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ON CO AND NO_x EMISSION IN THE KINETIC COMBUSTION OF PROPANE/NATURAL GAS MIXTURES

Concentrations of CO and NO_x during combustion of propane/natural gas mixtures in air and in air enriched with oxygen have been investigated. The mixtures were: low-propane (up to 10 vol. %) and high-propane (up to 45 vol. %) types. A large effect of the propane content on the CO concentration in combustion gases was observed; stronger for the low-propane mixtures. The increase in the NO_x concentration with increasing propane content was lower and similar for the two types of mixtures.

1. INTRODUCTION

Research on the combustion processes of higher hydrocarbons such as propane, both experimentally and based on kinetic modeling, is not as extensive as in the case of methane. It includes ignition characteristics, chemical kinetics of flame combustion, normal combustion rate, emission of contaminant gases CO and NO_x, the tendency for sooting [1–5], processes of fluidized combustion, catalytic combustion and combustion with oxygen carriers, referred to as chemical looping combustion [6–10].

Not less important than the processes of clean gas fuel combustion are issues connected with the combustion of gas fuel mixtures. This refers especially to the effect of higher hydrocarbons such as ethane, propane and butane, present in natural gas, on the combustion of methane. From the point of view kinetics of chemical reaction, natural gas combustion is a difficult issue. Natural gas is a basic fuel with an industrial application, as opposed to methane. In recent years, there has been more and more experimental research on the effect of other hydrocarbons present in natural gas on such aspects as ignition, gas and soot contaminant emission.

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It is known that a trace presence of ethane and propane has a strong effect on ignition and methane oxidation [11, 12]. Ethane and propane oxidize more easily, and the formed intermediate products and radicals such as OH, H and O, begin to react with methane. That is why methane oxidization in their presence is initiated at a lower temperature than in the case of pure methane. Without those alkanes, methane oxidization begins with thermal dissociation and a reaction with oxygen particles, which require higher temperature. Promoting methane oxidization with higher alkanes is strongly dependent on their concentration but is revealed already in the case of small amounts.

The effect of propane on sooting in diffusion flames during the combustion of propane mixtures with methane, ethane and ethene has been investigated [13]. A synergistic effect in the propane/ethene mixtures was observed. The sooting per fuel mixture unit was higher than that in the case of a separate combustion of those two fuels. In the experiments involving a constant temperature of the flame, the synergistic effect for this mixture did not depend on temperature. No synergistic effect was observed in the case of mixtures of methane and propane or of propane and ethane.

Tests were also conducted on the effect of low amounts of propane in the mixture with methane on catalytic combustion, with respect to the effect of propane on the catalyst life [14]. This issue is significant because of the industrial application of catalytic combustion of natural gas.

2. EXPERIMENTAL

The combustion using kinetic burners of propane/natural gas mixture in air and in air enriched with 25 and 27 vol. % of oxygen and with an addition of CO_2 was studied. The mixture was composed of high-methane city gas and propane from a cylinder. The fuels were fed into a burner separately and mixed there. The natural gas was composed of 97.8 vol. % of CH_4 and 1 vol. % of ethane, propane and butane together. The purity of propane was 99.99%. When the combustion was carried out in a modified atmosphere, air, oxygen and CO_2 were supplied into a gas mixer before feeding the burner.

The inner dimensions of the combustion chamber were: length – 120 cm and diameter – 16 cm. The chamber walls were covered with ceramic fibre16 cm thick. The cross section of the chamber is shown in Fig. 1. The flame temperature was measured at point 4. The species concentrations and the temperature of the combustion gas were measured at points 5, 6a, 6b, located axially at various distances from the burner. Temperature was measured with thermocouples, for determining the concentration of combustion gas components a Lancom Series II analyser was used. The concentrations refer to dry combustion gas.

Combustion of two types of fuel mixtures was examined:

- high propane mixtures (type I): 0.4 m^3/h stream of natural gas with 12.5–45 vol. % of propane burned in air,

- low propane mixtures (type II): 0.6 m^3/h stream of natural gas with up to 10 vol. % of propane burned in air and in air enriched with oxygen with addition of CO_2.

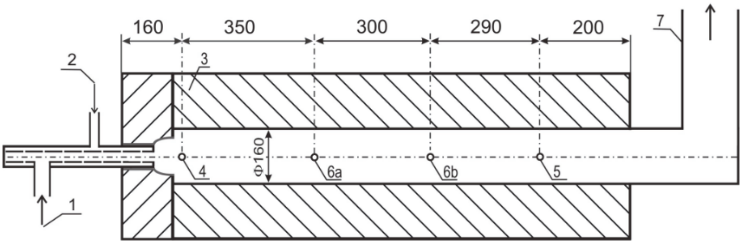

Fig. 1. Chamber cross section: 1, 2 – inlets to burner of fuel and oxidizing mixture, 3 –insulation, 4 – flame temperature measurement, 5 – main port for measurement of composition of combustion gas , 6a, b – additional measurement ports, 7 – outlet of flue gas

The burned mixtures were lean ($\phi < 1$)[2]. The fuel mixtures and the combustion conditions are summarized in Table 1.

Table 1

Experimental conditions for the combustion studies

No.	Natural gas–propane mixture			Oxidizing mixture	Equivalence ratio ϕ
	Fuel stream [m^3/h]		C_3H_8 [vol. %]		
	CH_4	C_3H_8			
Type I. High-propane mixtures					
1	0.35	0.05	12.5	air	0.625–0.83
2	0.30	0.10	25		
3	0.25	0.15	37.5		
4	0.22	0.18	45		
5	–	0.18	100		
6	–	0.30	100		
Type II. Low-propane mixtures					
7	0.60	–		a) air + 0–4% of CO_2 b) 25% of O_2 + air + 0–20% of CO_2 c) 27% of O_2 + air + 0–20% of CO_2	0.71–0.91
8		0.012	2		
9		0.038	6		
10		0.067	10		

The burners for the combustion of the two types of fuel mixtures had different nozzle diameters, because propane requires 2.5 times more air for combustion than

[2]The fuel-air equivalence ratio, ϕ, is the ratio of the actual fuel-to-oxidizer ratio to the stoichiometric fuel-to-oxidizer ratio).

methane. The burner used for the type I mixture of a high propane content had a smaller nozzle diameter, in order to shorten the flame.

3. RESULTS

3.1. MIXTURES WITH HIGH CONTENTS OF PROPANE

0.4 m^3/h streams of type I mixtures (Table 1) which contained 12.5, 25, 37.5 and 45 vol. % of propane were burned in air, with the range of equivalence ratio ϕ of 0.625–0.83. For comparison, the combustion of 0.18 and 0.3 m^3/h streams of pure propane was also studied.

The first port (4 in Fig.1) for measuring the flame zone temperature was shifted a little from the chamber axis, to minimize the perturbation of the flame by the thermocouple. Further measurements were performed in the axis of the chamber at the distances of 51, 81 and 120 cm from the wall of the chamber (ports 6a, 6b and 5 in Fig. 1).

Figure 2 presents the temperature along the chamber axis during the combustion of natural gas with 12.5 and 45 vol. % of propane.

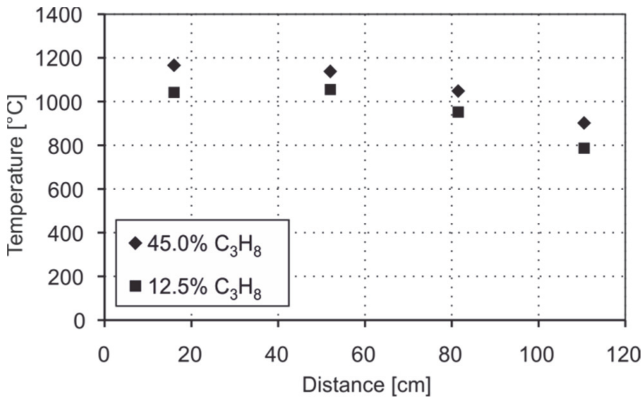

Fig. 2. Temperature along the axis of the chamber during combustion of propane/ natural gas mixture in air; 0.4 m^3/h stream for ϕ = 0.67

CO concentrations along the axis of the chamber are presented in Figs. 3–6, and those for NO_x in Figs. 7–10. Figures 3 and 4 show the effect of propane content in the mixtures on CO concentration for ϕ = 0.77 (Fig. 3) and ϕ = 0.71 (Fig. 4). In Figure 4, the results for the combustion of pure propane at 0.18 m^3/h (which equals the propane part in the stream of mixture No. 4 in Table 1) and 0.3 m^3/h (lower than the stream of the studied mixtures) are also shown.

The experimental data presented in Figs. 3 and 4 show that the CO concentration in the combustion gas increases with the enrichment of the fuel mixture in propane.

The combustion of pure propane of 0.3 m^3/h stream emits CO of a higher concentration than that emitted by the combustion of mixtures of 0.4 m^3/h streams.

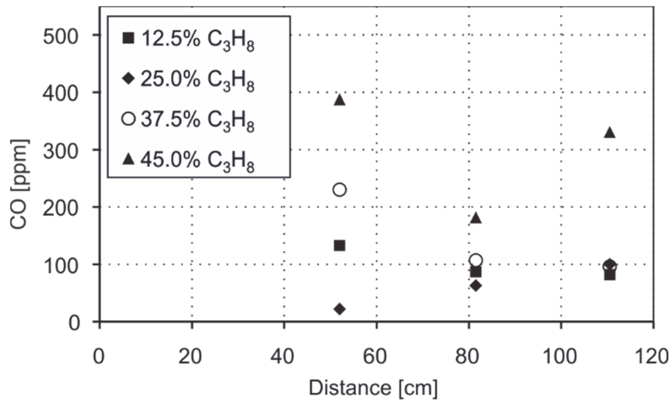

Fig. 3. CO concentration along the chamber axis for various propane contents in propane/natural gas mixture burned in air for $\phi = 0.77$, 0.4 m^3/h stream

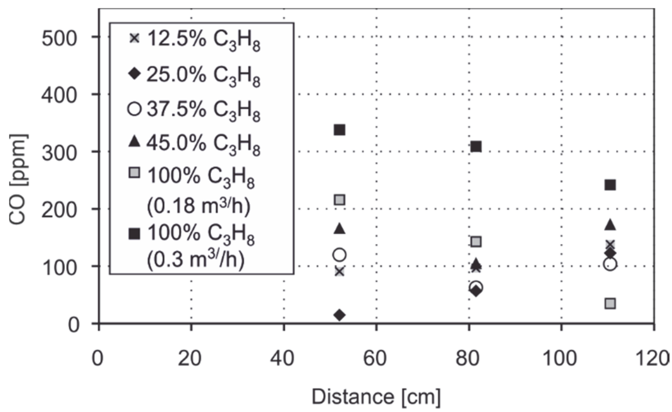

Fig. 4. CO concentration along the chamber axis for various propane contents in propane/natural gas mixture burned in air for $\phi = 0.71$, 0.4 m^3/h stream as well as for pure propane 0.18 m^3/h and 0.3 m^3/h streams

The effects of the equivalence ratio ϕ on the CO concentration in the combustion of the mixture with 12.5 vol. % and 45 vol. % of propane are shown in Figs. 5 and 6, respectively. In the ϕ range of 0.67–0.77, the CO concentrations at a 51 cm distance did not exceed 150 ppm for the mixtures with 12.5 vol. % of propane, but reach nearly 400 ppm for the mixtures with 45 vol. % of propane. The decrease of the equivalence ratio ϕ (increasing the excess air) caused a decrease in the CO concentration in the combustion gas. The effect is stronger when the propane content in the mixture is higher.

The CO concentration in combustion gases shows a high variability along the furnace axis (Figs. 3–6). This can result from, e.g. an increase in the propane content in the mixture which causes an increase of the volume of the air needed for combustion, as propane uses 2.5 times more air than methane. The increase of the air stream changes the aerodynamic conditions in the chamber. This may cause instability of the CO concentration in the chamber axis. Another reason can be a change in the propane content in the mixture, causing a change in the flame length. The combustion gas uptake points for the analysis change their location with respect to the flame front, which significantly affects the CO concentration.

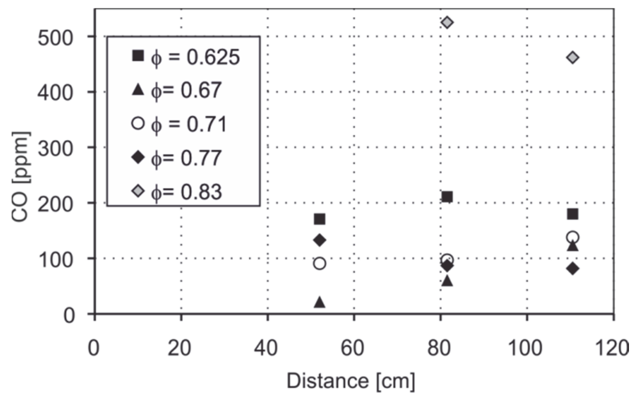

Fig. 5. CO concentration along the chamber axis for various ϕ during combustion of propane (12.5 vol. %)/natural gas mixture in air

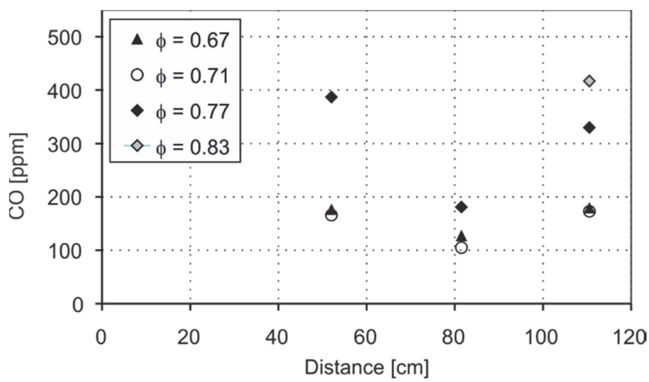

Fig. 6. CO concentration along the chamber axis for various ϕ during combustion of propane (45 vol. %)/natural gas mixture in air

Despite CO concentrations demonstrating a high variability along the chamber axis, one can conclude that the increase of the propane content in the mixture results in an increase of the CO concentration in the combustion gas.

The NO_x concentrations, measured at three locations along the axis of the combustion chamber, are presented in the subsequent figures. As the concentration of the NO_2 species did not exceed 1–3 ppm, the symbol NO, instead of NO_x, is used in these figures.

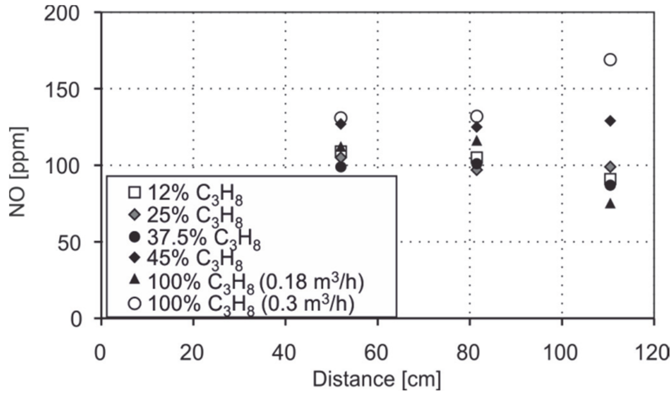

Fig. 7. NO concentration along the chamber axis for various propane contents in the propane/natural gas mixture burned in air for $\phi = 0.71$, 0.4 m^3/h stream, as well as for combustion of pure propane, 0.18 m^3/h and 0.3 m^3/h streams

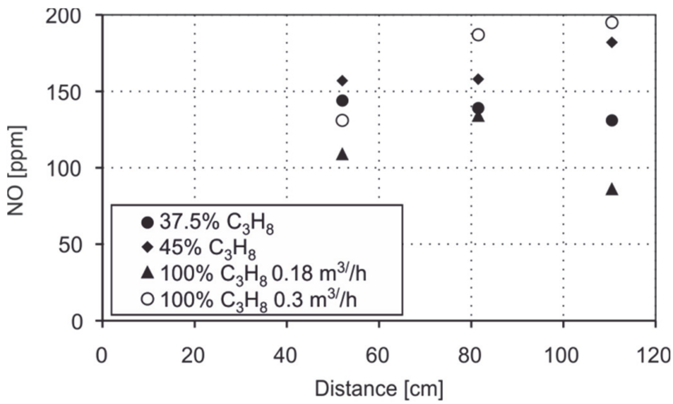

Fig. 8. NO concentration along the chamber axis for various propane contents in propane/natural gas mixture burned in air for $\phi = 0.83$, 0.4 m^3/h stream, as well as for combustion of pure propane, 0.18 m^3/h and 0.3 m^3/h streams

The effect of propane content on the NO_x concentration is shown in Figs. 7 and 8, for ϕ equal to 0.71 and 0.83, respectively. In both figures, the results are also shown for the combustion of pure propane of 0.18 m^3/h and 0.3 m^3/h streams. The effect of the equivalence ratio ϕ on the NO_x concentration for the mixtures with 12.5 and 45 vol. % of propane is shown in Figs. 9 and 10. The results shown in Fig 7 for $\phi = 0.71$ indicate that the NO_x concentrations for the mixtures of propane contents from 12.5% to 37.5% are very close – they are in the range of 95–105 ppm at the distance of 81 cm. The NO_x concentration for the mixture of 45% of propane is clearly higher, at about 125 ppm. The corresponding combustion temperatures, measured at port 4 in Fig. 1, were: 1055 –1090 °C for 12.5–37.5% and 1200 °C for 45%. The NO_x concentration during the combustion of pure propane of 0.3 m^3/h stream, shown in Fig.7, is the highest – it is equal to ca. 135 ppm at 1217 °C. For propane of a very low stream of 0.18 m^3/h at 1130 °C, the measured concentration of NO_x revealed a high degree of variability. Nevertheless, the results were always below those for the mixture of 45% of propane (0.4 m^3/h stream of that mixture is composed of 0.18 m^3/h of propane). For the mixtures burned with $\phi = 0.83$, the NO_x concentrations are higher by ca. 30–40 ppm. For the distance of 81 cm, they are: 155 ppm for the mixture of 45% of propane (1245 °C) and 186 ppm for the propane of 0.3 m^3/h stream (1200 °C).

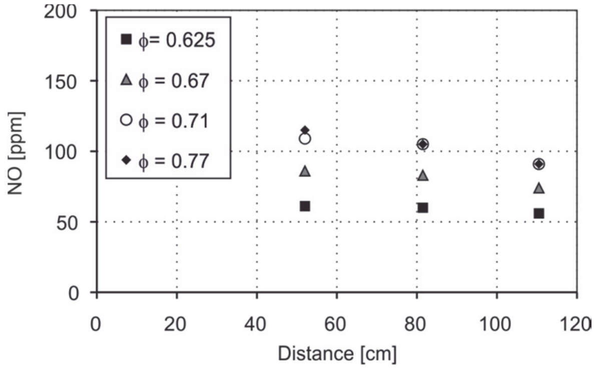

Fig. 9. NO concentration along the chamber axis for various ϕ during combustion of propane (12.5 vol. %)/natural gas mixture in air

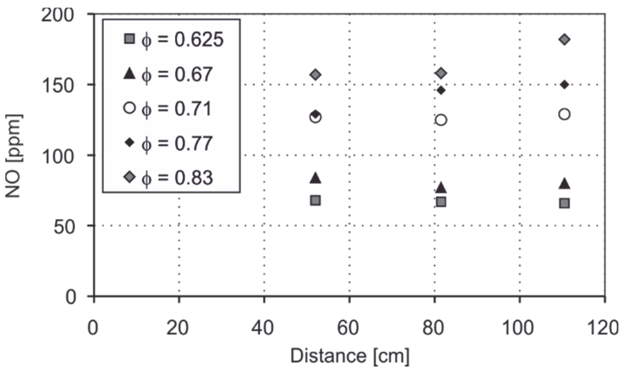

Fig. 10. NO concentration along the chamber axis for various ϕ during combustion of propane (45 vol. %)/natural gas mixture in air

With an increase of ϕ from 0.625 to 0.77 (Figs. 9, 10), the concentrations of NO_x measured at the distance of 81 cm are in the range of 60–106 ppm for 12.5% of propane (combustion temperature of ca. 1040–1070 °C) and of 68–146 ppm for 45% of propane (combustion temperature of ca. 1150–1220 °C).

The results presented in Figs. 7–10 indicate that an increase of the propane content in the mixture causes a little increase in the NO_x concentration. It cannot, however, be deduced if this increase results from the thermal (dependent on temperature) or prompt (dependent on the radicals arising from the fuel) mechanisms of formation of the NO_x oxides.

3.2. MIXTURES WITH LOW CONTENTS OF PROPANE

In natural gas of 0.6 m^3/h stream with a small addition of propane burned in air and air enriched with oxygen the propane concentration in the mixture was in the range of 1–10 vol. % (type II mixture in Table 1). The air enriched with oxygen contained 25 and 27 vol. % of O_2 and up to 20 vol. % of CO_2. The concentrations of species in combustion gas were measured at port 5 of the chamber (Fig. 1).

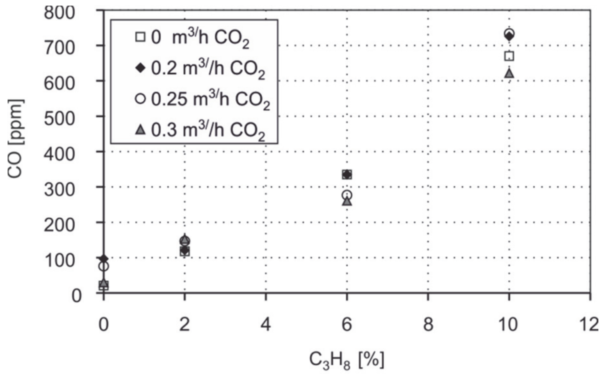

Fig. 11. Effect of propane content on CO concentration during combustion of propane/natural gas mixture, 0.6 m^3/h stream, with some addition of CO_2 for $\phi = 0.83$

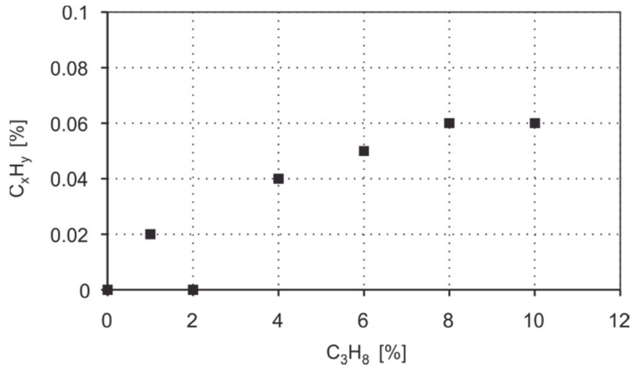

Fig. 12. Effect of propane content on concentration of unburned hydrocarbons during combustion of propane/natural gas mixture, 0.6 m^3/h stream, with no addition of CO_2 for $\phi = 0.83$

The effect of the propane content (2, 6, 10 vol. %) in the fuel mixture on the CO concentration during combustion in air, for $\phi = 0.83$, is presented in Fig. 11. The air was supplemented with the addition of CO_2, stream 0.2, 0.25 and 0.3 m^3/h. The effect of the CO_2 addition is not clear – the changes in the CO concentration seem rather to be due to the variations in the combustion gas content, typically observed for CO. All the results strongly indicate that the increase in CO concentration is caused by the increase of the propane content in the mixture. The concentration of CO increases from 100–150 ppm, for a 2% of propane mixture, to 600–700 ppm for 10% of propane. Figure 12 demonstrates the effect of propane in the mixture combusted in air (without CO_2 addition) for the same value of ϕ, on the unburned hydrocarbon concentration in the combustion gas, generally C_xH_y. As can be seen, together with the increase in the propane content, the hydrocarbon concentration in the combustion gas also increases.

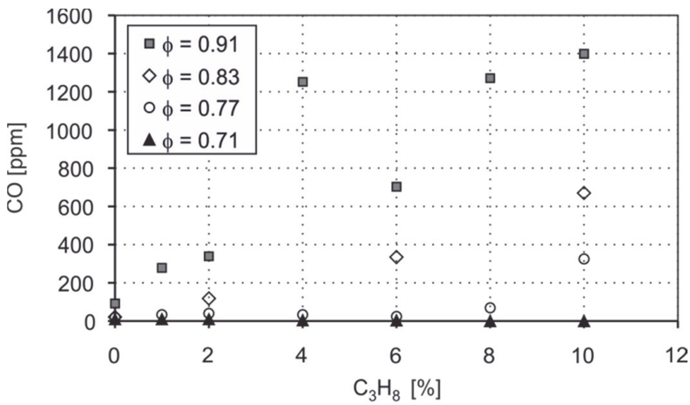

Fig. 13. Effect of propane content on CO concentration during combustion of propane/natural gas mixture in air, 0.6 m^3/h stream for $\phi = (0.71–0.91)$

Figure 13 shows the effect of the propane content on the CO concentration in the combustion gas for equivalence ratio ϕ in the range of 0.71–0.91. Despite the fluctuations in the CO concentration observed for $\phi = 0.91$, it can be seen that the increase of the propane content causes an increase in the CO concentration. The effect is very strong for the nearly stoichiometric mixture ($\phi = 0.91$). With the decrease of ϕ (increasing the excess air), it is obvious that the effect fades, for example for $\phi = 0.71$, the CO concentration is very low for the whole range of propane contents.

It is interesting to compare the effect of propane concentration in low-propane (type II) and high-propane (type I) mixtures on the increase of the CO concentration during combustion in air. An increase of the propane content by about 8% causes a much greater increase in the CO concentration in the case of the low-propane mixture (Fig. 13, cf. the increase from 2% to 10% of propane, for $\phi = 0.77$) than for a high-propane mixture (Fig. 3, cf. the increase from 37.5% to 45% of propane, for $\phi = 0.77$).

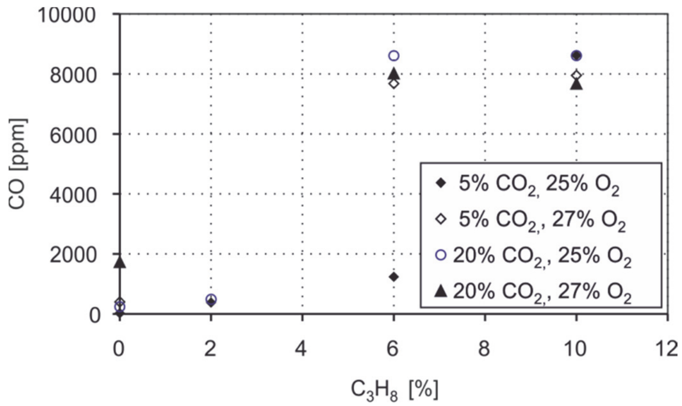

Fig. 14. Effect of propane content on CO concentration during combustion of propane/natural gas mixture, 0.6 m^3/h stream, enriched with oxygen and carbon dioxide added for $\phi = 0.91$

Effect of propane content on CO concentration during combustion of propane/natural gas mixture, 0.6 m^3/h stream, enriched with oxygen and carbon dioxide added for $\phi = 0.91$ is shown in Fig. 14. Combustion in air enriched with oxygen increases the CO concentration in the combustion gas, compared with combustion in air, more in the case of mixtures of 6 and 10 vol. % of propane than for combustion of natural gas alone. A 20% addition of CO_2 significantly further increases the CO concentration. In this case, the increase of the oxygen concentration from 25% to 27% seems not to have any strong effect on the concentration of CO, although, due to the very broad range of CO concentrations in Fig. 14, this conclusion is only approximate.

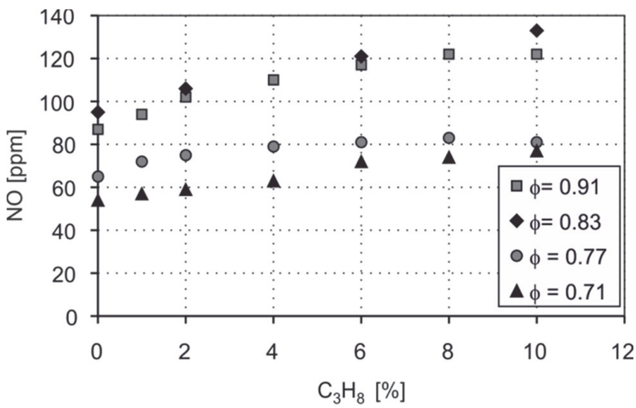

Fig. 15. Effect of propane content on NO_x concentration during combustion of propane/natural gas mixture, 0.6 m^3/h stream for $\phi = (0.71–0.91)$

The dependence of the NO_x concentration on propane content in the mixture with natural gas is presented in Figs. 15–17. In Figure 15, the results for the combustion in air, for the equivalence ratio ϕ in the range of 0.71–0.91, are shown. NO_x concentrations in the combustion gas increase in a moderate way with the increase of the propane contents in the mixtures. For ϕ = (0.91–0.83), the NO_x concentration during the combustion of the mixture of 10 vol. % of propane (combustion temperature 1170–1200 °C) is higher by about 35–40 ppm, compared to the case of natural gas (combustion temperature 1110–1140 °C). When ϕ = 0.77 and 0.71, the appropriate difference is lower and equals 15–20 ppm only. For all the mixtures, high concentrations of NO_x were obtained for ϕ = 0.83; only a little lower for ϕ = 0.91.

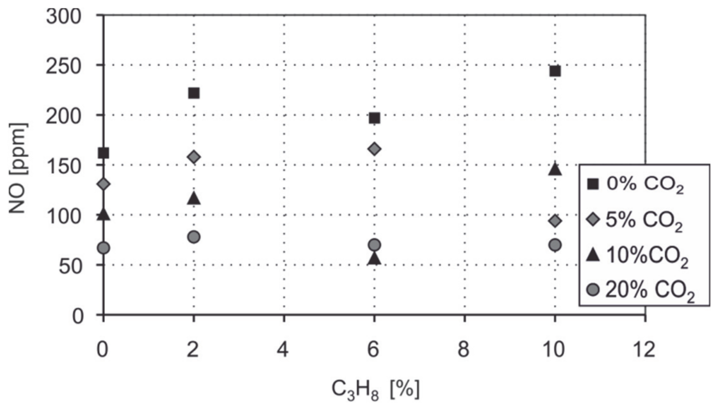

Fig. 16. Effect of propane content on NO_x concentration during combustion of propane/natural gas mixture, 0.6 m^3/h stream, in air enriched with oxygen (25%) and carbon dioxide added for ϕ = 0.91

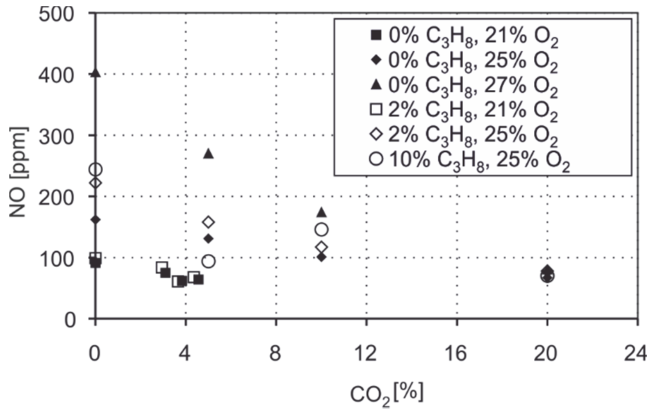

Fig. 17. Effect of fuel composition and oxygen concentration on NO_x concentration during combustion of propane/natural gas mixture in function of CO_2 content for ϕ = 0.91

The effect of the propane concentration in low-propane mixtures and high-propane mixtures on the NO_x concentration during combustion in air can be evaluated by comparing Fig. 15 with Fig. 7. An increase of the propane content by about 8% causes a lower increase of the NO_x concentration in the case of low-propane mixtures (comparison of the results for 2% and 10% of propane, for $\phi = 0.71$, Fig. 15), than for high-propane mixtures (comparison of results for 37.5% and 45% of propane, for $\phi = 0.71$, in Fig. 7). The opposite effect was observed in the case of the concentration of CO.

The combustion of mixtures with the content of 2, 6 and 10 vol. % of propane in the atmosphere with a higher oxygen concentrations, up to 25 vol. %, and an addition of CO_2 up to 20 vol. %, for $\phi = 0.91$, is presented in Fig. 16.

During the combustion in air enriched with oxygen, the concentrations of NO_x were characterized by high instability. An increase in oxygen concentration caused a significant increase of the NO_x concentration. When $\phi = 0.91$, the combustion of the mixture containing 6–10 vol. % of propane created a 200–250 ppm concentration of NO_x, when the air enriched with oxygen did not contain a CO_2 addition. The combustion temperatures then were 1195–1220 °C. When combustion took place in the atmospheric air (Fig. 15), the concentration of NO_x reached about 120 ppm. The addition of 10–20 vol. % of CO_2 lowered the NO_x concentration down to that for combustion in air. The comparison of the NO_x concentration results obtained for natural gas and the mixtures with propane burned in air with different contents of oxygen, as a function of the CO_2 addition, is presented in Fig. 17.

The NO_x concentration for natural gas and the mixtures with 2 and 10 vol. % of propane burned in the atmosphere are very sensitive to the CO_2 addition upon increasing O_2 concentration. In all the experiments, the NO_x concentration tends to reach a similar value when the CO_2 concentration increases up to 20 vol. %.

4. CONCLUSIONS

Addition of propane to natural gas increases CO concentration in the combustion gas within the combustion chamber. An increase of the CO concentration is observed even with only a slight content of propane in the mixture. A change in the propane concentration from 2 to 10 vol. % causes a greater increase of the CO concentration than a change from 37.5% to 45%.

The presence of propane in the mixture with natural gas has a slighter effect on the concentration of nitrogen oxides. The increase of the NO_x concentration together with the increase of the propane content in a mixture with natural gas is insignificant. Contrary to the case of CO, a slightly reduced increase of the NO_x concentration is observed in the case of increased propane content in low-propane mixtures than that in high-propane mixtures.

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