Combustion of hydrogen-natural gas mixtures applied to the cooking of ceramic products: emissions and flame properties

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Abstract:

In the coming years, the high temperature industry must face a very ambitious challenge to adapt to the demands of reducing CO_2 emissions, and this adaptation will only be possible with major technological changes, together with the use of alternative energy sources. One of the elements that can contribute to decarbonisation is the use of fuel hydrogen, with the aim of obtaining by direct combustion the necessary heat in the drying and cooking processes. The great advantage of this process is that the combustion of hydrogen does not generate CO_2 emissions, and therefore the current emissions associated with the fuel would be completely eliminated.

In this technical work, a technical study is presented, without considering the economic aspects. In the first part, a theoretical study of the combustion of hydrogen-natural gas mixtures is carried out, and in the second part, the experimental results obtained in some preliminary hydrogen-oxygen combustion tests in an oxy-fuel burner specifically adapted for this work are presented.

For the detailed study, a combustion chamber has been designed in which it will be possible to determine the main combustion parameters: geometric characteristics and temperature profile of the flames, heat transmission coefficients, as well as the composition of the combustion gases. . The results obtained will be key to study, in future works, the technical-economic feasibility of using this fuel in the kilns of the ceramic industry.

Introduction

The ceramic sector is an intensive sector in the use of thermal energy, obtained mainly by the combustion of natural gas, which is a source of generation of CO_2 emissions. It is well known that it is a greenhouse gas (GHG), so its emissions are subject to international monitoring and control, given its relationship with global warming of the planet and consequently on Climate Change.

The technologies and fuels currently used in the ceramic product manufacturing process have a high degree of maturity, so the margin for reducing direct emissions from the process is certainly limited. Consequently, to meet the ambitious emission reduction targets that have been established at European level, the sector will have to radically modify the technologies and energy sources used in its production process.

Among the decarbonisation options that are in the portfolio of the European high temperature process industry, the use of hydrogen as fuel (either alone or mixed with natural gas) stands out, specifically the so-called green hydrogen, which is generated by electrolysis of water using renewable electricity as an energy source. The economic viability of this process is based on using as an energy source the surpluses of renewable electrical energy that are mainly produced by frequent episodes of decoupling between production and demand.

In the case of the ceramic sector, the hydrogen generated could be used as fuel, partially or totally replacing natural gas to generate heat at high temperatures. The great advantage of this process is that its combustion only produces water vapor, and if the energy for its production is of renewable origin, its associated direct emission of CO_2 would be zero or very low, and therefore of great interest to achieve the objectives decarbonisation planned.

However, the use of hydrogen as fuel in industrial processes is a technology that is not very mature from a technical point of view, which requires a detailed study to know the influence that this change of fuel can produce on the physicochemical reactions that go to suffer the processed materials, the possible effects on the construction materials of the industrial equipment, as well as on the process variables and atmospheric emissions.

This work is part of a series of studies carried out to analyze the viability of the different decarbonisation options in the ceramic industry.

Objective

The objective of this work is to show the theoretical parameters of combustion of hydrogen mixtures with natural gas, to study in detail the combustion of mixtures of both fuels and their impact on the generation and transmission of heat, the composition of the resulting combustion gases, as well such as changes in the flame profile to achieve high-quality and energy-efficient cooking, paying special attention to the emissions generated.

The economic aspects are outside the scope of this work, and will be considered in later stages.

Theoretical study of the combustion of natural gas and hydrogen

Fuel properties of hydrogen versus natural gas

Depending on the origin of the raw materials used, a distinction can be made between blue or gray hydrogen, which is obtained from fossil sources, and green hydrogen, obtained from water, using electricity from renewable sources, would be the only one that has meaning from the point of view of the decarbonization of the process.

Hydrogen could be used as a fuel in the ceramic sector in those processes where natural gas is currently used. Table 1 shows the characteristics of both gases for their use as fuels.

The main advantage of hydrogen combustion compared to fossil fuel combustion is that it does not present CO_2 emissions, as can be seen in the combustion reactions detailed in table 2.

Although it should be noted that the combustion of air with hydrogen can generate a greater amount of thermal NO_x, since it has a higher flame temperature (over 170° C higher), this parameter being very critical from temperatures of the order of 1400°C. NO_x emissions present emission limit values in the integrated environmental authorizations (variable depending on the process stage).

In fact, the development of burners and / or operating conditions that reduce the formation of NO_x in combustion is one of the aspects planned to be studied in this project.

Table 1. Main characteristics of natural gas and hydrogen.

Parameters	H_2	Natural gas
Composition considered	100%	90% methane 7.5% ethane 1.5% propane 0.4% butane 0.6% N_2
HV (kWh/Nm^3)	2997	10,617
Gas density (kg/Nm^3)	0.0899	0.7955
Flammability range (% vol.)	4-75 (Air)	5-15 (Air)
	4-94 (Oxygen)	5-61 (Oxygen)
Laminar flame velocity (cm/s)	270 (Air)	35 (Air)
	290 (Oxygen)	330 (Oxygen)
Adiabatic flame T (ºC)	2,045 (Air)	1,875 (Air)
	2,805 (Oxygen)	2,780 (Oxygen)
Flame visibility	No	Yes

Table 2. Combustion reactions of hydrogen with air.

Combustion reactions	Stoichiometric ratio
$H_2(g) + 0.5\cdot(O_2\ (g) + 3.76\cdot N_2)\ (g) \rightarrow H_2O(g) + 1.88\cdot N_2\ (g)$	Volumetric 2.38 Nm^3 air/Nm^3 H_2
$H_2(g) + 8\cdot O_2\ (g) + 26{,}5\cdot N_2\ (g) \rightarrow 9\cdot H_2O(g) + 26.5\cdot N_2\ (g)$	Mass 34.5 kg air/kg H_2

Theoretical study of natural gas and hydrogen combustion with air.

Table 3 and table 4 show the combustion products from the combustion of natural gas with air and hydrogen with air, respectively, for different stoichiometric air-fuel ratios (n).

Table 4 shows that, in the combustion of hydrogen with air, the percentage of water vapor present in the combustion gases increases significantly, if compared with the gases resulting from the combustion of natural gas, where the vapor value of water for stoichiometric combustion amounts to 18.53% (table 3).

Combustion of methane-hydrogen mixtures with air

By adding hydrogen to natural gas, the properties of the resulting mixture are significantly modified. The results obtained from the variation of the energetic properties of mixtures of natural gas with hydrogen are shown below until reaching a hydrogen concentration of 100% by volume (volumetric fraction $x\ H_2 = 1$). The calculations have been carried out under standard conditions of pressure and temperature (P = 1 atm, T = 273.15 K).

Table 5 shows the calculations obtained in the upper and lower calorific value of the resulting mixture, per unit volume, Wobbe index and its variation, for the different mixtures of natural gas and hydrogen.

It has been considered interesting to calculate the Wobbe index since it is a very important parameter when it comes to determining the interchangeability of combustible gases. Two gases are interchangeable when for a given burner, with the same supply conditions (P and T), the same combustion characteristics are maintained: heat flow and flame behavior.

Table 3. Combustion products (in %) of natural gas with air according to different indices of excess air. Calculation basis: 1 Nm^3 of natural gas.

n	Composition of humid fumes			
	CO_2 (%)	H_2O (%)	O_2(%)	N_2 (%)
1	9.78	18.53	0.00	71.69
1.2	8.28	15.68	3.22	72.81
1.4	7.18	13.60	5.59	73.64
1.6	6.33	12.00	7.40	74.27
1.8	5.67	10.74	8.83	74.76
2	5.13	9.72	9.99	75.17

Table 4. Combustion products (in %) of hydrogen with air according to different indices of excess air. Calculation basis: 1 Nm^3 of hydrogen.

n	Composition of humid fumes			
	CO_2 (%)	H_2O (%)	O_2(%)	N_2 (%)
1	0	34.71	0	65.29
1.2	0	29.79	2.98	67.23
1.4	0	26.09	5.22	68.70
1.6	0	23.20	6.96	69.83
1.8	0	20.90	8.36	70.75
2	0	19.00	9.50	71.49

Table 5. Upper and lower calorific value per unit volume, Wobbe index and its variation, for the different mixtures of natural gas and hydrogen.

Natural gas (% by vol.)	Hydrogen (% by vol.)	HHV (kWh/Nm^3)	LHV (kWh/Nm^3)	Wobbe index (kWh/Nm^3)	% Variation Wobbe Index
100	0	11.78	10.62	54.16	-
90	10	10.96	9.85	52.76	2.57
80	20	10.13	9.09	51.36	5.17
70	30	9.31	8.33	49.95	7.77
60	40	8.49	7.57	48.56	10.34
50	50	7.66	6.81	47.20	12.84
40	60	6.84	6.04	45.95	15.16
30	70	6.01	5.28	44.88	17.12
20	80	5.19	4.52	44.25	18.30
10	90	4.37	3.76	44.65	17.55
0	100	3.54	3.00	48.36	10.71

The Wobbe Index is used to compare the energy provided by gaseous fuels of different composition in the same burner. Two fuels that have the same Wobbe Index can be used in the same burner, without changing the operating conditions. Variations of up to 5% are acceptable without the need to introduce changes in the burner, but higher variations will require adjustments of the equipment or even its change.

It can be observed that the calorific value of the mixtures decreases as the amount of hydrogen increases, that is, the energy contained per unit volume decreases progressively, since hydrogen has a lower calorific value per unit volume (table 1).

For example, it is observed that under standard conditions, when the volumetric fraction of hydrogen reaches a value of 0.10 (10% hydrogen by volume in the mixture) it causes a 7% decrease in the value of the calorific value. If this percentage is increased to 50% hydrogen by volume in the mixture, the calorific value is reduced by 35%.

With regard to interchangeability, it should be noted that, according to the values in the table and taking as a criterion a tolerance in the variation of the Wobbe index of 5%, the incorporation of up to 20% of hydrogen by volume to natural gas, would allow working with the same burners and combustion system. For higher percentages, modifications should be made, and even changes in the design of the burners.

Variation in the composition of the furnace combustion gases as a function of the percentage of hydrogen in the mixture

When using natural gas-hydrogen mixtures, the composition of the resulting combustion gases is significantly modified. Figure 1 shows how the composition of the gases formed in complete combustion (CO_2, H_2O) varies for different mixtures of natural gas and hydrogen.

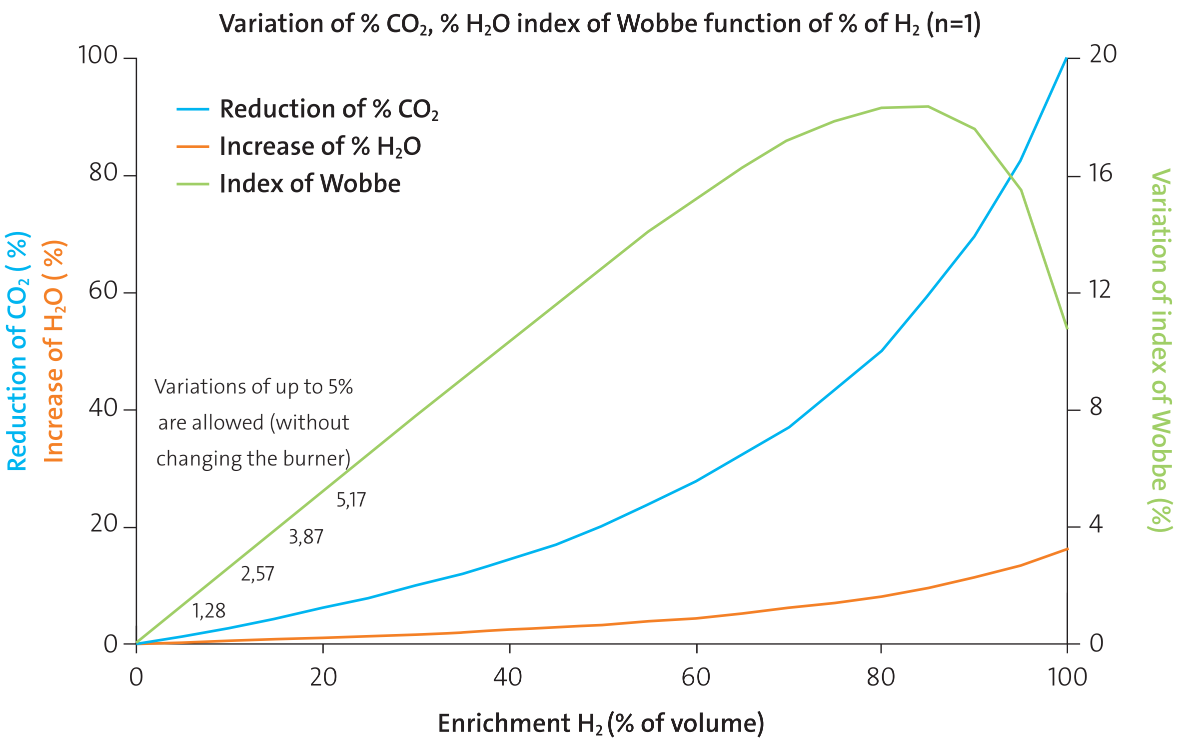
From the observation of the figure, the following aspects should be highlighted:

- To significantly reduce CO_2 emissions, mixtures that are very rich in hydrogen must be used, due to their low calorific value. For example, it is observed that adding 10% hydrogen by volume to the natural gas mixture only reduces the CO_2 generated by 2.52%. To achieve a reduction of the order of 50% of carbon dioxide, it is necessary to use mixtures with more than 80% of hydrogen.

- Another important aspect to consider is the variation in the percentage of H_2O vapor in the combustion chamber. The use of hydrogen-rich mixtures entails an enrichment of water vapor in the combustion gases. For example, in a 50% hydrogen mixture, the H_2O vapor increase reaches 3.27%. In the case of working with 100% hydrogen, the increase in the percentage of water vapor in the combustion products would reach 16.18%.

- The effects that the increase in the amount of water vapor will have, both in the product and in the refractory, are difficult to predict theoretically and, therefore, experimental studies will be necessary to evaluate its effect.

Figure 1. Variation of the composition of the products of complete combustion (CO_2, H_2O) and variation of the Wobbe Index, for different mixtures of natural gas and hydrogen.



Preliminary experimental study of combustion of natural gas and hydrogen mixtures

Cleanfire® HR_x™ Hydrogen Burners

In this project, work is being done on adapting the Air Products Cleanfire® HR_x ™ burner to be able to work with hydrogen, both for use in the ceramic and frit sectors. It is an oxy-fuel burner (oxygen combustion) with a flat flame that was originally designed for the glass industry (figure 2). It has several key features including up to 95% oxygen directing ability, a foam reduction mode to improve heat absorption in ovens, low NO_x emissions, and optional sensors for remote performance monitoring.

The Cleanfire® HR_x ™ burner block has three outlet gantries; a central precombustor gantry where the fuel and primary oxygen initiate combustion and the flame is formed and stabilized, and two oxygen directing gantries, upper and lower.

One of the burner's notable capabilities is that the introduction of oxygen can be directionally controlled, allowing it to be diverted through the upper or lower porticoes (or divided between the two) that surround the primary pre-burner. The oxygen staging modes include the "Foam Control" mode for foam control, the "Melt" mode for fusion, and the "Split" mode for staging division.

Such directional control of oxygen in stages provides several benefits, including adjusting the length, rate and brightness of the flame.

Figure 2. Image of the Cleanfire® HR_x™ burner with a detail of the hot side of the burner block.

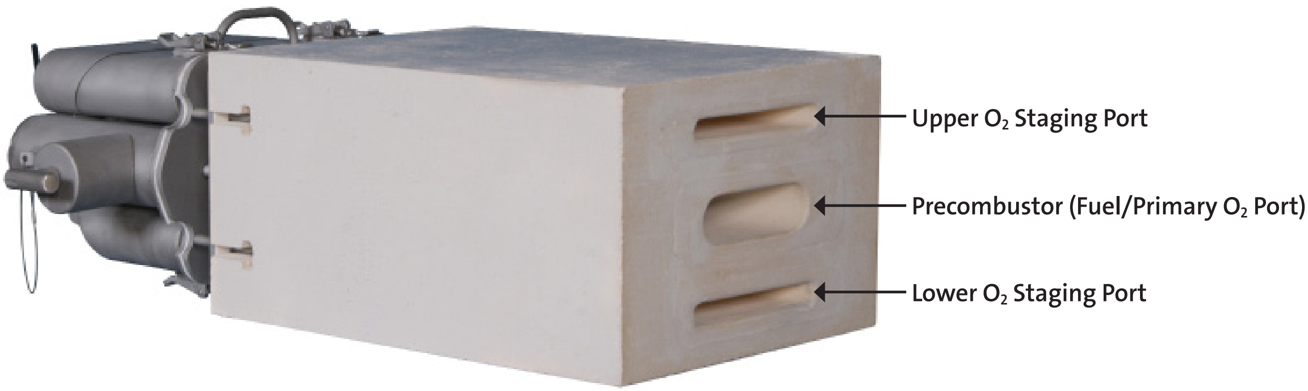
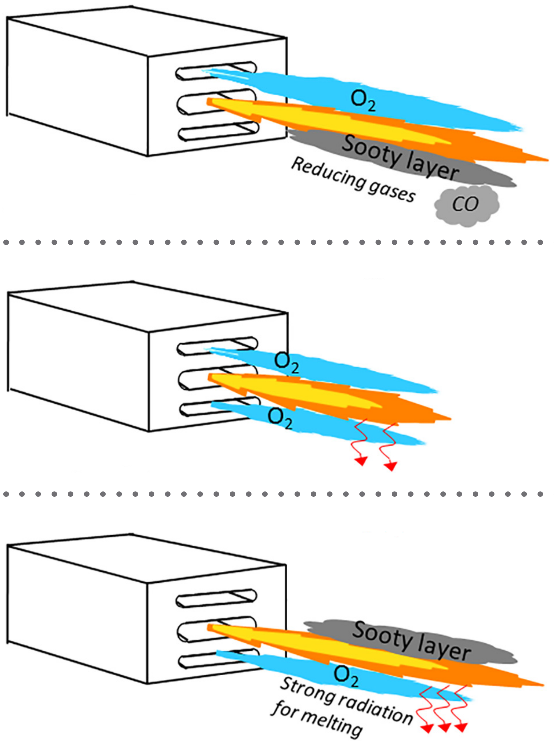


Figure 3: Various staging modes of the HR_x™ burner



Foam Control Mode

- Staging O_2 on top of primary flame
- Produces long, staged flame with sooty underlayer, containing reducing gases (CO)
- Will reduce foam on surface of glass

Split Mode

- Staging O_2 on top and bottom of primary flame
- Produces shorter, stable flame with high radiance
- Good for boosting applications and/or locations with high turbulence (near flue)

Melt Mode

- Staging O_2 on bottom of primary flame, similar to traditional HR_i burner
- Produces long, flame with high radiance on underside for faster melting

Figure 3 shows the different operating modes of the HR_x burner.

Oxygen staging is performed to avoid the formation of NO_x, by delaying the mixing of oxygen and fuel, resulting in a lower maximum flame temperature, in areas where the highest flame occurs. part of thermal NO_x. The burner is equipped with a valve, called the primary O_2 valve, which controls the amount of primary oxygen that flows through the main portico of the burner, as well as the secondary oxygen that is fed selectively and directionally, so that it is distributed independently of the different porticoes of the burner block.

• **Split Mode.** In "Split" mode, an equal amount of oxygen is directed to the upper and lower oxygen directing gates. This results in a shorter, brighter, and more stable flame. The "Split" mode can be especially useful in turbulent oxy-fuel furnace locations (eg, near the stack) and for oxy-fuel booster applications.

• **Melt Mode.** In fusion mode, oxygen is directed to the lower oxygen directing gantry of the burner block, which is located below the main flame. The flame will develop a bright bottom surface due to thermal radiation caused by localized combustion of directed oxygen with the gases on the bottom surface of the flame. The high radiation produced in melting mode is directed downward towards the surface of the material and has been shown to speed up the melting process in glass production.

• **Foam Control Mode.** In foam control mode, oxygen is directed to the upper oxygen directing gantry of the burner block, which is above the main flame. The resulting flame appears to be covered with soot on its lower edge, which contains reducing gases composed mainly of carbon monoxide (in concentrations of several percent). The reducing atmosphere created by the flame extends above the surface of the material and acts to dissipate the foam on the surface of the glass.

Hydrogen tests

Experimental tests have been carried out with the Cleanfire® HR_x™ burner using different mixtures of hydrogen with natural gas, from 100% natural gas to 100% with H_2, mainly using oxygen as an oxidizer.

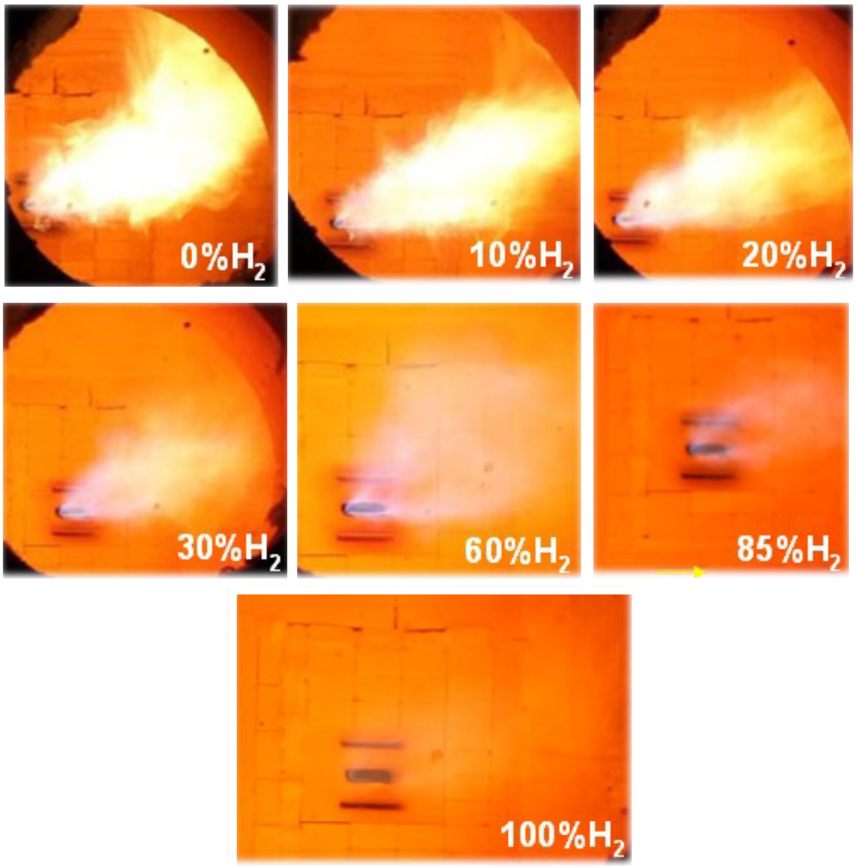
To work with hydrogen, small modifications were made in the configuration of the burner and the characteristics of the flame, such as its shape and luminosity, were observed. Figure 3 shows an example of how the natural gas / H_2 mix ratio affects these characteristics.

As can be seen in figure 4, as the hydrogen content in the mixture increases, the luminosity of the flame decreases. When it reaches 100% hydrogen the flame appears almost invisible.

The shape of the flame also changes with increasing hydrogen. In this case, the length of the flame decreases due to the higher reaction rate of combustion. The impact that this new heat release profile can have, with shorter flames, must be taken into consideration, to ensure optimal heat transfer to the product.

It should be noted that, during the experimental tests, no degradation effects were observed in the combustion chamber due to the new atmosphere generated, and no hot spots were observed on the face of the burner block.

Figure 4. Images of the Cleanfire® HR_x™ burner flame with different volumetric hydrogen-natural gas mixtures.



Conclusions

The results of this study show that the replacement of natural gas with hydrogen will imply the adaptation and / or replacement of current burners or equipment, given the special characteristics of hydrogen.

Therefore, future work should:

• Invest in the development of new hydrogen burners of the dimensions and power required in the ceramic sector.

• Work to minimize the formation of NO_x during the combustion of hydrogen with air.

• Study its adaptation to the characteristics of the process. It will be necessary to carry out an in-depth study to know the behavior of the ceramic materials processed, as well as the construction materials of the kiln, in the face of the replacement of natural gas by hydrogen, with the new atmosphere generated in the kiln.

• Pay special attention to the quality of the final product, since in the firing of ceramic tiles this is greatly influenced by the shape and characteristics of the flames.

• Analyze the effects of the increase in the amount of water vapor generated in combustion, which a priori, are difficult to predict.

Final considerations

This work is part of a project in development, in the case of being selected for its exhibition, the additional results that are available will be exhibited.

Acknowledgments

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