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Effect of the Oxidizer Composition on the CO and NO_x Emissions from a Laboratory Combustor Operating under Oxy-Fuel Conditions

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ABSTRACT: This article reports a parametric study on CO and NO_x emissions under oxy-fuel combustion conditions. The investigation was conducted in a laboratory combustor fired with methane, doped with NH₃ to simulate the fuel bound nitrogen present in many solid fuels. The results reported include flue gas composition data for various combustor operating conditions that allowed evaluating the influence of the oxidizer composition on CO and NO_x emissions and, also, of the concentration of NH₃ added to the fuel on NO_x emissions. The results revealed that (i) the impact of the oxidizer velocity on the CO and NO_x emissions is generally very small, suggesting that the flow aerodynamics, associated with the velocities considered in this study, plays a minor role on the establishment of the emissions, whose behavior can be mainly attributed to chemical and thermal effects; (ii) the CO emissions are significantly higher for the combustion in an oxidizer with 20.9% O₂/79.1% CO₂ than for the combustion in air, and, under oxy-fuel conditions, the CO emissions decrease as the O₂ concentration in the oxidizer increases, with the oxidizer composed of 35% O₂/65% CO₂ presenting levels of CO emissions similar to those obtained for the combustion in air; (iii) the addition of H₂O to the oxidizer originates no meaningful differences on CO emissions for any of the conditions analyzed; (iv) the oxidizer composition affects the NO_x emissions only for the highest NH₃ concentrations analyzed, where the NO_x levels are generally lower for the oxidizers that present lower CO₂ concentrations; and (v) under oxy-fuel conditions, the NH₃-to-NO_x conversion rates increase significantly with the increase in the O₂ concentration in the oxidizer, and the conversion rates in air and in a 20.9% O₂/79.1% CO₂ oxidizer are similar.

1. INTRODUCTION

Recent energy scenarios from international agencies^{1,2} predict that the consumption of fossil fuels will dominate the energy generation market in the next decades. Under these conditions, it is necessary to find technologies to reduce the CO₂ emissions to meet the targets set by the Kyoto Protocol. Among the most promising technologies, oxy-fuel combustion with flue gas recirculation emerges as one of the best options for carbon capture and storage. In this technology, the combustion of the fossil fuels takes place with pure oxygen, instead of atmospheric air, which, combined with flue gas recirculation, allows obtaining combustion products rich in CO₂ that greatly facilitates its capture.

This article investigates the CO and NO_x emissions during the oxy-fuel combustion of methane, doped with NH₃ to simulate the fuel bound nitrogen, in a laboratory combustor. Related studies centered on CO formation and emissions include those of Glarborg and Bentzen,³ Abián et al.,⁴ Amato et al.,⁵ Heil et al.,⁶ and Giménez-López et al.,⁷ among others, and on NO formation and NO_x emissions include those of Kim et al.,⁸ Andersson et al.,⁹ Normann et al.,¹⁰ Mendiara and Glarborg,¹¹ Giménez-López et al.,¹² Shaddix and Molina,¹³ Sun et al.,¹⁴ and Zhang et al.,¹⁵ among others.

On the CO formation/emissions side, Glarborg and Bentzen³ studied experimentally the chemical effects of high concentrations of CO₂ in the oxy-fuel combustion of methane in a plug flow reactor. The authors interpreted the results in terms of a detailed chemical kinetic mechanism for hydrocarbon oxidation and concluded that oxy-fuel combustion will lead to high levels of CO in the near burner zone. The CO₂ present competes with O₂ for atomic hydrogen (H) and leads to formation of CO through the reaction $\text{CO}_2 + \text{H} \rightleftharpoons \text{CO} +$

OH. They suggest that the high local CO levels may have implications for near burner corrosion and slagging, but they do not anticipate increased problems with CO emissions in oxy-fuel combustion. More recently, Heil et al.⁶ also investigated the importance of the chemical effects of high CO₂ concentrations in a methane-fired 25 kW furnace operating under flameless oxidation conditions. They found that, in O₂/N₂ atmospheres, the oxidizer O₂ concentration does not affect the CO production and oxidation rates, but in O₂/CO₂ atmospheres, an increase of the oxidizer O₂ concentration from 18% to 21% leads to a reduction of almost 2 times of the measured CO levels in the reaction zone, thus showing lower CO production rates. Abián et al.⁴ studied the impact of CO₂ and H₂O concentrations on the oxidation of CO in a plug flow reactor similar to that used by Glarborg and Bentzen.³ They also interpreted the experimental data in terms of detailed kinetic modeling. The authors concluded that, in general, the effect of adding CO₂ is to inhibit CO oxidation, this suppression being more pronounced for fuel-rich mixtures and low concentrations of CO₂. Additionally, they found that the addition of steam increases the conversion of CO to CO₂. Amato et al.⁵ analyzed experimentally and numerically the CO (and O₂) emissions from a swirl stabilized methane-fired laboratory combustor operating under oxy-fuel conditions. They concluded that CO emissions are higher in combustion with O₂ diluted with CO₂ than in combustion with air. Moreover, for a given residence time, the CO emissions from

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oxy-fuel combustion are higher because of the slow oxidation of the intermediate CO formed in the flame. Also, they found that CO emissions increase exponentially with the flame temperature and predicted that an increase in pressure would lower the emissions. Giménez-López et al.⁷ studied the effects of SO₂ on the oxidation of CO to CO₂ in atmospheres simulating oxy-fuel conditions in a plug flow reactor. They concluded that, for a given stoichiometry and temperature, the conversion of CO to CO₂ is always higher in atmospheres rich in N₂ than in atmospheres rich in CO₂, as in Glarborg and Bentzen.³ Giménez-López et al.⁷ also observed that the presence of SO₂ inhibits the oxidation of CO in both N₂- and CO₂-rich atmospheres for all stoichiometries studied.

On the NO formation/NO_x emissions side, Mendiara and Glarborg¹¹ studied experimentally the oxidation of NH₃ during the oxy-fuel combustion of methane in a plug flow reactor and interpreted the results in terms of a detailed chemical kinetic model. The results showed that a high CO₂ level enhanced NO formation under reducing conditions, whereas it inhibited NO under stoichiometric and lean conditions. According to the authors, the enhanced CO concentrations and alteration in the amount and partitioning of O/H radicals are responsible for the effect of a high CO₂ concentration on NH₃ conversion. Giménez-López et al.¹² investigated the oxidation of HCN in an O₂/CO₂ atmosphere in a plug flow reactor similar to that used by Mendiara and Glarborg¹¹ and also with the aid of a kinetic model. The authors concluded that the presence of high CO₂ concentration levels clearly inhibits HCN oxidation, since CO₂ competes with O₂ for atomic hydrogen through the CO₂ + H \rightleftharpoons CO + OH reaction, reducing the formation of chain carriers via O₂ + H \rightleftharpoons O + OH. The lower HCN burning rate observed in a CO₂ atmosphere is accompanied by a higher CO and HNCO formation and lower NO and N₂O concentrations compared to air combustion. Andersson et al.⁹ carried out an experimental and numerical study in a lignite-fired 100 kW furnace, designed for oxy-fuel combustion with flue gas recycling. They confirmed earlier findings that, during oxy-firing with gas recirculation, the amount of NO emitted per unit of energy supplied is reduced by 70–75% of the emissions at air firing. The modeling of the experimental results showed that the NO reduction is caused by an increased destruction of formed and recycled NO in oxy-fuel compared to air fuel conditions. Moreover, they observed that the conversion of fuel-N to NO is similar or even slightly higher during oxy-firing. Shaddix and Molina¹³ investigated the formation of NO during the oxy-fuel combustion of pulverized coals in a turbulent entrained flow reactor. The authors observed that the fuel-N conversion to NO_x increases significantly with increasing the bath oxygen concentration for both N₂ and CO₂ environments, though the conversion is generally lower in CO₂ environments. Sun et al.¹⁴ also examined the behavior of the fuel-N conversion to NO during the oxy-fuel combustion of pulverized coal in a laminar drop tube furnace. The results showed that fuel-N conversion to NO in O₂/CO₂ is lower than that in O₂/N₂, in accordance with the results of Shaddix and Molina.¹³

Despite the studies mentioned above, there is a lack of systematic experimental studies addressing simultaneously CO and NO_x emissions under oxy-fuel conditions. In this context, the main objective of this study is to evaluate the impact of the oxidizer composition on CO and NO_x emissions and, also, of the concentration of NH₃ added to the fuel on NO_x emissions from a methane-fired laboratory combustor operating under oxy-fuel conditions. The present combustor has been designed

to operate stably over a wide range of operating conditions¹⁶ so that this has allowed us to vary extensively the operating conditions, namely, the oxidizer composition.

2. MATERIALS AND METHODS

Figure 1 shows a schematic of the combustor used in this study. The combustion chamber is a quartz-glass cylinder with an inner diameter

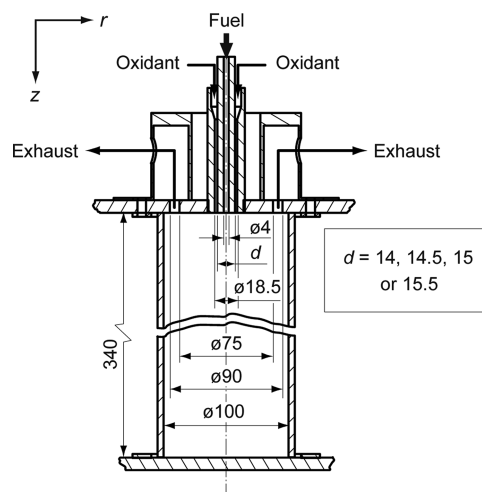


Figure 1. Schematic of the combustor.

of 100 mm and a length of 340 mm. During the tests, the quartz cylinder was insulated with a 30 mm thick ceramic fiber blanket. The burner and the exhaust port are mounted at the top end of the combustion chamber. The burner consists of a central orifice with an inner diameter of 4 mm, through which the fuel is supplied, surrounded by an annular orifice with a variable inner diameter ($d = 14, 14.5, 15,$ and 15.5 mm in this study) and an 18.5 mm outer diameter for the oxidizer supply. The exhaust consists of an annular orifice, concentric with the burner, with a 75 mm inner diameter and a 90 mm outer diameter. A stainless steel plate is used to close the bottom end of the combustion chamber. The oxidizer is preheated by an electrical heating system that allows inlet temperatures up to 700 °C, which are monitored by a type K thermocouple installed at the entrance of the burner.

Figure 2 shows a schematic of the fuel and oxidizer feeding systems. Methane and small amounts of NH₃, from gas cylinders, are fed to the

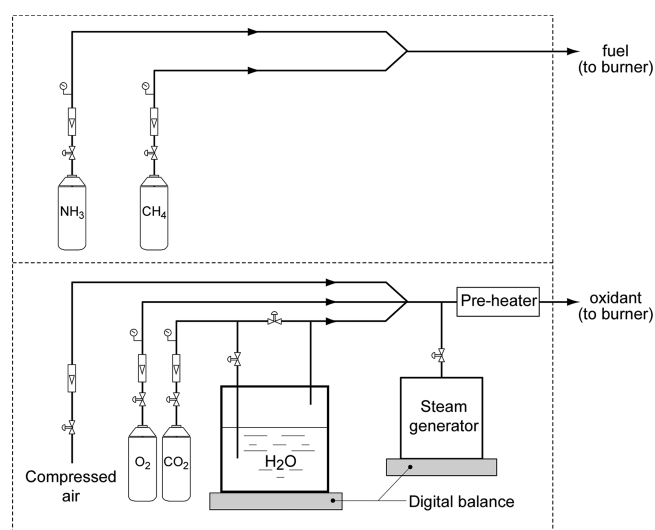


Figure 2. Schematic of the fuel and oxidizer feeding systems.

Table 1. Experimental Conditions^a

trial series number	$d(\text{mm})$	$\dot{m}_{\text{NH}_3}(\text{kg/s})$	oxidizer										flue gas (dry)				
			$\dot{m}_{\text{O}_2}(\text{kg/s})$	$x_{\text{O}_2}(\text{vol \%})$	$\dot{m}_{\text{CO}_2}(\text{kg/s})$	$x_{\text{CO}_2}(\text{vol \%})$	$\dot{m}_{\text{N}_2}(\text{kg/s})$	$x_{\text{N}_2}(\text{vol \%})$	$\dot{m}_{\text{H}_2\text{O}}(\text{kg/s})$	$x_{\text{H}_2\text{O}}(\text{vol \%})$	$v_{\text{ox}}(\text{m/s})$	$\text{Re}(-)$	$x_{\text{O}_2}(\text{vol \%})$	$x_{\text{CO}}(\text{vol ppm})$	$x_{\text{NO}}(\text{vol ppm})$	$T_{\text{ad}}(\text{K})$	
I	14	$0-2.5 \times 10^{-7}$	5.2×10^{-4}	20.9				1.7×10^{-03}	79.1			16.6	5084	2.1	27-31	134-429	2271
				35-29.3	1.3×10^{-3}	65-54.4	$0-1.6 \times 10^{-4}$	0-16.3	9.9	4575	3.8	47-62	0-553	2333-2214			
				30-25.7	1.7×10^{-3}	70-59.9	$0-1.7 \times 10^{-4}$	0-14.4	11.6	5483	3.2	50-66	0-578	2180-2056			
				25-21.9	2.2×10^{-3}	75-65.6	$0-1.7 \times 10^{-4}$	0-12.5	13.9	6754	2.6	55-66	0-626	2001-1886			
				20.9-18.6	2.7×10^{-3}	79.1-70.5	$0-1.9 \times 10^{-4}$	0-11.9	16.6	8251	2.1	59-83	0-475	1832-1722			
II	14.5	$0-2.5 \times 10^{-7}$	5.2×10^{-4}	20.9				1.7×10^{-3}	79.1			18.4	5007	2.1	26-29	138-437	2271
				35-29.3	1.3×10^{-3}	65-54.4	$0-1.6 \times 10^{-4}$	0-16.3	11.0	4506	3.8	43-57	0-675	2333-2214			
				30-25.7	1.7×10^{-3}	70-59.9	$0-1.7 \times 10^{-4}$	0-14.4	12.8	5400	3.2	46-59	0-633	2180-2056			
				25-21.9	2.2×10^{-3}	75-65.6	$0-1.7 \times 10^{-4}$	0-12.5	15.4	6652	2.6	54-74	0-569	2001-1886			
				20.9-18.6	2.7×10^{-3}	79.1-70.5	$0-1.9 \times 10^{-4}$	0-11.9	18.4	8126	2.1	56-84	0-513	1832-1722			
III	15	$0-2.5 \times 10^{-7}$	5.2×10^{-4}	20.9				1.7×10^{-3}	79.1			20.7	4933	2.1	26-30	121-432	2271
				35-29.3	1.3×10^{-3}	65-54.4	$0-1.6 \times 10^{-4}$	0-16.3	12.4	4438	3.8	46-56	0-717	2333-2214			
				30-25.7	1.7×10^{-3}	70-59.9	$0-1.7 \times 10^{-4}$	0-14.4	14.5	5319	3.2	49-58	0-614	2180-2056			
				25-21.9	2.2×10^{-3}	75-65.6	$0-1.7 \times 10^{-4}$	0-12.5	17.3	6553	2.6	53-65	0-601	2001-1886			
				20.9-18.6	2.7×10^{-3}	79.1-70.5	$0-1.9 \times 10^{-4}$	0-11.9	20.7	8004	2.1	61-78	0-481	1832-1722			
IV	15.5	$0-2.5 \times 10^{-7}$	5.2×10^{-4}	20.9				1.7×10^{-3}	79.1			23.8	4860	2.1	26-31	125-408	2271
				35-29.3	1.3×10^{-3}	65-54.4	$0-1.6 \times 10^{-4}$	0-16.3	14.2	4373	3.8	48-56	0-643	2333-2214			
				30-25.7	1.7×10^{-3}	70-59.9	$0-1.7 \times 10^{-4}$	0-14.4	16.6	5241	3.2	51-57	0-677	2180-2056			
				25-21.9	2.2×10^{-3}	75-65.6	$0-1.7 \times 10^{-4}$	0-12.5	19.9	6456	2.6	55-65	0-584	2001-1886			
				20.9-18.6	2.7×10^{-3}	79.1-70.5	$0-1.9 \times 10^{-4}$	0-11.9	23.8	7887	2.1	62-80	0-468	1832-1722			

^aFor all conditions: thermal input = 6 kW; $\dot{m}_{\text{fuel}} = 1.2 \times 10^{-4}$ kg/s; $v_{\text{fuel}} = 14.4$ m/s; $\text{Re}_{\text{fuel}} = 2813$; $T_{\text{ox}} = 500$ °C; $\lambda_{\text{O}_2} = 1.1$.

combustor as fuel. As for the oxidizer, air, from a compressor, or mixtures of O_2 and CO_2 , from gas cylinders, and H_2O are supplied to the combustor, as shown in Figure 2. The H_2O was supplied to the oxidizer stream either from a steam generator or by saturating the CO_2 stream through a bubbling water system at room temperature. The flow rates of methane, NH_3 , air, O_2 , and CO_2 were measured with calibrated rotameters, whereas the flow rate of H_2O was determined with the aid of digital balances.

Flue gas composition data were obtained using a stainless steel water-cooled probe placed at the combustor exhaust. The probe was composed of a central 1.3 mm inner diameter tube through which quenched samples were evacuated. This central tube was surrounded by two concentric tubes for probe cooling. The gas sample was drawn through the probe and part of the system by an oil-free diaphragm pump. A condenser removed the main particulate burden and condensate. A filter and a drier removed any residual particles and moisture so that a constant supply of clean dry combustion gases was delivered to the analyzers through a manifold to give species concentration on a dry basis. The analytical instrumentation included a magnetic pressure analyzer for O_2 measurements, a nondispersive infrared gas analyzer for CO_2 and CO measurements, a flame ionization detector for hydrocarbons (HC) measurements, and a chemiluminescent analyzer for NO_x measurements. At the combustor exhaust, probe effects were negligible and errors arose mainly from quenching of chemical reactions, which was found to be adequate. Repeatability of the flue-gas data was, on average, within 10% of the mean value.

3. TEST CONDITIONS

Table 1 presents the experimental conditions used in this investigation. Five oxidizer compositions, including air, were tested, with each oxidizer being injected through four different oxidizer diameters to evaluate the effect of the oxidizer velocity on CO and NO_x emissions. When performing NO_x emission measurements, the fuel (methane) was doped with small quantities of NH_3 (see Table 1) to simulate the fuel bound nitrogen present in many solid fuels, particularly in coal. The experimental conditions allowed us to evaluate the influence of the oxidizer composition on CO and NO_x emissions and, also, of the concentration of NH_3 added to the fuel on NO_x emissions. As seen in Table 1, the O_2 mass flow was kept constant throughout the tests, while the CO_2 and H_2O mass flow rates were varied in order to establish oxidizers with distinct compositions. Finally, note that the table includes the measured O_2 , CO , and NO_x dry concentrations in the flue gas and the calculated adiabatic flame temperatures (T_{ad}).

4. RESULTS AND DISCUSSION

4.1. Qualitative Description of the Flow Structure.

Before examining the combustion data, a qualitative description of the flow structure in the present combustor will be of use in understanding the discussion that follows. Figure 3 shows the

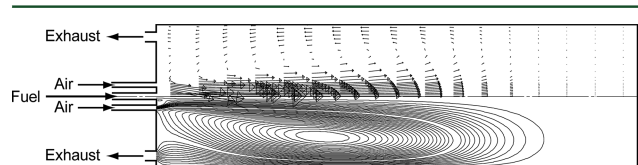


Figure 3. Predicted flow pattern for the first run in Table 1 (air combustion).

predicted flow pattern for the first run in Table 1 (air combustion), as predicted in a parallel mathematical modeling study.¹⁷ The figure shows the stream lines on the bottom side and the velocity vectors on the top side. The qualitative nature of the flow may be observed in these predictions. The flow is characterized by a large recirculation zone, around the central jet, that extends over a large part of the combustion chamber.

However, the velocities are quite small near the closed bottom of the combustor, where a quasi-stagnant region is present. The combustor configuration with the burner and the exhaust port mounted at the same end of the combustion chamber (Figure 1) causes a flow deceleration that promotes the stabilization process and enhances the mixing between the fresh reactants and the flue gas. Note that, according to the model predictions,¹⁷ the flow structure for all conditions studied is similar, including the central jet penetration into the combustion chamber, the mixing intensity, and the characteristic residence time.

In light of the discussion above, it may be supposed with reasonable justification that the effect of the flow structure/aerodynamics on changes in the pollutant emissions from this combustor for the present conditions will be reduced. Against this background, the variations in pollutant emissions observed in the present study (see below) are mainly attributed to chemical and thermal effects.

Figure 4 shows the appearance of the combustion process as viewed along the length of the combustion chamber for various

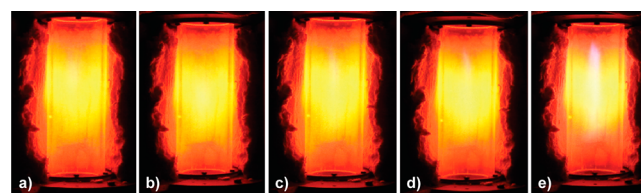


Figure 4. Typical appearance of the combustion process as viewed along the length of the combustion chamber for various oxidizers: (a) air; (b) 20.9% O_2 /79.1% CO_2 ; (c) 25% O_2 /75% CO_2 ; (d) 30% O_2 /70% CO_2 ; (e) 35% O_2 /65% CO_2 .

oxidizers. It is seen that the flame is hardly visible, which is a characteristic of the combustion under flameless conditions. The present reacting flows are characterized by a distributed reaction zone, located far from the burner, and relatively low spatial temperature and gas species concentration gradients.¹⁶ These features, which remain relatively unchanged for the range of oxidizer composition considered here, have also encouraged us to conduct this study in the present combustor.

4.2. CO Emissions. Figure 5 shows the CO emissions, expressed in ng/J , as a function of the oxidizer velocity for five

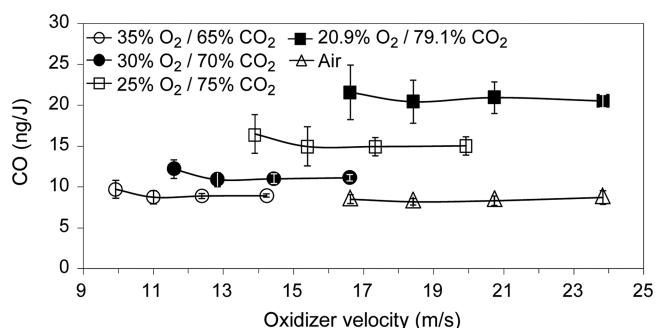


Figure 5. CO emissions as a function of the oxidizer velocity for five dry oxidizer compositions. The error bars are standard deviations.

dry oxidizer compositions. Each point in the figure represents the average value of a large number of measurements undertaken over 2 weeks, with the error bars giving a good idea about the quality of the present data. The figure reveals that, for a given

oxidizer composition, the oxidizer injection velocity has almost no effect on the CO emissions, except at the lowest oxidizer velocities where the CO emissions increase slightly. This independence indicates that the flow aerodynamics, associated with the velocities considered in this study, plays a minor role on the establishment of the CO emissions, as discussed in section 4.1.

Figure 5 reveals that the CO emissions are significantly higher for the combustion in an oxidizer with 20.9% O₂/79.1% CO₂ than for the combustion in air. Under oxy-fuel conditions, the CO emissions decrease as the O₂ concentration in the oxidizer increases, with the oxidizer composed of 35% O₂/65% CO₂ presenting levels of CO emissions similar to those obtained for the combustion in air.

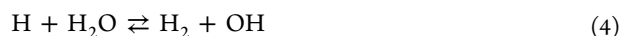
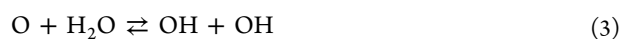
The presence of CO₂ in the oxidizer has an inhibiting effect in the fuel oxidation, which results from the competition between CO₂ and O₂ for H radicals, as expressed by the following reactions:^{3,7}



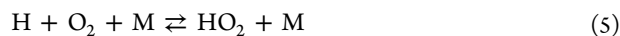
The importance of reaction 1 increases in the presence of large quantities of CO₂, and so the consumption of H radicals will also increase. The lower availability of atomic hydrogen diminishes the formation of chain carrier radicals, OH, through reaction 2, and thereby reduces the CO burning rate by the reverse reaction of 1,⁷ which explains the observed trends in Figure 5. It is important to note that the present results are generally consistent with those available in the literature for plug flow reactors (see, for example, Giménez-López et al.⁷) and for laboratory combustors (see, for example, Amato et al.⁵).

Figure 6 shows the CO emissions as a function of the oxidizer velocity for various wet oxidizer compositions. Given the magnitude of the error bars, it is evident from Figure 6 that the addition of H₂O to the oxidizer originates no meaningful differences on CO emissions for any of the conditions analyzed.

Following Abián et al.,⁴ the H₂O mainly participates in three reactions: directly, by interacting with O and H radicals, through reactions



and by acting as a very efficient collision partner in the following reaction:



Reaction 5 competes with reaction 2 for H radicals, which largely determines the oxidation regime of CO. Reaction 4 is only important in the absence of CO₂, and, thus, has little or no significance here. H₂O has a high efficiency as the third body in reaction 5, but there is still much uncertainty about this reaction.

The addition of H₂O to the oxidizer obviously moves reaction 3 in the forward direction, favoring the formation of OH radicals, which should lead to enhanced CO oxidation rates through the reverse reaction of 1. It is, however, clear that the addition of H₂O to the oxidizers in the present study does not enhance the CO oxidation (Figure 6). A possible explanation is as follows. It is likely that the increased OH concentration, promoted by the addition of H₂O, shifts reaction 2 to its reverse reaction, which will increase the concentration of hydrogen atoms. These H radicals will react with CO₂ (reaction 1), thus balancing the reverse reaction of 1 that was occurring due to the high concentration of OH radicals. In this way, the CO concentration is likely to be insensitive to the presence of H₂O in the oxidizer for the percentages studied.

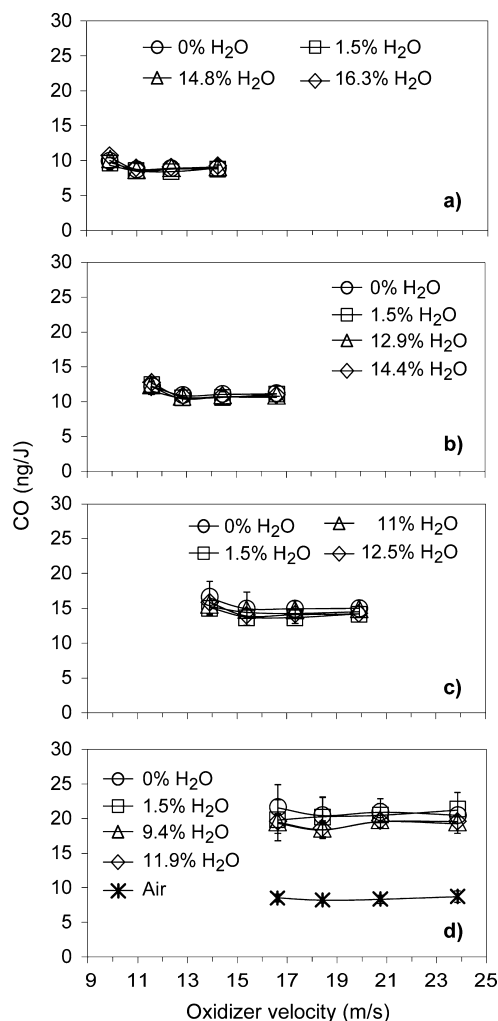


Figure 6. CO emissions as a function of the oxidizer velocity for various wet oxidizer compositions: (a) oxidizer composition: %O₂ + %CO₂ = 100% – %H₂O and %O₂/ %CO₂ = 35%/65%; (b) oxidizer composition: %O₂ + %CO₂ = 100% – %H₂O and %O₂/ %CO₂ = 30%/70%; (c) oxidizer composition: %O₂ + %CO₂ = 100% – %H₂O and %O₂/ %CO₂ = 25%/75%; (d) oxidizer composition: %O₂ + %CO₂ = 100% – %H₂O and %O₂/ %CO₂ = 20.9%/79.1%. The error bars are standard deviations.

It should be stressed that the present results are not entirely consistent with those reported by Abián et al.,⁴ who observed a promotion of CO oxidation as H₂O increases regardless of the oxidizer composition, namely, the CO₂ concentration.

4.3. NO_x Emissions. Figure 7 shows the NO_x emissions, expressed in ng/J, as a function of the oxidizer velocity for five oxidizer compositions and four NH₃ concentrations. Error bars are not included in the figure since they were rather small. It is seen that, for a given NH₃ concentration in the fuel, the oxidizer velocity has a modest effect on the NO_x emissions, regardless of the oxidizer composition, except at the lowest oxidizer velocity for the 35% O₂/65% CO₂ oxidizer. This is presumably because, for the range of oxidizer velocities used, the main characteristics of the flows remain rather analogous so that the observed changes in NO_x emissions can be attributed primarily to chemical and thermal effects, as discussed earlier.

Because of the absence of molecular nitrogen, the fuel-NO mechanism is responsible for all NO_x emissions under oxy-fuel combustion conditions. In air combustion, besides the fuel-NO

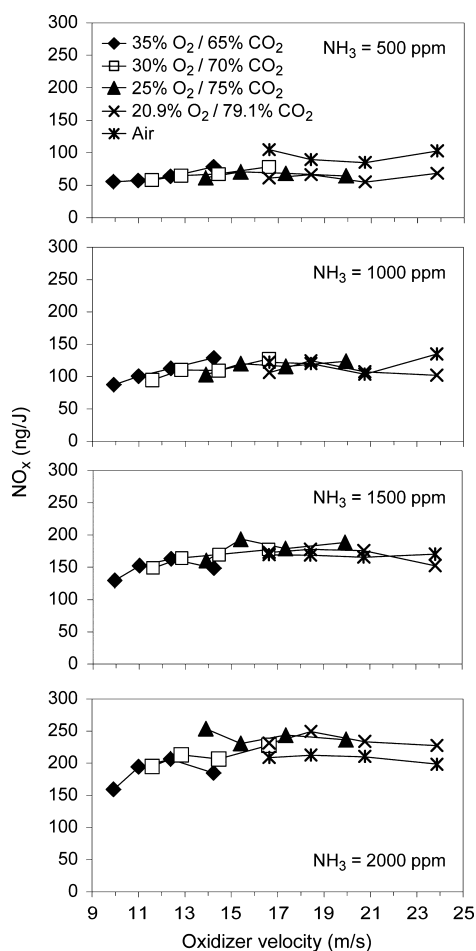


Figure 7. NO_x emissions as a function of the oxidizer velocity for five oxidizer compositions and four NH_3 concentrations.

mechanism, the thermal NO mechanism may play an important role. However, Figure 7 presents levels of NO_x emissions for combustion in air comparable to those for oxy-fuel combustion, which suggests that the NO -thermal mechanism in the present air flames plays a negligible role. This is indeed true for the present combustor, as discussed elsewhere.¹⁶

In Figure 7, it is seen that, under oxy-fuel conditions, for $\text{NH}_3 = 500$ and 1000 ppm, the NO_x emission levels are approximately constant regardless of the oxidizer composition, but, for $\text{NH}_3 = 1500$ and 2000 ppm, the NO_x levels are generally lower for the oxidizers that present lower CO_2 concentrations, which is presumably related to the enhanced CO concentrations and alteration in the amount and partitioning of O/H radicals under oxy-fuel conditions.¹¹ The present results are not entirely consistent with the conclusions of the fundamental study of Mendiara and Glaborg¹¹ on the NH_3 chemistry in oxy-fuel combustion, as discussed in section 1, but evidently the flow reactor and the experimental conditions used in their study are significantly different than those used in the present study.

Figure 7 suggests, therefore, that, for a given NH_3 concentration, the oxidizer composition has a minor influence on the NO_x emissions, but does the oxidizer composition affects, however, the NH_3 -to- NO_x conversion rate? To answer this question, Figure 8 shows the NO_x/NH_3 ratio as a function of the O_2 in the oxidizer for the four NH_3 concentrations. It is seen that the NH_3 -to- NO conversion rates in oxy-fuel conditions

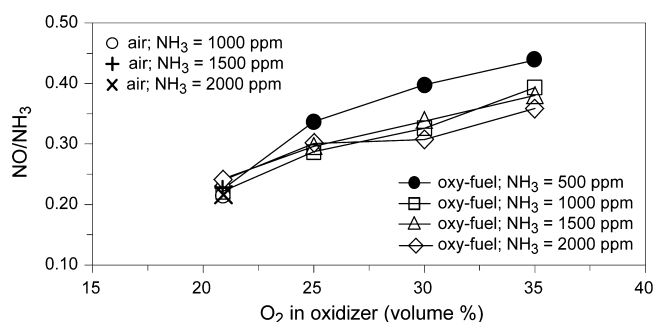


Figure 8. NO_x/NH_3 ratio as a function of the O_2 in the oxidizer.

increase significantly with the increase in the O_2 concentration in the oxidizer, which is consistent with the findings of Shaddix and Molina¹³ for the oxy-fuel combustion of pulverized coals. Moreover, the results show that the NH_3 conversions to NO_x in air and in a 20.9% $\text{O}_2/79.1\%$ CO_2 oxidizer are similar, which is in agreement with the results of Andersson et al.⁹ obtained for lignite.

Figure 8 also reveals that increasing the NH_3 concentration in the fuel yields higher NO_x emissions simply because more NH_3 is available to be converted to NO . However, it is important to notice in Figure 8 that higher NH_3 concentrations in the fuel originate lower conversion ratios to NO presumably because NO reduction by ammonia will occur under these circumstances.

5. CONCLUSIONS

This article reports a parametric study on the oxy-fuel combustion of methane in a laboratory combustor, whose main objective is to evaluate the impact of the oxidizer composition on CO and NO_x emissions and, also, of the concentration of NH_3 added to the fuel, which simulates the fuel bound nitrogen present in many solid fuels, on NO_x emissions. The main conclusions of the present study are as follows.

1. The impact of the oxidizer velocity on the CO and NO_x emissions is generally very small, suggesting that the flow aerodynamics, associated with the velocities considered in this study, plays a minor role on the establishment of the emissions, whose behavior can be mainly attributed to chemical and thermal effects.
2. The CO emissions are significantly higher for the combustion in an oxidizer with 20.9% $\text{O}_2/79.1\%$ CO_2 than for the combustion in air. Under oxy-fuel conditions, the CO emissions decrease as the oxidizer O_2 concentration increases, with the oxidizer composed of 35% $\text{O}_2/65\%$ CO_2 presenting levels of CO emissions similar to those obtained for the combustion in air. According to previous fundamental studies, this is because the high CO_2 concentration present in the atmosphere competes with O_2 for H radicals, which reduces the formation of OH radicals, inhibiting the CO oxidation.
3. The addition of H_2O to the oxidizer originates no meaningful differences on CO emissions for any of the conditions analyzed, which is not entirely consistent with the limited data from plug flow reactors available in the literature.
4. The oxidizer composition affects the NO_x emissions only for the highest NH_3 concentrations studied, where the NO_x levels are generally lower for the oxidizers that present lower CO_2 concentrations.

5. Under oxy-fuel conditions, the NH_3 -to- NO_x conversion rates increase significantly with the increase in the O_2 concentration in the oxidizer. The results also show that the conversion rates in air and in a 20.9% O_2 /79.1% CO_2 oxidizer are similar.

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Notes

The authors declare no competing financial interest.

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