THERMOCHEMICAL INSTABILITY OF HIGHLY DILUTED METHANE MILD COMBUSTION

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Abstract
The experimental and numerical investigation of oscillatory behaviors in methane MILD combustion is of interest to prevent undesired instable combustion regimes. In this study new speciation measurements were obtained in a jet stirred flow reactor (JSFR) for stoichiometric mixtures of CH_4 and O_2, diluted in N_2, CO_2 and N_2-H_2O, at p=1.1 atm and T=720-1200 K. Oscillations were experimentally detected under specific temperature ranges, where system reactivity is sufficient to promote ignition, but not high enough to sustain complete methane conversion.

Introduction
MILD combustion is a promising technology, which through strong preheating and high dilution of the reactants, simultaneously enhances thermal efficiency and decreases the pollutant formation. Despite the emission reduction potential of MILD combustion, fundamental difficulties associated with typical operating conditions exist [1,2].

Severe working conditions in fact, carry instability phenomena, caused by thermochemical oscillations. Experimental evidences of methane oscillatory behaviors in MILD conditions were reported in the literature and instability was classified on the basis of wave shapes [3]. De Joannon et al. [3–5] studied the MILD combustion of methane both experimentally and numerically. They identified several oscillation typologies where the frequencies and amplitudes depend on temperature and carbon/oxygen ratio. It was pointed out that the competition between CH_3 recombination and oxidation pathways is more emphasized under such circumstances, and the temperature oscillation modulation was affected by ethylene and acetylene formation. De Joannon and co-workers came to the conclusion that MILD combustion processes cannot be implemented without a preliminary assessment of the auto-ignition process.

Even though methane oscillatory behavior in MILD regime has been documented experimentally [1,3,5,6], very few studies addressed these issues from a kinetic

modelling perspective [7,8]. The aim of this study is to explore the thermochemical oscillation of methane, also focusing on the effect of different dilution gases (N_2, H_2O, CO_2) in promoting or inhibiting such instabilities.

Methodology

The oxidation process of methane under MILD operating conditions was studied in a Jet Stirred Flow Reactor (JSFR). The setup is described in detailed elsewhere [9], and only a brief description is provided here. It consists of a quartz sphere of 113 cm3. The main flow is composed of oxygen and a diluent species. It can be pre-heated up to 1200 K passing through a quartz tube located within an electrically heated ceramic fiber oven. It subsequently mixes with the fuel flow in a premixing chamber. Then the mixture enters the reactor through four injectors located at its center. Table 1 presents the mole fractions of the investigated mixtures. It refers to stoichiometric mixtures diluted with N_2 (reference case), CO_2 and 49.5% N_2-40.5% H_2O, keeping a fixed overall dilution degree of 90%.

Table 1. Experiment initial conditions.

Cases	CH_4	O_2	N_2	CO_2	H_2O
A	0.0333	0.0667	0.9	0.0	0.0
B	0.0333	0.0667	0.0	0.9	0.0
C	0.0333	0.0667	0.495	0.0	0.405

Numerical simulations have been carried out using the OpenSMOKE++ framework of Cuoci et al. [10]. Simulations refer to a non-isothermal perfectly stirred reactor with residence times of 0.5 s. The mechanism POLIMI-1704 containing the C1-C3 core mechanism of AramcoMech2.0 [11] has been chosen to analyze and discuss the experimental results.

Results and discussion

Stable oscillatory behaviours for three different diluted systems have been characterized. Figure 1 shows the measured and predicted temperature and CH_4 profiles. The oscillations can be found in distinct ranges of inlet temperatures for the three diluted systems: N_2 (1125-1195 K), N_2/H_2O (1120-1270K), and CO_2 (1140-1245K). It is clear that, in such highly diluted systems, heat capacity (Cp) plays a dominant role in determining the flame temperature. The variations of Cp associated with the different bath gases directly impact the range, amplitude and frequency of temperature oscillations. Flame temperature is inversely proportional to specific heat, therefore CO_2 diluted system presents the lowest temperature oscillation range (~ 300K), whereas the oscillation range of (N_2+H_2O) and N_2 systems are slightly lower and higher of ~ 500K, respectively.

CO_2 diluted system is analyzed at an intermediate temperature, T=1185 K, in the range of oscillations. Figure 2 shows the concentration profiles of major species. CH_4 spanning from ~2.5% down to 0%, with a period of ~1.6 s. The presence of a time interval of ~0.15 s without CH_4 is also noteworthy. These thermochemical

oscillations are typical of reacting systems where a sudden ignition is followed by a cooling phase with a new accumulation of reactants until a successive ignition. The same Figure 2 also reports the temperature profile. A maximum temperature of about 1500 K is observed, and a discontinuity is observed on the first derivative during the cooling phase.

Although the maximum temperature coincides with the time where methane is completely consumed, the discontinuity point corresponds to a new start of methane accumulation inside the reactor. In fact, during the cooling phase, the temperature is not high enough to sustain methane reactivity, at the given residence time. The sudden reduction of CH_3, OH and HO_2 radical concentrations observed in Figure 2, at this time is a further confirmation of this behaviour.
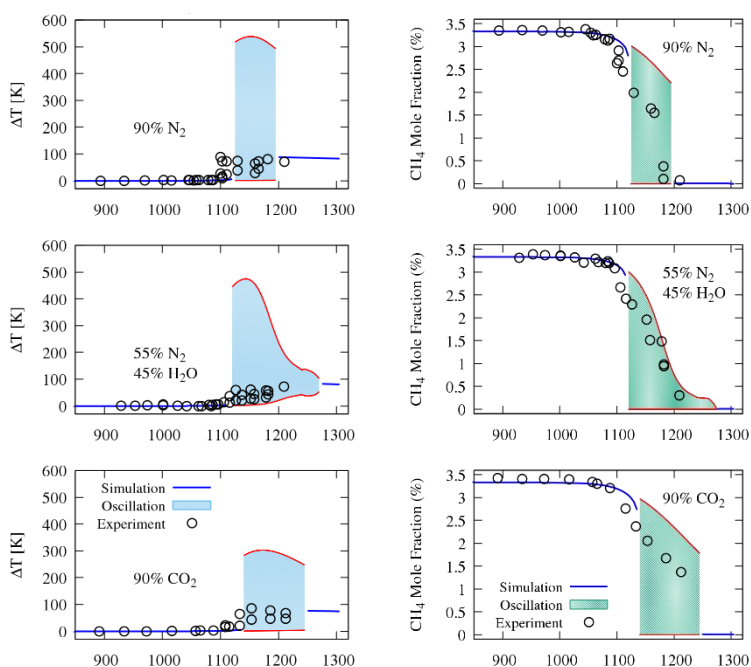

Figure 1. Range of oscillations of temperature ($\Delta T = T-T_{in}$) and CH_4 conversion versus inlet temperature, for the different dilution systems.

Once methane concentration starts to build up $H+O_2=OH+O$ and $CH_3+HO_2=CH_2O+OH$ emerge as the most sensitive reactions in increasing the system reactivity. On the contrary, methyl recombination reaction to form C_2H_6 acts as a termination reaction, reducing the overall radical concentrations. Another interesting feature is the competition between the two possible recombination/dismutation reactions of CH_3 and HO_2 radicals. Although the termination reaction to form CH_4 and O_2 reduces the system reactivity, the propagation reaction to form CH_3O and OH clearly increases methane conversion.

During this phase of methane accumulation, there is a significant formation of ethane and also of formaldehyde (CH_2O). The relatively high temperature (T>1200 K) justifies the importance of typical ethane pyrolysis reactions, confirmed by the significant amount of C_2H_4 and H_2 reported in Figure 2.

Figure 2 shows a clear visualization of the competition between pyrolytic and oxidative steps, in fact, while the maximum of methane concentration is reached at $\tau \sim 2$ s, the oxygen concentration builds up for slightly longer times reaching a maximum at $\tau \sim 2.2$ s. In other words, pyrolysis reactions, mostly involving ethyl radical and its dehydrogenation, progressively promote the onset of oxidation reactions and temperature increase up to the fast ignition of the system, with the peak temperature and the sudden decomposition of the intermediate species.
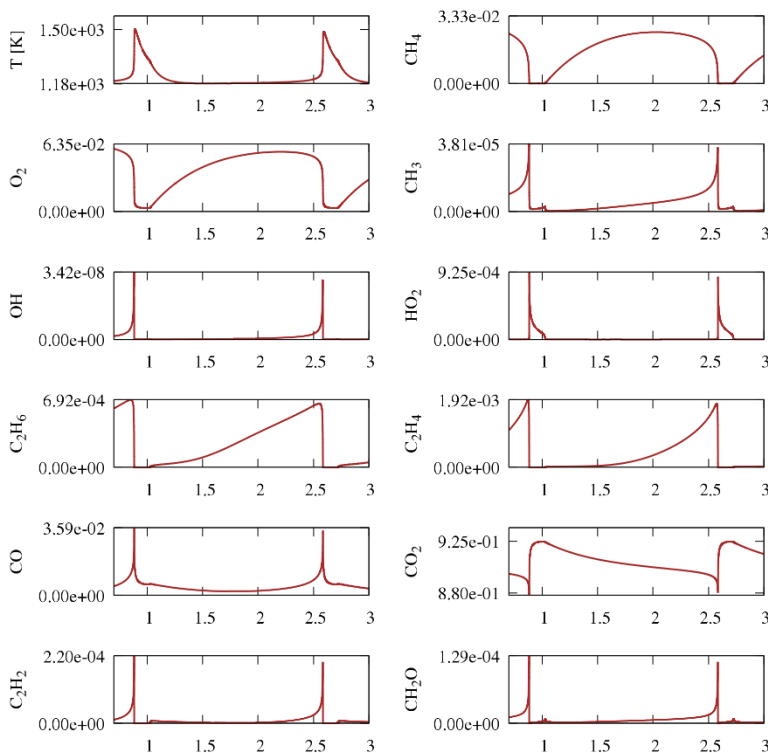

Figure 2. CH4 conversion at 1185 K, CO_2 dilution. Profile of major species.

Figure 3 compares induction times of N_2, CO_2, and (N_2+H2O) diluted systems. When comparing N_2 and (N_2+H2O) systems, one can observe the shorter ignition delay time for N_2 system in higher temperature. However, in the lower temperature region (T=1000 K), the induction times are very similar for two systems. On the contrary, CO_2 diluted system shows a different behaviour. In fact, the lower reactivity of the CO_2 diluted system is mainly due to the scavenging effect of CO_2 on H radicals with a promotion of CO formation through the reaction CO_2+H=OH+CO.
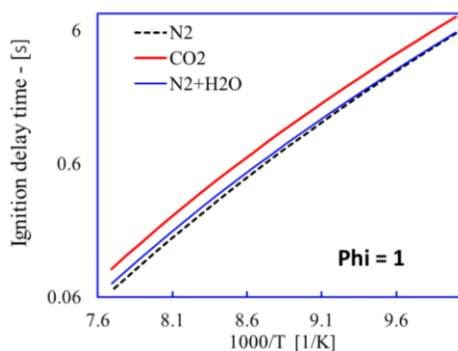
Figure 3. Induction time of three diluted systems in temperature range of 1000-1300 K.

Conclusion

Methane MILD combustion in JSR diluted with three different bath gases (N_2, CO_2 and N_2+H_2O) has been studied experimentally and numerically. The results show that oscillation happens as a result of competition between fuel conversion and accumulation during the induction time. The major conclusions of the study are as follows:

1. The competition between the two possible recombination/dismutation channels of CH_3 and HO_2 radicals is highlighted in both accumulation and ignition phases. Although the termination reaction to form CH_4 and O_2 reduces the system reactivity, the propagation reaction to form CH_3O and OH clearly increases methane conversion.
2. Pyrolysis reactions prevail over the oxidation ones during the induction phase. While the maximum of methane concentration is reached, the oxygen concentration builds up for slightly longer times reaching its maximum 0.2 s later.
3. CO_2 diluted system shows different induction time mainly due to the CO_2 reactivity. In fact, the lower reactivity of the CO_2 diluted system is mainly due to the scavenging effect of CO_2 on H radicals with a promotion of CO formation through the reaction $CO_2+H=OH+CO$.

Acknowledgement

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