



Emissions of NO_x and CO from Natural Gas Combustion with Adding CO_2 at Varying Distances from the Burner

Wojciech Jerzak

AGH University of Science and Technology

1. Introduction

The technology of oxygen-combustion of fuels is one of the most promising methods of controlling the emissions of greenhouse gases, such as CO_2 , N_2O , CH_4 . Applying the capturing of CO_2 from the combustion gas provides the possibility of the CO_2 being used for combustion gas recirculation or the dilution of combustion air. 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 . The explanation of the lower flame temperature is the greater heat capacity of CO_2 than that of N_2 . Nitrogen oxides contribute to the formation of toxic ozone. Both NO_x and SO_2 are jointly responsible for acid rains [6]. Unburned hydrocarbons may be the cause of eye, nose or throat irritations.

The emission of NO_x and CO during the combustion of natural gas in atmospheres of air enriched with oxygen is dependent, inter alia, on the temperature and the burner type. Natural gas combustion in an atmosphere of air enriched with oxygen up to 30% using a burner without the preliminary mixing of the fuel and the oxidizer was studied by Wu et al [11]. According to the studies [11], the increase in the oxygen fraction of air results in an increase in the concentrations of CO_2 and NO_x in the combustion gas. Enriching the air with oxygen up to 24%

results in a drop in CO concentration, and the continued increasing of the oxygen fraction of air causes an increase in CO concentration. In turn, Li, Zhou and Cen [7] employed a low-swirl burner for testing the combustion of methane in N₂/O₂ and CO₂/O₂ atmospheres. In the flame region, a higher temperature was achieved for the N₂/O₂ than for CO₂/O₂, which promotes the formation of thermal nitrogen oxides. A burner with the pre-mixing of natural gas and air enriched with oxygen up to 29% was used for the investigation of the combustion process by Kalicka et al [4]. During the addition of oxygen to the air, a scatter of CO concentrations in the combustion gas was observed. From numerical computation, on the other hand, an increase in CO concentration was obtained. Wilk et al [10] also used a pre-mixing burner for the combustion of natural gas in an atmosphere of air enriched with oxygen up to 29%. It was found from the experiments that the addition of oxygen to the combustion air caused an increase in CO and NO concentrations in the combustion gas. The investigation of the process of combustion in a swirl burner without fuel and oxygen pre-mixing was carried out by Merlo et al [8]. In this case, the CO emission decreased exponentially, while the (thermal) NO_x emission increased exponentially with increasing addition of oxygen to the air.

Carbon dioxide added to the combustion substrates 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. The addition of CO₂ reduces the emission of nitrogen oxides compared to their emission during air combustion [3–5]. In spite of using oxygen-fuel technologies, the complete elimination of nitrogen from the process is extremely difficult. The source of nitrogen may be: the fuel, air penetrating into the furnace through leaks, or the insufficient purity of air-derived oxygen.

The effect of the addition of CO₂ to the natural gas combustion process on the emission of CO, reported in literature [2–5,9], depends on various factors, such as the method and location of adding CO₂, the burner type, the flow pattern, temperature distribution, the time of combustion gas residence in the chamber, the gas flux, etc. Based on tests carried out in a plug flow reactor, Glarborg and Bentzen [2] found that the CO emission was higher for the O₂/CO₂ atmosphere than for air. Moreover, the CO concentration in combustion gas decreased with

increasing oxygen fraction of the O₂/CO₂ mixture. Experiments and calculations show that a high level of carbon dioxide in the oxygen combustion atmosphere (76% CO₂) prevents the oxidation of the fuel at high temperatures, while the increased availability of oxygen favours the oxidation to CO rather than to CO₂. In addition, CO₂ reacts with H radicals according to the following reaction:



Glarborg and Bentzen hold the view that the second important reaction contributing to the increase in CO concentration is the reaction with the participation of the methylene radical:



Generally, three causes of the increased CO concentration in the combustion gas can be indicated: combustion gas dilution with CO₂, the change in temperature, and the chemical effect resulting from the predominance of the reactions (1, 2). The greatest effect of increasing the CO concentration in the combustion gas is caused by the combustion gas dilution process, followed by the thermal effect; whereas, the least role is played here by the combustion reaction kinetics. Adding CO₂ to the substrate results in a reduction of combustion intensity, which associated with the reduction of temperature and the heat flux recovered in the furnace.

Numerical computations of combustion in the diffusion flame were carried out by Park et al [9]. They compared the rate of reaction (1) with the dilution of the oxidizer and methane with carbon dioxide. In the range of 10 < CO₂ < 30 vol.% of the oxidizer, the rate of reaction (1) increases, while in the case of diluting the fuel with carbon dioxide within the same range the reaction rate decreases. The addition of CO₂ influences 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 (1) [9].

The influence of CO₂ content on the variation of CO concentration in the combustion gas during natural gas combustion in the oxy-combustion process is the subject of ongoing research [1, 8].

2. Description of experimental tests

The addition of CO_2 to the oxidizing mixture hinders the process of mixing the fuel and the oxidizer. For the added carbon dioxide not to impede the combustible mixture forming process, a burner with a CO_2 feeding nozzle advancing in the axis was designed for these tests. The experiments were carried out using an experimental stand, as shown schematically in Fig. 1. The monitoring of temperature using S-type (Pt10Rh-Pt) thermocouples was conducted at three points denoted as no. 2 in Fig. 1 in the space between the quartz tube and the heating elements.

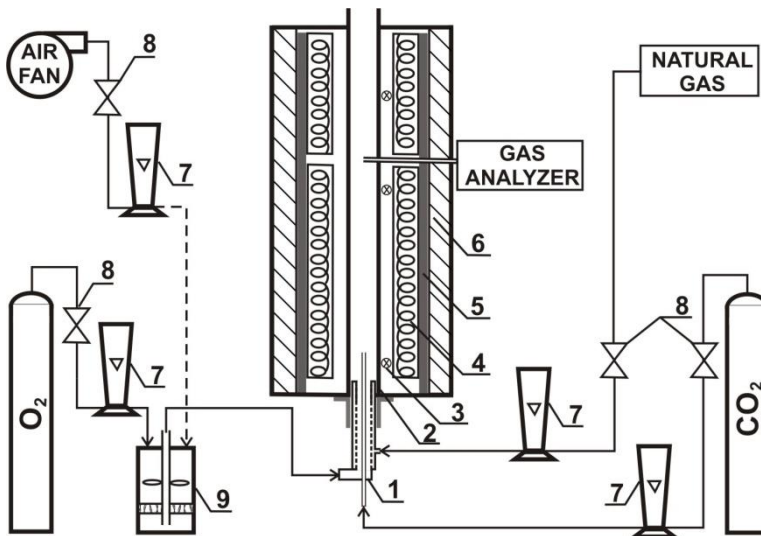


Fig. 1. Scheme of the experimental apparatus: 1. burner; 2. quartz tube; 3. thermocouple; 4. electric resistance wire; 5. ceramic tube; 6. ceramic fiber; 7. rotameter; 8. valve; 9. mixer

Rys. 1. Schemat stanowiska doświadczalnego: 1. palnik; 2. rura kwarcowa; 3. termopara; 4. drut oporowy; 5. rura ceramiczna; 6. włókno ceramiczne; 7. rotometr; 8. zawór; 9. mieszalnik

The measurements of dry combustion gas concentrations were taken in the combustion chamber axis at a distance of 0.58 m from the burner outlet using an Horiba PG-350 gas analyzer. The determination of the concentration of NO_x nitrogen oxides in the employed device is done using a chemiluminescence method being equivalent to the infrared absorption method. The chemiluminescence method is characterized by

higher sensitivity compared to other types of detection, which allows low measuring ranges to be used. The repeatability of measurements is $\pm 0.5\%$ for the range of $\text{NO}_x \geq 100$ ppm. The combustion gas analyzed operated in a continuous manner during the tests. A constant combustion gas flux of approx. $0.05 \text{ m}^3/\text{h}$ was taken for analysis, which was passed through the hot sample path (where a temperature of 110°C was maintained) and then got in excess to the gas cooler. From the cooler, the Horiba analyzer took dry combustion gas at a flow rate of approx. $0.03 \text{ m}^3/\text{h}$. High-methane natural gas from the municipal gas grid, which contained 97.8% vol. of CH_4 and 1% vol. of a mixture of ethane, propane and butane. For the calculation of the air flux settings, the following $\text{C}_2\text{-C}_4$ hydrocarbon volumetric fractions of natural gas were taken: 0.6 for ethane, 0.3 for propane and 0.1 for butane.

The experiments were conducted for a natural gas flow rate of $0.12 \text{ m}^3/\text{h}$. The excess air ratio, λ , was varied within the range of 1.15–1.25. The natural gas was combusted in air enriched with oxygen up to 25% vol. The effect of the advancement of the central CO_2 feeding burner nozzle on the emission of NO_x and CO in the combustion chamber was examined. The tests were carried out for the following CO_2 injection distances from the burner: 0; 0.05; 0.1; and 0.15m for the measurement settings listed in Table 1. The experiment was started with natural gas combustion in air enriched with oxygen up to a level of 25% with no CO_2 addition, and then carbon dioxide was added. With a constant flux of oxygen fed to the combustion process being maintained, for the excess air ratio examined, a decrease in the oxygen fraction occurs relative to the volume of the introduced gases down to a level of 18.7% with a CO_2 addition of 25% during the addition of CO_2 .

Table 1. Measurement settings for the excess air ratios examined

Tabela 1. Nastawy pomiarowe dla badanych nadmiarów powietrza

λ	Oxygen	Air	Carbon dioxide, %				
			5	10	15	20	25
-	dm^3/h						
1,15	55,9	1047	58	120	195	280	370
1,2	58,3	1093	60	125	200	290	385
1,25	60,7	1138	63	130	205	300	400

3. Measurement results

The variations of temperatures in the space between the quartz tube and the heating element are illustrated in Figure 2. The temperature measurement presented in Fig. 2 was performed at the height of the probe taking the combustion gas to the analyzer (the middle thermocouple in Fig. 1). The temperature measurement results apply to the natural gas combustion variant with the 25% CO_2 addition for the excess air ratios under consideration. With the increase in the excess air ratio, a decrease in temperature occurs. The distance of the CO_2 injection location from the burner results in a decrease of temperature in the combustion gas uptake location.

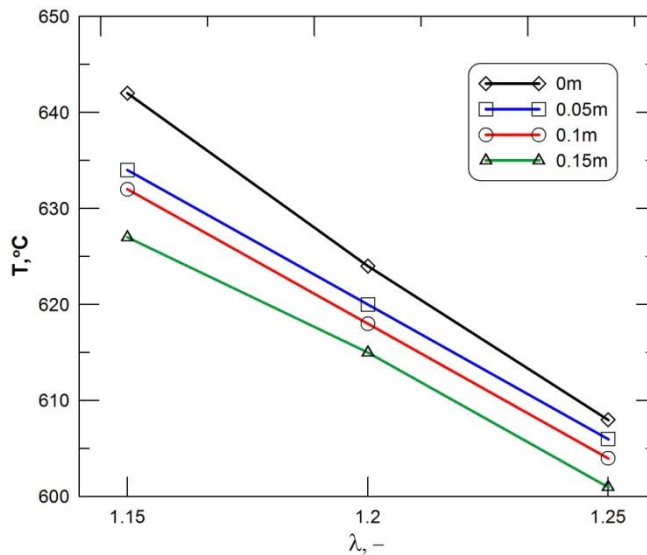


Fig. 2. The effect of CO_2 injection location on the temperature as a function of λ
Rys. 2. Wpływ miejsca wstrzykiwania CO_2 na temperaturę w zależności od λ

The following Figures 3a, 4a and 5a represent variations in NO_x concentrations in dry combustion gas during CO_2 injection at a distance of 0, 0.05, 0.1 and 0.15m, respectively, from the burner. As a result of combustion with $\lambda=1.15$ (Fig. 3a), the lowest combustion gas NO_x concentration values were obtained, whereas for $\lambda=1.25$ (Fig. 5a), the highest NO_x concentrations, regardless of the CO_2 injection distance. The

observed increase in NO_x concentration towards the fuel-lean mixture (Figs. 3a, 4a, 5a) is consistent with the calculation results [3], based on which the maximum NO_x concentration falls to $\lambda \sim 1.2$. By adding 20% CO_2 , the highest NO_x concentration was always obtained, when the CO_2 feeding nozzle was located at a distance of 0.05 m from the burner, for the excess air ratios examined. The advancement of the CO_2 injection nozzle by over 0.05 m would cause a drop of NO_x concentration in the combustion gas. For the employed burner design with gas and oxidizer pre-mixing, the effect of NO_x reduction is achieved by adding CO_2 at a distance of at least 0.1 m. It should be noted that the nozzle advancement alone without the CO_2 injection interferes with the flame and contributes to the variation in the concentrations of both CO and NO_x .

The variations in CO concentration in dry combustion gas during adding CO_2 at different distances from the burner are illustrated in Figures 3b, 4b and 5b. The highest CO concentration level for the examined excess air ratios occurs in the case of injecting CO_2 with no nozzle advancement (denoted in the figures by 0 m). In that case, the CO_2 is directed to the combustible mixture. The advancement of the CO_2 nozzle to a distance of 0.05 m results this time in the dilution of the flame rather than the combustible mixture. The farther the CO_2 was injected from the burner, the lower the CO concentration was noted in the dry combustion gas. Increasing the fraction of carbon dioxide (relative to the oxidizing mixture) injected at the distance of 0.15 m from the burner, depending on the excess air ratio, influences the changes in CO concentrations in the combustion gas. During combustion with $\lambda = 1.15$, an increase in CO concentration was observed (Fig. 3b). The absence of any significant changes in carbon monoxide concentration is visible in Fig. 4b for $\lambda = 1.2$, whereas for $\lambda = 1.25$, a decrease in CO concentration occurs. As illustrated in Fig. 5b), injecting CO_2 at a level of 5 and 10% at a distance of 0 and 0.05 m, respectively, reduces the CO concentration, while with a CO_2 addition above 15%, increases the CO concentration in the combustion gas.

The investigation results presented in this paper have proved that the distance of CO_2 injection from the burner substantially influences the concentrations of NO_x and CO during the combustion of natural gas.

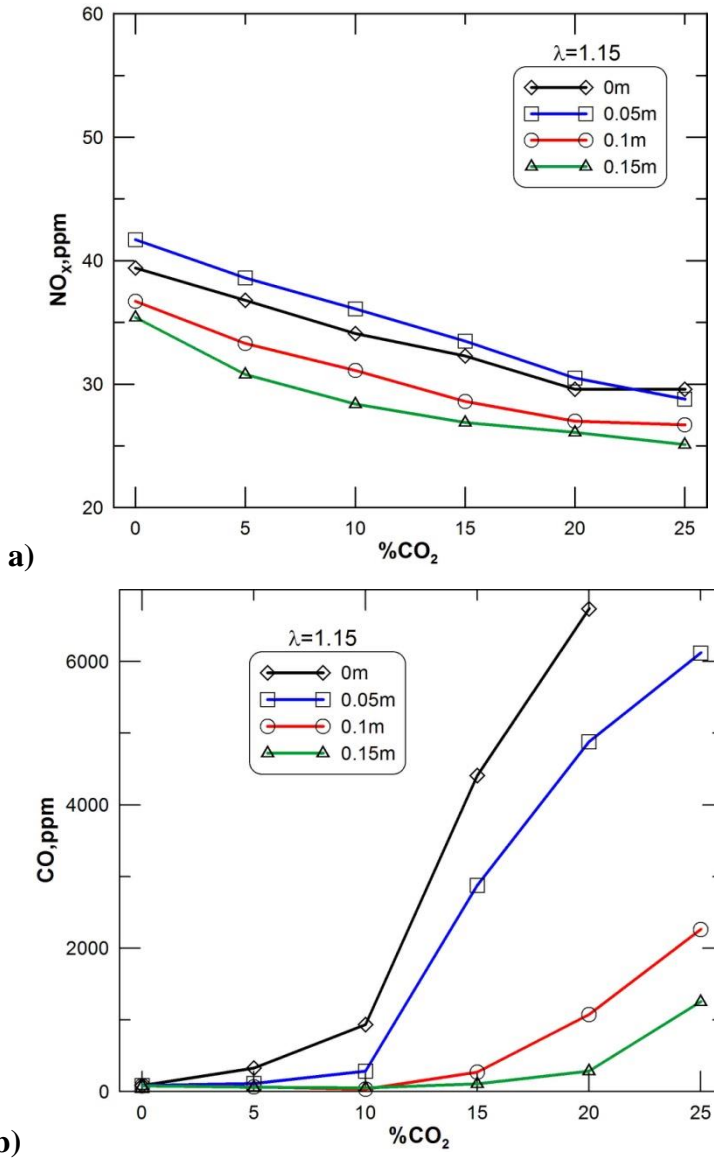


Fig. 3. The effect of CO_2 injection location on the concentrations of NO_x (a) and CO (b) for $\lambda=1.15$

Rys. 3. Wpływ miejsca wstrzykiwania CO_2 na stężenia NO_x (a) i CO(b) dla $\lambda=1.15$

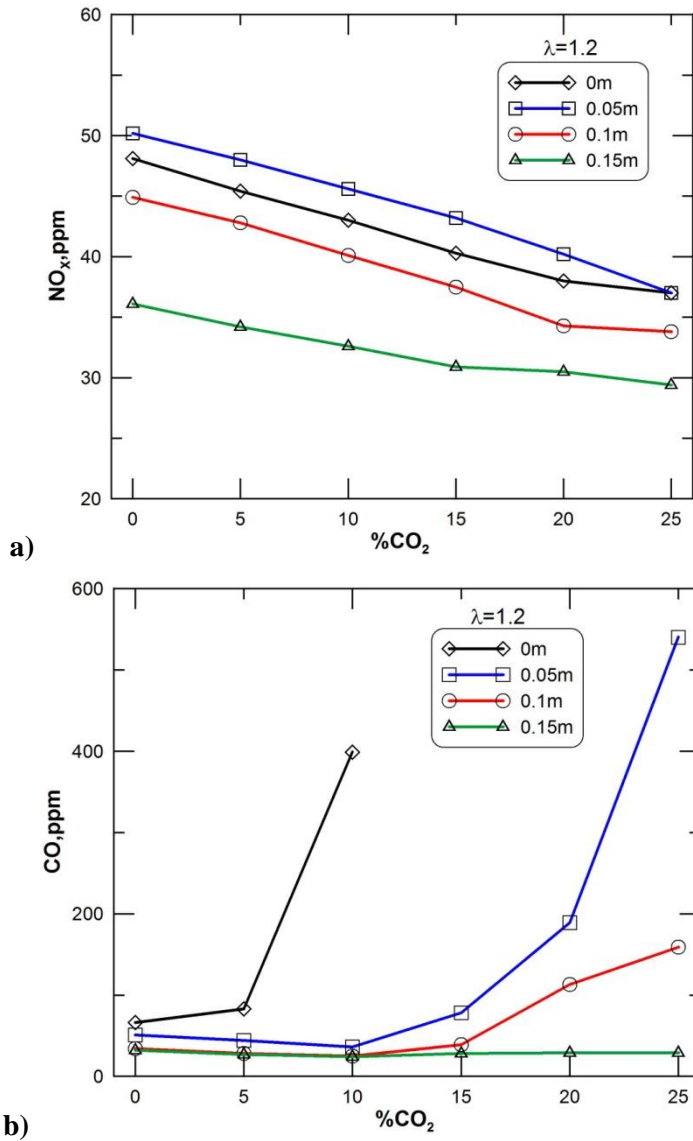


Fig. 4. The effect of CO₂ injection location on the concentrations of NO_x(a) and CO(b) for $\lambda=1.2$

Rys. 4. Wpływ miejsca wstrzykiwania CO₂ na stężenia NO_x(a) i CO(b) dla $\lambda=1.2$

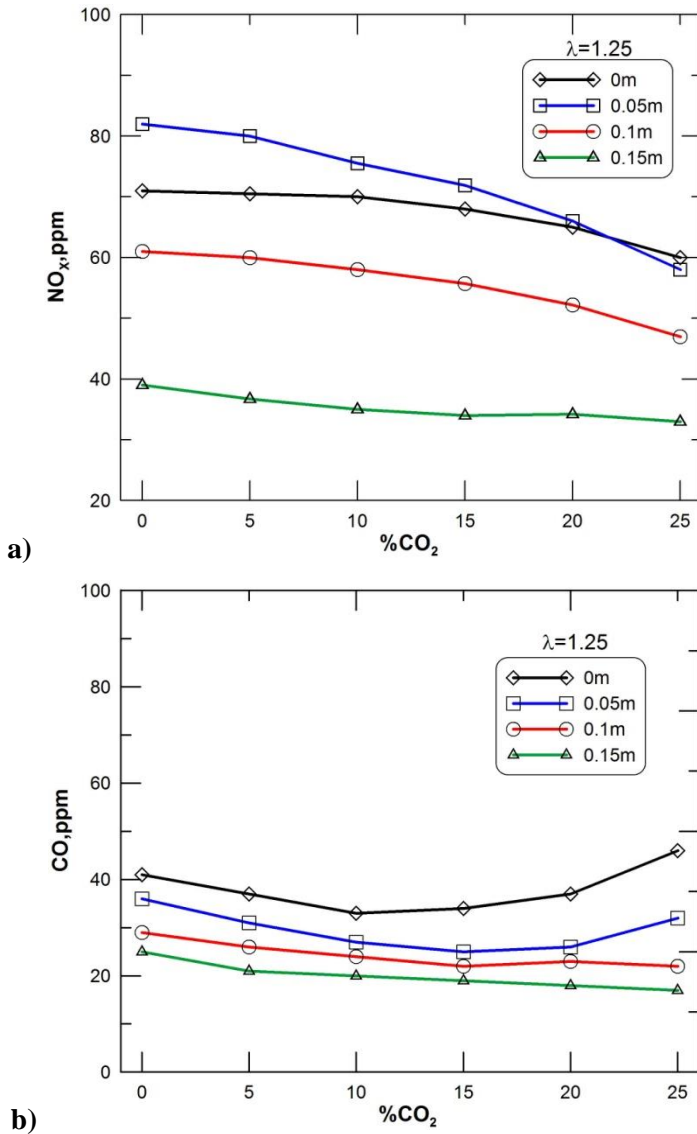


Fig. 5. The effect of CO_2 injection location on the concentrations of NO_x (a) and CO(b) for $\lambda=1.25$

Rys. 5. Wpływ miejsca wstrzykiwania CO_2 na stężenia NO_x (a) i CO(b) dla $\lambda=1.25$

4. Summary

The effect of the CO₂ injection distance on the emissions of NO_x and CO during the combustion of natural gas in air enriched with oxygen up to 25% vol. has been examined in the paper. On the basis of the experiments it has been demonstrated that injecting CO₂ at a distance of 0.05 m from the burner increases the concentration of NO_x, while the advancement of the CO₂ feed nozzle to a minimum of 0.1 m from the burner results in a reduction of NO_x.

Depending on the excess air ratio, the increase in the fraction of carbon dioxide injected at a distance of 0.15 m from the burner:

- a) results in an increase in combustion gas CO concentration for $\lambda=1.15$,
- b) has no effect of changing the CO concentration for $\lambda=1.2$, and
- c) reduces the combustion gas CO concentration when $\lambda=1.25$.

Adding CO₂ at a level of 5 and 10% at a distance of 0 and 0.05 m from the burner, respectively, in the case of combustion with $\lambda=1.25$, leads to a decrease in CO concentration, while with a CO₂ addition above 15%, an increase in CO concentration occurs.

Acknowledgement

The work was supported by grant no. AGH: 15.11.110.234

References

1. **Alves M., Rosa C., and Costa M.:** *Effect of the Oxidizer Composition on the CO and NO_x Emissions from a Laboratory Combustor Operating under Oxy-Fuel Conditions.* Energy & Fuels. No 1 Vol. 27, 561–567 (2013).
2. **Glarborg P. and Bentzen L. B.:** *Chemical Effect of a High CO₂ Concentration in Oxy-Fuel Combustion of Methane.* Energy & Fuels. No 1 Vol. 22, 291–296 (2002).
3. **Jerzak W., Kalicka Z., Kawecka Cebula E.:** *Obliczenia równowagowe a wyniki pomiarowe produktów spalania gazu ziemnego w atmosferze CO₂/O₂/N₂.* Archiwum Spalania, Nr 3 Vol. 12, 81–90 (2012).
4. **Kalicka Z., Jerzak W., Kawecka Cebula E.:** *The effect of combustion of natural gas with 21%–29% O₂/CO₂/N₂ mixtures on emission of carbon monoxide.* Archives of Environmental Protection. No 4 Vol. 39, 21–31 (2013).

5. **Kim H. K., Kim Y., Lee S. M., Ahn K. Y.:** *NO reduction in 0.03–0.2 MW oxy-fuel combustor using flue gas recirculation technology.* Proceedings of the Combustion Institute, No 2 Vol. 31, 3377–3384 (2007).
6. **Kordylewski W., Jakubiak M., Hardy T.:** *Pilot Plant Studies on Nox Removal Via No Ozonation and Absorption* Archives of Environmental Protection. Volume 39, Issue 3, Pages 93–106 (2013).
7. **Li G., Zhou H., Cen K.:** *Emission characteristics and combustion instabilities in an oxy-fuel swirl-stabilized combustor.* Journal of Zhejiang University SCIENCE A. No 9 Vol. 11, 1582–1589 (2008).
8. **Merlo N., Boushaki T. et al.:** *Experimental study of oxygen enrichment effect on turbulent non-premixed swirling flames.* Energy & Fuels. published online ahead of print, DOI: 10.1021/ef400843c (2013).
9. **Park J., Hwang D. J., Kim K.-T., Lee S.-B. and Keel S.-I.:** *Evaluation of chemical effect of added CO₂ according to flame location.* International Journal of Energy Research. No 6 Vol. 28, 551–565 (2004).
10. **Wilk M., Magdziarz A., Kuźnia M.:** *Wpływ dodatku tlenu do powietrza na proces spalania gazu ziemnego.* Rynek Energii, No 5, 32–36 (2010).
11. **Wu K.-K., Chang Y.-Ch., Chen Ch.-H., Chen Y.-D.:** *High-efficiency combustion of natural gas with 21–30% oxygen-enriched air.* Fuel. No 9 Vol. 89, 2455–2462 (2010).

Emisja NO_x i CO ze spalania gazu ziemnego podczas dodawania CO₂ w różnych odległościach od palnika

Streszczenie

W artykule badano wpływ wysunięcia centralnej dyszy palnika doprowadzającej CO₂, na emisję NO_x i CO podczas spalania gazu ziemnego w powietrzu wzbogaconym w tlen do 25%. Dwutlenek węgla wstrzykiwano w odległościach 0; 0,05; 0,1 i 0,15 m od palnika, w ilości do 25% obj. mieszanki utleniającej. Wzrost nadmiaru powietrza oraz oddalenie miejsca wstrzykiwania CO₂ od palnika, skutkowało obniżeniem temperatury w miejscu poboru spalin. Stwierdzono, iż miejsce wstrzykiwania CO₂ istotnie wpływa na emisję NO_x i CO podczas spalania gazu ziemnego. W analizowanym palniku ze wstępnym wymieszaniem paliwa i utleniacza, wysunięcie dyszy doprowadzającej CO₂ na odległość 0,05 m zwiększa stężenie NO_x w spalaniach suchych, a dalsze wysuwanie dyszy od palnika prowadzi do obniżenia stężeń NO_x dla badanych nadmiarów powietrza. Stężenia CO na skutek wysuwania dyszy doprowadzającej CO₂, wykazują odmienne tendencje w porównaniu z NO_x. Kierunek zmian

stężenia CO i NO_x istotnie uwarunkowany jest nie tylko od miejsca podawania czy udziału % CO₂, lecz również od nadmiaru powietrza. Wstrzykiwanie do 10% CO₂ w odległościach 0 oraz 0,05 m dla $\lambda=1.25$ prowadzi do spadku stężenia CO, a przy dodatku powyżej 15% obj. CO₂ mieszanki utleniającej następuje wzrost stężenia CO w spalinach suchych.

Słowa kluczowe: emisja NO_x, emisja CO, spalanie gazu ziemnego

Key words: emissions of NO_x, emissions of CO, natural gas combustion