Evaluation of the Effect of Natural Gas Enrichment with Hydrogen on Gas Turbine Emissions: Numerical Study Based on Chemical Equilibrium

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Abstract. Decarbonization involves the intensive use of renewable energy to obtain a sustainable energy matrix. Brazil has an electrical matrix strongly anchored in renewable sources, historically in hydraulic energy, and more recently, in solar, photovoltaic, and wind sources. The latter are stochastic and, therefore, have strong restrictions on their insertion into the matrix in a broad and dominant manner. Due to these limitations, excess supply can be used to produce green hydrogen and even methane in a process called methanation (chemical reaction between CO_2 and H_2). The use of electrical energy from renewable sources for the production of fuels is known in literature as power-to-gas. These fuel vectors (H_2 and CH_4) can be used directly to generate energy or can be mixed with natural gas to enrich it in terms of energy and potentially reduce emissions. This study evaluates the effect of enriching mixtures of natural gas and hydrogen on CO, CO_2, and NOx emissions, considering combustion applications in Gas Turbines. The analyses were numerical and involved the use of a thermodynamic combustion model with chemical equilibrium. The chemical equilibrium model is based on chemical equilibrium constants and assumes that the reactants and products are ideal gases. The volumetric fractions of H_2 in the mixture from 0 to 30% and the effect of the combustion pressure were investigated. The pressure was varied according to the application chosen. Gas turbines are part of the combined power cycles, and plants can operate with gas turbines of different pressure ratios according to the model, power, and manufacturer of the Gas Turbine. The analyses focused on medium and large gas turbines, and the chosen pressure range was 12:1 to 24:1.

Keywords: Green Hydrogen; NOx; Gas Turbines, Chemical Equilibrium Model; Numerical Simulation.

1 Introduction

The pursuit for decarbonizing the energy matrix is essential, and to achieve this goal is necessary to intensive use of renewable energy to make the matrix sustainable. According to the National Energy Balance 2023, Brazil has an electrical matrix predominantly from renewable sources, with a significant emphasis on hydroelectric power. In recent years, there has been an increase in electricity generation from other renewable sources such as photovoltaic solar and wind [1]. These sources are considered stochastic, that meaning their production varies randomly depending on environmental conditions like sun and wind availability. Due to these characteristics, electricity generation sometimes exceeds demand during certain periods of the day. This surplus energy can be used, among other applications, to produce green hydrogen and even methane. The use of electricity from renewable sources for fuel production is known in the literature as power-to-gas [2]. These fuel vectors, H_2 and CH_4, can be used directly for power generation or mixed with natural gas to enhance its energy content and potentially reduce emissions of pollutant gases.

As described by the IEA [3], Brazil announced at COP26 a long-term commitment to achieve net-zero emissions by 2050 and a plan to reduce carbon emissions by 50% by 2030, based on a national plan and a developing hydrogen strategy. The use of green hydrogen is often considered in the literature as a substitute for fossil fuels for low-carbon transitions. The concept of substitution makes this technology attractive because it offers the possibility of reducing emissions while maintaining the contemporary energy system [4].

Hydrogen has direct applications in energy through fuel cells or gas turbines. Currently, gas turbines are more economical and have a longer lifespan than fuel cell technologies. Gas turbines are part of combined cycle power plants, and these plants can operate with gas turbines of different pressure ratios depending on the model, power, and manufacturer of the gas turbine [5]. To some extent, gas turbines can also tolerate impurities in the fuel, such as CO, NH_3, and O_2, which can originate from biogas sources or fuel processing [6]. In pursuit of cleaner energy systems, gas turbines using H_2 are likely to become an important solution [7]. The combustion of H_2 and natural gas reduces the fraction of consumed hydrocarbons and the formation of CO_2 in combustion products [8]. The addition of hydrogen contributes to flame stability during combustion, especially in cases with excess air [9].

Several studies in the literature address the use of hydrogen in gas turbine power units. Arsalis [10] proposed a concept to couple an H_2/CH_4 powered gas turbine to a hybrid PV/H_2 system. This proposal demonstrated the versatility of gas turbines for sustainable energy generation systems. The combustion of H_2 and CH_4 was experimentally investigated in a combined heat and power microturbine [11]. Three fuel scenarios were evaluated: 100% CH_4 by volume, a mixture of 15% H_2 by volume with CH_4 and a mixture of 20% H_2 by volume with biogas. These mixtures were used to demonstrate the flexibility of the microturbine, simulating the addition of green H_2 to natural gas and biogas. For the H_2/biogas mixture, CO and NOx emissions showed respective reductions of 29.8% and 47.1% in energy-equivalent terms compared to using 100 vol% CH_4. However, this mixture exhibited a reduction of approximately 11.3% in maximum power and energy efficiency. Babahammou, Merabet, and Miles [12] analyzed the blending of different proportions of green H_2, produced through electrolysis using photovoltaic solar energy, to power a gas turbine. Using the Aspen HYSYS software simulator to analyze four cases with different hydrogen blend proportions: 5%, 10%, 15%, and 20%. The results showed that adding 20% H_2 by volume resulted in a 4.5% reduction in fuel consumption and adding just 5% H_2 reduced annual CO_2 emissions by 8,952 tons.

This study evaluates the effect of enriching natural gas with H_2 mixtures, on emissions of CO, CO_2, and NOx, considering combustion applications in gas turbines. The numerical analyses conducted involved the use of a thermodynamic combustion model with chemical equilibrium. The effects due to the addition of H_2 are evaluated concerning variations in parameters such as equivalence ratio and pressure ratio.

2 Methodology

Combustion is an essential process in energy generation, where the fuel reacts with an oxidant, usually oxygen from the air, to release energy. Stoichiometric combustion, also referred to as ideal, is characterized by the complete reaction of the fuel with the oxidant, without any remaining reactants present [13]. While useful, this model has significant limitations, especially under high temperature conditions where thermal dissociation can occur, leading to the formation of intermediate chemical species such as carbon monoxide (CO), hydrogen (H_2), hydroxyl (OH), and nitrogen oxides (NOx), for example. To address the limitations of the stoichiometric model, the concept of chemical equilibrium must be introduced, where it represents a state in which the rates of forward and reverse reactions are equal, resulting in constant concentrations of reactants and products over time [14].

At high temperatures, combustion products can dissociate, forming intermediate species, and dissociation increases the system's entropy but requires energy, affecting the total enthalpy of the system. An analysis of product dissociation can be performed using minimization of Gibbs free energy, considering contributions from all species present at equilibrium. As highlighted by Turns [13] and Klein [14], implementation of computational tools and numerical algorithms like EES, TPEQUIL, and HPFLAME becomes essential in solving complex problems in this field of study, where combustion reactions involve the interaction of multiple chemical species and the formation of a variety of products, considering formation enthalpies, heat capacities, and other thermodynamic properties of the species involved. As described, the analyses conducted in this study were numerical, and the following aspects were considered:

- The volumetric fraction of H_2 in the mixture was varied from 0 to 30%.
- The pressure was varied according to the application, focusing on medium to large gas turbines, with pressure ranges chosen from 12:1 to 24:1.

2.1 Thermodynamic Laws in Reacting Systems

The analysis of combustion reactions and reacting systems is directly rooted in the principles of thermodynamic laws. The first two laws are particularly indispensable in understanding the evolution of these systems towards equilibrium and how energy and entropy govern their application to combustion processes. The first law of thermodynamics, also known as the law of conservation of energy, states that energy cannot be created or destroyed, only transformed from one form to another. In mathematical terms, as stated by Bejan [15], this law can be expressed as the change in internal energy of the system (ΔU), given by the difference of heat added to the system (Q) minus the work done by the system (W), thus allowing for detailed energy balances to be developed.

In the context of combustion, as observed by Turns [13], this law implies that the energy released by the chemical reaction, in the form of heat, must equal the change in internal energy of the system plus the work done by the system. In adiabatic reactions, where there is no heat transfer with the surroundings ($Q = 0$), all the energy released by the reaction is converted into a change in internal energy and/or work. Therefore, considering a combustion reaction in a fixed volume, where the work done by the system is zero ($W = 0$), the change in internal energy of the system equals the released energy ($\Delta U = Q$), and for a complete combustion reaction, the energy released in the process can be calculated using the formation enthalpies of the reactants ($\Delta H_{f,reagents}$) and products ($\Delta H_{f,products}$). The formation enthalpy is the change in enthalpy when one mole of a substance is formed from its constituent elements in their standard states. The released energy, Q, is then described by eq. (1):

$$\mathrm{Q} = \Sigma(\Delta \mathrm{H_f produtos}) - \Sigma(\Delta \mathrm{H_f reagentes}) \tag{1}$$

Thus, based on Turns [13], applying the appropriate data allows for the calculation of the energy released by the reaction, which is then used to increase the temperature of the combustion products. For chemical reactions at constant pressure, the change in enthalpy (ΔH) equals the heat exchanged (Q_p), which is particularly relevant in combustion reactions, where the energy released by the chemical reaction is transferred as heat to the surroundings. In an adiabatic reaction, where there is no heat exchange with the surroundings, all the energy released by the reaction is used to increase the temperature of the combustion products.

The second law of thermodynamics states that the entropy of an isolated system tends to increase over time, reaching a maximum value at equilibrium. Entropy (S) is considered a measure of the disorder or randomness of a system, thus guiding towards chemical equilibrium where entropy is maximized. According to Bejan [15], in a combustion reaction, the second law of thermodynamics implies that the composition of reaction products at equilibrium maximizes the system's entropy, subject to energy and mass constraints where, according to equation (2), changes in entropy (ΔS) and enthalpy (ΔH) can be related through the change in Gibbs free energy (ΔG). The presence of intermediate species formed during the combustion process increases the system's entropy because there are more ways to distribute energy among different species.

$$\Delta \mathrm{G} = \Delta \mathrm{H} - \mathrm{T}\Delta \mathrm{S} \tag{2}$$

2.2 Enthalpy and Chemical Equilibrium

As described by Turns [13], chemical equilibrium is achieved when the rates of the forward and reverse reactions are equal, and the concentrations of reactants and products remain constant over time in each analysis. As mentioned earlier, the equilibrium condition can be determined by minimizing the Gibbs free energy of the system where, for a generic reaction, eq. (3), the equilibrium constant (K_p, or typically denoted simply as K) can be expressed in terms of partial pressures or concentrations of reactants and products, as shown in eq. (4).

$$aA + bB \text{ « } cD + dD \tag{3}$$

$$\mathrm{K} = ([\mathrm{C}]^{\mathrm{c}}[\mathrm{D}]^{\mathrm{d}})/([\mathrm{A}]^{\mathrm{a}}[\mathrm{B}]^{\mathrm{b}}) \tag{4}$$

From this latter equation, it is possible to establish a relationship between the equilibrium constant and the standard Gibbs free energy change ($\Delta G°$), which depends on the gas constant (R) and the absolute temperature (T), as presented in the following eq. (5):

$$\Delta G° = -RT(\ln K) \tag{5}$$

Based on Bejan [15], this relationship shows that for exothermic reactions ($\Delta H < 0$), the equilibrium constant increases with decreasing temperature, favoring the formation of products. For endothermic reactions ($\Delta H > 0$), the equilibrium constant increases with increasing temperature, also favoring the formation of products.

Now, in a situation where there is no loss or addition of energy to the external or internal environment of a system, at constant volume or pressure, the adiabatic flame temperature is the highest temperature achievable for the combustion products. For example, in the combustion of methane in natural gas turbines, the energy released by the reaction is used to heat the combustion products. Thus, according to Turns [13], the adiabatic flame temperature can be determined by solving the energy balance equation presented in eq. (6):

$$\Delta H = \Sigma(n_i C_{p,i} \Delta T) \tag{6}$$

Where:

- n_i is the amount of substance of the i-th product.
- $C_{p,i}$ is the molar heat capacity at constant pressure of the i-th product.
- ΔT is the temperature change.

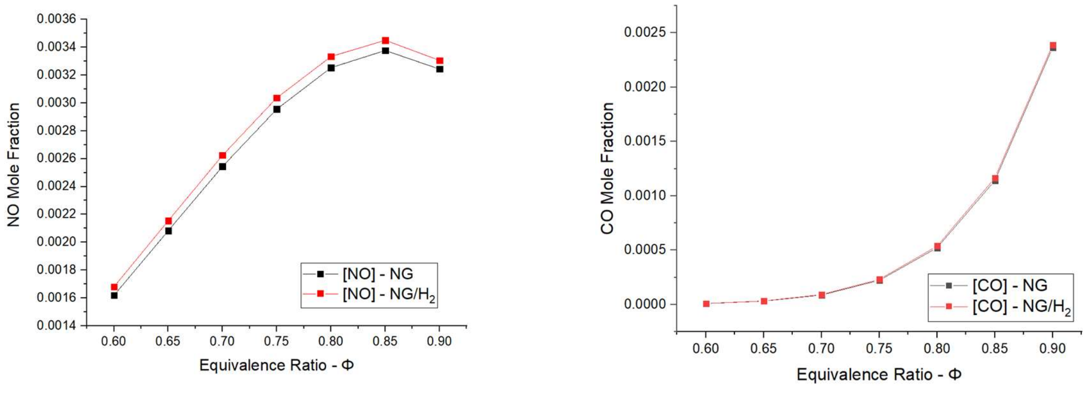
An important detail is that this calculation involves integrating the molar heat capacities at constant pressure (Cp) of the combustion products over the temperature range.

3 Results and discussions

Here are the main results obtained from the analyses conducted using the computational tools EES, TPEQUIL, and HPFLAME, along with their discussions. The results are first discussed in terms of the variation in equivalence ratio (Φ) and secondly by analyzing CO and NO emissions as a function of ratio and pressures.

3.1 Emissions according to equivalence ratio

The effects of enriching natural gas (NG) with H_2 were analyzed under constant pressure oxidation (1 bar), monitoring emissions as a function of equivalence ratio (Φ). These effects were compared with natural gas oxidation without H_2 addition. From the results, it is observed that variation in the equivalence ratio has minimal impact on emissions of both NO (Fig. 1a) and CO (Fig. 1b). Regarding NO formation, adding H_2 to natural gas leads to an increase in NO concentration; however, this does not imply that enrichment is detrimental. It is noteworthy that the amount of air used in oxidation is the same in both cases. Since less air is required to oxidize H_2 compared to natural gas, based on the graph in Fig. 1a, at a lower equivalence ratio under the same conditions, the same NO concentration would be achieved.



a) b)

Figure 1. Molar fraction of emissions as a function of equivalence ratio, a) NO; b) CO.

The adiabatic flame temperature also experiences an increase when natural gas is enriched with H_2 (Fig. 2). However, this effect is primarily associated with the properties of H_2 as a fuel, which exhibits a significantly higher heating value nearly three times greater than natural gas. Therefore, a greater amount of energy is obtained from its oxidation.

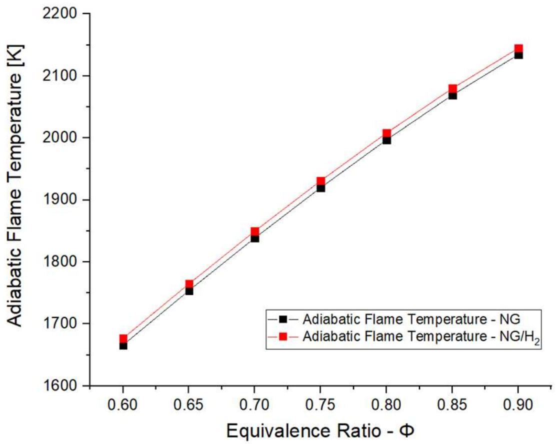


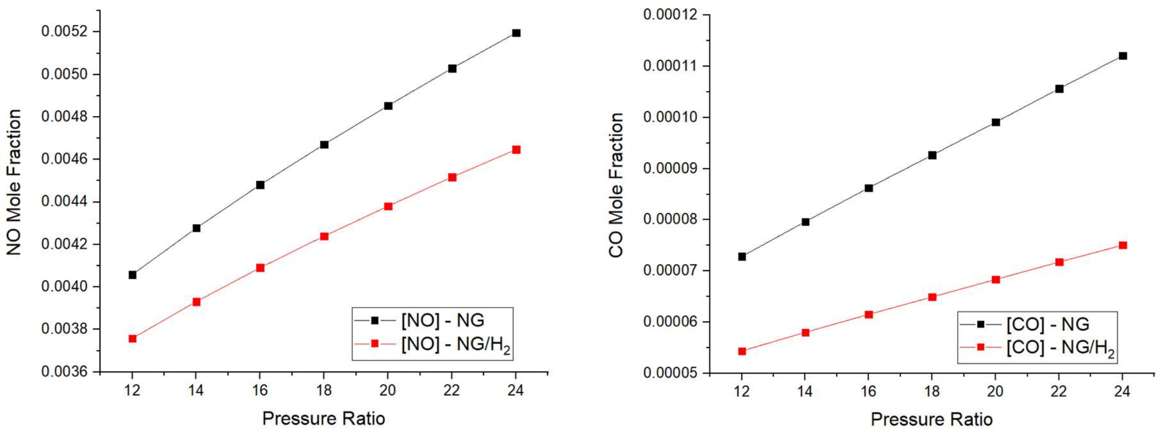
Figure 2. Flame temperature.

3.2 Emissions according to pressure ratio

The variation in pressure ratio exhibits a greater influence on pollutant formation compared to equivalence ratio differences (Fig. 3a and Fig. 3b). In both cases, the formation of NO and CO increases with higher pressure ratios during the oxidation process. However, with a fixed equivalence ratio (Φ = 0.65), adding 20% volume of H_2 to natural gas results in reduced emissions compared to unenriched natural gas. Indeed, the effects of H_2 addition become more pronounced as pressure ratios increase.

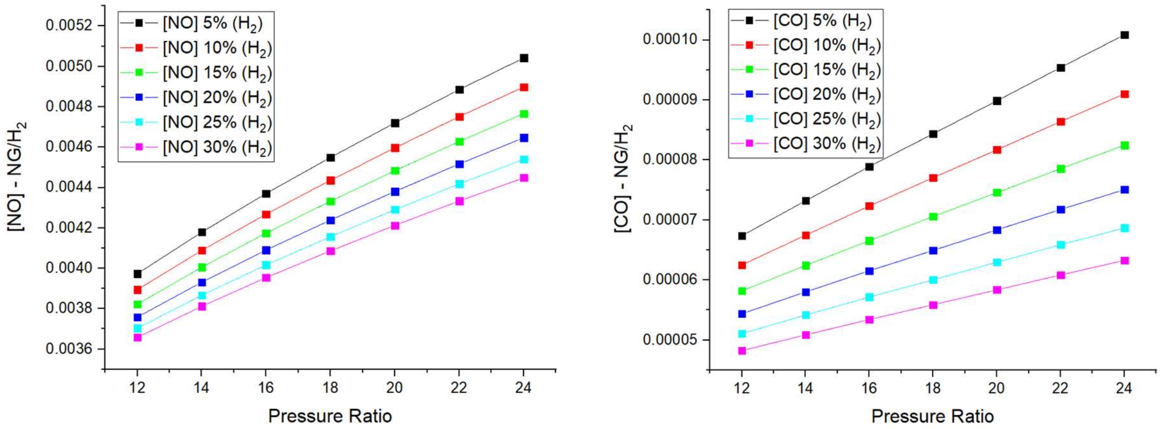
Similarly, increasing the volumetric fraction of H_2 in the mixture leads to greater emission reductions compared to combustion of natural gas without hydrogen addition (Fig. 4a and Fig. 4b). Therefore, from a pollutant emissions perspective, enriching natural gas with H_2 proves advantageous.

From an energy perspective, a decrease in adiabatic flame temperature is observed (Fig. 5). This could potentially reduce the useful work of the system and consequently the energy efficiency of the cycle, as discussed in the literature review. Additionally, increasing fuel consumption might be necessary to achieve similar temperatures. However, considering that combustion gases in a gas turbine have high temperatures after expansion processes, the energy losses may not outweigh the benefits associated with enriching natural gas with H_2.



a) b)

Figure 3. Molar fraction of emissions as a function of pressure ratio, a) NO; b) CO.



a) b)

Figure 4. Variation of molar fraction with respect to pressure ratio and H_2 addition, a) NO; b) CO

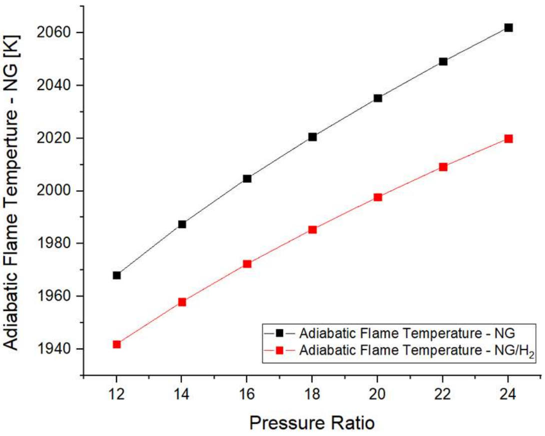


Figure 5. Flame Temperature.

4 Conclusions

In this study, the effect of enriching natural gas and H_2 mixtures on combustion emissions in gas turbines was evaluated through numerical analyses. The effects of H_2 addition were assessed concerning variations in parameters such as equivalence ratio and pressure ratio, the latter ranging from 12:1 to 24:1.

The results indicated that changes in the equivalence ratio had minimal impact on NO and CO emissions. However, variations in the pressure ratio led to significant changes in pollutant formation. Despite NO and CO formation increasing with higher pressure ratios during oxidation, adding H_2 to natural gas resulted in reduced emissions compared to unenriched natural gas.

From an environmental perspective, enriching natural gas with H_2 proved advantageous. However, from an energy standpoint, a decrease in adiabatic flame temperature was observed at high pressures. This could potentially lead to significant energy disadvantages if energy losses are substantial compared to the benefits of enriching natural gas with H_2. Nevertheless, it's crucial to consider the energy value of hydrogen compared to natural gas in this context.

5 Acknowledgements

This study was financed in part by the Coordination for the Improvement of Higher Education Personnel (CAPES in Portuguese) – Brazil – Finance Code 001. The fifth author would like to thank CAPES for the PhD scholarship. Additionally, the last author acknowledges CNPq for the Productivity Grant (Proc. 316482/2023-4).

6 Authorship statement

The authors hereby confirm that they are the sole liable persons responsible for the authorship of this work, and that all material that has been herein included as part of the present paper is either the property (and authorship) of the authors or has the permission of the owners to be included here.

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