates is geared to examining the process of combustion gas recirculation during oxy-fuel combustion.

Oxy-combustion technology has its advantages and drawbacks. The advantages include, e.g., a lower loss of thermal energy compared to air combustion, while the drawbacks primarily feature high technol-

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ogy expense resulting from the high cost involved in oxygen production and furnace modernization. Radiation burners for natural gas combustion can operate down to a low oxygen enrichment level (generally, lower than 28% O_2) without any modifications [4].

Combustion of coal in O_2/CO_2 atmospheres considerably reduces nitrogen oxide emissions compared to the emissions from air combustion [5–7]. Carbon dioxide is regarded not as an inert mixture component, but instead as a factor disturbing the combustion mechanism (reaction kinetics), thus affecting the process of both formation and destruction of NO_x. Increasing the CO_2 fraction of combustion substrates contributes to an increase in CO concentration in the combustion gas, irrespective of whether the mixture is lean or rich [5, 6]. Researchers indicate three causes of increase in the CO concentration in the combustion gas, namely: combustion gas dilution with CO_2, the change in temperature, and the chemical effect resulting from the predominance of the following reactions:

1. Boudouard reaction,

$$CO_2 + C \leftrightarrow 2CO \tag{1}$$

2. reaction of CO_2 with the hydrogen radical,

$$CO_2 + H \leftrightarrow CO + OH \tag{2}$$

3. CO_2 dissociation reaction.

$$CO_2 \leftrightarrow CO + 1/2O_2 \tag{3}$$

It has also been found that the ignition of volatile matter occurs more slowly in an O_2/CO_2 atmosphere [6].

Experimental and simulation studies of the distribution of coal combustion product concentrations along the length of the combustion chamber for air and $20\%O_2/80\%CO_2$ atmospheres were conducted by Zhao et al. [7]. In the initial part of the post-flame zone (400 mm from the start of the combustion chamber), a much higher CO concentration was noted for the O_2/CO_2 atmosphere than for air. With the increase in distance from the flame, a decrease in CO concentration was recorded for the O_2/CO_2 atmosphere to such an extent that at the end of the combustion chamber (1500mm from the start of the furnace) the concentration of CO from the air combustion atmosphere was higher.

The increase in the oxygen fraction of air during natural gas combustion reduces the CO concentration in the combustion gas [8, 9]. It should be emphasised, however, that with air enriched up to a level of $27\%O_2$, for various natural gas flows, a CO emission lower than for $30\%O_2$ [8] and $29\%O_2$ [9] was obtained on multiple occasions. As shown by investigations, the CO concentration depends on the following factors, among others: the temperature distribution in the combustion chamber, the gas flow, the time of combustion gas residence in the chamber, etc. Increasing the oxygen concentration in the air-fuel mixture increases the flame temperature and the NO_x concentration.

The effect of CO_2 as an additive (<30% CO_2) on the oxidation of gaseous fuels was examined in the flame [10], and in the tests of a flow reactor [8, 9], a jet stirred reactor [11] and IC engines [12].

Most authors agree that an increased presence of CO_2 in the combustion substrates contributes to an increase of CO in the combustion gas, with the combustion gas dilution process followed by the thermal effect being predominant here, while the combustion reaction kinetics play the least important role. Adding CO_2 to the substrate results in a reduction of combustion intensity, which is associated with a reduction of temperature and the heat flux recovered in the furnace.

In contrast to the above, some studies have found a marginal effect of CO_2 on the hydrocarbon oxidation process [11]. In addition, Liu at al. [13] found a better oxidation of ethylene through the addition of CO_2 in conditions of $\lambda<1$.

There is only a limited number of published studies of the oxidation of gaseous fuels at increased concentrations of carbon dioxide ($CO_2 \gg 50$) [1, 14–16]. Glarborg and Bentzen [1] presented tests on the effect of the methane combustion atmosphere (O_2/CO_2) conducted in a reactor with three separated zones (a heating zone, a 700 mm-long constant temperature zone, and a zone of rapid combustion gas cooling down to ambient temperature). Experiments and calculations show that a high level of carbon dioxide in the oxygen combustion atmosphere (76%

CO_2) prevents the oxidation of the fuel at high temperatures, while the increased availability of oxygen favors oxidation to CO rather than to CO_2. In addition, CO_2 reacts with H radicals according to reaction (2). However, the effect is most noticeable in rich mixture or stoichiometric conditions. There is no indication that the high CO_2 concentration influences the CO oxidation reaction at low temperatures (T<1300 K), in spite of the excess air. Glarborg and Bentzen hold the view that the second important reaction contributing to the increase in CO concentration is the reaction involving the methylene radical:

$$CO_2 + CH_2 \leftrightarrow CO + CH_2O \tag{4}$$

In the studies of the reaction rate of, e.g., reaction (2) of hydrogen oxidation in diffusion flame, Park et al. [15] noted that the method of supplying CO_2 to combustion played the key role. Namely, in the range of $10<CO_2<30$ v/v % of the oxidizer, the rate of reaction (2) increases, while in the case of diluting the fuel with carbon dioxide within the same range the reaction rate decreases. The addition of CO_2 has an effect on the location of the maximum flame temperature. The higher the temperature, the greater the H radical concentration, which does not always affect the rate of reaction (2) [15].

The effect of CO_2 addition (74 v/v %) and the combustion gas residence time on the concentration of, e.g., CO as a function of temperature for two combustion chambers made of different materials (quartz and alundum) was assessed by Gimenez-Lopez et al. [16]. They found that the reactions of hydrocarbon radicals with CO_2 were insignificant. A noteworthy chemical effect, on the other hand, is to be found in the reactions taking place with the participation of the chamber walls, which are intensified by the increased CO_2 concentration in the combustion gas.

The influence of CO_2 content on the variation of CO concentration in the combustion gas during natural gas combustion in the oxy-combustion process continues to be a subject of research.

2. Research description

2.1. Experimental tests

Later on in the paper, the notation of carbon dioxide is distinguished as follows: $CO_2{}^o$—added to the combustion process, CO_2—occurring in the combustion products.

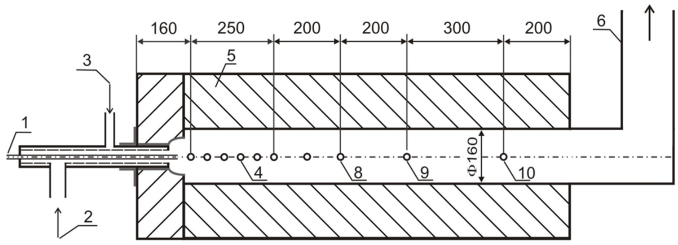

Figure 1: Furnace chamber with burner: 1. central nozzle $CO_2{}^o$; 2. air inlet; 3. gas inlet; 4,8,9,10. sight-glasses; 5. ceramic fiber; 6. exhaust gas system

The experiments were carried out on a test stand including a combustion chamber, as schematically shown in Fig. 1.

A constant natural gas flow of 0.6 m^3/h supplied to a double-pipe type kinetic burner was the subject of testing. Carbon dioxide was added in the amount of up to 15 v/v % of the oxidizing mixture (air + carbon dioxide) from a cylinder, on which a heater was installed to maintain its constant temperature at different flows. The nozzle delivering the $CO_2{}^o$ was designed coaxially inside the burner. Each nozzle end was located at a distance of 20 mm from the burner outlet at the flame/mixture interface. This technique allows the $CO_2{}^o$ to be fed directly into the high-temperature zone, thus not hindering the mixing of the fuel with the oxidizer. The combustion chamber is characterized by the following outer dimensions: the length, 1170 mm; and the diameter, 160 mm. The chamber walls were lined with 160 mm-thick ceramic fibre. A combustion air excess of λ=1.1, 1.15 and 1.2 respectively, was considered, and for each λ, two measurement series were carried out. The first series involved the recording of temperatures measured with (PtRh10-Pt) S-type thermocouples located in sight-glasses nos. 4, 8, 9 and 10 (as counted from the burner side). For the measurement of temperature variations in the cross-section of the combustion chamber in the location of combustion gas sampling for analysis, a FLIR ThermaCAM S60 portable thermovision camera and a thermoelement installed in the combustion gas analyzer were used. The second measurement series included analyses of dry combustion gas made by a LAND Lancom Series II analyzer at a distance of 740 mm from the burner (sight-glass no. 9 in Fig. 1) in the combustion chamber axis and 20 and 40 mm from the axis.

2.2. Computational procedure

Computer simulations were carried out using the latest version of the CHEMKIN-PRO software developed at the Sandia National Laboratories. A model considering combustion processes occurring in the Perfectly Stirred Reactor was adopted for the computations. The reactor can be briefly characterized as a system that exists in a steady state, the gases are regarded as ideal gases, the quotient of mixing time by chemical reaction time approaches zero, and the chemical reactions proceed in a gaseous phase. Two reactors in series were used for the computation. The first reactor reflected the process of air/natural gas mixture formation in the burner, while in the second reactor the addition of CO_2^o took place. The time of residence of the reagents in each reactor was 5 ms. Moreover, the following data was input to the program: the reagent mass flux, pressure, combustion chamber volume, temperature distribution over the chamber length, combustion temperature, reagent temperature at the outlet and air-fuel mixture composition in v/v %; natural gas: CH_4=97.8; C_2H_6=0.6; C_3H_8=0.3; CO_2=0.3, N_2=1; air: N_2=79; O_2=21.

The chemical mechanism was described with one of the most widely used methane combustion mechanisms, namely that of Miller-Bowman [17]. The mechanism employed in the computation was limited to 138 reactions and 37 elements and chemical compounds. The authors of the present study carried out a series of simulations using various chemical mechanisms and came to the conclusion that the Miller-Bowman mechanism best reflected the actual conditions of the investigation conducted by them. Moreover, the Miller-Bowman mechanism covers the methane oxidation reactions, including the nitrogen oxide formation mechanism. The reactions included in the Miller-Bowman mechanism were implemented in commonly known mechanisms, such as the GRI-Mech mechanism, version 3.0, developed by the Gas Research Institute.

3. Results

3.1. Measurement results

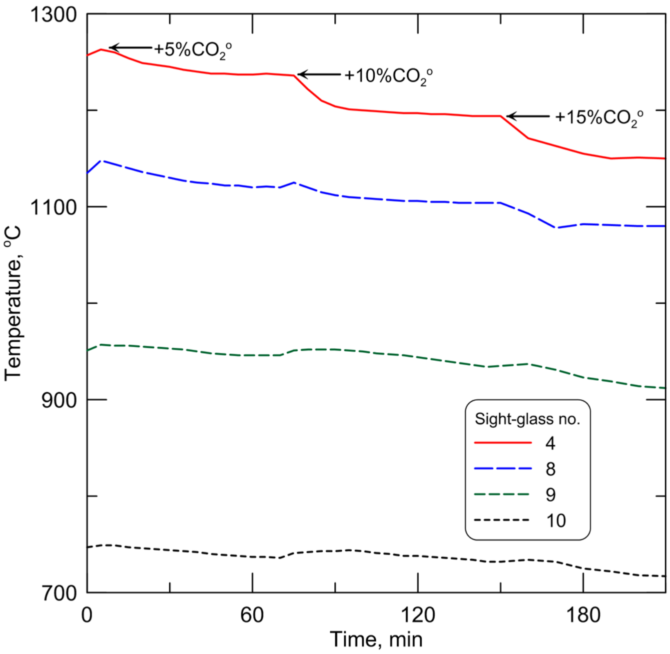

Figure 2: Thermal inertia of the chamber during the addition of CO_2^o for $\lambda=1.1$

The first measurement series conducted on the test stand concerned the distributions of temperatures in the furnace chamber during CO_2^o addition to the flame axis for the examined excess air ratios. Fig. 2 represents variations in temperature in the furnace axis in sight-glasses 4, 8, 9 and 10 as a function of measurement time for $\lambda=1.1$. The graph starts from the moment of temperature stabilization at four measurement points during air combustion of natural gas. As follows from Fig. 2, where the temperature was recorded every 5 min., a combustion gas temperature increase occurs at the moment of adding CO_2^o, which is caused by radiation of heat from the ceramic lining. The temperature stabilization after CO_2^o addition occurs slowest at measurement point no. 10 situated closest to the combustion gas discharge channel. A clear decrease in the temperature difference between sight-glasses nos. 4 and 8 should also be noted, which indicates a shift in the maximum flame temperature when CO_2^o is added. Based on the temperature measurement it was established that analyses of combustion gas should start from the highest CO_2^o concentration in order to eliminate the furnace chamber lining heating the combustion gas.

The next figure presents temperature variations recorded in the furnace cross-section (in the location of combustion gas sampling for analysis, sight-glass no. 9) during CO_2^o addition. The combustion gas temperatures shown in the graph originate from measurements taken with a thermocouple, with which the Lancom Series II combustion gas analyzer is equipped. At the same time, the temperature distribution in the cross-section was verified with the FLIR ThermaCAM S60 thermovision camera by introducing a specially prepared element with a pitch into sight-glass no. 9. The temperature resolution of the camera is 0.08°C, with the margin of error in temperature measurement being 2°C. The temperature measurement with the camera was made through the sight-glass situated in the combustion gas discharge channel. Identical temperature differences were obtained for the camera and the thermocouple. However, the temperature measured with the thermovision camera was 12°C higher than that obtained from the thermocouple.

The burner design undoubtedly has a significant effect on the distribution of concentrations, e.g., the distribution of CO_2, in dry combustion air in the chamber cross-section. The experimental results for CO_2 concentrations, obtained for the considered excess air values and CO_2^o additions, are summarized in Table 1. Regardless of the amount of added CO_2^o (in the furnace axis), for λ=1.1, the CO_2 concentration is always the lowest in the combustion chamber axis. For combustion with excess air of 1.2, the addition of CO_2^o resulted in the highest CO_2 concentration in the chamber axis. The measurements demonstrated there was no significant effect of the CO_2^o addition on the concentrations of the combusted hydrocarbons.

When examining Fig. 3a–c, it can be observed that regardless of the λ, the concentration of NO_x ($NO + NO_2$) in the combustion gas decreases as the CO_2^o is added.

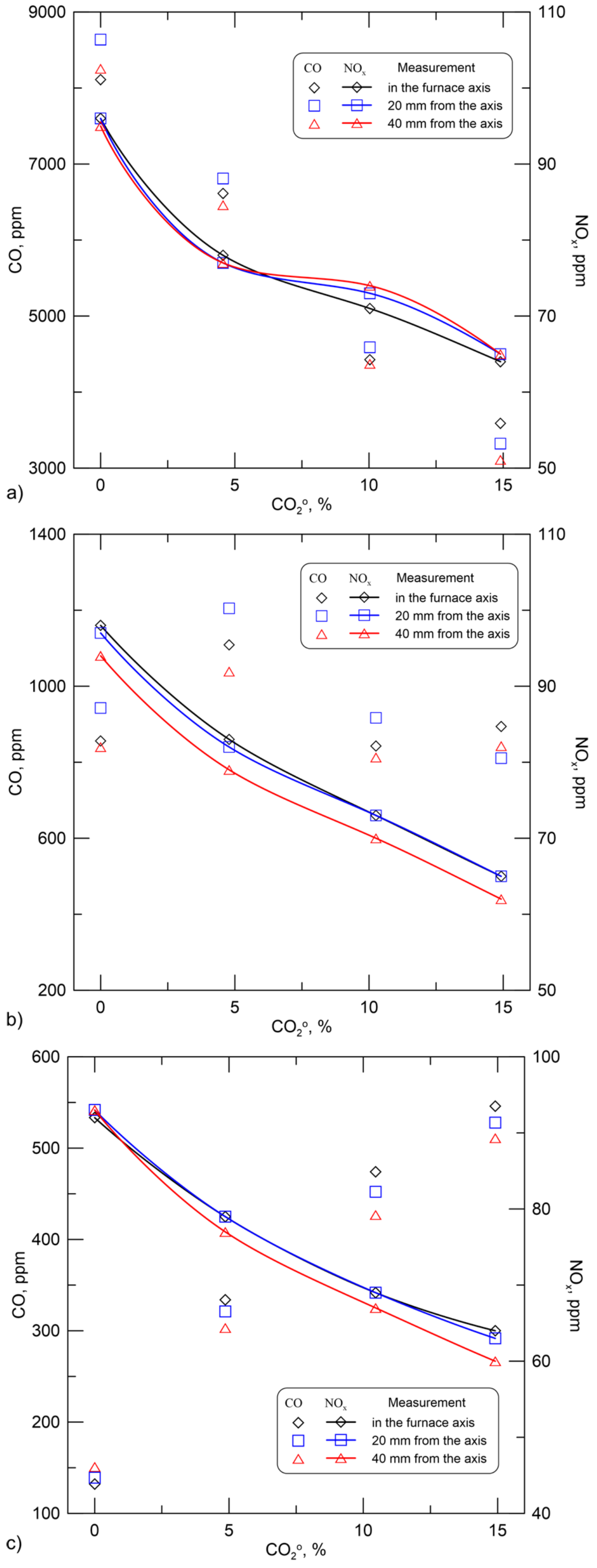

Figure 3: The effect of CO_2^o addition on the concentrations of CO and NO_x: a) λ=1.1; b) λ=1.15; c) λ=1.2

In a majority of analyses, the differences in NO_x concentration in the chamber cross-section are negligible (3 ppm, at the maximum), while the measuring error of the combustion gas analyzer is +/-1 ppm in this measuring range. The maximum NO_x concentration during air combustion of natural gas falls at λ=1.15. Generally, NO_x consists chiefly of NO, while NO_2 does not exceed 2 ppm. The lower the combustion temperature, the less NO_x in the combustion gas.

Much more difficult to interpret is the reduction in CO concentration during CO_2^o addition, as illustrated in Fig. 3a. The cause of the decreasing CO concentration is seen in the method of delivering the CO_2^o. For λ=1.1, the flame is situated closest to the burner, the consequence of which is the addition of CO_2^o to the axis of the flame (the main reaction zone). Due to the distortion of the flame pattern, we have a poorer dilution of the combustion gas with CO_2^o and, as a consequence, a reduction in CO concentration.

For λ=1.15, Fig. 3b, the CO_2^o addition takes place at the mixture/flame interface, while for λ=1.2, Fig. 3c, the CO_2^o gets to the mixture, because the flame is located farther from the burner. The variations in CO concentrations in Fig. 3b show a maximum for a CO_2^o addition of 5%. Regardless of the λ, the highest CO concentrations in the combustion chamber axis were only noted with a considerable fraction of added CO_2^o. The increase in CO concentration during CO_2^o addition was noted exclusively for λ=1.2.

The above-mentioned causes of the evolution in CO concentrations with the increase in λ are partially due to the CO_2^o flow guided by the same nozzle diameter, hence the variations in the velocity of CO_2^o discharge for successive excess air ratios. Factors that should be taken into consideration also include the differences in temperature of the added CO_2 (heated with a heater up to ambient temperature at larger flows) and the change in location of the maximum flame temperature influencing the distribution of CO concentrations along the combustion chamber. Investigations in the aspect of concentration distribution over the chamber length are planned for the future.

3.2. *Computation results*

Using the experimental results in the chamber cross-section given above, indicating a slight distribution of NO_x concentrations, an attempt was made to perform a numerical analysis of the problem of nitrogen oxide emissions during CO_2^o addition.

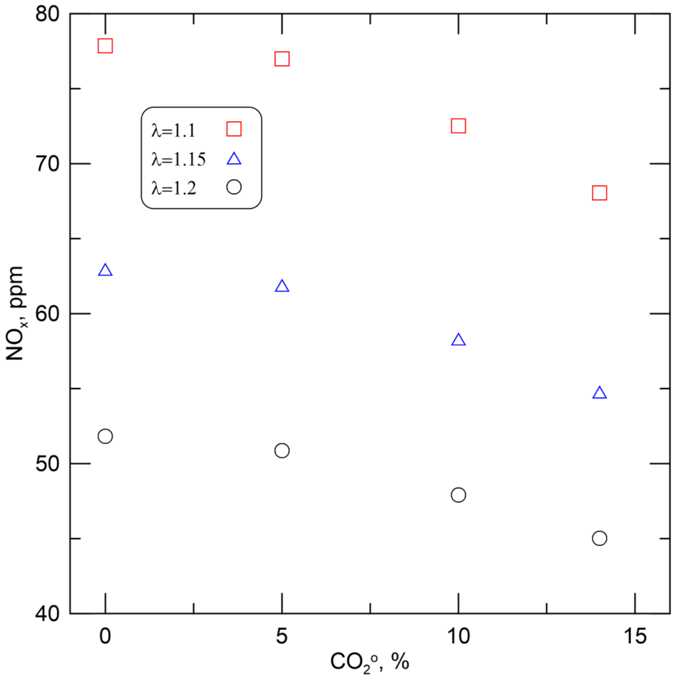

Figure 4: The effect of CO_2^o addition on the NO_x concentrations

For each concentration computation variant, there is NO_2 <1 ppm, which makes the notation of NO=NO_x correct. Lower values of NO concentrations in the dry combustion gas were obtained from the simulation computations, as shown in Fig. 4, compared to the NO_x from the experiment as shown in Fig. 3a–c.

The concentration difference might be due to all the combustion gas components in the chamber cross-section assumed for the calculation of the perfectly stirred reactors. However, the decrease in NO concentrations with CO_2^o addition, due to the reduction of temperature, is consistent. Looking at the data obtained from the experiments, while the NO_x concentration values for combustion with a 15% addition of CO_2^o for the considered excess air ratios are similar, in the case of the computations these differences are distinct.

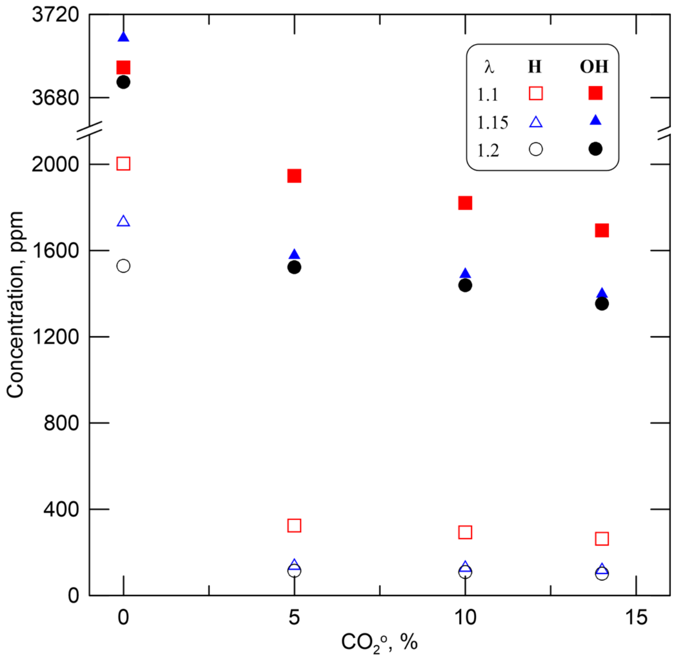

Figure 5: The effect of $CO_2{}^o$ addition on free radical concentrations

The next figure illustrates the effect of $CO_2{}^o$ addition on the variation in the concentrations of H and OH free radicals based on the computation. As can be seen from Fig. 5, there are many more OH radicals than H radicals in the combustion gas. Among the variants considered in this paper, the maximum temperature was shown by the excess air ratio of 1.1. In this particular case, there are the most free radicals that take part in reaction (2), among others. An exception is the OH radical for air combustion, where the maximum falls at λ=1.15. From the experimental tests, the increase in CO concentration in line with reaction (2) is unnoticeable, due to the poorer chemical effect relative to the combustion gas dilution.

A distinct decrease in the concentrations of H and OH free radicals can be noticed in the combustion gas upon adding 5% $CO_2{}^o$, and the increase in the $CO_2{}^o$ fraction leads to a reduction in free radical concentrations in the combustion chamber. The addition of 5% $CO_2{}^o$ has a five times greater free radical concentration effect for H radicals over OH radicals.

4. Summary

This paper analyzes the process of natural gas combustion at a distance of 740 mm from the start of the furnace, where the combustion gas temperature was contained in the range of 886–951°C during $CO_2{}^o$ addition. From the experiments performed, the following observations were made after the addition of $CO_2{}^o$ to the flame axis:

- the emissions of nitrogen oxides (NO_x) are reduced,
- slight changes occur in the distribution of NO_x concentrations in the chamber cross-section,
- the highest CO concentrations in the combustion chamber axis are only possible with a considerable fraction of added $CO_2{}^o$,
- the combustion temperature decreases,
- a shift occurs in the location of the maximum flame temperature, and
- a change occurs in the CO concentration.

By supplementing the experimental results with computations performed with the Chemkin-Pro program, a decrease in the concentrations of NO_x and OH and H free radicals was achieved during the addition of $CO_2{}^o$.

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Table 1: The effect of the quantity of added CO_2^o on the combustion gas CO_2 concentration in the chamber cross-section

λ	1.1			1.15			1.2		
Distance from axis, mm	0	20	40	0	20	40	0	20	40
CO_2^o, v/v % of air	Combustion gas CO_2 concentration in the chamber cross-section, %								
0	9.72	9.84	9.94	9.59	9.52	9.56	9.49	9.56	9.58
5	14.73	14.8	14.9	14.6	14.78	14.93	14.22	14.18	14.21
10	20.3	20.63	20.5	19.74	19.63	19.71	19.36	19.19	19.25
15	24.92	25.27*	25.05*	24.19	24.08	23.80	24.11	23.97	23.86

* the result exceeded the combustion gas analyzer's measuring range