# EMISSION RATES OF FORMALDEHYDE AND ACETALDEHYDE IN SYNGAS CONFINED FLAMES WITH OEC APPLICATION, ACETYLENE DOPING AND ACOUSTIC FORCING

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## ABSTRACT

The concept of environmental efficiency in equipment's is increasingly in tariff with the unfolding of global warming, and, among the industrial systems, 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 –, lean condition, acetylene doping (for thermal radiation efficiency) and acoustic forcing its interactions with emission rates of formaldehyde and acetaldehyde – precursors to produce tropospheric ozone and other atmospheric pollutants – in syngas 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 9%, 1% and 4% acetylene doping, 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 shows that works with OEC and acoustic forcing has important points for improving the thermal efficiency of combustion and pollutants reduction. These technologies 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.

## 1 INTRODUCTION

In the current context of environmental awareness and global efforts to mitigate climate change, the study of emissions resulting from industrial combustion has become crucial. Equipment such as industrial burners, fundamental in the combustion process, are under investigation due to their significant impact on pollutant emissions Maspanov et al. (2019). Among these pollutants, formaldehyde (HCHO) and acetaldehyde ($CH_3CHO$) stand out not only for their adverse health effects but also for their contribution to the formation of tropospheric ozone and other atmospheric pollutants [Lui et al. (2017), Santana et al. (2019), Zhang et al. (2019), and Chen et al. (2021)]. Considering this, the demand for environmentally more efficient burners, capable of reducing such emissions, is more pressing than ever, especially considering the gradual transition from fossil fuel sources to cleaner alternatives.

The present study addresses this demand through the experimental evaluation of advanced combustion techniques. Specifically, it investigates Oxygen-Enhanced Combustion (OEC) of synthesis gas, with doping with acetylene to improve the efficiency of thermal radiation with acoustic excitation. Such techniques are analyzed in terms of their interactions with the emission rates of formaldehyde and acetaldehyde in confined synthesis gas flames, using an oxygen enrichment that does not require significant changes in existing equipment.

This work builds on previous research demonstrating the potential of OEC and acoustic excitation in improving the thermal efficiency of combustion and reducing pollutants. Pereira et al. (2019) carried


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out an experimental evaluation of the emission rates of CO, NOx, formaldehyde and acetaldehyde in confined natural gas flames through a combustion chamber with OEC under acoustic excitation, observing reductions in CO and NOx emissions, in addition to a decrease in acetaldehyde emissions, although without a clear trend towards formaldehyde. On the other hand, Mutlu and Taşftan (2023) investigated the instability of combustion of oxygen-enriched propane under acoustic excitation, noting a reduction in flue gas emissions, particularly at 110 Hz, which resulted in stronger and more stable combustion.

Studies on the influence of the air/fuel equivalence ratio and the fuel composition on the emissions of these aldehydes, such as that conducted by Zervas et al. (2002), highlight the importance of exhaust temperature and the H/C ratio of the fuel in emission concentrations. Furthermore, the analysis of combustion characteristics of oxygen-enriched synthetic gas mixtures at various acoustic frequencies by Alabaş et al. (2021) offers valuable insights into optimizing combustion conditions to mitigate harmful emissions.

These studies highlight the relevance of integrated and innovative approaches to controlling emissions in combustion processes. Advances in the understanding of these techniques and their practical application can significantly contribute to the development of more sustainable standards and practices in the industry, aligning with the objectives of reducing emissions and improving air quality.

## 2 MATERIALS AND METHOD

A vertical cylindrical combustion chamber was designed to produce a confined diffuse flame, as presented in Figure 1. The experimental chamber, shown in Figure 2, is inspired by the combustion apparatus conceived by Pereira et al. (2019), which integrated a sound system with an external acoustic source (speaker). This study aimed to determine acoustic excitation parameters, where the investigation resulted in the identification of three sound pressure peaks, interpreted as harmonics associated with the equipment under test. The most pronounced pressure peak was recorded at a frequency of 220 Hz. Based on this result, 220 Hz was established as the reference frequency for subsequent application of acoustic excitation in experiments.

Furthermore, the combustion chamber reflects attributes of the burner designed by Santos (2010), intended to include an $O_2$ enrichment mechanism in the combustion air stream, in addition to instrumentation for data capture and analysis. Moreover, Figure 1 details the experimental scheme, presenting the supply lines for industrial gases — Hydrogen ($H_2$), Carbon Monoxide (CO), Nitrogen ($N_2$), and Acetylene ($C_2H_2$), for the formation of synthesis gas — accompanied by their respective flow meters (Rotameters) and valves for flow adjustment.

All gases are conducted to a pre-mixer to homogenize the mixture before being directed to the burner. Similarly, compressed air and oxygen are pre-mixed before their insertion into the combustion chamber.



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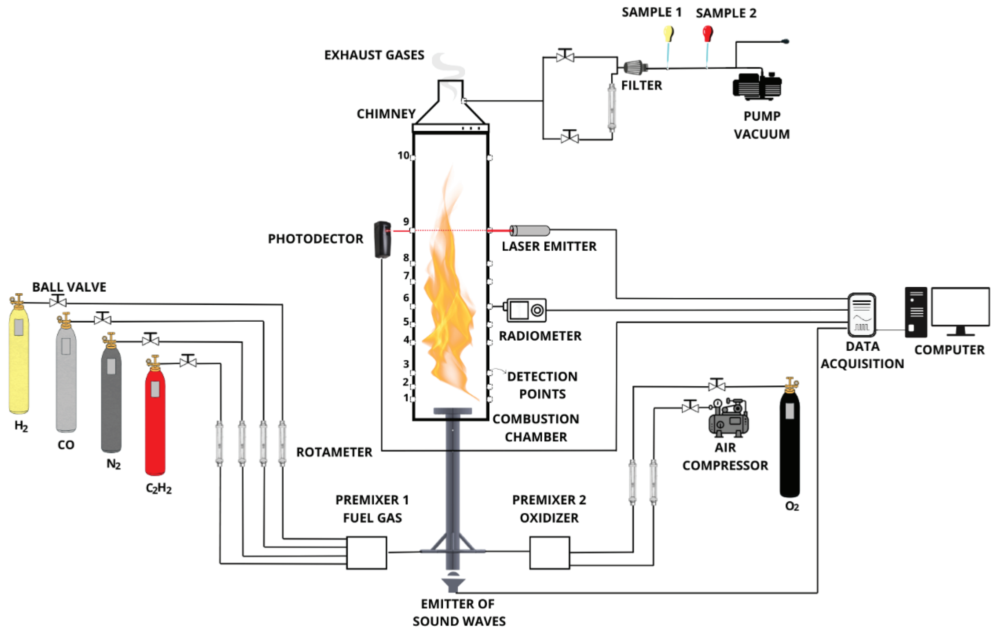


**Figure 1:** Experimental device scheme.

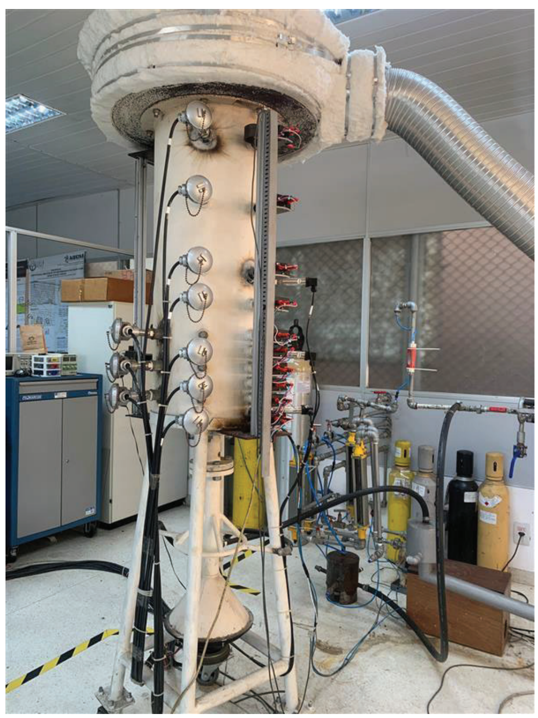

**Figure 2:** Vertical combustion chamber.

The gas collection system presented in Figure 3 was used to capture exhaust gases emanating from the combustion of synthesis gas in the combustion chamber. The sampling system consists of a thermal reservoir, for the accommodation and preservation of the coolant fluid (water) temperature of the derivatizing solution of 2,4-dinitrophenylhydrazine, used to capture molecules of the compounds to be analyzed (Formaldehyde and Acetaldehyde), a rotameter for measuring the flow rate of the collected exhaust gases, a vacuum pump for the suction of gases, as well as hoses, connections, and supports for


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routing the gases. The exhaust gases were collected at a flow rate of 0.4 L/min for five minutes. The collection and analysis procedure follows the same methodology applied in the article by Santos et al. (2016).

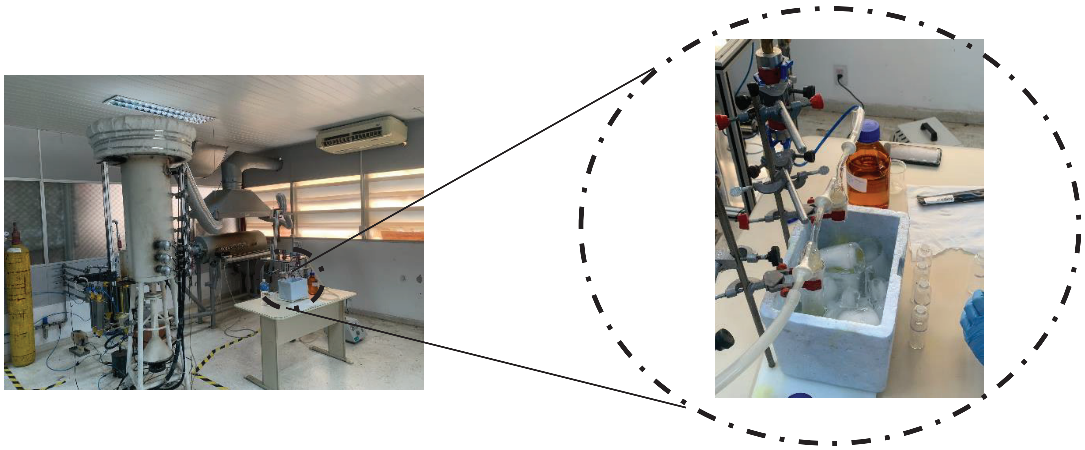

**Figure 3:** Gas collection system for quantifying formaldehyde and acetaldehyde.

Table 1 presents the parameters used for the identification of formaldehyde and acetaldehyde. These parameters adhere to the Brazilian standard ABNT 12026, and the methodology for defining these parameters can be found in the work by Guarieiro, Pereira, Torres, Rocha, and Andrade (2008).

**Table 1:** Parameters for compound identification.

| Compound | Working range (ug-L) | LOD | LOQ | Analytical Curve Equation | Correlation Coefficient |
|---|---|---|---|---|---|
| Acetaldehyde | 5,0 - 300 | 4,607 | 6,794 | y = 422,79x + 413,34 | $R^2 = 0{,}9999$ |
| Formaldehyde | 5,0 - 300 | 6,384 | 9,42 | y = 82,673x + 61,732 | $R^2 = 0{,}9999$ |

where LOD is the limit of detection and LOQ is the limit of quantification.

The Table 2 displays the conditions used in the tests. With proportions of Acetylene ($C_2H_2$) set at 0%, ~1%, and ~4%, a set of four experiments was organized for each concentration.

**Table 2:** Conditions used in the tests.

| Percentage of C2H2 (%) | Excess Air (λ) | Enrichment Level (%) | Acoustic Excitation (Hz) |
|---|---|---|---|
| 0 | 0.7 | 21.0 | 0 |
| 0 | 0.7 | 21.0 | 220 |
| 0 | 0.7 | 30.0 | 0 |
| 0 | 0.7 | 30.0 | 220 |
| 1 | 0.7 | 21.0 | 0 |
| 1 | 0.7 | 21.0 | 220 |
| 1 | 0.7 | 30.0 | 0 |
| 1 | 0.7 | 30.0 | 220 |
| 4 | 0.7 | 21.0 | 0 |
| 4 | 0.7 | 21.0 | 220 |
| 4 | 0.7 | 30.0 | 0 |
| 4 | 0.7 | 30.0 | 220 |

The Table 3 presents the percentage values of industrial gases for each condition.



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**Table 3:** Composition of the synthetic gases used in the tests.

| Composition and Characteristic | Condition 1 (0% C2H2) | Condition 2 (1% C2H2) | Condition 3 (4% C2H2) |
|---|---|---|---|
| $H_2$ | 39.95% | 38.50% | 36.10% |
| CO | 10.95% | 10.75% | 10.30% |
| $N^2$ | 49.10% | 50.01% | 49.84% |
| $C_2H_2$ | 0.00% | 0.74% | 3.76% |

## 3 RESULTS

Table 4 summarizes the experimental conditions performed, and the last two columns present the temperature and $O_2$ percentage values at the exit, respectively. It is noted that with the increase in acetylene doping, there is a higher temperature at the exit and a reduction in the $O_2$ percentage. Another interesting point is that for all experimental cases with acoustic excitation, the $O_2$ values are lower than those without acoustics, indicating an improvement in mixture diffusion, allowing better oxygen utilization. Comparing the experiment without acetylene doping to one with ~ 4% acetylene doping, both without acoustics and enrichment, the temperature increases by approximately 105% and the oxygen percentage decreases by approximately 18%. Now, for the same experiment with enrichment but without acoustics, the temperature is 88% higher with doping, and the oxygen percentage is 23% lower, meaning there is a gain in oxygen consumption when we enrich with oxygen and have acetylene doping, but the temperature gain is lower in percentage terms. Finally, for the experiment with doping, acoustics, and enrichment, the exit temperature is 80% higher compared to the case without doping, and the $O_2$ percentage at the exit is 25% lower. Therefore, we can conclude that with doping, acoustics, and enrichment, there is an increase in preferred pathways for oxygen consumption.
Another important comparison is between the extreme cases: one experiment without enrichment, acoustics, and doping, and another with all these techniques combined. It is observed that the temperature increases by 136% and the $O_2$ percentage at the exit is around 23%. This demonstrates that acetylene doping helps increase flame temperature and better oxygen consumption. This better consumption may be related to the higher flame temperature, which allows certain reactions to initiate preferentially over others.

**Table 4:** Summary of the experimental conditions including temperature and $O_2$ percentage, both at the exit.

| Percentage of C2H2 (%) | Excess Air (λ) | Enrichment Level (%) | Acoustic Excitation (Hz) | Temperature of Gas (°C) | $O_2$ (%) |
|---|---|---|---|---|---|
| 0 | 0.7 | 21.0 | 0 | 196 | 18,0 |
| 0 | 0.7 | 21.0 | 220 | 235 | 17,7 |
| 0 | 0.7 | 30.0 | 0 | 218 | 18,5 |
| 0 | 0.7 | 30.0 | 220 | 257 | 18,3 |
| 1 | 0.7 | 21.0 | 0 | 249 | 18,2 |
| 1 | 0.7 | 21.0 | 220 | 311 | 17,3 |
| 1 | 0.7 | 30.0 | 0 | 348 | 20,6 |
| 1 | 0.7 | 30.0 | 220 | 394 | 19,7 |
| 4 | 0.7 | 21.0 | 0 | 402 | 15,3 |
| 4 | 0.7 | 21.0 | 220 | 416 | 15,2 |
| 4 | 0.7 | 30.0 | 0 | 411 | 15,0 |
| 4 | 0.7 | 30.0 | 220 | 464 | 14,6 |


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Figures 4 and 5 present the results of formaldehyde concentration under different experimental conditions. These combustion conditions were evaluated with and without the presence of acoustic effects, at 220Hz and 0Hz, respectively. From the results shown in Figure 4, it is possible to observe a tendency for the reduction of formaldehyde concentration in the exhaust gases for conditions without acoustic excitation, with the increase of acetylene doping in the synthesis gas composition. For the conditions experimented with acoustic excitation, there is a scenario of reduced formaldehyde concentration with an increase in acetylene doping of ~1%. However, with ~4% acetylene doping, there is an observed increase of about 64% in the formaldehyde concentration compared to the acetylene doping of ~1%. The reaction for the formation of formaldehyde from methanol is presented in Equation (1), while Equation (2) shows the formation of acetaldehyde from methanol. Equation (3) describes the combustion reaction of acetylene. Observing these reactions, it is noted that the presence of acetylene adds a reaction that requires oxygen. This explains the lower formation of formaldehyde and acetaldehyde when this fuel is present in the combustion reaction. Furthermore, analyzing Figure 4, the acoustic effect in the reaction improves the diffusion between the fuel and the oxidant, resulting in a greater amount of carbonyl compounds. However, when the doping is approximately 4%, there is an increase in the formation of these compounds with the acoustic effect. Table 4 shows a significant increase in the gas outlet temperature with the increase in acetylene doping, providing more heat to the reaction system and favoring the formation of formaldehyde.

Formaldehyde

$$CH_3OH + {}^{1}/_{2}\, O_2 \rightarrow HCOH + H_2O \tag{1}$$

Acetaldehyde

$$CH_3OH + CO + H_2 \rightarrow CH_3CHO + H_2O \tag{2}$$

Acetylene

$$C_2H_2 + {}^{5}/_{2}\, O_2 \rightarrow 2CO_2 + H_2O \tag{3}$$

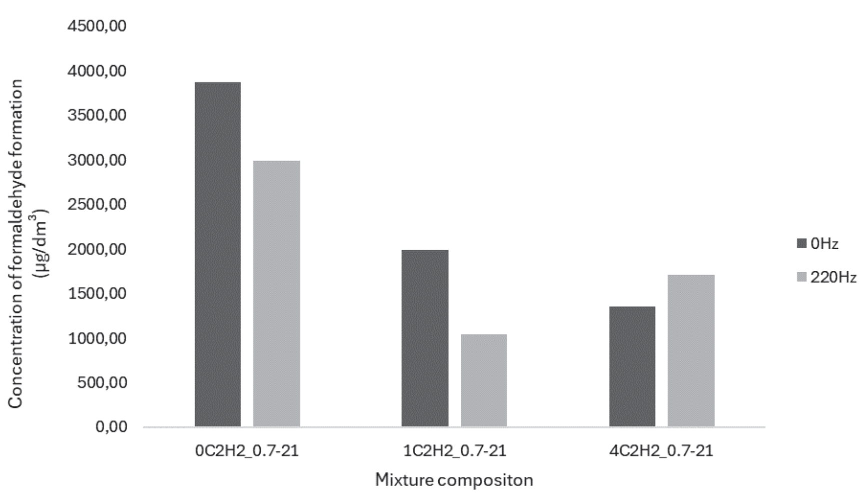


**Figure 4:** Concentration of Formaldehyde formation as a function of the effect of acoustics and acetylene doping.



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In Figure 5, the concentrations decreased with the presence of acoustics for the cases of 0% and ~1% acetylene doping, but for the case with ~4%, it was observed that the concentration is 26% higher with acoustic excitation compared to the case without excitation. The formation of formaldehyde with oxygen enrichment was lower, as shown in Figure 5. Observing the acetylene combustion reaction, Equation (3), it is noted that there is an oxygen demand. Since the system was enriched with oxygen, it is believed that this favored the combustion of this fuel to the detriment of the formation of formaldehyde, which also requires oxygen for its formation. Additionally, it can be observed that there is no clear trend in the reduction of formaldehyde concentration with the increase in acetylene doping in the mixture, and a lower concentration due to acoustic excitation.

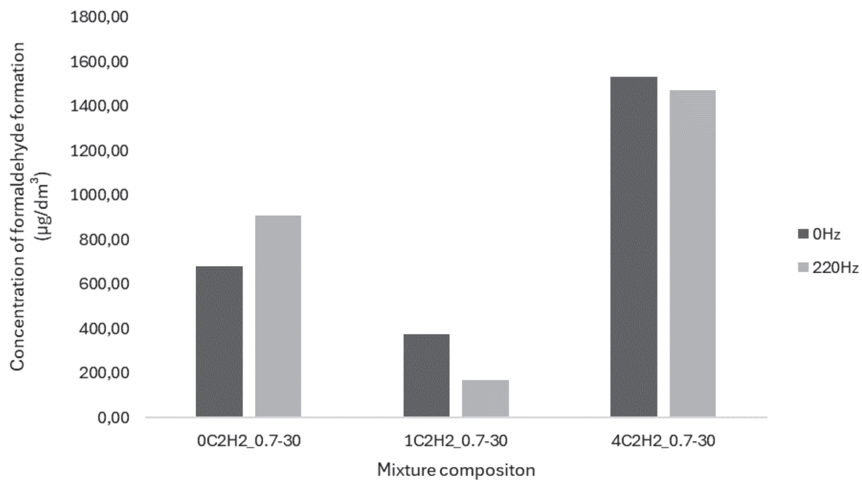


**Figure 5:** Concentration of Formaldehyde formation as a function of O2, acoustic effect and acetylene doping.

Figures 6 and 7 present the findings for acetaldehyde concentrations under different experimental conditions, similarly, evaluated as mentioned for formaldehyde. In Figure 6, a reduction in the concentration of acetaldehyde is observed when acoustic excitation is applied for the case without acetylene doping. In the condition of ~1% acetylene doping, there is a decrease in concentration compared to cases without acoustic excitation. However, when compared to conditions experimented with acoustic excitation, a significant increase in acetaldehyde concentration is noted. This increase may be related to a greater formation of secondary reactions that assist in the formation of acetaldehyde due to the enhanced diffusion of combustion. For the doping at ~4% of acetylene, there is no emission of acetaldehyde.

The behavior observed in the concentration of acetaldehyde with oxygen enrichment was lower, compared to the case without doping and without acoustic excitation, but for the condition with acoustic excitation and without doping, the concentration of acetaldehyde is much higher than the condition without $O_2$ enrichment. This increase may be related to the greater presence of oxygen in the reaction mixture. For the other cases, no formation of acetaldehyde was observed.


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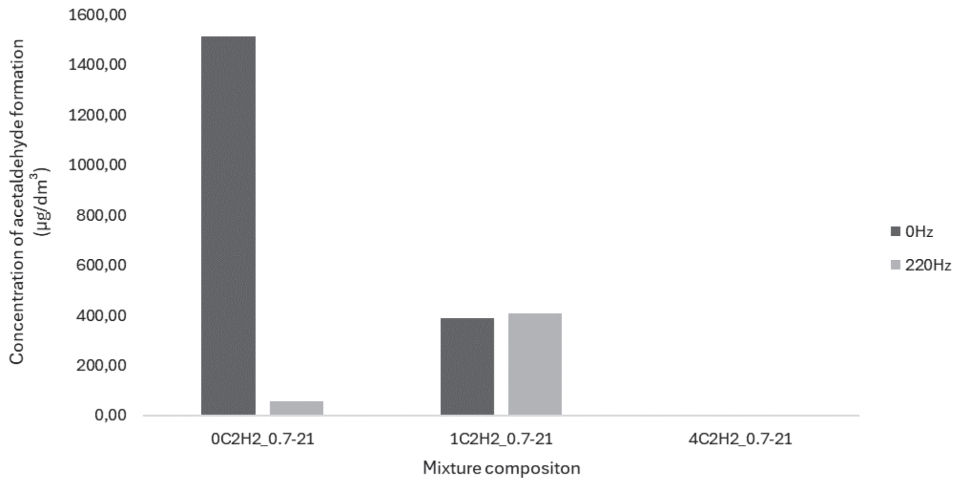


**Figure 6:** Concentration of Acetaldehyde formation as a function of the effect of acoustics and acetylene doping.

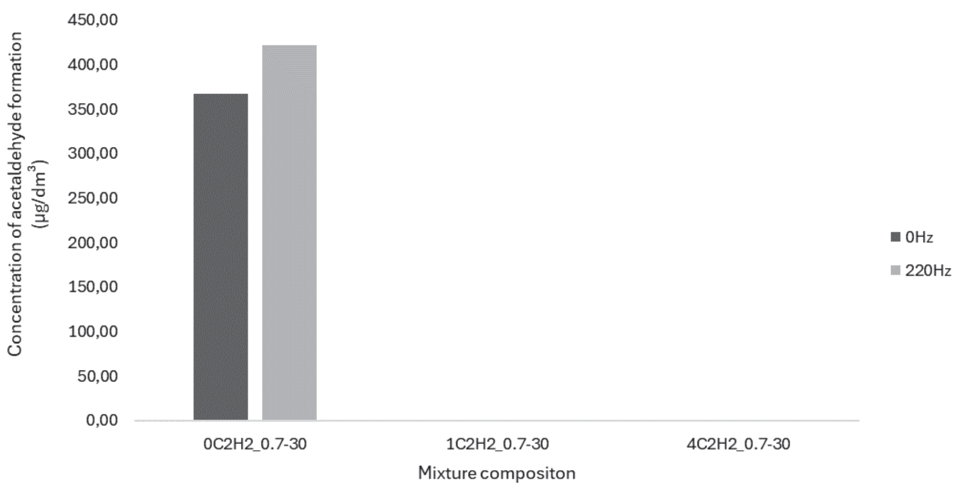


**Figure 7:** Concentration of Acetaldehyde formation as a function of O2, acoustic effect and acetylene doping.

## 4 CONCLUSION

The present study investigated the effect of acetylene doping in the synthesis gas composition and oxygen enrichment on the combustion of synthesis gas, as well as the effect of acoustic excitation on the formation of formaldehyde and acetaldehyde in the exhaust gases of the combustion chamber.
For the combustion tests, levels of acetylene doping at ~1% and ~4% of the synthesis gas composition, oxygen enrichment at 9%, and acoustic excitation at frequencies of 220 Hz were applied. These conditions can be applied in the modernization of combustion chambers and burners, where only minor modifications to the existing equipment are necessary.
The formation and emission of formaldehyde and acetaldehyde with acetylene doping in confined synthesis gas flames are influenced by oxygen enrichment and acoustic excitation. However, it was observed that at ~1% acetylene doping, lower values of formaldehyde and acetaldehyde concentrations were obtained in the exhaust gases for all experimental conditions.



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