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THE EFFECT OF COMBUSTION OF NATURAL GAS WITH 21–29% $O_2/CO_2/N_2$ MIXTURES ON EMISSION OF CARBON MONOXIDE

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Abstract: Natural gas combustion was carried out in air enriched with oxygen in the amount of 25 and 29% with addition of CO_2 in place of part of nitrogen. The research was carried out at different flow rates of gas and oxygen excess ratios. The concentration of CO and NO_x was analyzed. It has not been proved that the increased oxygen concentration influences significantly the CO concentration. However, the addition of CO_2 caused a substantial variability of CO concentration in the exhaust gas, in contrast to the concentration of NO_x which decreased monotonically. Model calculations, performed with use of FactSage, indicate an increase in the concentration of CO not only for the air enriched with oxygen, but after adding CO_2 too, as well.

INTRODUCTION

The term oxy-fuel combustion defines burning in oxygen itself or oxygen with the addition of CO_2, as the recycled flue gas (RFG), to reduce the temperature of the flame.

The motivation of such combustion is need to reduce the volume of exhaust gases by eliminating the burden, namely nitrogen, which is to facilitate the subsequent capture of carbon dioxide from the exhaust gases for its sequestration. Oxy-combustion studies were begun for coal, because this is the fuel which, per one unit of energy, puts the greatest amount of CO_2 into the atmosphere. For natural gas the studies have been conducted in recent years. The increased oxygen content and the presence of carbon dioxide in an oxidation mixture affect both the kinetics of combustion and thermal and dynamic processes in the combustion chamber. Carbon dioxide which replaces nitrogen in the oxidation mixture affects the burning speed because: a) it alters the transport and thermal properties of the mixture of gases, b) it can participate in reactions in the flame, c) increases the energy transfer by radiation.

Combustion of carbon in the atmosphere O_2/CO_2 reduces significantly the emission of nitrogen oxides but favors the increased carbon monoxide emissions [e.g. 1, 7, 9]. In the case of the combustion of natural gas, the impact on the emission of CO is not so clear.

The understanding of burning in air processes and the impact of different factors on the CO and NO_x concentrations in flue gas is more advanced. For example, the influences of the burner type and boiler power as well as the excess air ratio when burning natural gas have been thoroughly studied [e.g. 4, 5].

In [6] experiment, natural gas was burned in a mixture of oxygen (28% vol.) with the recirculated exhaust gases and the air enriched only with oxygen (28%) comparing the results of combustion in the air. Both the concentrations of CO and NO_x in the chamber were the highest for air enriched in oxygen, and the lowest for the same oxygen concentration but with an addition of CO_2. The distribution of concentrations and temperature in the chamber was also studied. It was noted that if the concentration of nitric oxide was stabilizing already at a short distance from the burner, the CO concentration was decreasing along the entire axis of the chamber. On the cross section of the chamber, the distribution of the concentrations was different for CO in comparison with NO_x – the concentration of CO was lower at the wall of the chamber, whereas the NO_x concentration was higher or almost unchanged.

In [8] experiment, the natural gas combustion in air enriched with oxygen to 30% was studied for the equivalence ratio of 0.952. The increase in oxygen concentration caused a higher temperature of the flame. Therefore, the NO_x concentration obviously significantly increased along with the enrichment of air in oxygen. However, the measurements of CO concentrations showed great variability. Depending on the conditions of combustion, the CO concentration decreased with increasing oxygen concentration or showed increases and decreases without a clear downward or decline trend. The important fact was that the increase of oxygen concentration resulted in greater inequality in the distribution of temperature in the furnace.

Model calculations of the burning speed of methane a) in air, b) in a mixture of oxygen, nitrogen and carbon dioxide, and c) in a mixture of oxygen and carbon dioxide without nitrogen, showed that the replacement of nitrogen by carbon dioxide significantly decreases the burning speed [2]. In order to verify that the result is only due to different thermophysical properties of carbon dioxide compared with nitrogen, the variant of calculations was carried out in which the added carbon dioxide, referred to as FCO_2 (fictitious), could not participate in the reactions. Then the calculated burning speeds were significantly higher, which means that the actual CO_2 takes part in reactions in the flame. The authors hypothesized that the chemical cause of the reduction of burning speed is the reduction of the hydrogen radicals concentration in the flame caused by the reaction $CO_2 + H \rightleftharpoons CO + OH$, as a result of which CO appears. Similar numerical calculations, this time for ethene [3], were performed to assess the effect of the CO_2 addition on the generation of soot and NO_x. The calculations included two variants of diffusive combustion – CO_2 was added to fuel or replaced nitrogen in air. The results were compared with calculations made with the participation of a fictitious, i.e. without the right to participate in chemical reactions, carbon dioxide (FCO_2). The authors also found that the major chemical reaction responsible for the chemical effect of adding CO_2 is the reaction with hydrogen radicals, $CO_2 + H \rightleftharpoons CO + OH$ and to a lesser extent, the reaction $CO_2 + CH \rightleftharpoons CO + HCO$, while the effect was stronger if CO_2 was added with air instead of fuel.

EXPERIMENTS

Natural gas combustion has been studied in oxidizing mixtures containing 25% and 29% of oxygen, with partial replacement of nitrogen into CO_2. The influence of oxygen concentration, the concentration of carbon dioxide, natural gas flow and the oxygen excess coefficient λ on the concentration of CO and NO_x in the exhaust gases was analyzed. Natural gas had the following composition: 97.8% vol. CH_4, 1% vol. of the ethane, propane and butane mixture. In calculating the oxygen demand, the following shares in a mixture of C_2-C_4 were assumed: 0.6 for ethane, 0.3 for propane, 0.1 for butane. The oxidizing mixture was made from the air and oxygen and CO_2 from the cylinder. The gases were supplied into a gas mixer before serving to the kinetic burner. The inner dimensions of the combustion chamber were the length of 131 cm and the diameter of 16 cm. The walls were covered with ceramic fibre 16 cm thick. The measuring ports for temperature were located at the distance of 16 cm (flame temperature), 42 cm, 62 cm, 110 cm, and for species concentration at the distance of 36 cm, 52 cm and 86 cm. The tip of the burner was at the distance of 11 cm. The main measurements for flue gas composition were carried out at 86 cm (75 cm from the burner outlet). Temperature was measured by thermocouples, species concentration in exhaust gas by Lancom Series II gas analyzer. Concentrations were expressed on a dry-volume basis.

Six series of measurements were performed. Each series concerned one flow of gas and one value of λ. The applied natural gas flows were 0.4; 0.6 and 0.8 m^3/h and the oxygen excess ratios were equal to 1.05; 1.15 and 1.25. The studies were carried out for air, air enriched with oxygen (25 and 29% O_2) and for mixtures of air with oxygen and CO_2, in which part of nitrogen was replaced by the same volume of dioxide. Table 1 summarizes the compositions of mixtures studied and their volumes per 1 m^3 of gas, compared with combustion in air.

Prior to each series of tests, the furnace was heated to similar temperatures. The measurements were started from the combustion in air, then the mixture of air with the oxygen content of 25% O_2 was added, and then gradually a part of nitrogen was replaced by CO_2 with a constant volume of the mixture, and finally similar measurements for a mixture containing 29% O_2 were performed. Gas analysis was started after 20 min after giving the mixture. The exhaust gases composition measurements were carried out in the axis of the chamber and additionally in some series, also at the chamber wall. The temperatures of flame and exhaust gases along the axis of the chamber were measured.

The upper limit of CO_2 concentrations given in Table 1 resulted from the maximum flow of CO_2 adapted to a heating device leveling the cooling of CO_2 with the expansion of the gas cylinder. The maximum concentration of CO_2 in the mixture could be higher, the smaller was the gas flow, the oxygen excess coefficient and a higher concentration of O_2 (that is, the smaller volume of the mixture).

RESULTS AND DISCUSSION

The analysis of the results concerned the impact of the increased concentration of oxygen and the presence of carbon dioxide on the amount of CO and NO_x contained in the exhaust gases. The basic measurements were made at a fixed distance from the burner.

Table 1. Compositions of combustion media studied

Oxygen excess ratio λ	Composition of $O_2/N_2/CO_2$ mixture		Volume of mixture per 1 m^3 of natural gas [m^3]
	$\%O_2$	$\%CO_2$	
1.05	air		10.00
	25% $O_2 + N_2$		8.39
	gas flow 0.6 m^3/h	14.6; 25.8	
	gas flow 0.8 m^3/h	14.6; 20.2	
	29% $O_2 + N_2$		7.24
	gas flow 0.6 m^3/h	13.9; 31.2; 39.9	
	gas flow 0.8 m^3/h	13.9; 23.6	
1.15	air		10.94
	25% $O_2 + N_2$		9.19
	gas flow 0.6 m^3/h	11.6; 21.9	
	29% $O_2 + N_2$		7.93
	gas flow 0.6 m^3/h	9.4; 25.2; 33.1	
1.25	air		11.90
	25% $O_2 + N_2$		9.99
	gas flow 0.4 m^3/h	9.2; 18.6; 32.7	
	gas flow 0.6 m^3/h	9.2; 18.6	
	gas flow 0.8 m^3/h	9.2; 13.9	
	29% $O_2 + N_2$		8.61
	gas flow 0.4 m^3/h	5.6; 19.8; 38.3	
	gas flow 0.6 m^3/h	5.6; 20.1; 27.4	
	gas flow 0.8 m^3/h	5.6; 13.8; 19.8	

In order to properly interpret the results, the knowledge about the impact of the place of measurements on the results is useful. The dependence of measurement results on the location is illustrated in Figures 1–4.

Figures 1 and 2 show the results of measuring the temperature along the axis of the chamber – depending on the percentage of O_2 (Fig. 1 for the gas flow 0.6 m^3/h and $\lambda = 1.05$) and depending on the gas flow (Fig. 2 for 29% O_2 and $\lambda = 1.25$). In neither of the above cases did the mixture contain CO_2. Figure 3 compares the change of the concentrations of CO and NO_x along the axis of the furnace for a mixture containing 25% oxygen and about 9% CO_2 at $\lambda = 1.25$ and a different flow of gas.

As one can see, the NO_x concentration is stabilized already at a short distance from the flame, regardless of flow speed of gases, while CO concentration shows a significant decrease along the chamber. This means that the measurements of CO are burdened with greater instability than the measurements of NO_x.

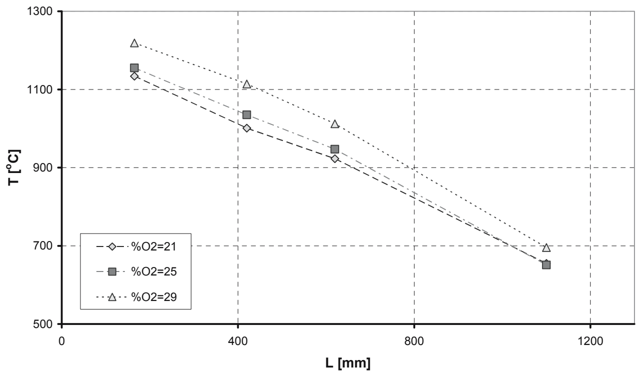

Fig. 1. Temperature drop along the axis of the chamber for different concentrations of oxygen (gas flow = 0.6 m³/h and λ = 1.05)

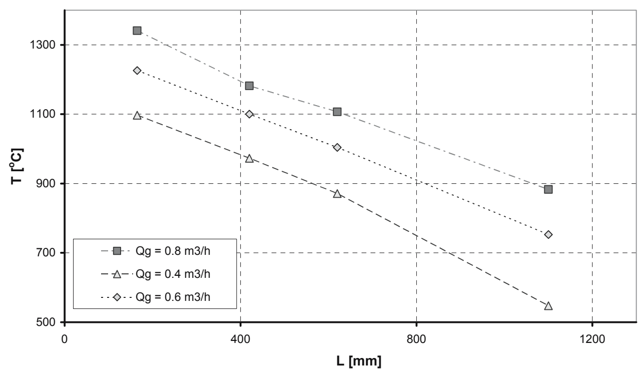

Fig. 2. Temperature drop along the axis of the chamber for different gas flows ($\%O_2$ = 29 and λ = 1.25)

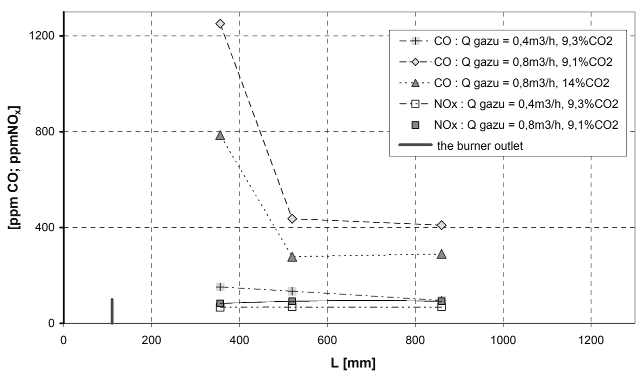

Fig. 3. Variation of CO and NO_x concentrations along the axis of the chamber for different gas flows ($\%O_2$ = 25 and λ = 1.25)

It is also an important piece of information of how the CO and NO_x concentrations vary on a cross section of the chamber. For this purpose, the measurements in the burner axis and near the chamber wall were performed, just in the distance of 86 cm (75 cm from the burner) for two series of measurements – $\%O_2 = 25$ and 29, $\lambda = 1.15$, the gas flow of 0.6 m³/h. The NO_x concentration at the wall turned out to be almost the same as in the axis, while the CO concentration showed large variability. The results for CO are shown in Figure 4.

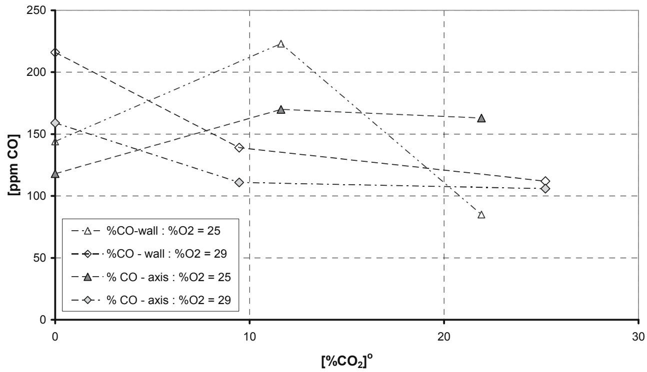

Fig. 4. Variation of CO concentration on a cross section of the chamber ($\lambda = 1.15$, gas flow 0.6 m³/h)

The results obtained from the main studies on the influence of oxygen concentration and carbon dioxide concentration on the concentration of CO and NO_x are summarized in Figures 5–6 (combustion without CO_2) and 7–11 (with CO_2 addition).

As shown in Figures 5 and 6, it cannot be categorically stated that burning in air enriched with oxygen causes an increase in the concentration of CO in the exhaust gases. The concentration of CO decreases, increases or remains almost constant, and what has the biggest influence on this behavior is the gas flow. Taking into account the fact that the concentration of CO, after leaving the flame, is still high, and then it falls for the length of the chamber (as presented in Fig. 3), an increase of the concentration obtained in CO between 21% and 29% O_2 (Fig. 6) for the largest flow of natural gas can be interpreted as an effect of too short residence time in the post-flame zone so that the final burning of the oxide is sufficient. However, in contrast to CO, the NO_x concentration shows a steady but significant increase when the oxygen concentration increases.

The effect of the presence of CO_2 in the oxidation mixture on the concentration of CO and NO_x in the exhaust gases is illustrated in Figures 7–11. The results of CO and NO_x concentrations as an effect of CO_2 addition were compared in Figure 7 for 25% O_2 and in Figure 8 for 29% O_2 for various ratios of λ when the gas flow is of 0.6 m³/h. The same results are presented in Figure 9 ($\lambda = 1.15$) and in Figure 10 ($\lambda = 1.25$) to compare the concentrations of 25% O_2 and 29% O_2.

As one can see, in each of the studied cases, the increase in CO_2 concentration had a significant influence on lowering the concentrations of NO_x, which is not the main point of the subject-matter of this paper but it is only a reference. The influence of CO_2

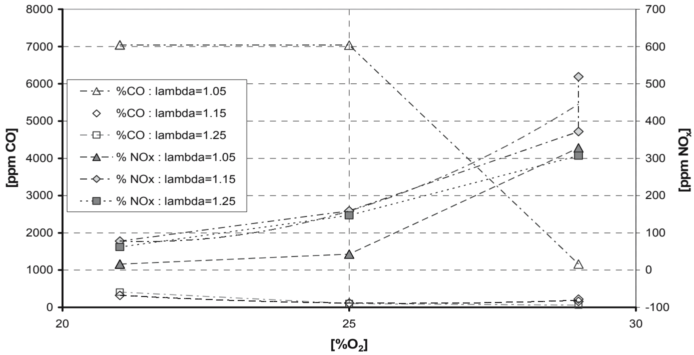

Fig. 5. Effect of oxygen concentration on CO and NO contents for different λ (gas flow of 0.6 m^3/h)

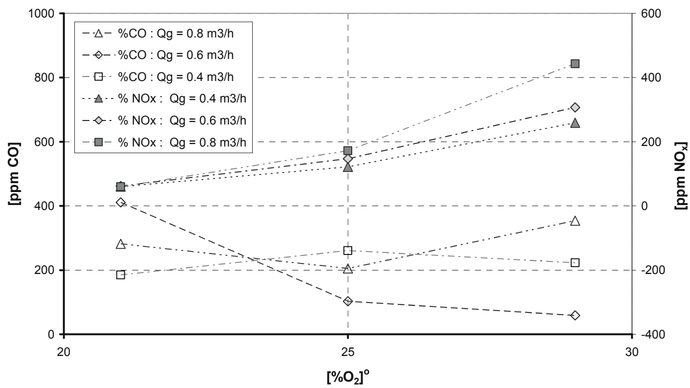

Fig. 6. Effect of oxygen concentration on CO and NO contents for different gas flows (λ=1.25)

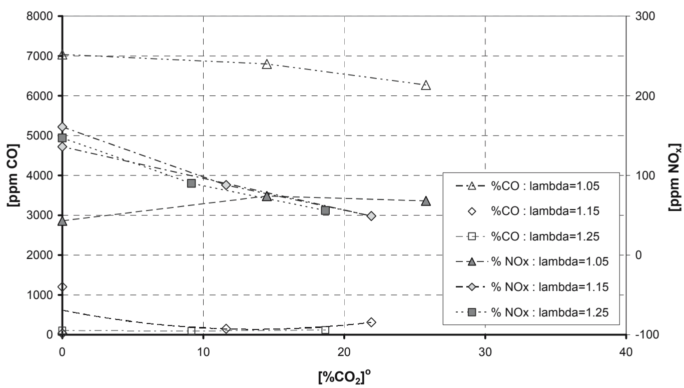

Fig. 7. Effect of CO_2 addition on CO and NO concentrations for 25% O_2 and different λ (gas flow 0.6 m^3/h)

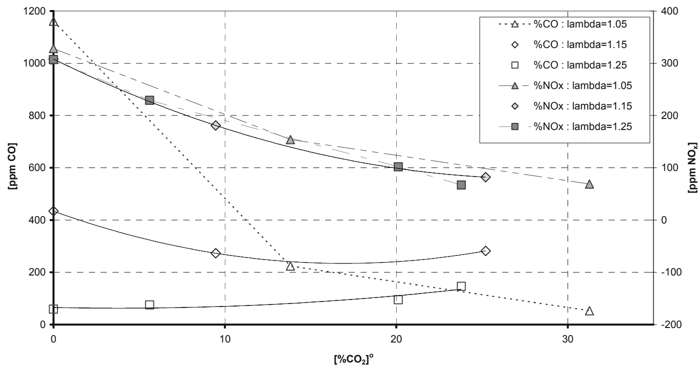

Fig. 8. Effect of CO_2 addition on CO and NO concentrations for 29% O_2 and different λ (gas flow 0.6 m^3/h)

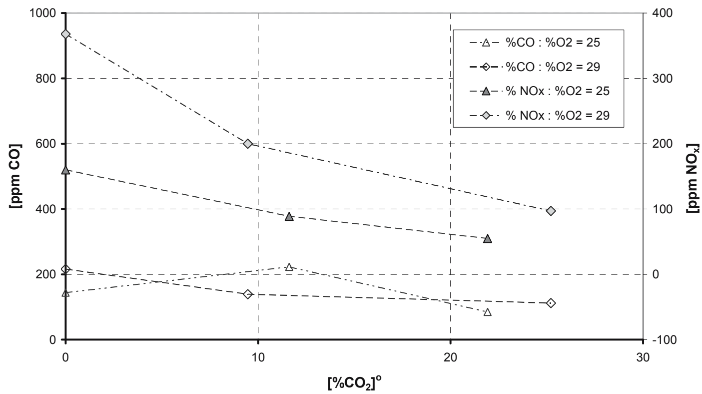

Fig. 9. Effect of CO_2 addition on CO and NO concentrations for different O_2 contents (λ = 1.15, gas flow 0.6 m^3/h)

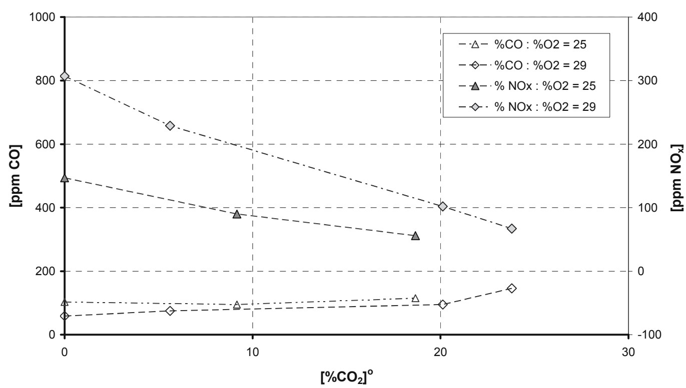

Fig. 10. Effect of CO_2 addition on CO and NO concentration for different O_2 contents (λ = 1.25, gas flow 0.6 m^3/h)

on the concentration of CO in combustion of methane is not so clear. There have been observed both a slight increase and decrease in CO caused by the addition of CO_2, but these changes are not big for the gas flow 0.6 m^3/h. So, the results for three gas flows were compared in Figure 11 for 29% O_2 where CO concentrations achieved with the largest flow are already high, but as before, they show variability which in such flow is even greater. It is difficult to assess surely how carbon dioxide affects the formation of CO while combusting methane.

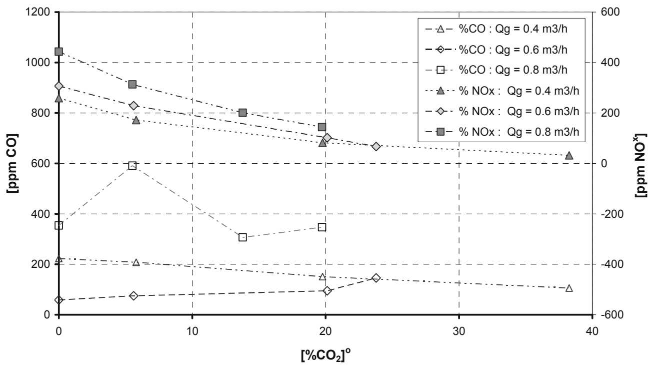

Fig. 11. Effect of CO_2 addition on CO and NO concentration for different gas flows (29% O_2, $\lambda = 1.25$)

NUMERICAL CALCULATIONS

With the assistance of FactSage program, containing a module of gases combustion, there were performed the calculations of the composition of the equilibrium of the reaction system after combustion of pure methane in air enriched with oxygen and in a mixture of oxygen, carbon dioxide and nitrogen. Calculations were performed for stoichiometric ratio ($\lambda = 1$) in the temperature range of 1000–1400°C. The results are presented in Figures 12 and 13.

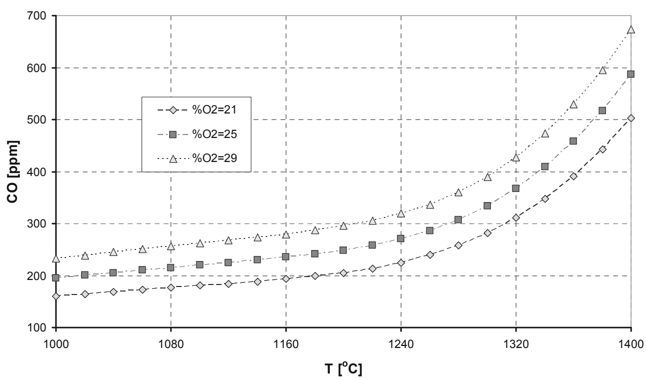

Fig. 12. Equilibrium concentration of CO depending on the temperature and oxygen concentration for stoichiometric combustion

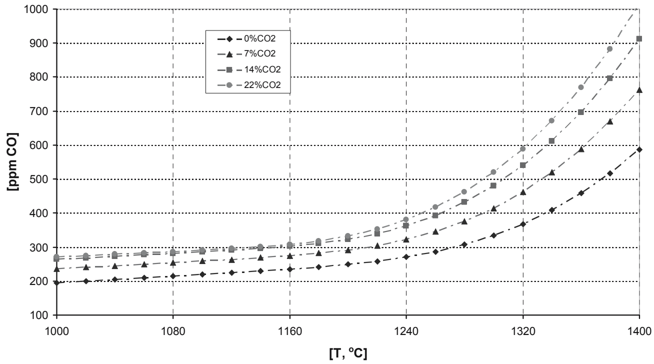

Fig. 13. Equilibrium concentration of CO depending on the temperature and CO_2 concentration in $25\%O_2/N_2/CO_2$ mixture for stoichiometric combustion

Figure 12 assesses the impact of increased oxygen concentration on CO emission as a function of combustion temperature. The increase of CO emission in air enriched with oxygen is visible. The results for 25% O_2 with 0; 7; 14 and 22% CO_2 (N_2 made up to 100%) are compared in Figure 13. A similar effect in CO concentration occurs when adding carbon dioxide, however, the greater the CO_2 addition is the smaller increase of CO emission is observed.

CONCLUDING REMARKS

When burning methane, the NO_x concentration stabilizes rapidly and shows no fluctuations during the measurements, while the concentration of CO is very diverse and the results of this analysis are subject to greater error.

While burning methane in air enriched with oxygen up to 29% the scatter of the concentrations of CO in the exhaust gases was observed, but there is no basis to state unequivocally that in the studied experiment the increase in oxygen concentration caused the increase of concentrations of CO in the exhaust gases. As a result of numerical calculations, the increase in CO concentration is obtained.

With the increase of CO_2 content in the oxidation mixture, the increased instability of measurements of concentration of CO was observed and because CO_2 lowers the burning speed, one may conclude that the CO measurement instability results from the increased concentrations of CO formed in the flame. In this case, in the numerical calculations there was obtained a growth of CO concentration but this effect was diminishing with the increase of CO_2 concentration.

The conclusions obtained with oxy-combustion (with recycled flue gas) of coal cannot be transferred directly to the combustion of methane, as the two reactions are differentiated primarily by the fact that combustion of coal is a heterogeneous reaction.

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WPŁYW SPALANIA GAZU ZIEMNEGO W MIESZANKACH 21–29% $O_2/CO_2/N_2$ NA EMISJĘ MONOTLENKU WĘGLA

Przeprowadzono spalanie gazu ziemnego w powietrzu wzbogaconym w tlen w ilości 25 i 29% z dodatkiem CO_2 w miejsce części azotu. Badania prowadzono przy różnych przepływach gazu i współczynnikach nadmiaru tlenu. Analizowano stężenie CO oraz NO_x. Nie stwierdzono, by zwiększone stężenie tlenu wpłynęło w sposób znaczący na stężenie CO. Natomiast dodatek CO_2 spowodował znaczną zmienność stężenia CO w spalinach, w przeciwieństwie do stężenia NO_x, które spadało monotonicznie. Obliczenia modelowe, przeprowadzone przy pomocy FactSage, wskazują na wzrost stężenia CO nie tylko dla powietrza wzbogaconego w tlen, ale także po dodaniu CO_2.