

# PYROLITIC AND OXIDATIVE STRUCTURES IN HODO MILD COMBUSTION.

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## Abstract

The typical reactive structure stabilized in a diffusion layer in standard conditions can be significantly modified whether injected flows are diluted and/or pre-heated.

The increase of the fuel and/or oxidant flow dilution up to extreme conditions could lead to the formation of not ignitable mixtures so that the oxidation processes could be sustained just in case the pre-heating temperature of one of the two flows is high enough to promote the auto-ignition of the system. The flows high initial enthalpy and the low fuel and/or oxygen concentration can drastically modify the structure of the oxidative and pyrolytic region due to change of the physical and chemical kinetics respect to conventional diffusion flame. Such operative conditions are typical of Mild Combustion processes. More specifically a combination of both heating and dilution of oxidant and/or fuel can yields to a not premixed combustion process named Hot Diluted Diffusion Ignition (HDDI).

The effect of inlet conditions on the stabilized reactive structure has been studied by analyzing the behavior of a steady, unidimensional diffusive layer. Numerical simulations have been carried out by means of OPPDIF application of ChemKin code and kinetic mechanisms available in literature, which simulates the behavior of two opposed jets. The change of the structures of the reactive region induced by a hot and diluted oxidant flow (HDDI-HODO) fed towards a fuel jet at environmental temperature has been numerically analyzed. Temperature and heat release profiles are considered as key parameters to understand the main features of the reactive region.

The oxidant flow dilution causes a lower maximum temperature and more uniform temperature profiles with respect to un-diluted traditional diffusion flames even though oxidant flow is pre-heated. At the same time, higher oxidant flow dilution levels affect drastically heat release profiles and cause the disappearance of fuel pyrolytic reactions (negative heat release values).

Further simulations were performed to understand the effect of water and carbon dioxide on flame structure.

## Introduction

Mild Combustion is a very promising process for the reduction of pollutants species emission, such as  $\text{NO}_x$  and particulate matter, and for the attainment of high thermal efficiency of combustion processes coupled with fuel savings [1, 2, 3].

The process presents unique, intrinsic structural properties as well as unique performance in terms of chemical conversion and depression of pollutant formation routes. Peculiar characteristics come out also in dependence of industrial or laboratory facilities where the process takes place. In this conceptual framework Mild Combustion has been evaluated in some well defined reactor configuration, namely in steady combustion processes evolving in a

Well Stirred Reactor [4, 5], in self ignition in quiescent oxidant environment as well as in premixed deflagrative combustion in Opposed Flow Reactor [6, 7, 8].

A further step toward the comprehension of the overall process is the study of the configuration, that is the analogous of the diffusion flame in back-fed combustion, i.e the one in which reactants are separated and inter-diffuse. In the contest of Mild Combustion a not-premixed combustion process is named Hot Diluted Diffusion Ignition (HDDI) whether:

- heating contributes significantly to the creation of an oxidative structure in the sense that no combustion process occurs without it;
- dilution is so intense that the maximum temperature attainable inside this structure is so low that, in turn, it affects significantly its placement in the mixture fraction domain, the structure itself and the physical and chemical kinetics when compared to a diffusion flame process.

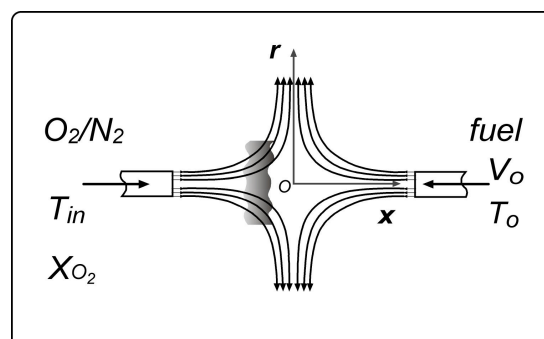
Different reactive structures compete to different combinations of hot, diluted fuel/oxidant flows. The ones associated with Hot Oxidant and Diluted Fuel (HODF) have been extensively studied and reported in literature [9, 10].

In this work the reactive structures stabilized in a unidimensional steady diffusive layer obtained from the interaction of a hot, diluted oxidant flow (Hot Oxidant Diluted Oxidant=HODO) with a undiluted fuel flow at ambient temperature have been considered. The effect of inlet temperature and dilution level of oxidant flow as well as of the presence of water and CO<sub>2</sub> as diluent are discussed in details.

### Configurations and numerical tools

The HDDI configuration has been schematized by means of opposed jets. and reported in figure 1. The presented scheme is referred as HODO (Hot Oxidant Diluted Oxidant) configuration, where a hot and diluted oxidant flow is fed towards a fuel flow at environmental temperature.

The oxidant flow and the fuel flow are characterized by inlet temperatures, respectively  $T_{in}$  and  $T_o$ . The fuel has a inlet velocity  $V_o$ , while the oxidant flow velocity comes from the assumption that the kinetic energies of the two flows are equal so that the stagnation point is located, in any case, in the middle of the two injection planes, located at a relative distance  $D$  equal to 2 cm. The asymptotic strain rate  $K_o$  is defined with respect to the fuel flow velocity as  $V_o/D$ . For the HODO configurations the dilution degree is expressed respectively by the oxygen molar fraction  $X_{O_2}$ . A first analysis refers to nitrogen as diluent species and methane as fuel. Then, the effect of diluent nature has been studied by replacing nitrogen with water or CO<sub>2</sub> in the oxidant flow.



**Figure 1.** Hot Oxidant Diluted Oxidant configuration.

Numerical analysis was carried out by means of Oppdif [11] application of ChemKin [12] package by using the GRI 3.0 [13] detailed mechanism for methane oxidation. Oppdif application computes the diffusion flame between two opposed nozzles.

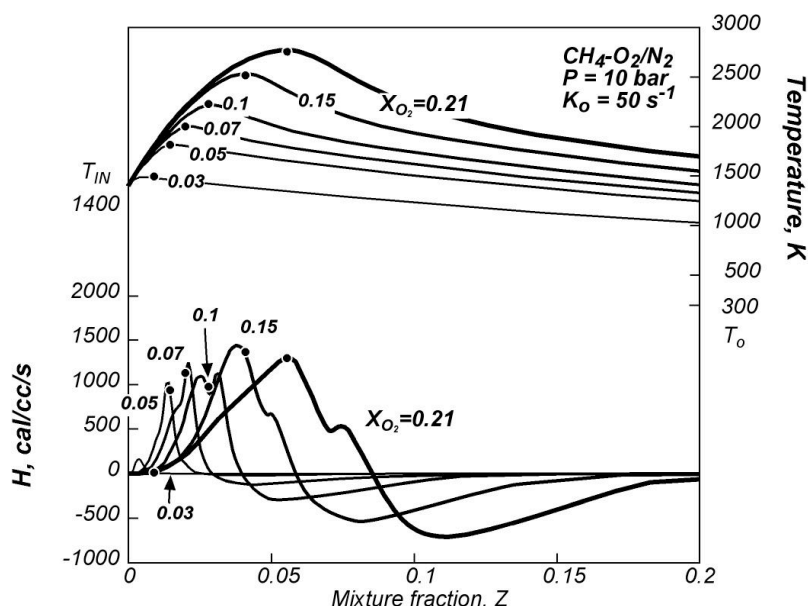
The structure of reactive zone was analyzed by an evaluation of temperature  $T$  and heat release rate  $H$  profiles as a function of mixture fraction  $Z$  along the axial coordinate of the system. Several simulations were carried out over a wide range of  $T_{in}$  at different dilution level of fuel jet and strain rate  $K_o$  in adiabatic conditions in correspondence of 1 and 10 bar.

In particular, for the lack of room, the results reported in this paper are relative to systems at high pressure but results are congruent with the ones obtained at atmospheric pressure.

## Numerical results

Figure 2 shows the temperature (upper part) and the heat release (lower part) profiles along the coordinate  $Z$  on curves parametric in the dilution level of the  $N_2/O_2$  pre-heated flow. The inlet temperature  $T_{in}$  is equal to 1400K, while the pressure is 10 bar. Methane is fed at ambient temperature with an inlet velocity  $V_o$  equal to 100 cm/s that corresponds to a strain rate  $K_o$  of  $50 s^{-1}$ .

Solid lines, representing  $T$  and  $H$ , decrease their thickness with  $X_{O_2}$ , whereas black dots indicate the stoichiometric values of  $Z$ .



**Figure 2.** Temperature (upper part) and heat release rate (lower part) versus mixture fraction, parametric on  $X_{O_2}$  at  $T_o = 300$ K,  $T_{in} = 1400$ K and  $p = 10$  bar, for the system  $CH_4-O_2/N_2$ .

The analysis of numerical results have been realized on the basis of the consideration that positive values of  $H$  are symptomatic of oxidation reaction occurrence, whilst negative values suggest the establishment of pyrolytic reactions or the overcoming of decomposition reactions with respect to oxidation ones.

Since the reactive region in the  $Z$  coordinate develops in the neighborhood of the oxidant injection plane the analysis of the results have been restricted in the range 0 - 0.2 of the mixture fraction.

Profiles at  $X_{O_2} = 0.21$  corresponds to the case where the oxidant flow is air. In such a case the temperature slightly increases up to reach a maximum value equal to 2750 K, then it slowly decreases down to 300 K towards the methane injection plane.

At the same time, the heat release profiles shows two relative maxima values, the former, in correspondence of the maximum value of temperature, located at  $Z = Z_{st} = 0.055$ , the latter,

with a lower value, at  $Z = 0.06$ . At  $Z = 0.11$  it shows a minimum negative value. Afterwards it slowly increases towards the fuel injection plane up to zero.

As soon as nitrogen content in the oxidant flow is enhanced, in general the temperature and the heat release profiles show the same trend but the maxima and minimum values occur for lower values of  $Z$  and the region, in the  $Z$  space, where reactions occur becomes narrower with respect to the case with no oxidant dilution.

For  $X_{O_2} = 0.15$  the maximum temperature ( $T_{\max} = 2675$  K) occurs for at  $Z = 0.040 = Z_{\text{st}}$ . The H absolute maximum is localized at the same position, while the second one at  $Z = 0.051$ . Both the two maxima heat release values are higher than the ones showed in the previous case, whereas the negative minimum is lower in absolute value.

When the oxidant stream dilution degree is 90%, the decrease of the mixture calorific value leads to a lower system temperature. The maximum allowed temperature is positioned at  $Z = 0.0275$  which corresponds to  $Z_{\text{st}}$ . The heat release profile is similar to the previous cases, but the absolute maximum is not located in correspondence of the stoichiometric  $Z$  value. As matter of fact the first maximum is sited at  $Z = 0.025$ , whereas the second one at  $Z = 0.031$ . It means that the maximum heat release rate occurs in correspondence of a mixture with a fuel lean composition. In such a case the two maxima are of comparable magnitude, furthermore the extension of the negative heat release region is reduced and the minimum absolute value diminishes in comparison with lower dilution case.

For  $X_{O_2} = 0.07$  the temperature further on decreases in congruence with the mixture lower calorific power due to the dilution degree enhancement. The temperature maximum falls in correspondence of the stoichiometric  $Z$  value. At the same time heat release profile maxima change their relative importance, in particular the former becomes lower than the second one that almost disappears. The stoichiometric mixture fraction falls on the left side of the maximum heat release rate value. The pyrolytic region extension diminishes congruently with the trend found out in the previous conditions in dependence of the dilution level.

A further depletion of oxygen causes a merging of the heat release maxima values and the disappearance of the negative heat release region. As matter of fact in case of  $X_{O_2} = 0.05$  the H profile shows a single positive maximum in correspondence a  $Z$  value slightly lower than  $Z_{\text{st}}$ , while the pyrolytic region disappears.

In the last case the oxygen molar fraction is equal to 0.03. For such dilution the temperature increase is very limited and the maximum temperature is 1475 K, while the heat release presents a single maximum, very low in comparison with other cases. Neither the maximum temperature nor the maximum heat release is correlated with  $Z_{\text{st}}$ .

The heat release profile shapes have been considered as indicative of the structure of the oxidation region. In particular profiles that show two positive peaks and a negative minimum value are indicative of high temperature combustion. In this case the composition of the mixture ensures high heat release and high system temperatures so that the oxidation process is self-sustaining. On the other hand, heat release profiles that present a single positive peak and no negative values are symptomatic of Mild Combustion. In such case oxidation reactions occur just by means of the high enthalpy content provided by the hot oxidant flow.

The heat release profile can be used for pointing out a comprehensive classification by building up a map of behavior on a  $T_{in} - \Delta T$  ( $\Delta T$  = maximum allowable temperature - frozen temperature) plane where regions corresponding to the different combustion regimes were identified.

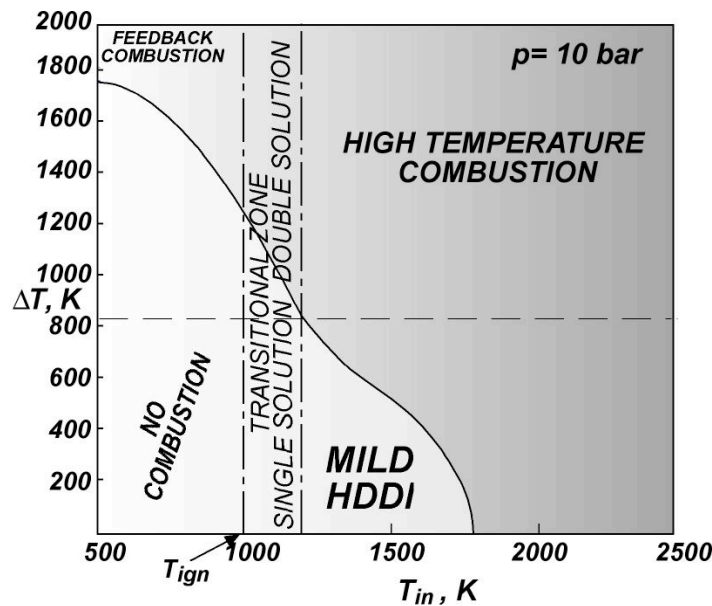
In Figure 3 the map obtained for  $K_0 = 50$  s<sup>-1</sup>,  $T_0 = 300$  K and  $p = 10$  bar has been reported for a pressure equal to 10 bar and a strain rate equal to 50 s<sup>-1</sup>.  $T_{in}$  was changed from 500 K up to 2500 K while  $\Delta T$  ranged from 0 to 2200 K.

Four different regions, respectively named “no combustion”, “feedback combustion”, high temperature combustion” and “Mild HDDI” are identifiable on the plane.

The region “no combustion” establishes in correspondence of inlet temperatures lower than the auto-ignition temperature of a stoichiometric mixture and for oxidant flow compositions very diluted so that the heat release associated to combustion is not sufficient to sustain the oxidation process.

If the composition of the mixture can satisfy such requirement, the oxidation process can evolve through traditional feed-back structures.

An inlet temperature increase causes the shifts towards the “high temperature combustion” region where both the pre-heating temperature and the mixture compositions also contribute to the oxidation reactions, but they do not change the main features of the diffusive structure.



**Figure 3.** Combustion regimes at  $p = 10$ bar,  $T_{in} = 300$ K,  $T_{in} = 1400$ K and  $K_o = 50$  s<sup>-1</sup> .

The last region is related to Mild-HDDI, where the high pre-heating oxidant flow temperature promotes and sustains the combustion process. It is identifiable for  $T_{in}$  comprised between 1200K and 1750K and  $\Delta T$  from 0 up to 800 K.

It is worth noting that the crossing from the “feedback combustion” to the “high temperature” regimes does happen through a transitional region where two different system steady states are allowed. This indicates a hysteresis behavior from low to high methane conversion solutions.

At the same time a transitional region is identifiable also for the passage from “no combustion” to “Mild Combustion” but numerical results show just a single solution indicating the disappearance of the hysteresis with a continuous transition from low to high fuel conversions.

The different reactive structures recognizable in a single profile along  $Z$  can be explained on the basis of the evolution of chemical conversion of the fuel and of intermediate species, which proceeds differently in dependence on the temperature and species concentration. Therefore, in order to have thorough knowledge of the oxidative structure in the mixing layer in the different operative conditions, the contribution of the heat release of production and destruction reactions of some significant species to the global heat release  $H$ , already reported in Figure 2, has been evaluated.

Figure 4 shows the global heat release and the contribute of some crucial species, indicative of the evolution of the oxidation process as a function of mixture fraction at a fixed inlet temperature and two different dilution levels.

A preliminary analysis has suggested the key species that mainly contribute to magnitude of the global heat release in the different step of the process.

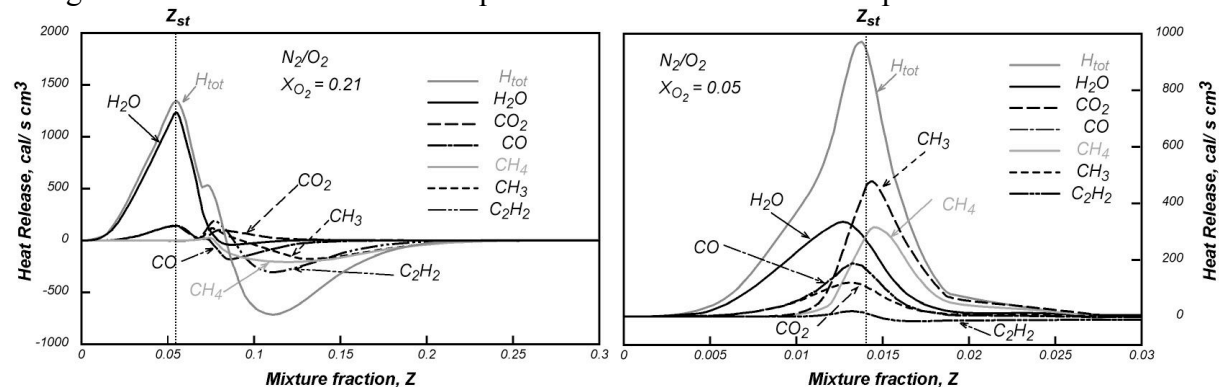
In particular Figure 4a shows the heat release distribution in the coordinate  $Z$  for a system in which the oxidant flow is not diluted and is pre-heated up to 1400K. The pressure is 10 bar and the strain rate is  $50 \text{ s}^{-1}$ . In the map of behavior, reported in Fig. 3, such condition falls in the High Temperature Combustion region, since no dilution and high inlet temperature are considered. The global heat release, reported in gray, extends in a  $Z$  range, from values very close to 0 up to 0.2.

The global  $H$  maximum value occurs in correspondence of  $Z_{st}$ , where  $\text{H}_2\text{O}$ ,  $\text{CO}$  and  $\text{CO}_2$  exhibit their maxima.

As soon as  $Z$  increases the global heat release decreases and shows a relative maximum for  $Z=0.074$ . Such a peak is mainly correlated to  $\text{CH}_3$ , then  $\text{CO}_2$  and  $\text{C}_2\text{H}_2$  species, while  $\text{CO}$  gives a negative contribution. It suggests that, in such neighborhood, methyl radicals and acetylene are mainly oxidized to intermediate species, while  $\text{CO}$  is largely formed through thermal decomposition reactions.

For  $Z > 0.074$ , the heat release decreases reaching a minimum negative value for  $Z=0.11$ . Acetylene, methane and methyl radical heat release mainly contribute to the negative region for higher values of  $Z$ . In this region, the depletion of oxygen and the relatively high temperatures promote endothermic reactions, such as methane thermal decomposition or methyl radical recombination and dehydrogenation, which respectively mainly produce  $\text{CH}_3$  and  $\text{C}_2\text{H}_2$ . As shown in Figure 6a, this latter strongly contributes to the negative value of  $H$ , along with all the  $\text{C}_2$  species that participate in the reaction channel that leads to the formation of  $\text{C}_2\text{H}_2$ .

The analysis of partial heat release shows that the structure of the oxidative region is very complex and several predominant phases occurring during the oxidation of  $\text{CH}_4$  are recognizable in relation to local composition of the mixture and temperature.



**Figure 4** Global heat release relative and heat release relative to selected species at  $T_{in}=1400\text{K}$  and (a)  $X_{O_2}=0.21$  and (b)  $X_{O_2}=0.03$ .

The heat release shown in Figure 4b is indicative of Mild Combustion regime. The global heat release shows a single peak that take place at a  $Z$  value slightly higher than the stoichiometric mixture fraction. The global heat release as well as the heat release relative to  $\text{H}_2\text{O}$ ,  $\text{CO}$  and  $\text{CO}_2$  present their maximum at  $Z = 0.013$ , while the methyl radical at  $Z$  slightly higher than stoichiometric value.

The high oxygen content and the low heat release and temperature values do not favor the methyl radical recombination reaction to ethane, so that the formation of  $\text{C}_2$  compounds. As

matter of a fact no predominant pyrolytic region is evident in the global heat profile. In addition the oxidation of methyl radicals to intermediate species and the full conversion of methane occurs almost in the same  $Z$  range. The heat release associated to such reactions compensates and overcomes the heat detracting to the system due to thermal decomposition and dehydrogenation reactions occurring in the same  $Z$  range.

The main result that can be evidenced by the analysis of the heat release profiles reported in Figure 4 is that the oxidative structure obtained in Mild Combustion conditions is uniform differently from the structure associated with high temperature combustion. This is in agreement with nearly homogeneous temperature and concentration profiles that characterize Mild Combustion [1].

### **HODO: Water and Carbon dioxide**

In industrial furnaces a common practice to ensure Mild Combustion conditions is by means of a recycling of hot exhaust gases since they provide for both the sensible enthalpy required for the fresh inlet mixture pre-heating and the mixture dilution [14]. Exhaust gases are mainly composed by steam and carbon dioxide. In the same way, high concentrations of water and  $\text{CO}_2$  assure the attainment of desired conditions in oxy-fuel combustion systems, which is coincident with a Mild Combustion process in the case of  $X_{\text{O}_2}$  lower than 0.21. Therefore the analyses of the oxidative structure in condition typical of Mild Combustion in systems diluted in  $\text{H}_2\text{O}$  and  $\text{CO}_2$  is very interesting. To this aim further simulations have been carried on in the HODO configuration in presence of such two species.

Figure 5 reports the  $T$  and  $H$  profiles versus  $Z$  for the system composed by a oxygen flow diluted in water and pre-heated up to 1400K, while the fuel flow is fed at ambient temperature. The inlet velocity  $V_0$  equal to 100 m/s, thus the asymptotic strain rate is equal to  $50 \text{ s}^{-1}$ . Curves are parametric in the oxidant flow dilution level specified by the oxygen molar fraction  $X_{\text{O}_2}$ .

The numerical simulations have been carried on varying the  $X_{\text{O}_2}$ , from air composition to very diluted conditions.

Solid lines decrease their thickness with  $X_{\text{O}_2}$ , whereas the black dots indicate, once the two flows completely mix, the stoichiometric values of the parameter  $Z$ .

As mentioned in the previous paragraph, numerical results are shown in the range 0-0.2 of the parameter  $Z$  since oxidation and pyrolytic reactions takes place in such range.

For  $X_{\text{O}_2} = 0.21$  the temperature slightly increases up to reach a maximum value equal to 2500 K, then it slowly decreases down to 300 K towards the methane injection plane.

At the same time, the heat release shows just one maximum value, in correspondence of the maximum value of temperature, located at  $Z = Z_{\text{st}} = 0.074$ . The second maximum, evident in the HODO configuration for the  $\text{CH}_4\text{-O}_2/\text{N}_2$  system at the same dilution level, is here substituted by an inflection point located at  $Z = 0.1$ . It suggests that the second maximum is almost merged inside the heat release curve.

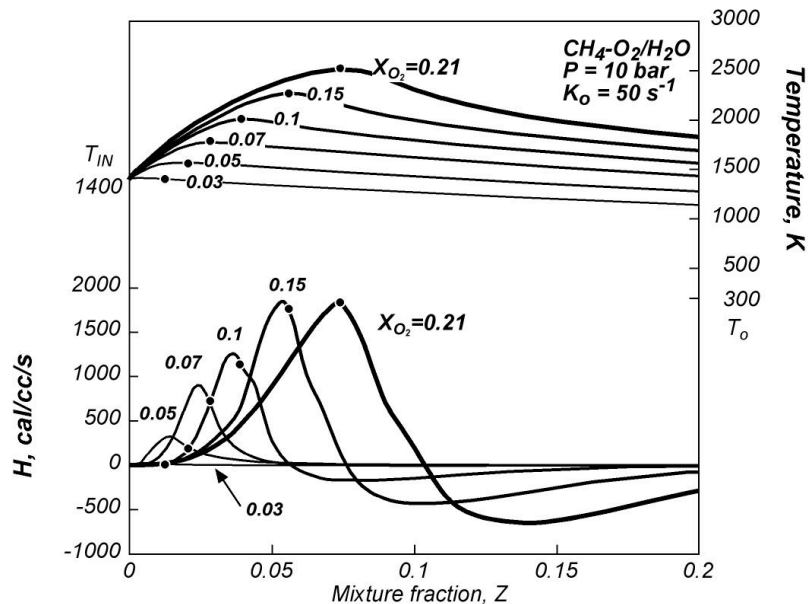
Afterwards the  $H$  curve decreases along the coordinate  $Z$  reaching a minimum negative value, and then it increases up to become zero.

As soon as water content in the oxidant flow is enhanced, the temperature and the heat release profiles show the same trend but the maximum and minimum values occur for lower values of  $Z$  and the region, in the  $Z$  space, where reactions occur, is narrower with respect to the case with no oxidant dilution.

For  $X_{\text{O}_2} = 0.15$  the maximum temperature ( $T_{\text{max}} = 2300 \text{ K}$ ) occurs for at  $Z = 0.0563 = Z_{\text{st}}$ . The  $H$  absolute maximum is localized at a  $Z$  value slightly lower than the stoichiometric one. The maximum  $H$  release intensity is comparable with respect to the previous case but the negative minimum is lower in absolute value.

In case of  $X_{O_2}=0.1$ , the enhancement of the heat capacity of the system leads to a lower system temperature. The maximum allowed temperature is positioned at  $Z = 0.0396$  which corresponds to  $Z_{st}$ .

The heat release profile is similar to the cases described earlier, but the absolute maximum is not localized in correspondence of the stoichiometric  $Z$  value. As matter of fact the maximum is sited at  $Z = 0.038$ , whereas the maximum at  $Z = 0.0396$ . The pyrolytic region disappears.



**Figure 5.** Temperature (upper part) and heat release rate (lower part) versus mixture fraction, parametric on  $X_{O_2}$  at  $T_o = 300$ K,  $T_{in} = 1400$ K and  $p = 10$  bar, for the system  $CH_4$ -  $O_2/H_2O$ .

Same considerations apply to the case  $X_{O_2} = 0.07$ , where the maxima of temperature and heat release decrease. The maximum temperature occurs in correspondence of the stoichiometric  $Z$  value while the maximum heat release for a  $Z$  slightly lower than  $Z_{st}$ . The inflection point completely disappears.

In the other cases ( $X_{O_2}=0.05, 0.03$ ) the temperature increment and the heat release are relatively modest. The maximum temperature always occurs for the stoichiometric mixture fraction, while the heat release is uncorrelated with  $Z_{st}$ .

Figure 6 shows the temperature and heat release profiles relative to the system  $CH_4$ - $O_2/CO_2$ . The approach to the problem is similar to the previous cases so the operative conditions, the dilution levels as well as the nomenclature are equal to the HODO configurations numerically exploited earlier in this work.

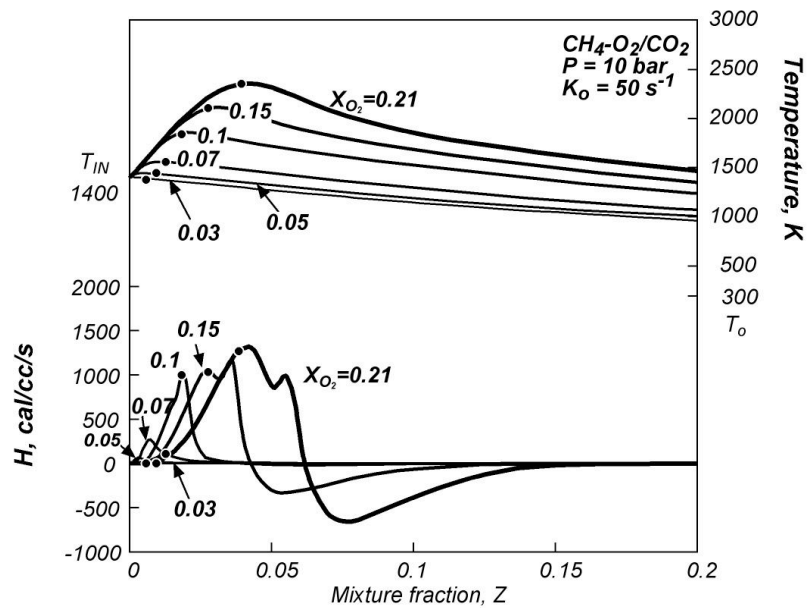
In case of  $X_{O_2} = 0.21$  the temperature slightly increases up to reach a maximum value, in correspondence of  $Z_{st} = 0.39$ , equal to 2350 K, then it slowly decreases down to 300 K towards the methane injection plane.

At the same time, the heat release profiles shows two relative maxima values. None of them occurs in correspondence of the stoichiometric value. In fact the  $Z_{st}$  is located on the left side of the absolute maximum value. The system shows a wide and significant pyrolytic region.

In general, as the  $CO_2$  concentration is increased, from 85% up to 97%, the temperature maximum decreases and shifts towards lower mixtures fraction values, while the two maxima as well as the absolute minimum value diminish their magnitude. The oxidative and pyrolytic regions shift to lower  $Z$  values while diminishing their extension.



Starting from  $X_{O_2}=0.1$  the heat release shows just a maximum value while the absolute minimum becomes zero.



**Figure 6.** Temperature (upper part) and heat release rate (lower part) versus mixture fraction, parametric on  $X_{O_2}$  at  $T_o = 300\text{K}$ ,  $T_{in} = 1400\text{K}$  and  $p = 10 \text{ bar}$ , for the system  $CH_4 - O_2/CO_2$ .

In highly diluted conditions the heat release is uncorrelated to the position of the stoichiometric mixture fraction.

All the HODO systems numerically analyzed have shown the same features relatively to the modification of the reactive structure of the combustion process in dependence of the dilution level increase. Nonetheless same peculiar characteristics can be underlined comparing the configurations among them for the same system external parameters and dilution level.

Figure 7 shows the temperature and heat release profiles for the systems  $CH_4 - O_2/N_2$ ,  $CH_4 - O_2/H_2O$  and  $CH_4 - O_2/CO_2$  in operative in case of  $X_{O_2} = 0.21$  and  $0.05$ .

The temperature profiles at  $X_{O_2} = 0.21$  clearly indicate that the nitrogen diluted system has the highest maximum temperature, followed by water and carbon dioxide. In any case systems show the maximum temperature increment in correspondence of their stoichiometric mixture fraction value that changes in dependence of mixture composition.

The heat release curves have similar shapes. The  $N_2$  and  $CO_2$  diluted systems show two maxima peaks and a negative minimum value. In case of water dilution the heat release curve shows just an absolute maximum and minimum.

The highest heat release competes to the system diluted in water while the other two systems are comparable in intensity maximum values.

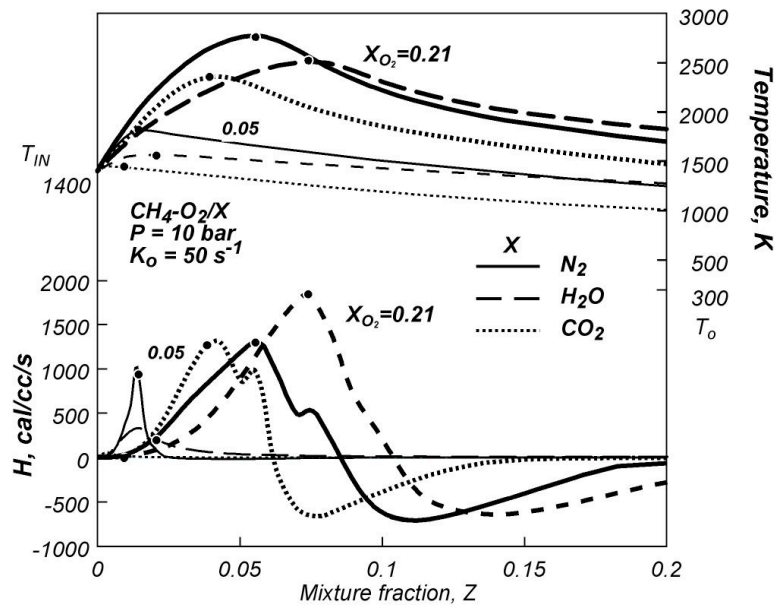
H profiles suggest clearly that the region where oxidation and pyrolytic reactions take place is wider in case of water dilution. The negative heat release rate for  $X_{O_2} = 0.21$  is located in different position in the  $Z$  space, but the magnitude is comparable for all the considered systems.

In case the dilution of the oxidant flow is increased up to 95%, the nitrogen diluted system presents the highest temperature because of the nitrogen lower heat capacity with respect to  $CO_2$  and  $H_2O$ .

The heat release profiles exhibit a single peak without negative values, so that the heat release associated to pyrolytic reactions does not overcome oxidation reactions heat release.

Comparing Figure 2, 3 and 4 it is worth noting that such condition is reached, for systems diluted in water and carbon dioxide, for a dilution level equal to  $X_{O_2}=0.1$ , while for the nitrogen diluted system for  $X_{O_2}=0.07$ .

The last one presents, in very diluted conditions, the highest heat release maximum, followed by the one diluted in water, then in carbon dioxide.



**Figure 7.** Comparison among  $CH_4-O_2/N_2$ ,  $CH_4-O_2/H_2O$  and  $CH_4-O_2/CO_2$  systems.

Such behaviors are mainly due to water and  $CO_2$  thermal effect, since their higher heat capacity with respect to nitrogen, and kinetic effects since, in condition typical of Mild Combustion, they can decompose and give rise to radical species, thus modifying the evolution of the oxidation process [15, 16]. Such aspect deserves further analysis but in this paper the attention has been focused on the structure of the reactive region so that any results on the kinetic evolution of the combustion process in so highly diluted systems is not reported.

## Conclusion

The numerical results highlight a drastic change of the structure of the reactive region in HODO system with respect to traditional diffusion flame configuration. In particular they can be reassumed as follows:

1. The oxidation processes evolves only because the pre-heating temperature of one of the two flows is high enough to promote the auto-ignition of the system.
2. The maximum local temperature of the systems is lower with respect to the undiluted traditional diffusion flames even though one of the reactant is pre-heated. This implies a reduction of undesired by-products such as  $NO_x$  species.
3. The double heat release peak, typical of High Temperature Air Combustion, disappears as the dilution degree is increased leading to a single peak profile and to the absence of the pyrolytic region, associated to Mild Combustion processes. Such condition implies the reduction of soot precursor species.
4. Once approaching Mild operative conditions, the maximum temperature always occurs in correspondence of the stoichiometric value of mixture fraction whereas the heat release maximum is uncorrelated with  $Z_{st}$  and occurs for leaner compositions respect to the stoichiometric one. The region in the  $Z$  space where reactions occur decreases as the highly diluted (Mild combustion) conditions are reached.

5. The nature of diluting species significantly affect the reaction region structures, affecting both the temperatures and the heat release profiles extension and shape in the Z coordinate. Due to higher thermal capacity of the system with respect to nitrogen diluted system, the maxima of temperature are lower, thus the production of undesired species, such as  $\text{NO}_x$  and soot, is further disadvantaged.

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