Emission Rates of Formaldehyde and Acetaldehyde in Natural Gas Confined Flames with OEC Application

Alex Álisson Bandeira Santos[a], *Pedro Afonso de Paula Pereira*[b], *Ednildo Andrade Torres*[c]

[a] *SENAI CIMATEC, Salvador/BA, Brazil, alex.santos@fieb.org.br,* ***CA***
[b] *CiEnAm – Interdisciplinary Center of Energy and Environmental– Federal University of Bahia, Salvador/BA, Brazil, pedroapp@ufba.br*
[c] *CiEnAm – Interdisciplinary Center of Energy and Environmental– Federal University of Bahia, Salvador/BA, Brazil, ednildo@ufba.br*

Abstract:

The concept of environmental efficiency in equipments is increasingly in tariff with the unfolding of global warming, and, among the industrial equipments, the burners have a major impact in this discussion because it is an equipment of industrial combustion. Demand for environmentally more efficient burners, with the reduction of emissions is essential for the proper use of fossil fuels during the transition between this energy sources for alternatives energy, which can last more than fifty years. This study evaluates experimentally the technique of oxygen enhanced combustion – OEC – and its interaction with emission rates of formaldehyde and acetaldehyde – precursors for the production of tropospheric ozone and other atmospheric pollutants – in natural gas confined flames. In the experiment was used low enriched with oxygen, which does not require significant existing equipment changes. The emission rates were verified by analysis in liquid chromatography. With the use of oxidizer enrichment of 2 and 4%, the emission rates of formaldehyde and acetaldehyde were reduced with the use of OEC in comparison with the use of atmospheric air as oxidant. The literature show that works with OEC has important points for improving the thermal efficiency of combustion and pollutants reduction. This technology can be an important tool for the adequacy of the industry in general, particularly in oil and gas, for the technological challenge of reducing global warming.

Keywords:
OEC, formaldehyde, acetaldehyde, natural gas.

1. Introduction

Oxygen enhanced combustion (OEC), mentioned by [1], can improve the combustion process by producing improved flame characteristics (larger inflammability limit, better ignition, stability and shape control); smaller combustion gas volumes; increased productivity and thermal efficiency (larger heat transfer process efficiency, improved product quality; fuel consumption reduction, raw material costs reduction, reduced costs of new equipment and possibly production increase in existing equipment).

Atmospheric air contains about 21% of oxygen in volume. Low levels of enrichment of the combustion air with oxygen, i.e. an O_2 index below 30%, are usually used in retrofit applications in which only small modifications to the existing equipment are necessary.

In a diffusion flame – the major of industrial burners – the reactants are initially separated, and reaction occurs only at the interface between the fuel and the oxidizer where mixing and reaction both take place. The addition of oxygen in diffusion flames can be carried out by direct addition to the fuel, or to the combustion air in a burner with an annular, parallel or counterflow oxidizer.

Literature about the addition of oxygen to combustion air in a burner with a parallel annular oxidizer flow includes [1-10].

The industrial burners are an important source of emission of pollutants into the atmosphere, among others, NOx, particulate matter and aldehydes as well as formaldehyde and acetaldehyde, which are important precursors in the ozone formation and photochemical oxidants in the atmosphere. The emission of formaldehyde and acetaldehyde in the atmosphere was studied [11-17].

The formaldehyde and acetaldehyde emissions on the internal combustion engines were evaluated [11]. The atmospheric carbonyl compounds – including formaldehyde and acetaldehyde – its sources, reactivity, concentration levels and toxicological effects were evaluated [12].

Apart from formation of formaldehyde and acetaldehyde in a variety of important photochemical reactions [18], they also have direct emissions from anthropogenic (especially auto exhausts) and biogenic source [13].

In [14] the authors studied a carbon isotope analysis for source identification of formaldehyde and acetaldehyde, and the results showed the carbon isotope method might be a valuable indicator for sources identification of atmospheric aldehyde compounds.

Studies were not identified in the literature about the influence of the OEC in the emissions of formaldehyde and acetaldehyde as also about emissions of these compounds in industrial burners. This indicates a gap of research about these emissions in industrial applications.

The objective of the present work is to explore the effect of the oxygen content in the oxidizer of the combustion on the emission rates of formaldehyde and acetaldehyde of a natural gas diffusion confined flame produced in a combustion chamber with a parallel annular coaxial oxidizer flow, such that the natural gas discharge is surrounded by a flow of air, or oxygen-enriched air. The applied enrichment levels were 23 and 25% O_2 and they were used in retrofit applications where only small modifications in the existing equipment are required.

2. Experimental Setup and Methods

The experimental setup is shown in Fig. l. The flame was generated in a horizontal cylindrical combustion chamber, which consisted of burner with two concentric tubes: a 5mm i.d. central tube, and a 100mm i.d. external tube, and a chamber 1.35m in length. Natural gas flowed up through the internal tube, while air, or enriched air, flowed through the annular region between this tube and the larger diameter concentric tube. Gas flow rates were controlled by valves and metered by rotameters. Diffusion air and oxygen were premixed before being fed into the combustion chamber.

The sampling system shown in Fig. 2 was used for the collection of formaldehyde and acetaldehyde present in the exhaust gases at the combustion chamber exit. The identification and quantification of these compounds were made in a liquid chromatograph coupled to a detector in the ultraviolet-visible absorption (HPLC-UV/VIS).

The sampling system consisted of flow regulator type rotameter, bubblers bottles containing the derivatizing solution of 2, 4-dinitrophenylhydrazine and vacuum pump. The gases leaving the chamber were suctioned by vacuum pump and a flow rate of 0.4L/min for five minutes, and bubble in the solution of 2, 4-dinitrofenilhidraniza derivatizing reagent, reaction and formation of the respective hydrazones. After collecting the solutions were transferred to volumetric flask, swelled to 10 mL with acetonitrile and stored in a refrigerator until the analysis.

The separation was made in column Xterra ® MS C18 5µm 2.1x250mm by injecting 0.2µL sample. The mobile phase consisted of acetonitrile (A) and water (B), according to the following schedule of gradient: 40% de B (0 minutes) → 60% de B (8 minutes) → 60% de B (10 minutes). The flow rate was 0.30 mL / min. The quantification was done by standard curves for external standards. Injection, sampling and analysis were performed in duplicate.

To examine the effect of the oxygen content of the combustion air, tests were performed comparing experiments with 23 and 25% O_2 to experiments with plain air (21% O_2). In the tests the equivalence ratios were maintained over a wide range (1.3 – 0.7). The natural gas flow was $0.0003 m^3/s$ (18 L/min), referred to 20°C and atmospheric pressure. The burner power was 9.76kW.

Fig. 1. Experimental setup.

Fig. 2. The sampling system of formaldehyde and acetaldehyde.

Table 1 summarizes the conditions used in the tests. Table 2 presents the natural gas composition and characteristics used in the tests. The gas flow was in transition regime (laminar to turbulence).

Table 1. Conditions used in the tests.

O_2 index	Equivalence ratio
21, 23 and 25%	1.3, 1.1, 1.0, 0.9 and 0.7

Table 2. Natural gas composition and characteristics used in the tests.

Composition and characteristics	Values
Methane	88.82% vol.
Ethane	8.41% vol.
Propane	0.55% vol.
N_2	1.62% vol.
CO_2	0.60% vol.
HHV (kJ/m^3)	39,329.60
LHV (kJ/m^3)	35,564.00

3. Results and Discussion

The formation of aldehydes under the conditions studied was assessed based on emission rates of formaldehyde and acetaldehyde at the outlet of the combustion chamber, since these two carbonyl compounds are most commonly formed by burning natural gas.

Figs. 3 and 4 present the results for emission rates of formaldehyde and acetaldehyde, respectively, at the exit of the combustion chamber.

The analysis of Fig. 3 shows that there is a trend of reduction in emission rates of formaldehyde with increasing oxygen content in the mixture. This is possibly due to increased flame temperature, which, with the highest content of oxygen allows the decomposition by oxidation of carbonyl compounds formed. Emission rates also showed a decrease for higher equivalence ratios, since these correspond to lower concentrations of oxidant in the mixture oxidizer / fuel. The behavior observed for acetaldehyde was broadly similar to that of formaldehyde, as shown in Fig. 4.

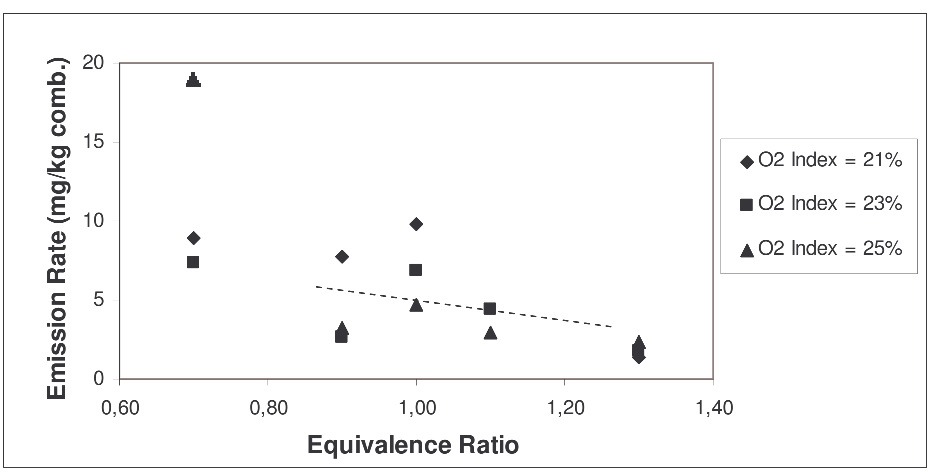

Fig. 3. Emission rate of formaldehyde as a function of equivalence ratio and O_2 index in the oxidizer.

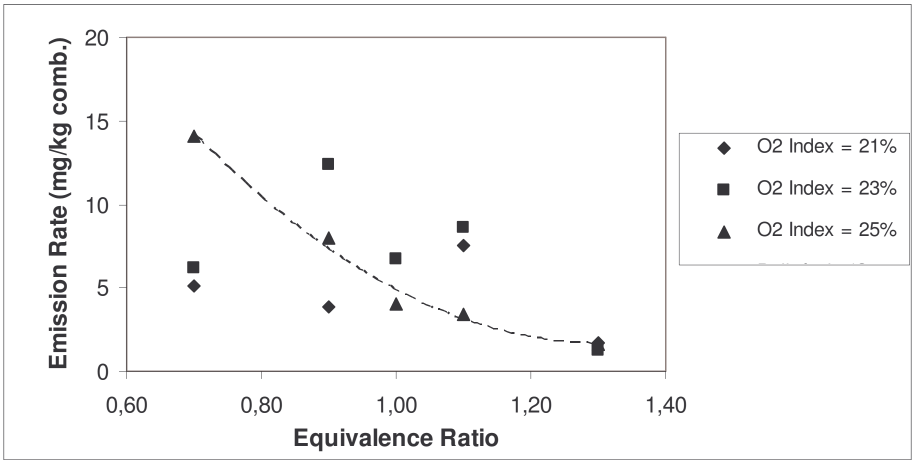

Fig. 4. Emission rate of acetaldehyde as a function of equivalence ratio and O_2 index in the oxidizer.

The Figs. 5 and 6 show the average values for formaldehyde/acetaldehyde ratios based, respectively, equivalence ratio and oxygen content. The values ranged between 0.7 and 1.5 for different equivalence ratios between 0.9 and 1.5 for different levels of oxygen in the flame. No jobs were found in the literature related to the emission of aldehydes in industrial burners. However, results for internal combustion engines using natural gas [11] reported reasons formaldehyde / acetaldehyde about three times higher. Table 3 presents the results of this comparison.

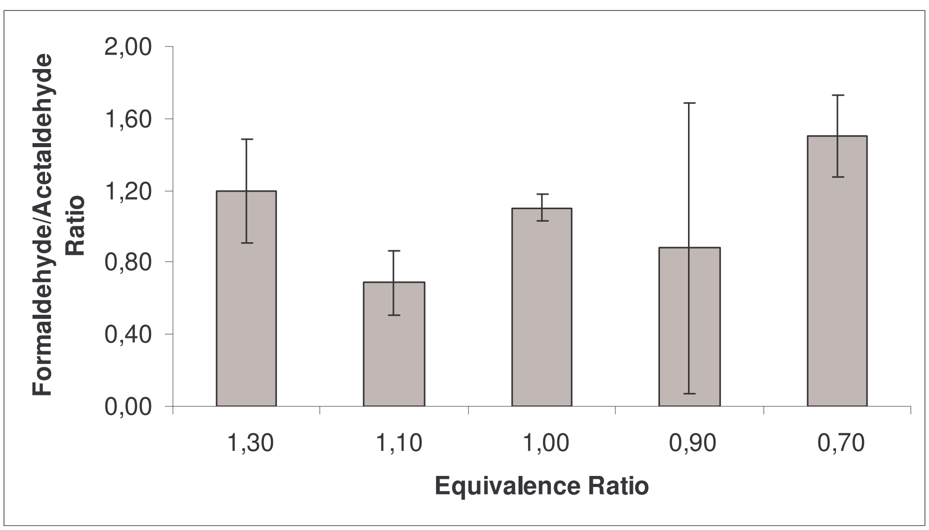

Fig. 5. Formaldehyde/acetaldehyde ratio as a function of equivalence ratio.

Natural gas is composed primarily of methane, and consequently its oxidation will generate formaldehyde as the carbonyl, the formaldehyde / acetaldehyde ratios close to 1.0 found here are derived from a probable reduction in the formation and emission of formaldehyde in combustion conditions employed possibly deriving from the difference in technology and the equivalence ratios employed. This constitutes an environmental benefit, since this compound is highly toxic when present in the atmosphere and participates in the formation of ozone and photochemical oxidants.

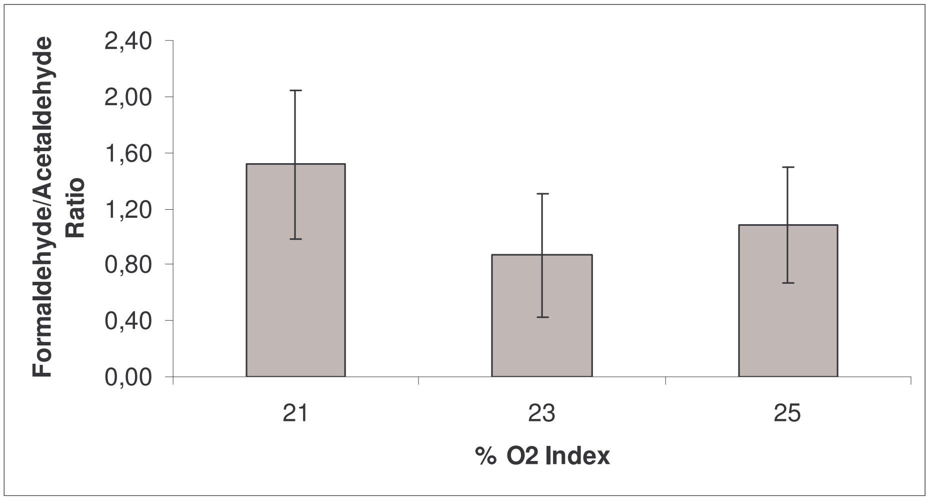

Fig. 6. Formaldehyde/acetaldehyde ratio as a function of O_2 index in the oxidizer.

Table 3. Comparison of experimental results of emission of formaldehyde and acetaldehyde with the literature.

Conditions of Tests	Concentration (ppm)		Formaldehyde/ Acetaldehyde Ratio
	Formaldehyde	Acetaldehyde	
O_2 Index = 21% Natural Gas	6.94	4.56	1.51
O_2 Index= 23% Natural Gas	4.60	7.02	0.87
O_2 Index = 25% Natural Gas	3.31	4.25	1.08
O_2 Index = 21% Natural Gás [11]*	15.54	4.66	3.42

* tests in internal combustion engine

4. Conclusions

This present work investigated the effect of the oxygen index in the oxidizer of the combustion on the emission rates of formaldehyde and acetaldehyde of a natural gas diffusion confined flame. The levels of air enrichment that were applied were 2% and 4% and can applied in retrofit burners, where only small modifications in the existing equipment are required.

The formation and the emission of formaldehyde and acetaldehyde with OEC on the natural gas confined flames are influenced by oxygen concentration and equivalence ratio in the mixture of oxidizer / fuel. The higher amounts of oxygen and equivalence ratios reduced these emissions. The formaldehyde/acetaldehyde ratio on the tested conditions indicates a probable preferential reduction of formaldehyde emissions.

Acknowledgments

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Nomenclature

Subscripts and superscripts

comb. fuel

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